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THE PERIODIC TABLE.\*

PERIODS.	GROUP O.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period .	2 He 4·0022	3 Li 6·940	4 Be 9·02	5 B 10·83	6 C 12·0036	7 N 14·008	8 O 16·0000	9 F 19·00	
Second short period .	10 Ne 20·18	11 Na 23·000	12 Mg 24·30	13 Al 26·97	14 Si 28·08	15 P 30·982	16 S 32·066	17 Cl 35·457	
First long period { Even series .	18 Ar 39·94	19 K 39·106	20 Ca 40·09	21 Sc 45·15	22 Ti 47·90	23 V 50·95	24 Cr 52·04	25 Mn 54·95	26 Fe 55·84
long period { Odd " .		29 Cu 63·55	30 Zn 65·38	31 Ga 69·72	32 Ge 72·60	33 As 74·984	34 Se 79·2	35 Br 79·915	28 Ni 58·69
Second long period { Even series .	36 Kr 82·9	37 Rb 85·48	38 Sr 87·63	39 Y 88·93	40 Zr 91·2	41 Nb 93·3	42 Mo 96·0	43 Ma ..	44 Ru 101·65
long period { Odd " .		47 Ag 107·880	48 Cd 112·40	49 In 114·8	50 Sn 118·70	51 Sb 121·76	52 Te 127·5	53 I 126·982	45 Rh 102·9
Third long period .	54 Xe 130·2	55 Cs 132·81	56 Ba 137·36	57 La 138·90	58 Ce 140·2	59 Pr 140·9	60 Nd 144·25	61 Pm ..	62 Sm 160·48
Fourth long period .		66 Dy 162·46	67 Ho 168·5	68 Er 167·6	69 Tm 169·4	70 Yb 178·0	71 Lu 175·0	72 Hf 178·6	63 Eu 162·0
Fifth long period { Even series .	86 Rn 222	87 ..	88 Ra 225·95	89 Ac ..	90 Th 232·15	91 Pa ..	92 U 238·15	73 Ta 181·3	64 Gd 167·0
long period { Odd " .								74 W 184·1	65 Tb 169·2
Volume in this series of text-books.	1	2	3	4	5	6	7	8	9

\* The Revised International Atomic Weights for 1929 as accepted by the Council of the Chemical Society are adopted in this Table.

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J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,  
CARNEGIE GOLD MEDALLIST.

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VOLUME VI. PART III.  
VANADIUM, NIOBIUM, AND TANTALUM.

BY  
SYDNEY MARKS, M.Sc., A.I.C.



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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 O, 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 ferro-cyanides 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 to 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.	Oxygen	=	16.000.
Sodium	=	22.996.	Sulphur	=	32.065.
Potassium	=	39.100.	Fluorine	=	19.015.
Silver	=	107.880.	Chlorine	=	35.457.
Carbon	=	12.008.	Bromine	=	79.916.
Nitrogen	=	14.008.	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 lists, pp. xv-xvii.

The addition of the *Table of Dates of Issue of Journals* (pp. xix-xxvi) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

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.

July 1929



## P R E F A C E.

THIS volume deals with the chemistry of vanadium, niobium, and tantalum. These elements are all of comparatively recent discovery, none of them being known before the nineteenth century.

Vanadium, niobium, and tantalum are metals which possess the capacity of forming both basic and acidic oxides, and, as they also display several degrees of combining power, the types of compounds they produce are very varied and often complex. The chemistry of these elements is, therefore, of considerable interest. In consequence of the difficulty experienced in separating niobium and tantalum satisfactorily, the compounds of these two elements have not been extensively explored; their further investigation certainly offers an attractive field for research.

Vanadium has found important application in the manufacture of special steels, and tantalum is being increasingly employed for electrolytic "rectifiers." It seems probable that the industrial application of these elements will increase in the future, and that uses will also be found for niobium.

In this volume only the inorganic compounds of the three elements are described, but references to the literature of the better known organic compounds have been given. The literature references throughout are complete up to December 1928, and every effort has been made to render them accurate. Information on several points has been obtained from Abegg & Auerbach's and from Gmelin-Kraut's *Handbuch der anorganischen Chemie*.

The Author's best thanks are due to the Editor, Dr. J. Newton Friend, for his advice and for reading both the manuscript and the proofs, as well as to Miss A. R. Russell, B.Sc., A.I.C., for reading the final proofs.

SYDNEY MARKS.

July 1929.



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## LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Afhandl. Fys. Kem.</i> . . .	Afhandlingar i Fysik, Kemi och Mineralogi.
<i>Amer. Chem. J.</i> . . .	American Chemical Journal.
<i>Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . .	The Analyst.
<i>Annalen</i> . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim.</i> . . .	Annales de Chimie (1719-1815, and 1914+).
<i>Ann. Chim. anal.</i> . . .	Annales de Chimie analytique appliquées à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
<i>Ann. Chim. Phys.</i> . . .	Annales de Chimie et de Physique (Paris) (1816-1913).
<i>Ann. Mines</i> . . .	Annales des Mines.
<i>Ann. Pharm.</i> . . .	Annalen der Pharmacie (1832-1839).
<i>Ann. Phys. Chem.</i> . . .	Annalen der Physik und Chemie (1819-1899).
<i>Ann. Physik</i> . . .	Annalen der Physik (1799-1818, and 1900+).
<i>Ann. Physik, Beibl.</i> . . .	Annalen der Physik, Beiblättes.
<i>Ann. Sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.
<i>Arbeiten Kaiserl. Gesundheits- amte</i> . . .	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
<i>Arch. exp. Pathol. Pharmak.</i> . . .	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i> . . .	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i> . . .	Archives des Sciences physiques et naturelles, Genève.
<i>Atti Acc. Torino</i> . . .	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i> . . .	Atti della Reale Accademia Lincei.
<i>B. A. Reports</i> . . .	British Association Reports.
<i>Ber.</i> . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Akad. Ber.</i> . . .	See <i>Sitzungsber. K. Akad. Wiss. Berlin</i> .
<i>Ber. Deut. physikal. Ges.</i> . . .	Berichte der Deutschen physikalischen Gesellschaft.
<i>Bull. Sci. Pharmacol.</i> . . .	Bulletin des Sciences Pharmacologiques.
<i>Bot. Zeit.</i> . . .	Botanische Zeitung.
<i>Bul. Soc. Stiințe Cluj.</i> . . .	Buletinul Societății de Științe din Cluj.
<i>Bull. Acad. roy. Belg.</i> . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i> . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. de Belg.</i> . . .	Bulletin de la Société chimique Belgique.
<i>Ber. Deut. pharm. Ges.</i> . . .	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Bull. Soc. chim.</i> . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. franç. Min.</i> . . .	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. min. de France</i> . . .	Bulletin de la Société minéralogique de France.
<i>Bull. U. S. Geol. Survey</i> . . .	Bulletins of the United States Geological Survey.
<i>Centr. Min.</i> . . .	Centralblatt für Mineralogie.
<i>Chem. Ind.</i> . . .	Die Chemische Industrie.
<i>Chem. News</i> . . .	Chemical News.
<i>Chem. Weekblad</i> . . .	Chemisch Weekblad.
<i>Chem. Zeit.</i> . . .	Chemiker Zeitung (Cöthen).
<i>Chem. Zentr.</i> . . .	Chemisches Zentralblatt.
<i>Compt. rend.</i> . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
<i>Crell's Annalen</i> . . .	Chemische Annalen für die Freunde der Naturlehre, von L. Crellé.
<i>Dingl. poly. J.</i> . . .	Dingler's polytechnisches Journal.

ABBREVIATED TITLE,	JOURNAL,
<i>Drude's Annalen</i> . . . . .	Annalen der Physik (1900-1906).
<i>Electroch. Met. Ind.</i> . . . . .	Electrochemical and Metallurgical Industry.
<i>Eng. and Min. J.</i> . . . . .	Engineering and Mining Journal.
<i>Gazzetta</i> . . . . .	Gazzetta chimica italiana.
<i>Gehlen's Allg. J. Chem.</i> . . . . .	Allgemeines Journal der Chemie.
<i>Geol. Mag.</i> . . . . .	Geological Magazine.
<i>Gilbert's Annalen</i> . . . . .	Annalen der Physik (1799-1824).
<i>Giorn. di Scienze Naturali ed Econ.</i> . . . . .	Giornale di Scienze Naturali ed Economiche.
<i>Helv. Chim. Acta</i> . . . . .	Helvetica Chim. Acta.
<i>Int. Zeitsch. Metallographie</i> . . . . .	Internationale Zeitschrift fur Metallographie.
<i>Jahrb. kh. geol. Reichsanst.</i> . . . . .	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
<i>Jahrb. Miner.</i> . . . . .	Jahrbuch fur Mineralogie.
<i>Jahresber.</i> . . . . .	Jahresbericht uber die Fortschritte der Chemie.
<i>Jenaische Zeitsch.</i> . . . . .	Jenaische Zeitschrift fur Naturwissenschaft.
<i>J. Amer. Chem. Soc.</i> . . . . .	Journal of the American Chemical Society.
<i>J. Chem. Soc.</i> . . . . .	Journal of the Chemical Society
<i>J. Chim. phys.</i> . . . . .	Journal de Chimie physique.
<i>J. Gasbeleuchtung</i> . . . . .	Journal fur Gasbeleuchtung.
<i>J. Geology</i> . . . . .	Journal of Geology.
<i>J. Ind. Eng. Chem.</i> . . . . .	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Metals</i> . . . . .	Journal of the Institute of Metals.
<i>J. Miner. Soc.</i> . . . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>J. Pharm. Chim.</i> . . . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . . . .	Journal of Physical Chemistry.
<i>J. Physique</i> . . . . .	Journal de Physique.
<i>J. prakt. Chem.</i> . . . . .	Journal fur praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> . . . . .	Journal of the Physical and Chemical Society of Russia (Petrograd).
<i>J. Soc. Chem. Ind.</i> . . . . .	Journal of the Society of Chemical Industry.
<i>Landw. Jahrb.</i> . . . . .	Landwirtschaftliche Jahrbücher.
<i>Mém. Paris Acad.</i> . . . . .	Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France.
<i>Mem. Coll. Sci. Kyōtō.</i> . . . . .	Memoirs of the College of Science, Kyōtō Imperial University.
<i>Monatsh.</i> . . . . .	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. scient.</i> . . . . .	Moniteur scientifique.
<i>Munch. Med. Wochenschr.</i> . . . . .	Munchener Medizinische Wochenschrift.
<i>Nature</i> . . . . .	Nature.
<i>Nuovo Cim.</i> . . . . .	Il nuovo Cimento.
<i>Oesterr. Chem. Zeit.</i> . . . . .	Oesterreichische Chemiker-Zeitung.
<i>Öfvers. K. Vet.-Akad. Förh.</i> . . . . .	Öfversigt af Kongliga Vetenskaps-Akademiens Forhandlingar.
<i>Pflüger's Archiv</i> . . . . .	Archiv fur die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. Post</i> . . . . .	Pharmazeutische Post.
<i>Pharm. Zentr.-h.</i> . . . . .	Pharmazeutische Zentralhalle.
<i>Phil. Mag.</i> . . . . .	Philosophical Magazine (The London, Edinburgh, and Dublin).
<i>Phil. Trans.</i> . . . . .	Philosophical Transactions of the Royal Society of London.
<i>Phys. Review</i> . . . . .	Physical Review.
<i>Physikal. Zeitsch.</i> . . . . .	Physikalische Zeitschrift.
<i>Pogg. Annalen</i> . . . . .	Poggendorff's Annalen der Physik und Chemie (1824-1877).
<i>Proc. Chem. Soc.</i> . . . . .	Proceedings of the Chemical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i> . . . . .	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
<i>Proc. Roy. Irish Acad.</i> . . . . .	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Phil. Soc. Glasgow</i> . . . . .	Proceedings of the Royal Philosophical Society of Glasgow.
<i>Proc. Roy. Soc.</i> . . . . .	Proceedings of the Royal Society of London.
<i>Proc. Roy. Soc. Edin.</i> . . . . .	Proceedings of the Royal Society of Edinburgh.

ABBREVIATED TITLE.	JOURNAL.
<i>Rec. Trav. chim.</i> . . .	Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
<i>Roy. Inst. Reports</i> . . .	Reports of the Royal Institution.
<i>Schweigger's J.</i> . . .	Journal für Chemie und Physik.
<i>Sci. Proc. Roy. Dubl. Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> . . .	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. Wiss. Wien.</i> . . .	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
<i>Techn. Jahresber.</i> . . .	Jahresbericht über die Leistungen der Chemischen Technologie.
<i>Trans. Amer. Electrochem. Soc.</i> . . .	Transactions of the American Electrochemical Society.
<i>Trans. Chem. Soc.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Inst. Min. Eng.</i> . . .	Transactions of the Institution of Mining Engineers.
<i>Trav. et Mém. du Bureau intern. des Poids et Mes.</i> . . .	Travaux et Mémoires du Bureau International des Poids et Mesures.
<i>Verh. Ges. deut. Naturforsch. Aerzte.</i> . . .	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Wied. Annalen</i> . . .	Wiedemann's Annalen der Physik und Chemie (1877-1899).
<i>Wissenschaftl. Abhandl. phys.-tech. Reichsanst.</i> . . .	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
<i>Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Chem.</i> . . .	Kritische Zeitschrift für Chemie.
<i>Zeitsch. Chem. Ind. Kolloide</i> . . .	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
<i>Zeitsch. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . . .	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. Nahr. Genuss-m.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. wiss. Photochem.</i> . . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik, und Photochemie.



## TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year	Amer. J Sci	Ann Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg Annalen.
1800	...	(1) 32-35	...	...	...	4-6	...	5-8	90	...
1	...	36-39	...	...	...	7-9	...	8-11	91	...
2	...	40-43	...	...	...	10-12	...	11-14	92	...
3	...	44-47	...	...	...	13-15	...	14-17	93	...
4	..	48-51	...	...	...	16-18	...	17-20	94	...
1805	..	52-55	...	...	...	19-21	...	20-23	95	...
6	...	56-60	...	...	...	22-24	...	23-26	96	...
7	...	61-64	...	...	...	25-27	...	26-29	97	...
8	...	65-68	...	...	...	28-30	...	29-32	98	...
9	..	69-72	...	...	...	31-33	(1) 1*	33, 34	99	...
1810	...	73-76	...	...	...	34-36	2	35, 36	100	...
11	...	77-80	...	...	...	37-39	3	37, 38	101	...
12	...	81-84	...	...	...	40-42	4	39, 40	102	...
13	...	85-88	...	...	...	43-45	5	41, 42	103	...
14	...	89-92	...	...	...	46-48	6	43, 44	104	...
1815	...	93-96	...	...	...	49-51	(2) 1	45, 46	105	...
16	...	(2) 1-3	...	...	...	52-54	2	47, 48	106	...
17	...	4-6	1, 2	...	...	55-57	3	49, 50	107	...
18	...	7-9	3	...	...	58-60	4	51, 52	108	...
19	(1) 1	10-12	4	...	...	61-63	5	53, 54	109	...
1820	2	13-15	5	...	1-3	64-66	6	55, 56	110	...
21	3	16-18	6	...	4-6	67-69	7	57, 58	111	..
22	4, 5	19-21	7	1, 2	7-9	70-72	8	59, 60	112	...
23	6	22-24	8	3-6	10-12	73-75	9	61, 62	113	...
24	7, 8	25-27	9	7-10	13-15	76	10	63, 64	114	1, 2
1825	9	28-30	10, 11	11-14	16-18	Continued as Pogg. Annalen.	11	65, 66	115	3-5
26	10, 11	31-33	12, 13	15-19	19-22		12	67, 68	116	6-8
27	12	34-36	(2) 1, 2	20-23	23-26		13	(2) 1, 2	117	9-11
28	1, 3, 14	37-39	3, 4	24-26	27-30		14	3, 4	118	12-14
29	15, 16	40-42	5, 6	27-30	31-34		15	5, 6	119	15-17

\* First series known as *Bulletin de Pharmacie*.

Year.	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon. scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
1880	17, 18	...	43-45	7-8	31-34	...	...	35-38	16	...	...	7, 8	120	18-20	...	...	...
31	19, 20	...	46-48	...	35-39	...	...	39-42	17	...	...	9, 10	121	21-23	...	...	...
32	21, 22	1-4	49-51	(8) 1, 2	40-43	...	...	43-47	18	...	...	11 (3) 1	122	24-26	1	...	...
33	23, 24	5-8	52-55	3, 4	44-47	...	...	48-50	19	...	...	2, 3	123	27-30	2	...	...
34	25-27	9-12	56-57	5, 6	48-50	...	...	51-54	20	1-3	...	4, 5	124	31-33	...	...	...
1835	28, 29	13-16	58-60	7, 8	(2) 1-4	...	1	55-58	21	4-6	...	6, 7	125	34-36	...	...	...
36	30, 31	17-20	61-63	9, 10	5-8	...	2, 3	59-62	22	7-9	...	8, 9	126	37-39	...	...	...
37	32, 33	21-24	64-66	11, 12	9-12	...	4, 5	63-66	23	10-12	...	10, 11	127	40-42	3	...	...
38	34, 35	25-28	67-69	13, 14	13-16	...	6, 7	67-70	24	13-15	...	12, 13	128	43-45	...	...	...
39	36, 37	29-32	70-72	15, 16	17-20	...	8, 9	71-74	25	16-18	...	13, 15	129	46-48	...	...	...
1840	38, 39	33-36	73-75	17, 18	21-24	...	10, 11	75-78	26	19-21	...	16, 17	130	49-51	...	...	...
41	40, 41	37-40	(3) 1-3	19, 20	25-28	...	12, 13	79-82	27	22-24	...	18, 19	131	52-54	...	...	...
42	42, 43	41-44	7-9	(4) 1, 2	29-32	...	14, 15	83-86	(3) 1, 2	25-27	...	20, 21	132	55-57	...	...	...
43	44, 45	45-48	7-9	3, 4	33-36	...	16, 17	87-90	3, 4	28-30	...	22, 23	133	58-60	4	...	...
44	46, 47	49-52	10-12	5, 6	37-40	...	18, 19	91-94	5, 6	31-33	...	23, 25	134	61-63	...	...	...
1845	48-50	53-56	18-15	7, 8	41-44	...	20, 21	95-98	7, 8	34-36	...	26, 27	135	64-66	...	...	...
46	(2) 1, 2	57-60	16-18	9, 10	45-48	...	22, 23	99-102	9, 10	37-39	...	28, 29	136	67-69	...	...	...
47	3, 4	61-64	19-21	11, 12	49-52	...	24, 25	103-106	11, 12	40-42	...	30, 31	137	70-72	...	...	...
48	5, 6	65-68	22-24	13, 14	53-56	...	26, 27	107-110	13, 14	43-45	...	32, 33	138	73-75	...	1	...
49	7, 8	69-72	25-27	15, 16	57-60	...	28, 29	111-113	15, 16	46-48	...	34, 35	139	76-78	...	1, 2	...
1850	9, 10	73-76	28-30	17, 18	61-64	...	30, 31	115-118	17, 18	49-51	...	36, 37	140	79-81	...	3	4, 5
51	11, 12	77-80	31-33	19, 20	65-68	...	32, 33	119-122	19, 20	52-54	...	(4) 1, 2	141	82-84	5	6, 7	15-18
52	13, 14	81-84	34-36	(5) 1, 2	69-72	...	34, 35	123-126	21, 22	55-57	...	3, 4	142	85-87	...	8, 9	19-22
53	15, 16	85-88	37-39	3, 4	73-76	...	36, 37	127-130	23, 24	58-60	...	5, 6	143	88-90	...	10	23-27
54	17, 18	89-92	40-42	5, 6	77-80	...	38, 39	131-133	25, 26	61-63	...	7, 8	144	91-93	...	6	28-33
1855	19, 20	93-96	43-45	7, 8	81-84	...	40, 41	135-138	27, 28	64-66	...	9, 10	145	94-96	7	8	34-38
56	21, 22	97-100	46-48	9, 10	85-88	...	42, 43	139-142	29, 30	67-69	...	11, 12	146	97-99	8	9	...
57	23, 24	101-104	49-51	11, 12	89-92	...	44, 45	143-146	31, 32	70-72	(1) 1	13, 14	147	100-102	9	10	...
58	25, 26	105-108	52-54	13, 14	93-96	1	46, 47	147-150	33, 34	73-75	2	15, 16	148	103-105	9	11	...
59	27, 28	109-112	55-57	15, 16	97-100	1	48, 49	151-153	35, 36	76-78	3	17, 18	149	106-108	9, 10	12	...

\* Often referred to by Series : Series 3, vols. 1-16, 1871-1886 ; Series 4, vols. 1-24, 1887-1910 ; Series 5, vols. 1-9, 1911-1919 (one vol. yearly).

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Zeit.
1860	...	29, 30	...	113-116	...	58-60	17, 18	101-104	...	2	1, 2	...	...
61	...	31, 32	...	117-120	1	61-63	19, 20	105-108	...	3	3, 4	...	...
62	...	33, 34	...	121-124	2	64-66	(6) 1, 2	109-112	...	4	5, 6	...	...
63	...	35, 36	...	125-128	2	67-69	3, 4	113-116	...	5	7, 8	...	...
64	...	37, 38	...	129-132	3	(4) 1-3	5, 6	117-120	...	(2) 1, 2	9, 10	...	...
1865	...	39, 40	...	133-136	3, 4	4-6	7, 8	121-124	...	8, 4	11, 12	...	...
66	...	41, 42	...	137-140	4	7-9	9, 10	125-128	...	5, 6	13, 14	...	...
67	...	43, 44	...	141-144	5	10-12	11, 12	129-132	...	7, 8	15, 16	...	...
68	...	45, 46	...	145-148	6	13-15	13, 14	133-136	...	9, 10	17, 18	...	...
69	...	47, 48	...	149-152	...	16-18	15, 16	137-140	...	11, 12	19, 20	...	...
1870	...	49, 50	...	153-156	7	19-21	17, 18	141-144	...	13, 14	21, 22	...	...
71	...	(3) 1, 2	...	157-160	...	22-24	19, 20	145-148	...	15, 16	23, 24	...	...
72	...	3, 4	...	161-164	8	25-27	(7) 1, 2	149-150, 201*	...	17, 18	25, 26	...	...
73	...	5, 6	...	165-170	...	28-30	3, 4	201-203	...	19, 20	27, 28	...	...
74	...	7, 8	...	171-174	...	(5) 1-3	5, 6	204, 205	...	21, 22	29, 30	...	...
1875	...	9, 10	...	175-179	...	4-6	7, 8	206, 207	...	23, 24	31, 32	...	...
76	...	11, 12	...	180-183	...	7-9	9, 10	208, 209	...	25, 26	33, 34	...	...
77	...	13, 14	...	184-189	...	10-12	11, 12	210, 211	...	27, 28	35, 36	...	...
78	...	15, 16	...	190-194	...	13-15	13, 14	212, 213	...	29, 30	37, 38	...	...
79	...	17, 18	...	195-199	...	16-18	15, 16	214, 215	...	31, 32	39, 40	...	...
1880	...	19, 20	...	200-205	...	19-21	17, 18	216, 217	...	13	41, 42	...	...
81	...	21, 22	...	206-210	...	22-24	19, 20	218, 219	...	14	43, 44	...	...
82	...	23, 24	...	211-215	...	25-27	(8) 1, 2	220	...	15	45, 46	...	...
83	...	25, 26	...	216-221	...	28-30	3, 4	221	...	16	47, 48	...	...
84	...	27, 28	...	222-226	...	(6) 1-3	5, 6	222	...	17	49, 50	...	...
1885	...	29, 30	...	227-231	...	4-6	7, 8	223	...	18	51, 52	...	...
86	...	31, 32	...	232-236	...	7-9	9, 10	224	...	19	53, 54	...	...
87	...	33, 34	...	237-242	...	10-12	11, 12	225	...	20	55, 56	...	...
88	...	35, 36	...	243-249	...	13-15	13, 14	226	...	21	57, 58	...	...
89	...	37, 38	...	250-255	...	16-18	15, 16	227	...	22	59, 60	...	...

\* Joining Series 1 and 2 together. Also written as (8) 1, 2, 3, etc.

Year.	Compt. rend.	Dingl. poly. J.	Gazetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Pharm. Chm.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon. scient.*	Nature.	Phil Mag.
1860	50, 51	155-158	...	...	...	37, 38	79-81	...	...	...	4	...	19, 20
61	52, 53	159-162	...	...	...	39, 40	82-84	...	...	...	...	...	21, 22
62	54, 55	163-166	...	...	...	41, 42	85-87	...	...	...	...	...	23, 24
63	56, 57	167-170	...	...	...	43, 44	88-90	...	...	...	...	...	25, 26
64	58, 59	171-174	...	...	...	45, 46	91-93	...	...	...	...	...	27, 28
1865	60, 61	175-178	...	...	...	(4) 1, 2	94-96	...	...	...	7	...	29, 30
66	62, 63	179-182	...	...	...	3, 4	97-99	...	...	...	8	...	31, 32
67	64, 65	183-186	...	...	...	5, 6	100-102	...	...	...	9	...	33, 34
68	66, 67	187-190	...	...	...	7, 8	103-105	...	...	...	10	...	35, 36
69	68, 69	191-194	...	...	...	9, 10	106-108	...	...	...	11	...	37, 38
1870	70, 71	195-198	...	...	...	11, 12	(2) 1, 2	...	...	...	12	...	39, 40
71	72, 73	199-202	...	...	...	13, 14	3, 4	...	...	...	13	...	41, 42
72	74, 75	203-206	...	...	...	15, 16	5, 6	...	...	...	14	...	43, 44
73	76, 77	207-210	...	...	...	17, 18	7, 8	...	...	...	15	...	45, 46
74	78, 79	211-214	...	...	...	19, 20	9, 10	...	...	...	16	...	47, 48
1875	80, 81	215-218	...	...	...	21, 22	11, 12	...	...	...	17	...	49, 50
76	82, 83	219-222	...	...	...	23, 24	13, 14	...	...	...	18	...	(5) 1, 2
77	84, 85	223-226	...	...	...	25, 26	15, 16	...	...	...	19	...	3, 4
78	86, 87	227-230	...	...	...	27, 28	17, 18	...	...	...	20	...	5, 6
79	88, 89	231-234	...	...	...	29, 30	19, 20	...	...	...	21	...	7, 8
1880	90, 91	235-238	...	...	...	(5) 1, 2	21, 22	...	...	...	22	...	9, 10
81	92, 93	239-242	...	...	...	3, 4	23, 24	...	...	...	23	...	11, 12
82	94, 95	243-246	...	...	...	5, 6	25, 26	...	...	...	24	...	13, 14
83	96, 97	247-250	...	...	...	7, 8	27, 28	...	...	...	25	...	15, 16
84	98, 99	251-254	...	...	...	9, 10	29, 30	...	...	...	26	...	17, 18
1885	100, 101	255-258	...	...	...	11, 12	31, 32	...	...	...	27	...	19, 20
86	102, 103	259-262	...	...	...	13, 14	33, 34	...	...	...	28	...	21, 22
87	104, 105	263-266	...	...	...	15, 16	35, 36	...	...	...	29, 30	...	23, 24
88	106, 107	267-270	...	...	...	17, 18	37, 38	...	...	...	31, 32	...	25, 26
89	108, 109	271-274	...	...	...	19, 20	39, 40	...	...	...	33, 34	...	27, 28

\* See footnote, p. xx.



Year.	Phil. Trans.	Pogg. Annalen.	Proc. Chem. Soc.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1860	150	109-111	...	10, 11	18	...	39-42	...	...	...	...	...	...
61	151	112-114	...	11	14	...	43, 44	...	...	...	...	...	...
62	152	115-117	...	11, 12	Continued	...	45, 46	...	...	1	...	...	...
63	153	118-120	...	12, 13	as J.	...	47, 48	...	...	2	...	...	...
64	154	121-123	...	13	Chem. Soc.	...	49, 50	...	...	3	...	...	...
1865	155	124-126	...	14	...	...	51, 52	...	...	4	...	...	...
66	156	127-129	...	15	...	...	53, 54	...	...	5	...	...	...
67	157	130-132	...	15, 16	...	...	55, 56	...	...	6	...	...	...
68	158	133-135	...	16, 17	...	...	57, 58	...	...	7	...	...	...
69	159	136-138	...	17, 18	...	...	59, 60	...	...	8	...	...	...
1870	160	139-141	...	18, 19	...	...	61, 62	...	...	9	...	...	...
71	161	142-144	...	19, 20	...	...	63, 64	...	...	10	...	...	...
72	162	145-147	...	20, 21	...	...	65, 66	...	...	11	...	...	...
73	163	148-150	...	21, 22	...	...	67, 68	...	...	12	...	...	...
74	164	151-153	...	22, 23	...	...	69, 70	...	...	13	...	...	...
1875	165	154-156	...	23, 24	...	...	71, 72	...	...	14	...	...	...
76	166	157-159	...	24, 25	...	...	73, 74	...	...	15	...	...	...
77	167	160	...	25, 26	...	...	75, 76	...	...	16	...	1, 2	...
78	168, 169	Continued	...	27, 28	...	...	77, 78	...	...	17	...	2, 3	...
79	170	as Wied. Annalen.	...	28, 29, 30	...	...	79, 80	...	...	18	...	3, 4	...
1880	171	...	...	30, 31	...	...	81, 82	...	...	19	...	4, 5	...
81	172	...	...	31, 32, 33	...	...	83, 84	...	...	20	...	5, 6	...
82	173	...	...	33, 34	...	1	85, 86	...	...	21	...	6, 7	...
83	174	...	...	34, 35, 36	...	2	87, 88	...	...	22	...	7, 8	...
84	175	...	...	36, 37, 38	...	3	89, 90	...	...	23	...	8, 9, 10	...
1885	176	...	1	38, 39	...	4	91, 92	...	...	24	...	10, 11	...
86	177	...	2	40, 41	...	5	93, 94	...	...	25	...	11, 12	...
87	A, 178	...	3	42, 43	...	6	95, 96	...	...	26	...	12, 13	...
88	179	...	4	43, 44, 45	...	7	97	...	...	27	...	13, 14, 15	...
89	180	...	5	45, 46, 47	...	8	98	...	...	28	...	15	...

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Weekblad.	Chem. Zeit.	Compt. rend
1890	12	39, 40	15	256-260	19-21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
91	13	41, 42	16	261-266	22-24	19, 20	229	24	5, 6	63, 64	8, 9	...	15	112, 113
92	14	43, 44	17	267-271	25-27	(9) 1, 2	230	25	7, 8	65, 66	10, 11	...	16	114, 115
93	15	45, 46	18	272-277	28-30	3, 4	231	26	9, 10	67, 68	12, 13	...	17	116, 117
94	16	47, 48	19	278-283	(7) 1-3	5, 6	232	27	11, 12	69, 70	14, 15	...	18	118, 119
1895	17	49, 50	20	284-288	4-6	7, 8	233	28	13, 14	71, 72	16, 17	...	19	120, 121
96	18	(4) 1, 2	21	289-293	7-9	9, 10	234	29	15, 16	73, 74	18, 19	...	20	122, 123
97	19	5, 4	22	294-298	10-12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299-308	13-15	13, 14	236	31	19, 20	77, 78	22, 23	...	22	126, 127
99	21, 22	7, 8	24	304-309	16-18	15, 16	237	32	21, 22	79, 80	24, 25	...	23	128, 129
1900	23, 24	9, 10	25	310-318	19-21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
01	25, 26	11, 12	26	314-319	22-24	19, 20	239	34	25, 26	83, 84	28, 29	...	25	132, 133
02	27, 28	13, 14	27	320-325	25-27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	...	26	134, 135
03	29, 30	15, 16	28	326-329	28-30	3, 4	241	36	29, 30	87, 88	32, 33	...	27	136, 137
04	31, 32	17, 18	29	330-337	(8) 1-3	5, 6	242	37	31, 32	89, 90	34, 35	...	28	138, 139
1905	33, 34	19, 20	30	338-343	4-6	7, 8	243	38	33, 34	91, 92	36, 37	...	29	140, 141
06	35, 36	21, 22	31	344-350	7-9	9, 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
07	37, 38	23, 24	32	351-357	10-12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	4	31	144, 145
08	39, 40	25, 26	33	358-363	13-15	13, 14	246	41	3, 4	97, 98	42, 43	5	32	146, 147
09	41, 42	27, 28	34	364-371	16-18	15, 16	247	42	5, 6	99, 100	44, 45	6	33	148, 149
1910	43, 44	29, 30	35	372-377	19-21	17, 18	248	43	7, 8	101, 102	46, 47	7	34	150, 151
11	45, 46	31, 32	36	378-385	22-24	19, 20	249	44	9, 10	103, 104	48, 49	8	35	152, 153
12	47, 48	33, 34	37	386-394	26-27	(11) 1, 2	250	45	11, 12	105, 106	50, 51	9	36	154, 155
13	49, 50	35, 36	38	395-401	28-30	3, 4	251	46	13, 14	107, 108	52, 53	10	37	156, 157
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1915	ceased	39, 40	40	...	...	...	253	48	17, 18	111, 112	56, 57	12	39	160, 161
16	...	41, 42	41	...	...	...	254	49	19, 20	113, 114	58, 59	13	40	162, 163
17	...	43, 44	42	...	...	...	255	50	21, 22	115, 116	60, 61	14	41	164, 165
18	...	45, 46	43	...	...	...	...	51	23, 24	117	62, 63	15	42	166, 167
19	...	47, 48	44	...	...	...	...	52	25, 26	118, 119	64, 65	16	43	168, 169

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1890	275-278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279-282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283-286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287-290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291-294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295-298	25	17	67, 68	...	(0)1, 2	...	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299-302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303-306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307-310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311-314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
01	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6)1, 2
02	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
03	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
04	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
06	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
07	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
08	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
09	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79-82	17, 18
1910	325	40	32	97, 98	2	(7)1, 2	14	81, 82	42	29	31	72, 73	82-85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85-88	21, 22
12	...	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	...	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	...	44	36	105, 106	6	9, 10	18	89, 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100-102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102-104	37, 38

\* See footnote, p. xx.

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1890	A. 181	...	6-	47, 48, 49	9	99	10	39-41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42-44	30	4	...	...	19, 20	7, 8
92	188	...	8	50, 51, 52	11	101	12	45-47	31	5	...	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48-50	32	6	...	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51-53	33	7	...	...	23, 24	13-15
1895	186	...	11	57, 58, 59	14	104	15	54-56	34	8	...	...	24, 25	16-18
96	187, 188	...	12	59, 60	15	105	16	57-59	35	9	...	...	26-28	19-21
97	189, 190	...	13	60, 61, 62	16	106	17	60-63	36	10	...	...	28, 29	22-24
98	191	...	14	62, 63, 64	17	107	18	64-66	37	11	...	...	29-31	25-27
99	192, 193	...	15	64, 65, 66	18	108	19	67-69	38	12	...	...	31, 32	28-31
1900	194, 195	1	16	66, 67	19	109	20	Con-	39	13	...	...	32-34	32-35
01	196, 197	2	17	68, 69	20	110	21	tinued as	40	14	...	...	34-36	36-38
02	198, 199	3	18	69, 70	21	111	22	Annalen	41	15	...	...	36, 37	39-42
03	200-202	4	19	71, 72	22	112	23	der	42	16	...	...	37-39	43-46
04	203	5	20	72, 73, 74	23	113	24	Physik.	43	17	...	...	39, 40	47-49
1905	204, 205	6	21	74-76	24	114	25	...	44	18	...	...	40-42	50-53
06	206	7	22	A. 77, 78	25	115	26	...	45	19	...	...	42, 43	54-57
07	207	8	23	78, 79, 80	26	116	27	...	46	20	...	...	43, 44	58-60
08	207-209	9	24	80, 81	27	117	28	...	47	21	...	...	44-46	61-64
09	209, 210	10	25	82, 83	28	118	29	...	48	22	...	...	46, 47	65-69
1910	210	11	26	83, 84	29	119	30	...	49	23	...	...	48, 49	70-74
11	210, 211	12	27	84, 85, 86	30	120	31	...	50	24	...	...	49, 50	75-77
12	211, 212	13	28	86, 87	31	121	32	...	51	25	...	...	50-52	78-80
13	212, 213	14	29	88, 89	32	122	33	...	52	26	...	...	52, 53	81-86
14	213, 214	15	30	89, 90	33	123	34	...	53	27	...	...	54	86-88
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16	216, 217	17	of matter	...	35	...	36	...	55	29	...	...	56	91, 92
17	217	18	of scientific	...	36, 37	...	37	...	56	30	...	...	57	92
18	217	19	interest now	...	37	...	38	...	57	31	...	...	No	92
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\* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF  
INORGANIC CHEMISTRY.  
VOLUME VI. PART III.



# A TEXT-BOOK OF INORGANIC CHEMISTRY

## VOL. VI. PART III. VANADIUM, NIOBIUM, AND TANTALUM.

### CHAPTER I.

#### GENERAL CHARACTERISTICS OF THE ELEMENTS OF GROUP V., SUBDIVISION A.

THE elements vanadium, niobium, tantalum and protoactinium constitute Subdivision A of the Fifth Group of the Periodic Classification. The general properties of Subdivision B are considered elsewhere in this series.<sup>1</sup> Niobium is also known

Group IV.	Group V.		Group VI.
A.	A.	B.	A.
		7 N	
		15 P	
22 Ti	23 V		24 Cr
		33 As	
40 Zr	41 Nb		42 Mo
		51 Sb	
72 Hf	73 Ta		74 W
		83 Bi	
90 Th	91 Pa		92 U

as columbium. Protoactinium, also known as *eka-tantalum*, is a radioactive element which is also described elsewhere in this series.<sup>2</sup> Vanadium occurs in the first long period of the periodic system. It is, in fact, the first member of a set of nine elements (*viz.* vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium) which fall in the centre of the period and for which there are no analogues in the short periods. Niobium occupies an analogous position in the second long period, and tantalum in the third very long period. These three elements display the characteristic properties of "transition" elements in that they are distinctly metallic substances of high density and melting-point, associated with great hardness and other valuable mechanical properties. They display marked resemblances both

in the elemental state and in their compounds to the corresponding members of the A Subdivisions of Groups VI. and IV.<sup>3</sup> The analogy

<sup>1</sup> Vol. VI., Part I. (1928), p. 3.

<sup>2</sup> Vol. VII., Part III. (1926), p. 349.

<sup>3</sup> These subdivisions are included in the foregoing table.

of the elements with the B Subdivision of Group V. is mainly restricted to the pentavalent compounds; vanadium, for instance, is on the whole more closely parallel in properties to chromium than to phosphorus and arsenic. Indeed the resemblance is in this case so marked that vanadium was at one time included in the chromium family of elements, and analogous but erroneous formulæ were assigned to its compounds. The physical properties of these elements are set out in the following table. Chromium has been added to the table for the sake of comparison.<sup>1</sup>

Property.	Vanadium.	Niobium.	Tantalum.	Chromium.
Atomic weight .	50.95	93.3	181.3	52.04
Density . . .	6.0	12.7	16.6	6.9
Atomic volume .	8.5	7.3 *	10.93	7.5
Specific heat .	0.120	0.071	0.0365	0.1208
Melting-point .	1720° C.	1950° C.	2850° C.	1550° C.
Specific electrical resistance (in ohms per cc.).	$26 \times 10^{-6}$	$18.7 \times 10^{-6}$	$14.6 \times 10^{-6}$	$2.6 \times 10^{-6}$

The metals are not readily attacked by acids, but when they pass into solution they lose their metallic character and yield derivatives of the acid pentoxides,  $V_2O_5$ ,  $Nb_2O_5$  and  $Ta_2O_5$ . These derivatives include the vanadates, niobates and tantalates, which are among the commonest and most stable compounds of these metals.

A gradual increase is observable in the electropositeness of the metals in the order  $V \rightarrow Nb \rightarrow Ta$  (increase in atomic weight), as in the case of the elements of the B Subdivision of this group,  $N \rightarrow P \rightarrow As \rightarrow Sb \rightarrow Bi$ . It is also worthy of notice that, consistent with the usual rule, the A Subdivision on the whole is more strongly electropositive than the B Subdivision. The following observations show these facts clearly:—

(a) The decrease in the acidity of the pentoxides with increase in atomic weight. Vanadium pentoxide is the most acidic of the three, and is somewhat comparable with chromic acid in its behaviour; niobium pentoxide is much weaker, and tantalum pentoxide is still slightly weaker. These latter two acids are, in fact, extremely weak, and are comparable with titanous acid and zirconous acid (their neighbours in Group IV.), so much so that considerable difficulty is experienced in separating niobium and tantalum quantitatively from the Group IV. elements.

(b) The increase in the stability of the pentahalides with increase in atomic weight. Tantalum yields a pentahalide with each of the halogens, a pentiodide of niobium is unknown, and in the case of vanadium only the pentafluoride has been prepared. The existence of

<sup>1</sup> For a comparison of the physical properties of tantalum, tungsten, molybdenum, platinum, copper and nickel, see Balke, *Chem. Met. Eng.*, 1922, 27, 1273.

\* This value disturbs the gradation, but it is probable that the density (12.7) used in its calculation is too high (see p. 135).



tantalum pentiodide is, in fact, remarkable, because no other element in Groups IV. to VIII. displays the maximum valency of its group towards iodine. The variation in the readiness with which the pentafluorides undergo hydrolysis is shown in the fact that when the pentoxides of vanadium, niobium, and tantalum are dissolved in hydrofluoric acid and treated with potassium fluoride under the same conditions, the following double salts are most readily precipitated:  $x\text{KF.VO}_2\text{F}$ ;  $x\text{KF.NbOF}_3$ ;  $x\text{KF.TaF}_5$ . With increase in the concentration of hydrofluoric acid the double salts of vanadium oxytrifluoride,  $\text{VOF}_3$ , and of niobium pentafluoride,  $\text{NbF}_5$ , can be obtained. The double fluorides and oxyfluorides of niobium and tantalum are among the commonest compounds of these two elements, and form the classical means whereby the two metals are separated from each other. Double fluorides of analogous type are also given by antimony, e.g.  $2\text{KF.SbF}_5.\text{H}_2\text{O}$ , and by molybdenum, tungsten, etc., e.g.  $2\text{KF.MoF}_3.\text{H}_2\text{O}$  and  $\text{KF.WO}_2\text{F.H}_2\text{O}$ . The double alkali fluorides formed by the metals which belong to neighbouring groups are frequently isomorphous with the corresponding double fluorides of vanadium, niobium, and tantalum, and in many instances a fluorine atom is able to undergo replacement by an oxygen atom without disturbing the crystalline form. The following are examples of pairs of isomorphous compounds:  $2\text{NH}_4\text{F.NbOF}_3$  and  $2\text{NH}_4\text{F.WO}_2\text{F}_2$ ;  $3\text{KF.NbOF}_3.\text{HF}$  and  $3\text{KF.SnF}_4.\text{HF}$ ;  $\text{ZnF}_2.\text{NbOF}_3.6\text{H}_2\text{O}$  and  $\text{ZnF}_2.\text{TiF}_4.6\text{H}_2\text{O}$ ; the compounds  $3\text{NH}_4\text{F.NbOF}_3$  and  $3\text{NH}_4\text{F.TaOF}_3$  are isomorphous with the compounds  $3\text{NH}_4\text{F.TiF}_4$  and  $3\text{NH}_4\text{F.ZrF}_4$ ; and the compound  $2\text{KF.NbOF}_3.\text{H}_2\text{O}$  is isomorphous with  $2\text{KF.WO}_3\text{F}_2.\text{H}_2\text{O}$  and with  $2\text{KF.TiF}_4.\text{H}_2\text{O}$ .

As is usual with transitional elements, vanadium possesses considerable freedom in its valencies; with niobium and tantalum, however, this freedom is less marked. This can be seen in the variation of the readiness displayed by the compounds of these elements to undergo reduction:

(a) Vanadates can be successively reduced in stages, and thus be made to furnish tetra-, tri- and di-valent vanadium salts by varying the reducing agent and other conditions employed. Divalent vanadium salts are obtained with nascent hydrogen; niobates in acid solution are reduced by nascent hydrogen approximately to the trivalent<sup>1</sup> state, but no niobium salts of lower valency than five have hitherto been isolated from the solutions produced; tantalates do not undergo reduction at all with nascent hydrogen, and, apart from the halides and the disulphide (which do not possess saline character), only penta-valent compounds of tantalum are known.

(b) Vanadium pentoxide can be reduced to the metal by the action of hydrogen at high temperatures and pressures; niobium pentoxide is more stable, and yields the trivalent oxide  $\text{Nb}_2\text{O}_3$ , whereas tantalum pentoxide has not hitherto been reduced by hydrogen.

The following table summarises the more important types of compounds given by these three elements.

Nitrates and carbonates of vanadium, niobium, and tantalum have not been prepared. Niobium and tantalum salts of other weak acids, e.g. boric acid, hydrocyanic acid, phosphoric acid, are also unknown, and in the case of vanadium are not well defined.

<sup>1</sup> See p. 131.

**TYPICAL COMPOUNDS OF VANADIUM, NIOBIUM,  
AND TANTALUM.**

Type.	Vanadium.	Niobium.	Tantalum.
RF <sub>5</sub>	VF <sub>5</sub>	NbF <sub>5</sub>	TaF <sub>5</sub>
ROF <sub>3</sub>	VOF <sub>3</sub>	NbOF <sub>3</sub>	TaOF <sub>3</sub> *
RCl <sub>5</sub>	..	NbCl <sub>5</sub>	TaCl <sub>5</sub>
ROCl <sub>3</sub>	VOCl <sub>3</sub>	NbOCl <sub>3</sub>	TaOCl <sub>3</sub> *
RBr <sub>5</sub>	..	NbBr <sub>5</sub>	TaBr <sub>5</sub>
ROBr <sub>3</sub>	VOBr <sub>3</sub>	NbOBr <sub>3</sub>	TaOBr <sub>3</sub>
RI <sub>5</sub>	..	..	TaI <sub>5</sub>
RCl <sub>4</sub>	VCl <sub>4</sub>	..	..
ROCl <sub>2</sub>	VOCl <sub>2</sub>	..	..
RCl <sub>3</sub>	VCl <sub>3</sub>	NbCl <sub>3</sub>	TaCl <sub>3</sub>
R <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>
RO <sub>2</sub>	VO <sub>2</sub>	NbO <sub>2</sub>	TaO <sub>2</sub>
R <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>3</sub>	Nb <sub>2</sub> O <sub>3</sub>	..
RO	VO	NbO †	..
3K <sub>2</sub> O.R <sub>2</sub> O <sub>5</sub>	K <sub>3</sub> VO <sub>4</sub>	..	..
2K <sub>2</sub> O.R <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	..	..
K <sub>2</sub> O.R <sub>2</sub> O <sub>5</sub>	KVO <sub>3</sub>	NaNbO <sub>3</sub>	NaTaO <sub>3</sub>
xK <sub>2</sub> O.yR <sub>2</sub> O <sub>5</sub>	2K <sub>2</sub> O.3V <sub>2</sub> O <sub>5</sub> .6H <sub>2</sub> O	4K <sub>2</sub> O.3Nb <sub>2</sub> O <sub>5</sub> .16H <sub>2</sub> O	4K <sub>2</sub> O.3Ta <sub>2</sub> O <sub>5</sub> .16H <sub>2</sub> O ‡
HR <sub>4</sub>	HVO <sub>4</sub> .xH <sub>2</sub> O	HNbO <sub>4</sub> .xH <sub>2</sub> O	HTaO <sub>4</sub> .xH <sub>2</sub> O
Per-salts	KVO <sub>4</sub>	K <sub>3</sub> NbO <sub>8</sub>	K <sub>3</sub> TaO <sub>8</sub> .½H <sub>2</sub> O
RS	VS	..	..
R <sub>2</sub> S <sub>3</sub>	V <sub>2</sub> S <sub>3</sub>	..	..
RS <sub>2</sub>	..	NbS <sub>2</sub> †	TaS <sub>2</sub>
RS <sub>5</sub>	VS <sub>5</sub>	..	..

*Pentavalent Compounds.*—Vanadates display isomorphism with the corresponding phosphates; e.g. Na<sub>3</sub>PO<sub>4</sub>.12H<sub>2</sub>O and Na<sub>3</sub>VO<sub>4</sub>.12H<sub>2</sub>O are isomorphous. More remarkable is the isomorphism displayed by some of the double chlorovanadates with the corresponding chlorophosphates and chloroarsenates. The isomorphism shown by *vanadinite*, 3Pb<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>.PbCl<sub>2</sub>, *mimetesite*, 3Pb<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>.PbCl<sub>2</sub>, and *pyromorphite*, 3Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.PbCl<sub>2</sub>, led to vanadium being grouped with phosphorus and arsenic instead of with chromium. Vanadates differ from phosphates mainly in the ease with which they undergo reduction, and in the fact that while *orthophosphates* are more stable than *pyro-* or *meta-*phosphates, in the case of the vanadates the order of stability is reversed. Solutions of vanadates appear to contain the ions of all three types of salts, i.e. [VO<sub>4</sub>]<sup>'''</sup>, [V<sub>2</sub>O<sub>7</sub>]<sup>'''</sup> and [VO<sub>3</sub>]<sup>'</sup>, and can be made to precipitate any one of the salts by suitable alteration of the conditions. In the case of niobates and tantalates only the *meta-*salts and a few *pyro-*salts have been prepared.

Solutions of vanadates undergo change in the presence of dilute acids to produce polyvanadates which contain highly polymerised ions analogous to the polymerised chromate and molybdate ions.<sup>1</sup> Hence a numerous series of salts is known possessing the general formula xR<sub>2</sub>O<sub>5</sub>.yV<sub>2</sub>O<sub>5</sub>, to which analogous phosphates do not exist. The

\* Not known in the free state.

† Existence doubtful.

‡ Also formulated 7K<sub>2</sub>O.5Ta<sub>2</sub>O<sub>5</sub>.24H<sub>2</sub>O (see p. 199).

<sup>1</sup> See this series, Vol. VII., Part III. (1926), pp. 45, 135.

best known are the 2 : 3 salts,  $2R_2O_5 \cdot 3V_2O_5$ . Niobates and tantalates are decomposed by dilute acids, or even on being boiled in aqueous solution, with the precipitation of hydrated niobium pentoxide and tantalum pentoxide (also known as niobic acid and tantallic acid respectively), which readily form *sols*. Complex niobates and tantalates analogous to the polyvanadates are, however, produced by heating the pentoxides with bases in varying proportions, or by the double decomposition of the oxyfluorides of niobium and tantalum with alkalis, but the commonest salts in the cases of niobium and tantalum are the 4 : 3 salts. It is remarkable that the alkali tantalates which contain small proportions of the base are insoluble in water; this recalls the sparing solubility of potassium pyroantimonate,  $K_2H_2Sb_2O_7 \cdot 6H_2O$ .

Vanadic acid differs also from niobic and tantallic acids in that it forms a number of complex acids with other acids, and a large number of heteropolyvanadates are known. Niobic acid and tantallic acid show little tendency to form complex acids; oxalonibates and oxalotantalates have, however, been prepared.

The pentoxides of vanadium, niobium, and tantalum react with hydrogen peroxide to produce per-acids of the general formula  $HRO_4 \cdot xH_2O$ . These per-acids increase in stability with increase in atomic weight. Pertantallic acid is a white solid which can be heated to  $100^\circ C$ . without undergoing decomposition. The oxyfluorides of these metals also take up active oxygen to yield peroxyfluorides, which are much better defined in the case of niobium and tantalum than with vanadium.

*Tetravalent Compounds.*—With reduction in valency the acid character of pentavalent vanadium gradually disappears and basic properties become manifest. The oxide  $VO_2$  is amphoteric, and yields both tetravalent vanadium salts and vanadites. A large number of basic salts containing the vanadyl radical  $VO^{\cdot\cdot}$ , e.g. vanadyl sulphate,  $VOSO_4$ , are also known. This radical recalls the  $CrO_2^{\cdot\cdot}$ ,  $MoO_2^{\cdot\cdot}$ ,  $WO_2^{\cdot\cdot}$ , and  $UO_2^{\cdot\cdot}$  radicals given by the elements of the neighbouring group. The corresponding oxides of niobium and tantalum,  $NbO_2$  and  $TaO_2$ , do not give rise to salts.

*Trivalent Compounds.*—In trivalent vanadium compounds the basic character of the element is well developed, and both normal and oxy-salts of the sesquioxide  $V_2O_3$  are well defined, e.g. vanadous sulphate,  $V_2(SO_4)_3$ , and vanadium oxymonochloride,  $VOCl$ . It has been previously mentioned that resemblances between the elements of the A and B Subdivisions of Group V. are mainly restricted to the *pentavalent* compounds; it is of interest to note that the oxychloride has analogues in the *trivalent* antimony and bismuth basic chlorides,  $SbOCl$  and  $BiOCl$ . Trivalent vanadium also displays considerable analogy, however, with other trivalent transitional elements, as shown by the following:—

(a) A series of vanadium alums, e.g.  $V_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ , is known which are isomorphous with the alums furnished by trivalent iron, chromium, cobalt, manganese and titanium.

(b) Double cyanides of trivalent vanadium have been prepared which show the properties of co-ordinated compounds, e.g.  $K_3[V(CN)_6]$ ; compare with  $K_3[Cr(CN)_6]$  and  $K_3[Fe(CN)_6]$ .

(c) Double thiocyanates of corresponding compositions are also known, e.g.  $3KSCN \cdot V(SCN)_3 \cdot 4H_2O$ ; compare with  $3KSCN \cdot Cr(SCN)_3 \cdot 4H_2O$  and  $3KSCN \cdot Mo(SCN)_3 \cdot 4H_2O$ .

(d) Ammines of trivalent vanadium have recently been obtained

which are closely analogous to the cobalt-ammines, *e.g.*  $[V(NH_3)_6]Cl_3$ ; compare with  $[Cr(NH_3)_6]Cl_3$  and  $[Co(NH_3)_6]Cl_3$ .

The hydroxide  $V(OH)_3$  is distinguished from the corresponding hydroxides of phosphorus, arsenic and antimony in that it is wholly basic. It is insoluble in alkalis, so that there do not exist any compounds of vanadium which would correspond to the phosphites, arsenites, and antimonites, or to the ferrites, aluminates, and chromites.

In addition to the halides the only trivalent salt of niobium is the uncertain double sulphate  $(NH_4)_2SO_4 \cdot Nb_2(SO_4)_3 \cdot 6H_2O$ . Tantalum has not given any trivalent salts.

*Divalent Compounds.*—In divalent vanadium compounds the basic character is at a maximum. As might be anticipated these salts are extremely strong reducing agents, and evolve hydrogen from their aqueous solutions. Analogy with other transitional elements in the divalent state is again shown: (*a*) In the formation of double cyanides, *e.g.*  $K_4[V(CN)_6]$ ; compare with  $K_4[Cr(CN)_6]$  and  $K_4[Fe(CN)_6]$ ; and (*b*) in the isomorphism and analogous composition of some of the sulphates, *e.g.*  $VSO_4 \cdot 7H_2O$  is isomorphous with  $FeSO_4 \cdot 7H_2O$ , and also forms mixed crystals with  $CrSO_4 \cdot 7H_2O$  and  $MgSO_4 \cdot 7H_2O$ . It is of interest to note that the stability of the divalent salts of the even members of the first long series, Ti, V, Cr, Mn, Fe, Co, Ni, increases with increase in atomic weight of the metals. Divalent titanium compounds are also decomposed by water with evolution of hydrogen, whereas ferrous sulphate solution is stable in the absence of air, and nickel sulphate solution does not oxidise under ordinary conditions of exposure. Substitution of a molecule of ammonium sulphate for a molecule of water in the hydrated sulphates imparts stability to the compounds; thus both the solid double sulphates,  $VSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  and  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ , are less easily oxidised on exposure to air than are the simple salts.

Niobium and tantalum so far have not appeared to give rise to divalent salts, but evidence for the existence of divalent chlorides of these elements has recently been obtained.<sup>1</sup>

It will perhaps have been observed from the foregoing outline of the chemistry of vanadium, niobium, and tantalum that while these three elements form a closely related triad, vanadium undoubtedly possesses many chemical characteristics that are not displayed by either niobium or tantalum. Indeed the last two elements are so closely parallel in their reactions that considerable time elapsed before their separate identities were definitely established, and their separation from one another is still not an easy matter. The natural occurrence of the three elements under discussion is also here worthy of note, for while vanadium is almost always found in association with phosphorus and other elements of Group V., niobium and tantalum invariably occur with metals belonging to other groups, namely, iron, manganese, zirconium, titanium, and the rare earths, suggesting that the genesis of niobium and tantalum is different from that of vanadium. In this volume the occurrence, history, extraction, detection, and estimation of niobium and tantalum will be considered together in Chapter V.

<sup>1</sup> See pp. 149 and 192.

## CHAPTER II.

### VANADIUM AND ITS ALLOYS.

Symbol, V. Atomic Weight, 50.95 (O=16)..

**Occurrence.**—Although vanadium does not occur free in nature, compounds of vanadium occur widely distributed in small quantities in many rocks, and even in the ashes of plants. According to Clarke,<sup>1</sup> the amount of vanadium in the earth's crust is 0.017 per cent. The corresponding figures for copper, zinc, and lead are 0.0104 per cent., 0.0039 per cent., and 0.0020 per cent. respectively, so that it is incorrect to refer to vanadium as a "rare" element, although it is true that vanadium ores from which the metal can be economically extracted occur in only a few localities. The principal industrial deposit is an impure vanadium sulphide, containing considerable quantities of free sulphur and carbonaceous matter, known as *patronite*, after its discoverer, and found in Peru. Analysis gave the following composition (per cent.):<sup>2</sup> S, 58.79; V, 19.53; SiO<sub>2</sub>, 6.88; C, 3.47; Fe, 2.92; Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>, 2.00; TiO<sub>2</sub>, 1.53; Ni, 1.87; Fe<sub>2</sub>O<sub>3</sub>, 0.20; Mo, 0.18; O, 0.38; H<sub>2</sub>O, 1.90. Total=99.65 per cent. Particulars of the most important ores are set out in the table on the next page.

Vanadium ores are mainly of igneous origin. The vanadium sources which are of present or potential economic value can be classified under several headings.<sup>3</sup>

I. In association with titaniferous *magnetites* and *ilmenites*. The best known deposit of this type is the Taberg iron ore in Sweden, where vanadium was first definitely discovered.

II. In veins of hydrothermal origin, where the vanadium is associated with either uranium or gold. This division includes *roscoelite* and *mottramite*.

III. In sulphide ores in which the mineral is associated with hydrocarbons. This class includes the *patronite* deposits of Peru and various vanadium-bearing *asphaltites*. It is probable that these *asphaltites* are the residuary seepage of petroleum deposits, and that they have been formed by the action of (a) hydrocarbons and (b) sulphur or hydrogen sulphide on a fairly porous rock which has been impregnated with a vanadium compound.

IV. In the oxidised upper levels of certain veins of lead and copper. This class is numerous and widely distributed, and includes the various vanadates of lead, copper, zinc, etc. They may have been formed by

<sup>1</sup> Clarke, *The Data of Geochemistry*, Bulletin 616, U.S. Geol. Survey, Washington, 1916.

<sup>2</sup> Hillebrand, *Amer. J. Sci.*, 1907, [iv], 24, 141.

<sup>3</sup> See Monograph on *Vanadium Ores*, Imperial Institute, London, 1924, p. 4.

## MINERALS CONTAINING VANADIUM.

ame.	Locality.	Density.	Proximate Formula.	Authorities.
vanadinite	Peru . . .	2.65	$V_2S_5 + nS$	Hillebrand, <i>loc. cit.</i> ; Hewett, <i>Trans. Amer. Inst. Min. Eng.</i> , 1910, 40, 274.
vanadinite	Colorado, Utah, Australia.	4.14	$2U_2O_3 \cdot V_2O_5 \cdot K_2O \cdot 3H_2O$	Friedel and Cumenge, <i>Compt. rend.</i> , 1899, 128, 532; Boutwell, <i>Bulletin</i> 260, <i>U.S. Geol. Survey</i> , 1904, pp. 200-210; Fritchle, <i>Chem. News</i> , 1900, 82, 258; Hillebrand and Ransome, <i>Amer. J. Sci.</i> , 1900, [iv], 10, 120; Crook and Blake, <i>Min. Mag.</i> , 1910, 15, 271; Wherry, <i>Amer. J. Sci.</i> , 1912, [iv], 33, 574; Hillebrand, <i>ibid.</i> , 1913, [iv], 35, 439; Lind and Whittemore, <i>J. Amer. Chem. Soc.</i> , 1914, 36, 2066; Plum, <i>ibid.</i> , 1915, 37, 1797; Schlundt, <i>J. Phys. Chem.</i> , 1916, 20, 485; Loomis and Schlundt, <i>J. Ind. Eng. Chem.</i> , 1916, 8, 990; Schoep, <i>J. Chem. Soc., Abs.</i> , 1923, ii, 124, 870; Cannori and Postelli, <i>Gazzetta</i> , 1924, 54, 561; Kammer and Silverman, <i>J. Amer. Chem. Soc.</i> , 1925, 47, 2514.
vanadinite	Colorado, California, W. Australia.	2.90	(A muscovite containing about 28.6 per cent. $V_2O_5$ .)	Roscoe, <i>Proc. Roy. Soc.</i> , 1876, 25, 109; Hillebrand, <i>Amer. J. Sci.</i> , 1899, 7, 451; <i>ibid.</i> , 1900, 10, 120; Pearce, <i>J. Chem. Soc., Abs.</i> , 1903, ii, 84, 380.
vanadinite	Arizona, Mexico, Argentine, Spain, Transvaal, Scotland, Ireland.	6.60-7.23	$3Pb_3(VO_4)_2 \cdot PbCl_2$	Rose, <i>Pogg. Annalen</i> , 1833, 29, 455; Roscoe, <i>Phil. Trans.</i> , 1868, 158, 1; Schrauf, <i>Proc. Roy. Soc.</i> , 1871, 451; Storey-Maskelyne and Flight, <i>J. Chem. Soc.</i> , 1872, 25, 1053; Frenzel, <i>Jahrb. Miner.</i> , 1875, 673; Nordström, <i>ibid.</i> , 1879, 895; Nordstrom, <i>Ber.</i> , 1879, 12, 1723; Silliman, <i>J. Chem. Soc., Abs.</i> , 1881, 40, 1108; Rammelsberg, <i>Jahrb. Miner.</i> , 1881, 2, 26; Wobsky, <i>ibid.</i> , 1881, 2, 24, 25; Blake, <i>Amer. J. Sci.</i> , 1884, [iii], 28, 145; Doring, <i>Jahrb. Miner.</i> , 1885, 1, 204; Genth and vom Rath, <i>Zeitsch. Kryst. Min.</i> , 1885, 10, 458; Penfield, <i>Amer. J. Sci.</i> , 1886, [iii], 32, 441; Genth, <i>Jahrb. Miner.</i> , 1888, 187; Collie, <i>J. Chem. Soc.</i> , 1889, 55, 94; Lovisato, <i>Atti R. Accad. Lincei</i> , 1903, [v], 12, ii, 81; Comucci, <i>ibid.</i> , 1926, [vi], 3, 335; Carobbi and Restaino, <i>Gazzetta</i> , 1926, 56, 59.

MINERALS CONTAINING VANADIUM—*continued.*

Name.	Locality.	Density.	Proximate Formula.	Authorities.
Desclozite	La Plata, Nevada, N.W. Rhodesia.	5.9-6.2	$2\text{Pb}(\text{Zn})\text{O}\cdot\text{V}_2\text{O}_5$	Damour, <i>Ann. Chim. Phys.</i> , 1854, [3], 41, 72; Hillebrand, <i>Amer. J. Sci.</i> , 1889, [3], 37, 434; Penfield, <i>ibid.</i> , 1883, [iii], 26, 361; see also Schrauf, <i>loc. cit.</i> ; Frenzel, <i>loc. cit.</i> ; Silliman, <i>loc. cit.</i> ; Rammelsberg, <i>loc. cit.</i> ; Websky, <i>loc. cit.</i> ; Genth and vom Rath, <i>loc. cit.</i> ; Genth, <i>loc. cit.</i> ; Bensaude, <i>J. Chem. Soc., Abs.</i> , 1921, 120, 54.
Deschenite	Germany . . .	5.6-5.81	$\text{Pb}(\text{Zn})\text{VO}_4$	Bergemann, <i>Pogg. Annalen</i> , 1850, 80, 393; Tschermak, <i>Pogg. Annalen</i> , 1862, 117, 349; Schrauf, <i>ibid.</i> , 1862, 116, 355.
Mottramite	Cheshire, Eng- land.	5.89	$3(\text{PbCu})(\text{VO}_4)_2$	Roscoe, <i>Proc. Roy. Soc.</i> , 1876, 25, 109; Silliman, <i>loc. cit.</i> ; Rammelsberg, <i>loc. cit.</i>
Chileite . . .	Chili . . .	..	$3\text{Cu}_2\text{O}\cdot 3\text{PbO}\cdot\text{V}_2\text{O}_5$	Domeyko, <i>Ann. Mines</i> , 1850, [4], 19, 145; <i>Compt. rend.</i> , 1847, 24, 793; Silliman, <i>loc. cit.</i>
Psittacinite	Montana . . .	..	$3(\text{PbCu})(\text{VO}_4)_2\cdot 3\text{Cu}(\text{OH})_2\cdot 6\text{H}_2\text{O}$	Genth, <i>Amer. J. Sci.</i> , 1876, [3], 12, 32; Pisani, <i>Compt. rend.</i> , 1881, 92, 1292; Döring, <i>loc. cit.</i> ; Rammelsberg, <i>loc. cit.</i>
Volborthite	Urals . . .	3.55	$3(\text{CuCa})(\text{VO}_4)_2\cdot\text{H}_2\text{O}$	Genth, <i>Jahresber.</i> , 1878, 1227; Silliman, <i>loc. cit.</i> ; Rammelsberg, <i>loc. cit.</i>
Sulvanite . . .	S. Australia . . .	4.0	$3\text{Cu}_2\text{S}\cdot\text{V}_2\text{S}_5$	Goyder, <i>J. Chem. Soc.</i> , 1900, 77, 1094.

the action of percolating vanadiferous waters on compounds of lead,<sup>1</sup> but their origin is doubtful.

V. In sedimentary rocks. These minerals also contain oxidised vanadium, and consist of vanadates of iron, aluminium, lead, copper, etc. The *carnotite* deposits of Colorado are of this type.

In Great Britain vanadium has been found associated with the lead ores at Wanlockhead, in the Lead Hills, Dumfriesshire, as *vanadinite*,<sup>2</sup> and associated with the copper deposits at Alderley Edge and at Mottram St. Andrews, Cheshire, as *mottramite*. The latter was at one time mined and treated for its vanadium, but commercially profitable supplies of this ore have now given out. Vanadium has also been reported to occur in titaniferous iron ores at Antrim,<sup>3</sup> and in rocks at Wicklow and Giant's Causeway.<sup>4</sup>

The foregoing account deals with the main distribution of vanadium; the presence of this element in very small quantities has also been established in a variety of substances. Among these the following

<sup>1</sup> Ditte, *Compt. rend.*, 1904, 138, 1303.

<sup>2</sup> Collie, *J. Chem. Soc.*, 1889, 55, 94.

<sup>3</sup> Hodges, *Chem. News*, 1872, 26, 238.

<sup>4</sup> Apjohn, *ibid.*, 1872, 26, 183; Sonstadt, *ibid.*, 1872, 26, 214; Thomson, *Jahrb. Miner.*, 1837, 322.

may be mentioned: Clays and shales,<sup>1</sup> *bauxite*, *cryolite*, *rutile*<sup>2</sup> and *pitchblende*. Vanadium is absorbed by plants from the soil, and hence is found in the ash of some coals and lignites;<sup>3</sup> a lignite from San Rafael, Argentine, gave 0.63 per cent. of ash which contained 38.22 per cent. of vanadium estimated as the pentoxide,<sup>4</sup> and the flue dust from the burning of a South Yorkshire coal contained an appreciable proportion of vanadium.<sup>5</sup> The presence of vanadium has been observed in petroleum hydrocarbons, asphalt, volcanic sublimations on Mount Vesuvius,<sup>6</sup> and meteorites;<sup>7</sup> in technical products, e.g. caustic potash, sodium carbonate;<sup>8</sup> and in the blood-cells of certain *ascidia*,<sup>9</sup> where it apparently replaces iron.

**History.**—In 1801 Manuel del Rio discovered the presence of a new metallic substance, which was subsequently called *erythronium*, in a lead ore found at Zimapan in Mexico. The discovery was communicated to the Académie des Sciences de Paris,<sup>10</sup> and the ore was examined by Collet-Descostils, who reported, however, that the new metal was impure chromium.<sup>11</sup> In 1830 Sefström definitely established the presence of a new element in a remarkably tenacious and ductile specimen of wrought iron which had been prepared from Taberg (Småland) ore. To this Sefström gave the name *vanadium*, from Vanadis, a cognomen of the Scandinavian goddess Freia.<sup>12</sup> About the same time Wöhler re-examined the Zimapan ore and found del Rio's *erythronium* to be identical with vanadium.<sup>13</sup> Considerable numbers of vanadium compounds were then prepared and examined by Berzelius, who formed the conclusion that vanadium belonged to the same family as chromium and molybdenum.<sup>14</sup> This conclusion was subsequently shown by Roscoe to be in error, because Berzelius had been handling the oxide or nitride when he thought he was dealing with the free metal. This error was due to the extreme difficulty experienced in reducing vanadium compounds to the metal. Roscoe conducted some classical researches on vanadium from 1868 to 1870, and found that the metal forms an oxide, VO, which enters into reactions as the vanadyl radical [VO]<sup>·</sup>, in an analogous manner to the uranyl radical [UO<sub>2</sub>]<sup>·</sup>. He also established the intimate relation that exists between vanadium and the members of the nitrogen family.<sup>15</sup> Ditte continued the work by his extensive investigations into the preparation and behaviour of a large number of vanadium compounds.<sup>16</sup>

<sup>1</sup> Phipson, *Chem. News*, 1863, 7, 210.

<sup>2</sup> Deville, *Ann. Chim. Phys.*, 1861, [iii], 61, 309, 342.

<sup>3</sup> Baskerville, *J. Chem. Soc.*, 1899, 76, 666; Mingaye, *ibid.*, 1904, 86, 420.

<sup>4</sup> Kyle, *Chem. News*, 1892, 66, 211. <sup>5</sup> Ramage, *Nature*, 1927, 119, 783.

<sup>6</sup> Carobbi, *Atti R. Accad. Lincei*, 1926, [vi], 4, 306, 382.

<sup>7</sup> Apjohn, *J. Chem. Soc.*, 1874, 27, 104; Hasselberg, *Öfvers. K. Vet.-Akad. Förh.*, 1899, 56, 131, from *J. Chem. Soc., Abs.*, 1901, 80, ii, 251.

<sup>8</sup> Thorpe, *J. Chem. Soc.*, 1872, 25, 660; Robinson, *Chem. News*, 1894, 70, 199; Smith, *ibid.*, 1890, 61, 20.

<sup>9</sup> Henze, *Zeitsch. physiol. Chem.*, 1911, 72, 494.

<sup>10</sup> Humboldt, *Gilbert's Annalen*, 1804, 18, 118.

<sup>11</sup> Descostils, *Ann. Chim. Phys.*, 1805, [i], 53, 260; *Gilbert's Annalen*, 1822, 71, 7.

<sup>12</sup> Sefström, *Pogg. Annalen*, 1831, 21, 43.

<sup>13</sup> Wöhler, *ibid.*, 1831, 21, 49.

<sup>14</sup> Berzelius, *ibid.*, 1831, 22, 1.

<sup>15</sup> Roscoe, *Phil. Trans.*, 1863, 153, 1; 1869, 159, 679; 1870, 160, 317.

<sup>16</sup> Ditte, *Compt. rend.*, 1883, 96, 846; 1885, 101, 698, 1487; 1886, 102, 757, 918, 1019, 1105, 1310; 1886, 103, 55; 1887, 104, 902, 982, 1061, 1168, 1705, 1844; 1887, 105, 813, 1067; 1888, 106, 270.



Roscoe obtained his vanadium from the residual lime precipitate which was thrown down during the extraction of cobalt from the copper deposits at Alderley Edge and Mottram St. Andrews in Cheshire, England. Although the total amount of vanadium in the ore was only small (the lime precipitate contained about 2 per cent. of vanadium), these deposits for a long time formed an important source of supply of vanadium compounds. Until the year 1900 the only industrial applications of vanadium compounds lay in their employment as catalysts in the manufacture of aniline-black, and in their use as mordants in dyeing and calico-printing. The Cheshire source for these purposes was supplemented and later displaced by supplies obtained from the Spanish lead mines and from the basic steel slags produced at Le Creusot Steel Works in France. It was found that these slags contained over 1 per cent. of vanadium.<sup>1</sup>

The industrial application of vanadium received its main impetus, however, when the metal entered the domain of metallurgy. In 1893 Moissan applied his electric furnace to the making of alloys of vanadium, and produced ferrovanadium in large quantity. The mechanical properties of vanadium steels were noted by Hélouis in 1896,<sup>2</sup> but were first thoroughly investigated at Sheffield, England, by Professor Arnold in 1900 (see p. 26), whose work was followed by that of Sankey and Smith in 1904.<sup>3</sup> The discovery of the vast Peruvian deposits in 1905 was followed by the successful preparation from them of a ferrovanadium alloy which could readily be employed in the manufacture of vanadium steels. This process now absorbs nearly all the world's production of vanadium.

**Commercial Sources of Vanadium.**—The world's most important vanadium supply comes from the deposits of *patronite* in Peru. The ore occurs in the coal deposits at Minas Raga, and is essentially a sulphide of vanadium containing 10 per cent. or more of vanadium and 30 per cent. or more of free sulphur.<sup>4</sup> The substance is hard, and has the appearance of a black, slaty coal. The surrounding earth is impregnated with vanadates or other vanadium compounds, and contains numerous deposits of *asphaltites*, the ash from which yields from 20 to 40 per cent. of vanadium pentoxide. The patronite deposits are supposed to have been formed by the upward movement of asphaltic petroleum and its subsequent evaporation, the vanadium being derived from the vegetable matter which gave rise to the petroleum. The mines at Minas Raga are the highest in the world, and are about 16,000 feet above sea-level. The ore is here submitted to a preliminary roasting, whereby the vanadium content is increased to about 20 per cent. with almost total elimination of sulphur. The mines are connected by rail to Callao, whence shipment of the material takes place to the United States for further treatment.

A secondary source of supply lies in the *carnotite* deposits of Colorado and Utah. The vanadium content in these is very low, being only about 1 per cent. or even less, and the ore is really worked for its radium and uranium content, the vanadium forming a by-product. The deposits of *carnotite* are considerable.

<sup>1</sup> Witz and Osmond, *Chem. News*, 1882, 46, 47.

<sup>2</sup> Hélouis, *J. Soc. Chem. Ind., Abs.*, 1896, 15, 657.

<sup>3</sup> Sankey and Smith, *J. Soc. Chem. Ind.*, 1905, 24, 444.

<sup>4</sup> Hillebrand, *Amer. J. Sci.*, 1907, [iv], 24, 141.

Commercial sources of vanadium which are now disused are the *roscoelite* deposits in Colorado, the *vanadinite* deposits near Santa Marta in Spain, and the *mottramite* deposits in Cheshire and Shrewsbury.<sup>1</sup> It is of some interest to note that efforts are being made to extract the vanadium from the Taberg iron ores or slags, in which vanadium was originally discovered,<sup>2</sup> and from the Rhodesian deposits.<sup>3</sup>

### Extraction of Vanadium.

For industrial purposes vanadium is not required in the elemental state. More than 90 per cent. of the world's production of vanadium is used in the manufacture of special steels, for which purpose an iron-vanadium alloy, known as *ferrovanadium*, containing from 30 to 40 per cent. of vanadium, is marketed. The method of manufacture of this alloy from vanadium-bearing ores varies considerably with the composition of the ore and the value of the by-products. The process is conveniently divided into two stages :

- I. The preparation of a complex mixture of vanadates or of crude vanadium pentoxide or of crude iron vanadate.
- II. The conversion of these products into the iron-vanadium alloy.

#### I. *The Preparation of a Complex Mixture of Vanadates or of Crude Vanadium Pentoxide or of Crude Iron Vanadate.*

A. *Dry Process.*—The ore is roasted in a reverberatory furnace of about eighty tons capacity. The time occupied in passing the ore through the furnace is about two days, this time being necessary in order to burn off the asphaltic material which, together with any free sulphur also present, renders the addition of fuel unnecessary except towards the end of the heating. The roasted product contains from 40 to 50 per cent. of vanadium pentoxide and not more than 0.5 per cent. of sulphur, the rest being made up of silica, alumina, lime, magnesia, iron and nickel in varying proportions. This material is mixed with suitable fluxes and subjected to a matte smelting in a second reverberatory furnace. A matte is formed of all the foreign metals present in the ore, and a supernatant slag is produced, which contains all the vanadium combined with the gangue material (silica, lime, alumina, magnesia) as mixed vanadates.<sup>4</sup>

B. *Wet Processes.*—These vary considerably in detail according to the nature and amount of constituents other than vanadium in the ore. An outline of the operations involved in the case of *patronite* is as follows: The ore is roasted with common salt or sodium carbonate and then extracted either (a) with water to give an alkaline solution of sodium vanadate and soluble vanadates of other metals, any lead, zinc, copper, etc., being left in the residue; or (b) with sulphuric acid to produce a solution of vanadyl sulphate. Acid extraction is usually employed when the vanadium content of the material is low. The alkaline extract from (a) is treated with excess of sodium carbonate in order to precipitate calcium and aluminium, after removal of which,

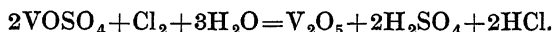
<sup>1</sup> Smith, *J. Soc. Chem. Ind.*, 1901, 20, 1183; Gerland, *ibid.*, 1901, 20, 1188; Gin, *Trans. Amer. Electrochem. Soc.*, 1909, 16, 409.

<sup>2</sup> See *Chem. Met. Eng.*, 1922, 27, 321; *Amer. Chem., Abs.*, 1925, 19, 3234; 1927, 21, 2638; Kjellberg, *Eng. and Min. J.*, 1927, 123, 521.

<sup>3</sup> Walker, *ibid.*, 1928, 125, 733.

<sup>4</sup> Saklatwalla, *Trans. Amer. Electrochem. Soc.*, 1920, 37, 341.

addition of ferrous sulphate throws down a precipitate of iron vanadate of uncertain composition.<sup>1</sup> The acid solution of vanadyl sulphate from (b) is either evaporated to a cake and the residue calcined to vanadium pentoxide, or the solution is treated directly with oxidising agents, e.g. hypochlorites, whereupon precipitation of vanadium pentoxide takes place :



For the treatment of *carnotite* several methods are available. The method recommended by the *United States Bureau of Mines*<sup>2</sup> is as follows: The ore is leached with concentrated nitric acid at 100° C., neutralised with caustic soda, and barium chloride and sulphuric acid added to the solution to precipitate the radium as barium-radium sulphate. The precipitate settles in three or four days, after which time the clear liquid is decanted into tanks and is treated with excess of boiling sodium carbonate solution in order to precipitate any iron, aluminium and chromium present. The solution now contains sodium uranyl carbonate and sodium vanadate. It is nearly neutralised with nitric acid, and caustic soda is added in sufficient quantity to precipitate the uranium as sodium uranate. After filtering, the remaining solution is neutralised with nitric acid and ferrous sulphate added, whereupon iron vanadate is thrown down. By this method it is claimed that 90 per cent. of the radium, all the uranium, and 50 per cent. of the vanadium in the *carnotite* are recovered.

Electrolytic methods for the separation of vanadates of the metals have also been suggested, but do not appear to have come into general use.<sup>3</sup>

## II. *The Conversion of the Products of the Previous Stage into Iron-Vanadium Alloys.*

The preparation of the iron-vanadium alloy from the crude vanadates obtained in any of the foregoing processes is carried out almost entirely at Bridgville, Pennsylvania. The process consists in reduction of the material with carbon in the electric furnace. Three graphite rods of 12-inch diameter are suspended in an intimate mixture of vanadium compound, iron ore or scale, fluxing agent (lime or fluorspar), and coke, contained in a cast-iron furnace lined successively with bricks and carbon blocks. The material is moved by a worm-conveyor into the high-temperature zone, and thence is immediately removed in order to prevent reoxidation of the vanadium. Two tap-holes are provided, one for alloy and one for slag, and continuous feed is employed.<sup>4</sup> A good sample of the alloy produced in this manner gave the following analysis:—

Fe . . . . .	48·65 per cent.	Al . . . . .	0·31 per cent.
V . . . . .	49·20 „	Mn . . . . .	0·32 „
Si . . . . .	0·72 „	S . . . . .	0·15 „
C . . . . .	0·55 „	Ni . . . . .	0·10 „

<sup>1</sup> Saklatwalla, *loc. cit.*; Bleecker, *Met. Chem. Eng.*, 1911, 9, 499.

<sup>2</sup> See *U.S. Bureau of Mines*, Bulletin 104, 1915, p. 30; also Conley, *Chem. Met. Eng.*, 1919, 20, 514; d'Aguiar, *ibid.*, 1921, 25, 825; Doerner, *ibid.*, 1924, 31, 429; Thews and Heinle, *J. Ind. Eng. Chem.*, 1923, 15, 1159.

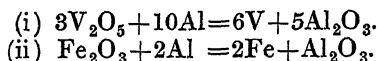
<sup>3</sup> Bleecker, *loc. cit.*

<sup>4</sup> Scott, *The Engineer*, 1923, 136, 636; Saklatwalla, *J. Ind. Eng. Chem.*, 1922, 14, 968; *Electrical World*, 1923, 81, 452.

The usual vanadium content of commercial ferrovanadium is, however, between 30 and 40 per cent.<sup>1</sup>

Carbon has a great tendency to combine with vanadium to form carbides, the presence of which in the alloy renders it unsuitable for use in steel manufacture. The successful employment of carbon as the reducing agent is in fact quite recent. Formerly silicon, an iron-silicon alloy, or aluminium was used in place of carbon, but it was difficult to obtain a product which was free from silicon or aluminium, and considerable loss of vanadium took place in the slags.<sup>2</sup>

Modifications of the Goldschmidt thermite process may also be employed for the preparation of the iron-vanadium alloy. The crushed vanadates or vanadium pentoxide are mixed with the necessary amount of iron scalings or turnings and fluxes, and introduced into a gas-fired open-hearth furnace or into an iron crucible provided with a refractory lining and previously heated to redness. The reactions taking place are :



With a vertical-shaft furnace a much higher temperature, 2500° to 2800° C., and a much larger output can be obtained than with a crucible. A furnace 9 feet 3 inches high and 4 feet 6 inches wide will produce 125,000 lb. of alloy in one "run."<sup>3</sup>

**Preparation of Vanadium.**—There is no demand for pure vanadium, and the isolation of the metal is therefore not an industrial process. Even on the small scale the operation is attended with considerable difficulty, owing to the very high temperature necessary for the reduction of vanadium compounds and the tendency for re-oxidation to take place. The following methods have given products of variable purity :—

(i) *Modifications of the Goldschmidt Process.*—Vanadium pentoxide,  $\text{V}_2\text{O}_5$ , is mixed with twice its weight of an alloy of the rare earths obtained in the manufacture of thorium nitrate, and consisting roughly of 45 per cent. cerium, 20 per cent. lanthanum, 15 per cent. "didymium," and about 20 per cent. of other rare metals. The reaction is carried out in a magnesia-lined crucible and is started with a firing mixture of barium peroxide, potassium chlorate, and aluminium powder. Considerable evolution of heat takes place.<sup>4</sup> It is claimed that vanadium of 99.7 per cent. purity can be obtained by this method.<sup>5</sup> Samples of vanadium, which in some cases were 100 per cent. pure, have recently been obtained by reducing the pentoxide with a mixture of finely milled calcium and calcium chloride in a bomb heated electrically for an hour at 900° to 950° C. The presence of hydrogen or carbon should be avoided, and the operation is best conducted *in vacuo*.<sup>6</sup>

Vanadium pentoxide is not easily reduced by means of aluminium,<sup>7</sup>

<sup>1</sup> For analyses of other samples see Monograph on *Vanadium Ores*, Imperial Institute, London, 1924, p. 13; Fourment, *Revue de Métallurgie*, 1926, 23, 135.

<sup>2</sup> Saklatwalla, *loc. cit.*; Vogel, *J. Soc. Chem. Ind.*, 1924, 43, 367.

<sup>3</sup> Matignon and Monnet, *Compt. rend.*, 1902, 134, 542; Saklatwalla, *Trans. Amer. Electrochem. Soc.*, 1920, 37, 341; *Chem. and Met. Eng.*, 1922, 26, 1141.

<sup>4</sup> Muthmann, *Chem. Zeit.*, 1904, 28, 506; Weiss and Aichel, *Annalen*, 1904, 337, 380.

<sup>5</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 59.

<sup>6</sup> Marden and Rich, *J. Ind. Eng. Chem.*, 1927, 19, 786.

<sup>7</sup> Goldschmidt, *Zeitsch. Elektrochem.*, 1898, 4, 494; Hittorf, *Physikal. Zeitsch.*, 1903, 4, 196.

which also tends to alloy with the product.<sup>1</sup> Even with the addition of carbon, calcium fluoride, or calcium carbide to the reaction mixture, complete reduction does not ensue.<sup>2</sup> Meyer and Backa obtained vanadium of only 93.5 per cent. purity using vanadium pentoxide and aluminium as in the Goldschmidt process.<sup>3</sup> Vogel and Tammann claim to have prepared vanadium of more than 99.07 per cent. purity by the same method, but did not ascertain the conditions necessary for success.<sup>4</sup> Ruff and Martin prepared 95 per cent. pure vanadium by using vanadium trioxide,  $V_2O_3$ , and aluminium.<sup>5</sup>

The use of calcium in place of the rare-earth alloy as the reducing agent gives a product containing from 91 to 93 per cent. of vanadium, while a mixture of calcium and aluminium produces 94.5 per cent. pure vanadium.<sup>6</sup> Lithium has been used as reducing agent, vanadium of 99 per cent. purity being claimed.<sup>7</sup>

(ii) *Reduction of Chlorides.*—Roscoe reduced vanadium dichloride,  $VCl_2$ , at a bright red heat with hydrogen, every precaution being taken to prevent the entry of moisture and oxygen into the apparatus. The product was 95.8 per cent. pure metal, the impurity being mainly hydrogen. This method is of interest in that by its means metallic vanadium was first obtained; the process is, however, very slow.<sup>8</sup> Reduction of the chlorides of vanadium by means of sodium gives a product of doubtful purity.<sup>9</sup> Billy claims to have prepared pure vanadium by passing the vapour of vanadium tetrachloride,  $VCl_4$ , over sodium hydride, prepared *in situ*, at  $400^\circ C$ .<sup>10</sup>

(iii) *Electrolytic Reduction at High Temperatures.*—The deposition of metallic vanadium by electrolysis of a solution of a vanadium salt at ordinary pressures has not hitherto proved successful.<sup>11</sup> The reason is that vanadium compounds of low valency frequently decompose water with evolution of hydrogen and undergo oxidation with increase of valency, so that the formation of the free metal does not ensue. The electrolytic isolation of other strongly electropositive metals is attended with the same difficulty. Electrolysis of anhydrous fused vanadium salts or reduction of vanadium oxides in the electric furnace can, however, be successfully employed.<sup>12</sup> Thus, the metal has been obtained by electrolyzing vanadium trioxide or pentoxide dissolved in a bath of molten vanadium tetrafluoride and calcium fluoride. The anode is made of carbon and the cathode of lead. A lead-vanadium alloy is obtained from which the lead is subsequently volatilised. This process is similar

<sup>1</sup> Moissan, *Compt. rend.*, 1896, 122, 1297.

<sup>2</sup> Koppel and Kaufmann, *Zeitsch. anorg. Chem.*, 1905, 45, 352; Prandtl and Bleyer, *Ber.*, 1910, 43, 2602.

<sup>3</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

<sup>4</sup> Vogel and Tammann, *ibid.*, 1909, 64, 225.

<sup>5</sup> Ruff and Martin, *Zeitsch. angew. Chem.*, 1912, 25, 49; but compare Prandtl and Manz, *Zeitsch. anorg. Chem.*, 1912, 79, 209.

<sup>6</sup> Prandtl and Bleyer, *ibid.*, 1909, 64, 217.

<sup>7</sup> Baughman, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 305, but details of his method are not given.

<sup>8</sup> Roscoe, *Phil. Trans.*, 1869, 159, 679.

<sup>9</sup> Roscoe, *loc. cit.*; Setterberg, *Öfvers. K. Vet.-Akad. Förh.*, 1882, 39, No. 10, 13; Prandtl and Manz, *Zeitsch. anorg. Chem.*, 1912, 79, 209; Hunter and Jones, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 28.

<sup>10</sup> Billy, *Compt. rend.*, 1914, 158, 578.

<sup>11</sup> Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 175.

<sup>12</sup> Compare Marden and Rich, *J. Ind. Eng. Chem.*, 1927, 19, 786.

to the Héroult method for the extraction of aluminium.<sup>1</sup> Gin electrolysed molten calcium fluoride using a steel cathode and an anode composed of a mixture of carbon and vanadium trioxide,  $V_2O_3$ . Vanadium trifluoride is formed on the anode, passes into the molten electrolyte and is then decomposed, the vanadium being deposited on the cathode.<sup>2</sup> Beckman electrolysed a vanadium oxide in a bath of molten lime.<sup>3</sup>

(iv) *Reduction of Oxides of Vanadium in the Electric Furnace.*—The reduction of vanadium pentoxide or trioxide by means of carbon yields a product which contains some of the carbon as carbide.<sup>4</sup> Friederich and Sittig were unable to obtain a sample containing more than 82 per cent. of vanadium when they reduced a mixture of vanadous oxide,  $V_2O_3$ , and carbon in an atmosphere of hydrogen.<sup>5</sup> Using sugar-charcoal and carrying out the reduction in an atmosphere of hydrogen in an electric furnace, Moissan was able to reduce the carbon content to 4.4 per cent.<sup>6</sup> Ruff and Martin obtained 98.11 per cent. vanadium by heating to  $1950^\circ\text{C}$ . a mixture of vanadium carbide and vanadium trioxide pressed into a rod in a zirconia crucible.<sup>7</sup> The reduction of vanadium trioxide has also been effected by passing an electric current through rods of the material in a good vacuum,<sup>8</sup> and by the action of hydrogen at a pressure of 5 atmospheres and a temperature of  $2500^\circ\text{C}$ .<sup>9</sup>

The isolation of vanadium can be effected on a very small scale, suitable as a lecture experiment, by passing an electric current through a platinum wire filament immersed in vanadium oxytrichloride,  $VOCl_3$ , either *in vacuo* or in an atmosphere of hydrogen.<sup>10</sup> The metal is obtained as a smooth, silver-grey deposit.

### Physical Properties of Vanadium.

The reported data are not always in good agreement owing to the fact that vanadium in varying conditions of purity has been used for the determination of constants by the various investigators. Vanadium has been variously described as: a bright grey metal which appears as lustrous, silver-white crystals under the microscope;<sup>11</sup> a grey powder in which glistening, needle-like crystals can be seen with the naked eye;<sup>12</sup> small crystals, of differing crystalline form, which appear blue or olive-green on the surface, and which possess flat, glistening faces;<sup>13</sup> silvery, well-formed crystals of twin rhomboids, belonging to the hexagonal system;<sup>14</sup> similar in appearance to cast

<sup>1</sup> Baughman, *Trans. Amer. Electrochem. Soc.*, 1909, 16, 439.

<sup>2</sup> Gin, *Zeitsch. Elektrochem.*, 1903, 9, 831; Baughman, *Trans. Amer. Electrochem. Soc.*, 1909, 16, 442.

<sup>3</sup> Beckman, *ibid.*, 1911, 19, 171.

<sup>4</sup> Moissan, *Compt. rend.*, 1893, 116, 1225.

<sup>5</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 143, 303.

<sup>6</sup> Moissan, *Compt. rend.*, 1896, 122, 1297.

<sup>7</sup> Ruff and Martin, *Zeitsch. angew. Chem.*, 1912, 25, 49.

<sup>8</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45; compare Baughman, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 310.

<sup>9</sup> Wartenberg, Broy, and Reinicke, *Zeitsch. Elektrochem.*, 1923, 29, 214.

<sup>10</sup> Edson and McIntosh, *Trans. Roy. Soc. Canada*, 1915, [iii], 9, 81.

<sup>11</sup> Roscoe, *Phil. Trans.*, 1869, 159, 679.

<sup>12</sup> Setterberg, *Öfvers. K. Vet.-Akad. Förh.*, 1882, 39, No. 10, 13.

<sup>13</sup> Brögger and Flink, *Zeitsch. Kryst. Min.*, 1884, 9, 232.

<sup>14</sup> Weiss and Aichel, *Annalen*, 1904, 337, 380.

iron which is rich in carbon, and sometimes forms long prisms.<sup>1</sup> X-ray analysis shows, however, that vanadium possesses a body-centred cubic lattice crystal of side equal to 3.04 Å; the distance between the nearest atoms is 2.63 Å.<sup>2</sup> The metal is rather brittle but extremely hard; its hardness on Mohr's scale is 7.5, so that it cannot be scratched even by quartz or steel. The density of pure vanadium is 6.0 at 22° C.,<sup>3</sup> 6.025 at 15° C.<sup>4</sup> Other reported figures vary with the purity of the sample: 5.688 at 18.7° C. for a specimen 98 per cent. pure;<sup>5</sup> 5.53,<sup>6</sup> 5.5 at 15° C.,<sup>7</sup> 5.8 at 20° C.,<sup>8</sup> 5.97<sup>9</sup> and 5.987 at 20° C.<sup>10</sup> for samples about 95 per cent. pure. The melting-point of the purest vanadium obtainable is given as 1720° ± 20° C.<sup>11</sup> Other reported figures are 1650° C.,<sup>12</sup> 1680° C.,<sup>13</sup> about 1700° C.,<sup>14</sup> 1715° C.,<sup>15</sup> 1750° ± 30° C.,<sup>16</sup> below 1760° C.<sup>17</sup> The specific heat of vanadium is 0.120 between 20° and 100° C.,<sup>18</sup> 0.1153 between 0° and 100° C.,<sup>19</sup> 0.1240,<sup>20</sup> 0.1259,<sup>21</sup> 0.1235 to 0.1258.<sup>22</sup> The metal is non-magnetic; even when subjected to a temperature of -259° C. it gives only very feeble indication of ferromagnetism.<sup>23</sup> The specific electrical resistance of cold-worked vanadium metal is 26 × 10<sup>-6</sup> ohms per cc. at 20° C.; the temperature coefficient of resistance between 20° and 150° C. is 0.0028. Vanadium can be cold-rolled into wire; it has a tendency to become harder when so treated and annealing is beneficial. Photomicrographs of vanadium metal are given in the reference cited.<sup>24</sup>

The refractive index of vanadium is 3.03, the coefficient of absorption 3.51, and the reflexion capacity 57.5 per cent. for yellow light of wave-length  $\lambda = 5790$ .<sup>25</sup> Vanadium compounds do not impart any coloration to the ordinary Bunsen flame, and do not furnish any characteristic line spectra even in the oxyacetylene flame. The flame produced between carbon electrodes consists of a reddish-purple core with a yellowish-green shell and a red edge.<sup>26</sup>

<sup>1</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 58.

<sup>2</sup> Hull, *Phys. Review*, 1922, 20, 113.

<sup>3</sup> Marden and Rich, *J. Ind. Eng. Chem.*, 1927, 19, 788. This figure was given by the cold-worked metal.

<sup>4</sup> Muthmann, Weiss, and Riedelbauch, *loc. cit.*

<sup>5</sup> Ruff and Martin, *Zeitsch. angew. Chem.*, 1912, 25, 49.

<sup>6</sup> Hunter and Jones, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 28.

<sup>7</sup> Roscoe, *J. Chem. Soc.*, 1870, 23, 357.

<sup>8</sup> Moissan, *Compt. rend.*, 1896, 122, 1297.

<sup>9</sup> Hunter and Jones, *loc. cit.*

<sup>10</sup> Prandtl and Manz, *Zeitsch. anorg. Chem.*, 1912, 79, 209.

<sup>11</sup> Burgess and Waltenburg, *J. Washington Acad. Sci.*, 1913, 3, 371; Baughman, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 286.

<sup>12</sup> Arsem, *ibid.*, 1923, 43, 313.

<sup>13</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45 (determined by the Lummer photometric method).

<sup>14</sup> Marden and Rich, *loc. cit.*

<sup>15</sup> Ruff and Martin, *loc. cit.* (determined by extrapolation).

<sup>16</sup> Vogel and Tammann, *Zeitsch. anorg. Chem.*, 1908, 58, 73.

<sup>17</sup> Slade and Higson, *J. Chem. Soc.*, 1919, 115, 209.

<sup>18</sup> Marden and Rich, *loc. cit.*

<sup>19</sup> Mache, *Sitzungsber. K. Akad. Wiss. Wien*, 1897, 106, 590.

<sup>20</sup> Muthmann, Weiss, and Riedelbauch, *loc. cit.*

<sup>21</sup> Setterberg, *Öfvers. K. Vet.-Akad. Förh.*, 1882, 39, No. 10, 21.

<sup>22</sup> Matignon and Monnet, *Compt. rend.*, 1902, 134, 542.

<sup>23</sup> Honda, *Ann. Physik*, 1910, 32, 1027; Loring, *Chem. News*, 1914, 109, 122; Weiss and Onnes, *Compt. rend.*, 1910, 150, 687; Weiss and Collet, *ibid.*, 1924, 178, 2146.

<sup>24</sup> Marden and Rich, *J. Ind. Eng. Chem.*, 1927, 19, 787.

<sup>25</sup> Wartenberg, *Verh. Deut. physikal. Ges.*, 1910, 12, 105.

<sup>26</sup> Mott, *Trans. Amer. Electrochem. Soc.*, 1917, 31, 272.

Lockyer and Baxendall<sup>1</sup> investigated the arc spectrum of vanadium by volatilising vanadium chloride and vanadium oxide between poles of pure silver. Using a Rowland grating, over 650 lines were obtained in the region between  $\lambda$  3887 and  $\lambda$  4932, the more intense of which are indicated in the following table:—

ARC SPECTRUM OF VANADIUM.<sup>2</sup>

Wave-length.	Intensity of Line. Max. = 10.	Wave-length.	Intensity of Line. Max. = 10.	Wave-length.	Intensity of Line. Max. = 10.
3890.3	7	4123.6	7	4452.2	7
3902.4	10	28.2	9	60.5	7
09.9	9	32.1	9	89.1	7
90.7	7	34.6	9	4545.6	7
92.9	7	4341.2	7	60.9	7
98.9	7	53.0	7	77.3	8
4090.7	8	79.4	10	80.6	8
92.8	8	84.9	9	86.5	9
95.6	7	90.1	9	94.3	10
99.9	9	95.4	8	4619.9	7-8
4105.3	7	4400.7	8	4851.7	7
09.9	8	06.8	7	64.9	7
12.0	10	07.8	7	75.7	7
15.3	9	38.0	7	81.7	7-8
16.6	8	41.9	7		

The most intense lines produced by vanadium in the spark spectrum are set out in the table on the opposite page.<sup>3</sup>

The most *intense* lines in the spark spectrum of a metal are not necessarily the most *persistent* when solutions containing the metal in gradually increasing dilution are sparked.<sup>4</sup> By photographing the spectra given by solutions containing one gram of the metal, usually in the form of its chloride, in every 100, 1000, 10,000, and 100,000 parts of solution, it has been possible to draw up a table (p. 22) showing the

<sup>1</sup> Lockyer and Baxendall, *Proc. Roy. Soc.*, 1901, 68, 189.

<sup>2</sup> Earlier determinations than the above are those of Thalén (*Nova acta regiæ societatis scientiarum*, Upsala, 1868, [iii], 6, 9, 36), Hasselberg (*Kongliga Svenska vetenskaps Academiens Handlingar*, 1899, 32, 2), and Rowland and Harrison (*Astrophys. J.*, 1900, 7, 273, 373). More recently a fresh determination in the region  $\lambda$  2207 to  $\lambda$  4606 has been carried out by Ludwig (*Zeitsch. wiss. Photochem.*, 1917, 16, 157). Additional lines in the arc spectrum from  $\lambda$  4500 to  $\lambda$  9522 have been tabulated by Kiess and Meggers (*U.S. Bureau of Standards, Bulletin*, 1920, 16, 51), and the spectra produced by volatilisation of the metal in the electric furnace have been investigated by King (*Astrophys. J.*, 1915, 41, 86; 1924, 60, 282), Hemsalech (*Phil. Mag.*, 1920, [vi], 39, 241), and by Gieseler and Grotrian (*Zeitsch. für physik.*, 1924, 25, 342). Regularities in the structure of the vanadium arc spectrum have also recently been studied by Kiess and Meggers (*J. Washington Acad. Science*, 1923, 13, 317; 1924, 14, 151), Bechert and Sommer (*Zeitsch. für physik.*, 1925, 31, 1), and Meggers (*ibid.*, 1925, 33, 509).

<sup>3</sup> Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1898, 107, [2]; see also Eppley, *J. Franklin Inst.*, 1926, 201, 333, and Russell, *Astrophys. J.*, 1927, 66, 184, 233.

<sup>4</sup> Hartley, *Proc. Roy. Soc.*, A. 1902, 69, 283.



## SPARK SPECTRUM OF VANADIUM.

Wave-length.	Relative Intensity of Line. <sup>1</sup>	Wave-length.	Relative Intensity of Line. <sup>1</sup>	Wave-length.	Relative Intensity of Line. <sup>1</sup>
2366.4	16	3271.3	20	4023.5	20
71.2	18	76.3	20	35.8	16
82.6	16	80.0	16	80.6	26
93.7	18	3504.6	16	90.8	16
2405.3	16	17.5	20	4100.0	16
2526.8	16	24.9	16	15.4	16
28.0	18	30.9	20	28.3	16
93.2	16	45.4	20	32.2	16
95.2	16	56.9	20	83.7	16
2641.1	16	89.9	18	4379.4	40
44.5	16	92.2	18	84.9	40
49.5	16	93.5	16	90.2	30
55.8	16	3669.5	16	95.5	20
63.4	18	3727.5	16	00.8	18
2715.8	16	71.1	20	4489.1	16
3093.2	16	3952.1	18		
3190.8	16	4005.9	16		

most persistent lines under these conditions. The application of the knowledge of the residuary lines given by a metal renders possible its estimation in a solution of unknown strength. The quantitative spectrum of vanadium is as shown in the table on the next page.<sup>2</sup>

The following marks of identification are employed in the table :—

$\phi$  = seen with 1.0 per cent. solutions but not with 0.1 per cent. solutions.  
 $\chi$  = " 0.1 " " " " 0.01 " "  
 $\psi$  = " 0.01 " " " " 0.001 " "

Measurements of wave-lengths in X-ray high frequency spectra are given in the references cited.<sup>3</sup> The electron configuration of vanadium atoms has been investigated.<sup>4</sup> Attempts have been made to bombard the vanadium atom with the view to obtaining hydrogen nuclei, but without result.<sup>5</sup> Vanadium is not radioactive.<sup>6</sup>

<sup>1</sup> There is a general want of uniformity in the standards that have been adopted by different observers for measuring the relative intensities of spectral lines. The intensity figures given in this table and in the preceding table do not refer to a common standard of measurement.

<sup>2</sup> Pollok, *Proc. Roy. Dublin Soc.*, 1909, 11, 331; Baly, *Spectroscopy* (Longmans, London), 1927, 2, 144; see also de Gramont, *Compt. rend.*, 1920, 171, 1106.

<sup>3</sup> K series: Hjalmar, *Phil. Mag.*, 1921, 41, 675; Dolejssek, *Compt. rend.*, 1922, 174, 441; Siegbahn and Dolejssek, *Zeitsch. Physik*, 1922, 10, 159; Coster, *ibid.*, 1924, 25, 83; Walter, *ibid.*, 1924, 30, 357; Lindh, *ibid.*, 1925, 31, 210; Larsson, *ibid.*, 1926, 35, 401; Levi, *Trans. Roy. Soc. Canada*, 1924, [iii], 18, 159; Hendricks and Wyckoff, *J. Phys. Chem.*, 1927, 31, 703. L series: Thoræus, *Phil. Mag.*, 1926, [vii], 2, 1007.

<sup>4</sup> Samuel and Markowitz, *Zeitsch. Physik*, 1926, 38, 22; Lessheim and Samuel, *ibid.*, 1926, 40, 220; Gibbs and White, *Phys. Review*, 1927, 29, 359, 426, 606, 655.

<sup>5</sup> Kirsch and Pettersen, *Phil. Mag.*, 1924, [vi], 47, 500.

<sup>6</sup> Strong, *Amer. Chem. J.*, 1909, 42, 147.

## QUANTITATIVE SPECTRUM OF VANADIUM.

Wave-length.	Intensity and Persistence of Line.	Wave-length.	Intensity and Persistence of Line.	Wave-length.	Intensity and Persistence of Line.
2630.7	3 $\phi$	2910.4	4 $\phi$	3267.6	20 $\chi$
2649.4	5 $\phi$	2920.4	3 $\phi$	3271.1	20 $\chi$
2655.7	6 $\phi$	2924.6	8 $\psi$	3276.1	20 $\chi$
2663.3	6 $\chi$	2941.4	10 $\chi$	3457.2	10 $\phi$
2672.0	3 $\chi$	2944.6	8 $\chi$	3517.3	20 $\chi$
2679.3	4 $\phi$	2952.1	8 $\phi$	3545.2	30 $\chi$
2683.1	2 $\chi$	2957.5	6 $\phi$	3593.3	15 $\phi$
2690.8	2 $\phi$	2968.4	10 $\phi$	3709.4	3 $\chi$
2702.2	3 $\chi$	2976.5	3 $\phi$	3715.5	20 $\phi$
2706.7	2 $\chi$	3001.2	8 $\chi$	3727.5	20 $\phi$
2714.2	2 $\phi$	3003.5	4 $\phi$	3732.8	20 $\phi$
2715.7	5 $\chi$	3008.6	5 $\phi$	3745.8	20 $\phi$
2723.6	5 $\chi$	3057.1	1 $\phi$	3750.9	4 $\phi$
2739.7	3 $\phi$	3063.3	4 $\phi$	3840.8	2 $\phi$
2742.4	2 $\phi$	3067.1	5 $\phi$	3855.8	3 $\phi$
2753.4	5 $\chi$	3093.1	15 $\psi$	3863.9	4 $\phi$
2775.8	3 $\phi$	3102.3	15 $\psi$	4005.7	20 $\phi$
2777.7	3 $\phi$	3110.7	15 $\psi$	4023.4	20 $\phi$
2810.3	8 $\phi$	3118.4	15 $\psi$	4111.8	20 $\phi$
2854.4	5 $\phi$	3130.3	10 $\phi$	4115.2	6 $\phi$
2869.1	5 $\phi$	3133.3	5 $\phi$	4128.1	10 $\phi$
2877.7	2 $\phi$	3134.9	8 $\phi$	4132.0	10 $\phi$
2880.1	5 $\phi$	3136.5	8 $\phi$	4379.2	30 $\psi$
2888.3	4 $\phi$	3139.8	8 $\phi$	4384.7	30 $\phi$
2889.6	4 $\phi$	3142.5	3 $\phi$	4390.0	20 $\phi$
2891.7	6 $\phi$	3133.4	2 $\chi$	4395.2	15 $\phi$
2896.3	4 $\phi$	3185.4	4 $\chi$	4400.6	10 $\phi$
2903.1	4 $\phi$	3187.7	8 $\phi$	4408.5	20 $\psi$
2908.8	7 $\phi$	3190.7	10 $\phi$	4460.3	10 $\psi$
2910.0	4 $\phi$	3217.1	10 $\phi$	4462.4	10 $\psi$

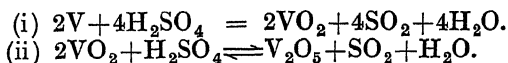
**Physiological Action.**—Vanadium compounds are poisonous when taken internally.<sup>1</sup> The usual symptoms are paralysis, convulsions, lowering of the body temperature, and feeble pulse. The fatal dose in the case of a rabbit is between 0.00918 and 0.01466 gram. Workmen exposed to fumes of vanadium compounds, especially those engaged on ore-reduction plants, are said to be susceptible to vanadium poisoning, but this has been denied.<sup>2</sup> Vanadium compounds have been shown

<sup>1</sup> Priestley, *Proc. Roy. Soc.*, 1875-76, 24, 40; Jackson, *Proc. Amer. Physiol. Soc.*, 1911, 23-24.

<sup>2</sup> Lees, *Eng. and Min. J.*, 1911, 92, 99.

to possess antiseptic action,<sup>1</sup> and in suitable form to be useful in medicine; <sup>2</sup> they are not, however, at present used in medicine.<sup>3</sup>

**Chemical Properties of Vanadium.**—Pure vanadium is stable and retains its lustre in damp air. On being rapidly heated in a stream of oxygen the powdered metal burns, forming vanadium pentoxide,  $V_2O_5$ ; the reaction is, however, incomplete.<sup>4</sup> At a bright red heat the metal combines with nitrogen to form a nitride. In excess of chlorine, vanadium burns to form a tetrachloride,  $VCl_4$ , which is also produced by the action of carbonyl, sulphuryl, thionyl, and sulphur chlorides at  $600^\circ C$ .<sup>5</sup> When heated in hydrogen the gas is absorbed.<sup>6</sup> Vanadium is not attacked by solutions of alkali chlorides, bromine water, or cold hydrochloric acid, whether dilute or concentrated. Hydrochloric acid gas, however, at  $300^\circ$  to  $400^\circ C$ . gives rise to the trichloride,  $VCl_3$ .<sup>7</sup> Vanadium is slowly attacked by hydrofluoric acid and by hot, concentrated sulphuric acid. A specimen of vanadium which contained 8.66 per cent. of carbon and 1.6 per cent. of other impurities, when treated with concentrated sulphuric acid at  $330^\circ C$ ., gave vanadium pentoxide,  $V_2O_5$ , with evolution of sulphur dioxide. At lower temperatures the dioxide,  $VO_2$ , was formed, but this was converted into the pentoxide when the temperature was raised, thus:<sup>8</sup>



Vanadium is readily attacked in the cold by dilute nitric acid and by concentrated nitric acid or aqua-regia, giving vanadic acid. This latter acid is also formed by the action of other oxidising agents on vanadium, as, for example, chloric acid, perchloric acid, bromic acid, potassium iodate. On being fused with sodium carbonate, caustic potash, or potassium nitrate, vanadates of sodium or potassium are produced. Vanadium reduces solutions of mercuric chloride, cupric chloride, and ferric chloride to mercurous chloride, cuprous chloride, and ferrous chloride respectively, and precipitates the metal from solutions of gold chloride, silver nitrate, platinum chloride, iridium chloride. Carbon monoxide attacks vanadium between  $500^\circ$  and  $800^\circ C$ . with the formation of a carbide. Glass and porcelain vessels absorb vanadium at high temperatures.<sup>9</sup> The metal can be rendered "passive," as in the case of iron, by immersion in oxidising agents, *e.g.* chromic acid, nitric acid, or by making the metal the anode in an electrolytic bath of various salts.<sup>10</sup> Cathodic treatment reconverts the vanadium to the "active"

<sup>1</sup> Witz and Osmond, *Bull. Soc. chim.*, 1886, [ii], 45, 309; Weber, *Pharmaceutische Zeitung*, 1898, 43, 667.

<sup>2</sup> Larmuth, *J. Anat. Physiol.*, 1877, 11, 251; Gamage and Larmuth, *ibid.*, 1877, 11, 235; Anon., *J. Soc. Chem. Ind.*, 1922, 41, 1373 R; Fournier, see *Amer. Chem. Abs.*, 1922, 16, 4283; Winkler, *ibid.*, 1925, 19, 1601; Spiro, *Ergebnisse Physiol.*, 1925, 24, 474; *U.S. Pat.* 1607196 (1927); Levaditi and others, *Compt. rend.*, 1928, 187, 434.

<sup>3</sup> Compare Partridge, *J. Ind. Eng. Chem.*, 1929, 21, 40.

<sup>4</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 58.

<sup>5</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

<sup>6</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 58; Prandtl and Manz, *Zeitsch. anorg. Chem.*, 1912, 79, 209; Huber, Kirschfeld, and Sieverts, *Ber.*, 1926, 59, 289.

<sup>7</sup> Meyer and Backa, *loc. cit.*

<sup>8</sup> Marino, *Zeitsch. anorg. Chem.*, 1904, 39, 152; compare p. 99 *et seq.*

<sup>9</sup> Roscoe, *J. Chem. Soc.*, 1870, 23, 358.

<sup>10</sup> Muthmann and Frauenberger, *Zeitsch. Elektrochem.*, 1904, 10, 929; Thiel and Hammerschmidt, *Zeitsch. anorg. Chem.*, 1924, 132, 15.

state. Marino, however, could not effect this change,<sup>1</sup> but this may have been due to differences in the purity of the vanadium specimens used.

**Atomic Weight of Vanadium.**—The early investigations into the atomic weight of vanadium provide a very interesting example of the application of Mitscherlich's Law of Isomorphism. Berzelius in 1831<sup>2</sup> obtained the value 68·5 by (a) reducing vanadic acid in hydrogen at a red heat, (b) reconvertng the reduced oxide to vanadic acid. Berzelius assumed in his calculations that the formula for vanadic acid was  $\text{VO}_3$ . In 1868 Roscoe<sup>3</sup> pointed out that the following minerals had been shown by Rammelsberg<sup>4</sup> to be isomorphous, but were not at that time represented by analogous formulæ :

- (i) *Vanadinite*,  $3\text{Pb}_3(\text{VO}_3)_2 \cdot \text{PbCl}_2$ .
- (ii) *Mimetesite*,  $3\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{PbCl}_2$ .
- (iii) *Pyromorphite*,  $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2$ .

If the Law of Isomorphism held good in this instance, the formula for *vanadinite* should be similar to those written down for the other minerals. The formula for vanadic anhydride should thus be  $\text{V}_2\text{O}_5$ , corresponding to  $\text{P}_2\text{O}_5$  and  $\text{As}_2\text{O}_5$  for phosphoric and arsenic anhydride respectively, and not  $\text{VO}_3$  as was supposed by Berzelius. Roscoe was able to show that the anhydride was correctly represented as  $\text{V}_2\text{O}_5$ , and that the substance regarded by Berzelius as metallic vanadium was in fact an oxide,  $\text{VO}$ . The formula for *vanadinite* thus becomes  $3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2$ , and the atomic weight of vanadium as originally determined becomes 68·5—16·0 or 52·5. Even this figure is incorrect, because the materials employed were not pure.<sup>5</sup>

Roscoe<sup>6</sup> carried out the first reliable determinations of the atomic weight of vanadium. He used three methods :

(a) Reduction of vanadium pentoxide to vanadium trioxide by means of hydrogen. From the ratio  $\text{V}_2\text{O}_5 : \text{V}_2\text{O}_3$ , the atomic weight of vanadium was found to be 51·382.<sup>7</sup>

(b) Vanadium oxytrichloride was treated with silver nitrate solution volumetrically until all the chlorine was removed. From the ratio  $\text{VOCl}_3 : 3\text{Ag}$ , the atomic weight of vanadium was 51·055.

(c) Vanadium oxytrichloride was treated with silver nitrate, and the precipitated silver chloride was collected, dried, and weighed. From the ratio  $\text{VOCl}_3 : 3\text{AgCl}$ , the atomic weight of vanadium was 51·259.

No further investigations were carried out until 1909, over forty years later, when Prandtl and Bleyer<sup>8</sup> repeated Methods (a) and (c) of Roscoe, but took care to avoid several sources of error. Method (a) gave the value 51·356, but the investigators found that the vanadium

<sup>1</sup> Marino, *loc. cit.*

<sup>2</sup> Berzelius, *Pogg. Annalen*, 1831, 22, 14.

<sup>3</sup> Roscoe, *J. Chem. Soc.*, 1868, 21, 322; *Phil. Trans.*, 1868, 158, 1.

<sup>4</sup> Rammelsberg, *Pogg. Annalen*, 1856, 98, 249.

<sup>5</sup> See also Czudnowitz, *ibid.*, 1863, 120, 17.

<sup>6</sup> Roscoe, *loc. cit.*

<sup>7</sup> The following atomic weight values have been used in calculating the atomic weights in this section :—

$$\text{O} = 16\cdot000; \quad \text{Cl} = 35\cdot457; \quad \text{Ag} = 107\cdot880; \quad \text{Na} = 22\cdot996.$$

Where necessary, the atomic weights have been recalculated from the original experimental data, using the above values.

<sup>8</sup> Prandtl and Bleyer, *Zeitsch. anorg. Chem.*, 1909, 65, 152; 1910, 67, 257.

trioxide obtained on reduction took up oxygen again so readily that its weight could not be obtained with certainty. The value obtained was therefore too high. Method (c) gave the value 51.074.

In 1914 Briscoe and Little<sup>1</sup> again analysed vanadium oxytrichloride, using Methods (b) and (c). The ratio  $\text{VOCl}_3 : 3\text{Ag}$  was studied in detail and gave an atomic weight of 50.950; two measurements of the ratio  $\text{VOCl}_3 : 3\text{AgCl}$  gave an atomic weight of 50.952. The investigators state, in reviewing the possible sources of error, that the figures are likely to prove a trifle low. Hence the atomic weight of vanadium lies between 50.95 and 50.96, and the higher number is most probably the more correct. This value is in good agreement with a determination carried out in 1910 by McAdam,<sup>2</sup> who employed a totally different reaction. A known weight of anhydrous sodium metavanadate was heated in a stream of hydrogen chloride gas and chlorine; the residual sodium chloride was fused and weighed. From the ratio  $\text{NaVO}_3 : \text{NaCl}$  an atomic weight of 50.960 was obtained.

The values for the atomic weight of vanadium as determined by various investigators since 1868 are summarised in the following table:—

ATOMIC WEIGHT OF VANADIUM.

Authority.	Date.	Ratio Determined.	No. of Determinations.	Atomic Weight of Vanadium.
Roscoe . . .	1868	$\text{V}_2\text{O}_5 : \text{V}_2\text{O}_3$	4	51.382
		$\text{VOCl}_3 : 3\text{Ag}$	9	51.055
		$\text{VOCl}_3 : 3\text{AgCl}$	8	51.259
Prandtl and Bleyer	1909	$\text{V}_2\text{O}_5 : \text{V}_2\text{O}_3$	4	51.356
		$\text{VOCl}_3 : 3\text{AgCl}$	9	51.074
McAdam . . .	1910	$\text{NaVO}_3 : \text{NaCl}$	5	50.960
Briscoe and Little	1914	$\text{VOCl}_3 : 3\text{Ag}$	9	50.950
		$\text{VOCl}_3 : 3\text{AgCl}$	2	50.952

The *International Committee on Atomic Weights* adopted the value 51.0 in 1911.<sup>3</sup> This was altered to 50.96 in 1925 and to 50.95 in 1929.<sup>4</sup>

The atomic number of vanadium is 23. Examination by the method of mass-spectra has shown that vanadium has no isotopes.<sup>5</sup>

**Uses of Vanadium.** (a) *Vanadium Steels.*—By far the largest proportion of the world's production of vanadium is absorbed in the production of ferrovanadium alloy for the manufacture of vanadium steels, which usually contain up to 0.8 per cent. of vanadium. The effect of the addition of vanadium to a steel is to increase its tensile strength enormously, also its hardness, and its resistance to shock and fatigue.<sup>6</sup> A good carbon steel containing about 1.10 per cent. of carbon has an elastic limit of about 80 tons per square inch and an ultimate

<sup>1</sup> Briscoe and Little, *J. Chem. Soc.*, 1914, 105, 1310.

<sup>2</sup> McAdam, *J. Amer. Chem. Soc.*, 1910, 32, 1803. <sup>3</sup> *J. Chem. Soc.*, 1911, 99, 1867.

<sup>4</sup> *Ibid.*, 1925, 127, 913; 1929, 218.

<sup>5</sup> Aston, *Phil. Mag.*, 1924, 47, 385.

<sup>6</sup> Guillet, *J. Iron Steel Inst.*, 1905, 68, 118; McWilliam and Barnes, *ibid.*, 1911, 83, 294; 1915, 91, 125; Portevin, *Carnegie Scholarship Memoirs, Iron and Steel Institute*, 1909, 1, 230.

stress of about 60 tons per square inch. Addition of 0.3 per cent. of vanadium to such a steel raises the elastic limit to 43 tons and the maximum stress to 76 tons per square inch, while addition of 0.6 per cent. of vanadium gives an elastic limit of 65 tons and a maximum stress of 85 tons per square inch.<sup>1</sup> Similar improvement in physical properties takes place with the incorporation of small quantities of vanadium into cast iron.<sup>2</sup> Vanadium steels are admirably suited to situations where they are subject to varying stresses and vibrations. They are used in the construction of transmission shafts, piston rods, axles, bolts, gears, motor-car parts, aeroplane parts, and in tools for punching, shearing, and drawing. The coefficients of thermal expansion of vanadium steels are given by Souder and Hidnert.<sup>3</sup>

It is found that the use of vanadium up to about 1 per cent. with tungsten and molybdenum in the manufacture of high-speed tools again exerts a favourable influence by imparting increased cutting efficiency under heavy working conditions. The presence of a small proportion of vanadium reduces the quantity of tungsten or molybdenum required to impart to the steel definite hardness and toughness. Used in conjunction with other alloying metals, *e.g.* in nickel steels, cobalt steels, chromium steels, and nickel-chromium steels, it produces equally useful results.<sup>4</sup> These special steels closely resemble the chrome-nickel steels, but have the advantage of greater freedom from surface imperfections. They are employed mainly in automobile construction. Some chromium-vanadium steel which has high resistance imparted by heat treatment is used for armour plate of medium thickness, gun shields, gun tubes, torpedo tubes, etc. The use of vanadium steel for the manufacture of Brinell balls has recently been suggested.<sup>5</sup>

The function of vanadium in steel appears to be twofold: (a) It acts as a "scavenger," removing traces of oxygen and nitrogen, and (b) it effects a more homogeneous distribution of carbon throughout the mass. The vanadium displaces the iron from the iron carbide,  $\text{Fe}_3\text{C}$ , in the steel, producing vanadium carbide,  $\text{V}_4\text{C}_3$ , which does not segregate as readily as cementite or pearlite, with the consequence that the carbon is more evenly distributed throughout the mass and a fine-grained structure results.<sup>6</sup> In the case of cast iron, vanadium also assists the retention of the carbon in the combined form.<sup>7</sup>

Vanadium finds application to a limited extent in the manufacture of non-ferrous alloys. The introduction of the metal up to about 0.5 per cent. into brasses which contain from 60 to 70 per cent. of copper and 30 to 40 per cent. of zinc is stated to increase the maximum stress and elongation.<sup>8</sup> Copper-vanadium and aluminium-vanadium alloys

<sup>1</sup> Arnold, *J. Iron Steel Inst.*, 1915, 91, 442; Smith, *J. Soc. Chem. Ind.*, 1901, 20, 1183.

<sup>2</sup> Norris, *Met. Chem. Eng.*, 1911, 9, 361.

<sup>3</sup> Souder and Hidnert, *American Bureau of Standards*, Scientific Papers, 1921, No. 433; see also Maurer and Schilling, *Stahl und Eisen*, 1925, 45, 1166.

<sup>4</sup> Guillet, *J. Iron Steel Inst.*, 1906, 70, 71; McWilliam and Barnes, *loc. cit.*; Portevin, *loc. cit.*; McAdam, *Chem. Met. Eng.*, 1921, 25, 1081; *Proc. Amer. Soc. for Testing Materials*, 1923, 56; 1924, 273, 574; *Trans. Amer. Soc. for Steel Treating*, 1924, 6, 393; 1925, 7, 54, 217, 581; Gillett and Mack, *Proc. Amer. Soc. for Testing Materials*, 1924, 476, 609, 760.

<sup>5</sup> Quick and Jordan, *Trans. Amer. Soc. for Steel Treating*, 1927, 12, 3.

<sup>6</sup> Arnold and Reed, *J. Iron Steel Inst.*, 1912, 85, 215; Grossmann and Bain, *ibid.*, 1924, 110, 263; compare Maurer, *Stahl und Eisen*, 1925, 45, 1629.

<sup>7</sup> Donaldson, *J. Iron Steel Inst.*, 1918, 98, 497; Hatfield, *ibid.*, 1911, 83, 318.

<sup>8</sup> Morris, *J. Franklin Inst.*, 1911, 171, 561; but compare Dunn and Hudson, *J. Inst. Metals*, 1914, 11, 152; Clark, *J. Soc. Chem. Ind., Abs.*, 1915, 34, 1097.

are used in aeroplane construction ; an aluminium-manganese-vanadium alloy is used for castings, and a copper-vanadium bronze is used in marine work.<sup>1</sup> Addition of vanadium also improves the tensile strength and the elastic limit of copper-aluminium bronzes and of copper-zinc-aluminium bronzes, but not beyond the amount due to its deoxidising properties.

(b) *Vanadium Catalysts*.—Vanadium compounds function as extremely efficient catalysts in various oxidative reactions of technical importance. They are used in the oxidation of aniline to aniline-black,<sup>2</sup> of naphthalene to phthalic anhydride,<sup>3</sup> of anthracene to anthraquinone, of benzene to maleic acid,<sup>4</sup> of toluene to benzaldehyde and benzoic acid, as well as in the conversion of acetylene into acetaldehyde.<sup>5</sup> Among important inorganic processes in which vanadium catalysts are employed are the oxidation of ammonia to nitric acid<sup>6</sup> and of sulphur dioxide to sulphur trioxide.<sup>7</sup> To prepare the catalyst for these operations, pure alumina, or other inert, porous material of the type of pumice or kieselguhr, may be mixed with about 10 per cent. of ammonium metavanadate or other vanadium salt and compressed into briquettes, which are then strongly heated ; the vanadate decomposes and leaves a porous block impregnated with finely divided vanadium pentoxide.<sup>8</sup> Alternatively, ferric chloride, or a soluble salt of another metal, is added to a solution of ammonium metavanadate which has been acidified with hydrochloric acid ; the precipitated vanadate is washed, dried, and gently ignited.<sup>9</sup> Recently, complex vanadium silicates have been introduced, particularly to replace platinum in the contact process for the manufacture of sulphuric acid. It is claimed for them that they are closely parallel to the best platinum catalysts with respect to optimum temperature, conversion equilibrium, and activity, and have the advantages of being cheaper and of not becoming poisoned by arsenic or hydrochloric acid.<sup>10</sup> In the laboratory the vanadium catalyst can be prepared by soaking asbestos fibre in a dilute solution of vanadyl sulphate,  $\text{VO}_2\text{SO}_4$ , which is obtained by reducing a boiling solution of ammonium vanadate with sulphur dioxide at 40° to 50° C. ; the solution is made alkaline with ammonia and evaporated almost to dryness ; the fibre is then dried and heated to about 500° C. to decompose ammonium salts.<sup>11</sup>

Vanadium salts have also been found to be effective as catalysts in various electrolytic oxidation and reduction processes ; for example in the preparation of hypochlorites,<sup>12</sup> the reduction of polynitro-aromatic compounds,<sup>13</sup> and in the sulphonation of aromatic compounds.<sup>14</sup> On

<sup>1</sup> See *Amer. Chem. Abs.*, 1921, 15, 3603.

<sup>2</sup> Guyard, *Bull. Soc. Chim.*, 1876, [ii], 25, 58, 351.

<sup>3</sup> Gibbs, *J. Ind. Eng. Chem.*, 1919, 11, 1031.

<sup>4</sup> Weiss and Downs, *ibid.*, 1920, 12, 228.

<sup>5</sup> See *Chem. Trade J.*, 1922, 71, 418 ; *Eng. Pat.* 238033 (1924) ; Maxted, *J. Soc. Chem. Ind.*, 1928, 47, 101.

<sup>6</sup> Neumann and Rose, *Zeitsch. angew. Chem.*, 1920, 33, 41, 45, 51.

<sup>7</sup> Miles, *Manufacture of Sulphuric Acid (Contact Process)*, vol. iv. (London, 1925), p. 120.

<sup>8</sup> Dyson, *Chem. Age, Metallurgical Section*, 1926, 14, 33 ; *U.S. Pat.* 1518043 (1925).

<sup>9</sup> *Eng. Pat.* 15174 (1913).

<sup>10</sup> Nickell, *Chem. Met. Eng.*, 1928, 35, 153.

<sup>11</sup> Efremov and Rosenberg, *J. Russ. Phys. Chem. Soc.*, 1927, 59, 701.

<sup>12</sup> Luther, *Zeitsch. Elektrochem.*, 1907, 13, 437 ; Allmand, *Applied Electrochemistry* (London, 1924), p. 370.

<sup>13</sup> Hofer and Jacob, *Ber.*, 1908, 41, 3187.

<sup>14</sup> Meyer, *Annalen*, 1923, 433, 327.

being incorporated into a drying oil in the form of a rosinate or linoleate, vanadium accelerates oxidation of the oil even more efficiently than lead or manganese, which are commonly used for the purpose, but not so efficiently as cobalt. The oxidised film is smooth and tough.<sup>1</sup> Vanadium cannot, however, be incorporated into oils to be used for white paints, as the film possesses a brown colour.<sup>2</sup>

(c) *Various Uses*.—On being fired at a red heat with pottery or glass, vanadium compounds impart a fine gold colour with a greenish tinge. Vanadium chlorides and other vanadium compounds are used with potassium ferricyanide in toning bromide prints; the green colour which is produced is attributed to the deposition of yellowish-green vanadium ferrocyanide together with Prussian blue.<sup>3</sup> A solution of vanadium pentoxide in sulphuric acid is used under the name of *Mandelin's Reagent* in testing for the presence of various alkaloids.

**Vanadium Alloys**.—Vanadium alloys readily with many metals, including aluminium, cobalt, copper, iron, manganese, molybdenum, nickel, platinum, and tin, also with silicon. These alloys have hitherto received scant attention, and little is known in most cases of the systems produced.

*Aluminium* appears to alloy with vanadium in all proportions. The alloys can be prepared by melting aluminium in a crucible and igniting a mixture of vanadium pentoxide on the top, or by reducing a mixture of aluminium, alumina, and vanadium pentoxide, with addition of cryolite and fluorspar, in the electric furnace.<sup>4</sup> They can also be produced by reducing vanadium pentoxide with carbon in the electric furnace in the presence of aluminium, but the product then contains appreciable quantities of carbide. Vanadium-aluminium alloys containing from 30 to 80 per cent. of vanadium have been obtained by the first-mentioned processes; fusion of these with aluminium gives products of lower vanadium content. By the regulated action of acids on these alloys crystals having the composition  $Al_3V$  and  $AlV$  have been isolated, and the existence of a third compound,  $AlV_2$ , has been suggested.<sup>5</sup> The mechanical properties of vanadium-aluminium alloys have not been fully studied, but it has been shown that 2 per cent. of vanadium in aluminium results in substantial increase in the strength and hardness of the rolled and annealed metal. The elongation of the annealed alloy falls, but even with 4 per cent. vanadium it is sufficiently high for most purposes.<sup>6</sup>

*Aluminium-Silicon*.—Vanadium possesses the property in common with a large number of other metals of forming complex alloys with aluminium and silicon.<sup>7</sup> Several of these vanadium-aluminium-silicides, each possessing different crystalline form, have been obtained

<sup>1</sup> Rhodes and Chen, *J. Ind. Eng. Chem.*, 1922, 14, 222; compare Hebler, *Farben-Zeitung*, 1927, 32, 2077.

<sup>2</sup> Swehten, *Farben-Zeitung*, 1927, 32, 1138; Gardner, *Paint Manufacturers' Assoc. of U.S.*, Circular 149 (1922).

<sup>3</sup> *Photography, Its Principles and Practice*, Neblette, p. 476 (Chapman & Hall, London), 1927.

<sup>4</sup> Clark, *J. Soc. Chem. Ind., Abs.*, 1915, 34, 1097; Czako, *Compt. rend.*, 1913, 156, 140; *Monograph on Vanadium Ores*, Imperial Institute, London, 1924, p. 9; Moissan, *Compt. rend.*, 1896, 122, 1297.

<sup>5</sup> Matignon and Monnet, *Compt. rend.*, 1902, 134, 542; Czako, *loc. cit.*

<sup>6</sup> Schirmeister, *Stahl und Eisen*, 1915, 25, 650; Keeney, *Mineral Industry*, 1917, 726.

<sup>7</sup> Vigouroux, *Compt. rend.*, 1905, 141, 951.



by fusing together potassium silicofluoride, aluminium, and ammonium metavanadate in varying proportions. One of the products formed in the presence of a large excess of silicon has the composition  $V_8Al_9Si_{13}$ .<sup>1</sup> It yields hexagonal, prismatic needles of density 4.3 and hardness 5. It is a remarkably stable compound, being unattacked by boiling concentrated hydrochloric acid, sulphuric acid, nitric acid, aqua-regia, or fused potassium chlorate. It reacts, however, with fused alkalis and with hydrofluoric acid to give, in the absence of air, a solution of hypovanadous fluoride,  $VF_2$ , which rapidly oxidises to vanadous fluoride,  $VF_3$ .

Compounds of vanadium and silicon are described on p. 107.

*Copper*.—Alloys of copper and vanadium are prepared by firing a mixture of vanadium pentoxide, copper oxide, aluminium shot, lime, soda-ash, and fluorspar with the aid of sodium peroxide in a magnesia-lined crucible.<sup>2</sup> Electrolytic methods have also been employed, and are applicable for the preparation of other vanadium alloys.<sup>3</sup> An alloy containing 3.38 per cent. of vanadium and 96.52 per cent. of copper was found to be harder than copper and could be drawn into wire. An aluminium-copper-vanadium alloy has been prepared.<sup>4</sup>

*Iron*.—The industrial preparation and uses of iron-vanadium alloys have already been described (see pp. 14 and 25). A laboratory method of preparation consists in passing a mixture of hydrogen and vanadium tetrachloride vapour over iron at  $900^\circ C$ .<sup>5</sup> Alloys of iron and vanadium which contained varying quantities of carbon were prepared by Moissan.<sup>6</sup> The freezing-point curve for alloys of iron and vanadium falls from the melting-point of iron ( $1530^\circ C$ .) to a minimum at 32 per cent. of vanadium, and then rises to the melting-point of vanadium ( $1750^\circ C$ .)<sup>7</sup> As the alloys are homogeneous the metals form a complete series of mixed crystals. A commercially useful alloy containing about 30 per cent. of vanadium is hard but not brittle, and is difficult to pulverise; its specific gravity is about 7.3 and its melting-point lies between  $1340^\circ$  and  $1400^\circ C$ . The presence of silicon in the alloy increases its hardness and brittleness. The temper-colours of iron-vanadium alloys have been studied by Tammann and Siebel.<sup>8</sup>

*Mercury*.—The solubility of vanadium in mercury is too small for measurement.<sup>9</sup>

*Nickel*.—Vanadium and nickel are miscible in all proportions in the liquid state up to 36 per cent. vanadium. The solid alloys, which contain up to 20 per cent. vanadium, appear to be homogeneous, but those richer in vanadium consist of two kinds of crystals.<sup>10</sup> These alloys are made by reducing a mixture of vanadium pentoxide and nickel oxide.<sup>11</sup>

*Silver*.—Vanadium does not alloy with silver.<sup>12</sup>

<sup>1</sup> Manchot and Fischer, *Annalen*, 1907, 357, 129.

<sup>2</sup> Keeney, *loc. cit.*

<sup>3</sup> Gin, *Chem. News*, 1903, 88, 38.

<sup>4</sup> Hélois, *Revue de Métallurgie*, 1905, 2, 588.

<sup>5</sup> Parravo and Mazzetti, *Rec. Trav. chim.*, 1923, 42, 821.

<sup>6</sup> Moissan, *loc. cit.*

<sup>7</sup> Vogel and Tammann, *Zeitsch. anorg. Chem.*, 1908, 58, 73; van Liempt, *Rec. Trav. chim.* 1926, 45, 203.

<sup>8</sup> Tammann and Siebel, *Zeitsch. anorg. Chem.*, 1925, 148, 297.

<sup>9</sup> Tammann and Hinnuber, *ibid.*, 1927, 160, 249.

<sup>10</sup> Giebelhausen, *ibid.*, 1915, 91, 251.

<sup>11</sup> Herrenschmidt, *Compt. rend.*, 1904, 139, 635.

<sup>12</sup> Giebelhausen, *loc. cit.*

## CHAPTER III.

### COMPOUNDS OF VANADIUM.

#### GENERAL PROPERTIES OF VANADIUM COMPOUNDS.<sup>1</sup>

THE compounds of vanadium are numerous and to some extent complicated; this is due to the variable valency of the element. It forms a series of oxides:  $\text{VO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ , and although the oxide  $\text{V}_2\text{O}_7$  has not hitherto been isolated, *pervanadates* derived from it are well defined. A monoxide having the formula  $\text{V}_2\text{O}$  has also been reported, but its existence is doubtful; compounds containing mono-valent vanadium are unknown. As is usual in the case of any one element, the acidity of the oxide increases with increasing oxygen content, and basic properties gradually become less marked.

**Hypovanadous Oxide**,  $\text{VO}$ , was originally mistaken by Berzelius for the element. As in the case of uranium it is difficult to separate vanadium from the last remaining oxygen atom, and this oxide is found to enter as the vanadyl radical into a large number of compounds. *Hypovanadous salts* can be isolated in the pure state only with difficulty because of the readiness with which they undergo oxidation; they are among the most powerful inorganic reducing agents known, and frequently evolve hydrogen from aqueous or acid solution. They are best prepared by electrolytic reduction in an inert atmosphere of more highly oxidised compounds. They are isomorphous with magnesium salts and with the divalent salts of iron, chromium, and manganese. *Double sulphates* of the type  $\text{VSO}_4 \cdot \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{VSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  are known, as well as a *complex cyanide*,  $\text{K}_4[\text{V}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ .

**Vanadous Oxide**,  $\text{V}_2\text{O}_3$ , is almost insoluble in acids, but salts containing trivalent vanadium can be prepared by reducing the tetra- or penta-valent compounds. *Vanadous salts* are also strong reducing agents. *Vanadous trichloride*,  $\text{VCl}_3$ , for instance, precipitates metallic silver from a solution of a silver salt, the charge on the  $\text{Ag}^+$  ion being taken up by the  $\text{V}^{3+}$  ion. Vanadous salts are comparable in their general behaviour with trivalent iron, aluminium, and chromium salts; they form *alums* with the alkali sulphates, e.g.  $\text{V}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ , as well as *double oxalates* of the type  $3(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{V}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ . The trivalent vanadium ion,  $\text{V}^{3+}$ , as in the case of the ferric ion,  $\text{Fe}^{3+}$ , has a strong tendency to produce complex ions, and hence the existence of such compounds as *potassium vanadicyanide*,  $\text{K}_3[\text{V}(\text{CN})_6]$ .

**Hypovanadic Oxide**,  $\text{VO}_2$ , is amphoteric, and dissolves both in alkalis and acids. In passing from trivalent to tetravalent vanadium, however, the basic character of the oxide becomes less pronounced and

<sup>1</sup> The general characteristics of vanadium compounds are outlined in Chapter I.

weakly acid properties become manifest. The corresponding hydroxide,  $V(OH)_4$ , has not been definitely isolated; it appears to be too weakly basic to form salts by the replacement of the four hydroxyl groups by acid radicals, and the salts produced possess the general formula  $VOX_2$ . Examples are *vanadyl sulphate*,  $VOSO_4$ , and *vanadyl dichloride*,  $VOCl_2$ , in which two hydroxyl groups only have undergone replacement. *Vanadium tetrafluoride*,  $VF_4$ , and *vanadium tetrachloride*,  $VCl_4$ , however, are known. Considerable numbers of *double vanadyl salts* are also known. When solutions of hypovanadic oxide in hot alkalis are cooled, salts which contain the vanadium in the anion are obtained. These are called *hypovanadates* or *vanadites*, and are probably derived from an acid having the composition  $4VO_2 \cdot H_2O$  or  $H_2V_4O_9$ . Hypovanadic oxide appears to be too weakly basic to give rise to salts without previously undergoing condensation, then giving salts of the type  $R_2O \cdot xVO_2$ .

**Vanadic Oxide** or *vanadium pentoxide* gives rise to the *vanadates*, the most numerous and important class of vanadium compounds. All vanadium compounds in a lower stage of oxidation have a tendency on being warmed to become converted into vanadates or derivatives of vanadates. Vanadium pentoxide hence is strongly acidic, but the basic character exhibited by the lower oxides is not completely lost, since the pentoxide dissolves in strong acids to give rise to salts, such as, for example,  $V_2O_5 \cdot 2SO_3$ . These salts, however, are not very well defined or stable, and readily undergo hydrolysis to give rise to compounds which contain the trivalent radical  $[VO]^{+++}$ , e.g. *vanadium oxytrichloride*,  $VOCl_3$ , or the monovalent radical  $[VO_2]^{+}$ , for example, *ammonium vanadium dioxyfluoride*,  $3NH_4F \cdot VO_2F$ . The pentavalent ion  $V^{+5}$  appears to be incapable of free existence, since no pentavalent compounds are known, excepting those with oxygen and sulphur, in which all the five valencies are saturated with negative elements or groups. As in the case of the lower oxide,  $VO_2$ , vanadium pentoxide has a strong tendency to form condensed *poly-acids* which give rise to salts of the type  $R_2O \cdot xV_2O_5$ . In this respect vanadium pentoxide is analogous with other weak acids which are formed from metallic elements; compare, for instance, tungstic acid<sup>1</sup> and chromic acid,<sup>2</sup> several molecules of which frequently combine with one molecule of a base to form a salt. The chromates and vanadates are in fact so comparable in their general behaviour that the formula  $VO_3$  was at one time assigned to vanadium pentoxide in harmony with  $CrO_3$  for chromic anhydride. Vanadium pentoxide has the further well-pronounced property of combining with other acid oxides to form *heteropoly-acids*. The most common acid oxides are phosphorus pentoxide, arsenic pentoxide, molybdenum trioxide, tungsten trioxide, silica. The heteropoly-acids yield well-defined, crystallisable salts with basic oxides.

**Heats of Formation of the Oxides of Vanadium.**—The difficulty that is experienced in reducing any of the oxides of vanadium to the metal is attributed partially to their very strongly exothermic nature. Ruff and Friedrich<sup>3</sup> obtained the following figures from combustions carried out in a bomb calorimeter:—

- (i)  $2V + 5(\frac{1}{2}O_2) = V_2O_5 + 437,000 \pm 7,000$  calories.  
(ii)  $2V + 3(\frac{1}{2}O_2) = V_2O_3 + 302,000 \pm 10,000$  „

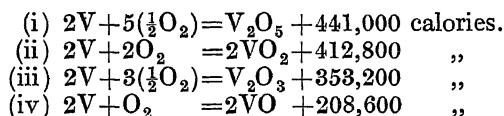
<sup>1</sup> See this series, Vol. VII., Part III. (1926), p. 208.

<sup>2</sup> *Ibid.*, p. 44.

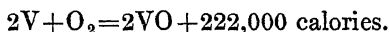
<sup>3</sup> Ruff and Friedrich, *Zeitsch. anorg. Chem.*, 1914, 89, 279.

Previous determinations of the heat of formation of the pentoxide gave 313,030 calories<sup>1</sup> and 250,315 calories.<sup>2</sup>

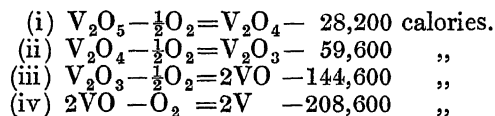
Mixer<sup>3</sup> investigated the thermal changes that ensue when the lower oxides are converted into the pentoxide, and from these data calculated the following :—



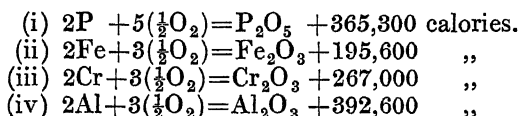
The last figure is in fair agreement with an indirect determination effected by Slade and Higson,<sup>4</sup> who obtained



It is of interest to note that, commencing with vanadium pentoxide, the amounts of heat absorbed in the successive formation of the next lower oxide rapidly increase as the metal is reached. The heat changes in the following equations have been calculated from Mixer's figures, given above :



The heats of formation of a few other oxides are here inserted for the sake of comparison :



The comparatively high heat of formation of vanadium pentoxide and the tendency of aluminium to alloy with metallic vanadium explain the non-success of the application of the thermite process for the production of pure vanadium from the pentoxide and from vanadates.

The table on the next page summarises the various types of vanadium compounds known.

*Vanadyl salts* are salts of tetravalent vanadium, and contain the divalent [VO]<sup>+</sup> radical. Many vanadium compounds are known which appear to contain a [VO] group, but the vanadium is either trivalent or pentavalent. Throughout this book the term *vanadyl* is restricted to compounds of tetravalent vanadium, that is, to salts of the oxide VO<sub>2</sub>. Hence, for example, the compound VOCl<sub>3</sub>, which contains pentavalent vanadium, is called *vanadium oxytrichloride*, and not by the more usual but less logical name "vanadyl chloride."

*Colours of Vanadium Salts.*<sup>5</sup>—As is usual with salts of metals which exhibit variable valency, those of vanadium are coloured in solution. The colour varies with the valency; salts of V<sub>2</sub>O<sub>5</sub> are yellow, those of

<sup>1</sup> Muthmann, Weiss, and Riedelbauch. *Annalen*, 1907, 355, 58.

<sup>2</sup> Ruff and Martin, *Zeitsch. angew. Chem.*, 1912, 25, 49.

<sup>3</sup> Mixer, *Amer. J. Sci.*, 1912, [iv], 34, 141.

<sup>4</sup> Slade and Higson, *J. Chem. Soc.*, 1919, 115, 205.

<sup>5</sup> Compare Bichowsky, *J. Amer. Chem. Soc.*, 1918, 40, 500.

VO<sub>2</sub> are blue, those of V<sub>2</sub>O<sub>3</sub> are green, and those of VO are lavender (see table). Remarkable colour changes can be observed by diluting considerably the reddish solution obtained by dissolving the pentoxide, V<sub>2</sub>O<sub>5</sub>, in hydrochloric or sulphuric acid and then adding metallic zinc. Under the influence of the nascent hydrogen produced the solution passes through all shades of blue and green, and finally assumes a lavender tint. The same effect can be produced by electrolytic reduction of the hydrochloric acid solution.<sup>1</sup> These characteristic colours cannot definitely be attributed to the existence of penta-, tetra-, tri-, and di-valent vanadium cations, since, as has been indicated, the various vanadium salts readily undergo hydrolysis in contact with water to give rise most probably to the following cations: [VO]<sup>3+</sup> or [VO<sub>2</sub>]<sup>+</sup> from V<sup>V</sup>, [VO]<sup>2+</sup> from V<sup>IV</sup>, and [VO]<sup>+</sup> from V<sup>III</sup>. These oxygenated radicals cannot be without influence on the different colours observed.<sup>2</sup>

VANADIUM COMPOUNDS.

Oxide.	Nature.	Name of Salts.	Colour of Salts in Aqueous Solution.	Examples.	Probable Ions in Solution.
VO	Basic	<i>Hypovanadous salts</i>	Lavender	VCl <sub>2</sub> ; VSO <sub>4</sub> .7H <sub>2</sub> O	V <sup>2+</sup>
V <sub>2</sub> O <sub>3</sub>	Basic	<i>Vanadous salts</i>	Green	VCl <sub>3</sub> ; VOCl	V <sup>3+</sup> , [VO] <sup>+</sup>
VO <sub>2</sub>	Basic and weakly acidic	<i>Hypovanadic salts and vanadyl salts.</i>	Blue	VCl <sub>4</sub> ; VOSO <sub>4</sub>	V <sup>4+</sup> , [VO] <sup>2+</sup>
	Weakly acidic	<i>Hypovanadates or vanadites.</i>		Na <sub>2</sub> V <sub>4</sub> O <sub>9</sub> .4H <sub>2</sub> O	[V <sub>4</sub> O <sub>9</sub> ] <sup>2-</sup>
V <sub>2</sub> O <sub>5</sub>	Weakly basic and acidic	<i>Vanadic salts.</i>	Black to brown.	VF <sub>5</sub> ; VOF <sub>3</sub> ; VO <sub>2</sub> F	V <sup>5+</sup> , [VO] <sup>3+</sup> , [VO <sub>2</sub> ] <sup>+</sup>
	Acidic	<i>Vanadates (ortho-, pyro-, meta-).</i>	Yellow to red.	Na <sub>3</sub> VO <sub>4</sub> ; Na <sub>4</sub> V <sub>2</sub> O <sub>7</sub> ; NaVO <sub>3</sub> .	[VO <sub>4</sub> ] <sup>3-</sup> , [V <sub>2</sub> O <sub>7</sub> ] <sup>4-</sup> , [VO <sub>3</sub> ] <sup>3-</sup> or [V <sub>2</sub> O <sub>6</sub> ] <sup>4-</sup>
(V <sub>4</sub> O <sub>9</sub> )*	Acidic	<i>Pervanadates (ortho-, pyro-, meta-).</i>	Various	NH <sub>4</sub> VO <sub>4</sub> ; NH <sub>4</sub> H <sub>2</sub> V <sub>2</sub> O <sub>9</sub> ; 2(NH <sub>4</sub> ) <sub>3</sub> VO <sub>6</sub> .5H <sub>2</sub> O.	[VO <sub>4</sub> ] <sup>3-</sup> , [V <sub>2</sub> O <sub>6</sub> ] <sup>4-</sup> , [VO <sub>3</sub> ] <sup>3-</sup>
			Yellowish-orange.		[V <sub>4</sub> O <sub>9</sub> ] <sup>2-</sup>

*Catalytic Activity of Vanadium Compounds.*—The technical application of vanadium compounds as catalysts has already been referred to (see p. 27). Several reactions, the velocities of which are affected by the presence of vanadium salts, have been quantitatively investigated.<sup>3</sup> It appears to be established that the compounds employed usually function as *oxygen carriers*, and that their effect depends, therefore, on the ease with which they undergo oxidation and reduction. To give two instances: (a) The reduction of chloric acid, HClO<sub>3</sub>, by hydriodic acid, HI, is accelerated by the addition of a vanadous salt, because chloric acid is much more rapidly reduced by a vanadous salt than by hydriodic acid; on the other hand, the reduction of persulphuric acid, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, with HI is not appreciably affected by addition of a vanadous salt, because the last named reduces persulphuric acid but slowly. (b) Vanadium pentoxide accelerates the oxidation of sucrose to oxalic acid by nitric acid, that of ethyl alcohol to acetaldehyde and

<sup>1</sup> Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 175.

<sup>2</sup> Someya, *Zeitsch. anorg. Chem.*, 1927, 161, 46.

<sup>3</sup> Ostwald, *Zeitsch. physikal. Chem.*, 1888, 2, 127.

\* Not hitherto isolated.

acetic acid by air, that of potassium iodide to iodine by hydrogen peroxide, and that of stannous salts by nitric acid. In these reactions the vanadium pentoxide gives up its oxygen to the oxidisable substance, being itself reformed at the expense of the oxidising agent.<sup>1</sup>

In some cases, however, the *modus operandi* is modified. In the oxidation of hydriodic acid with chromic acid, the data indicate that while liberation of iodine takes place, the vanadous or hypovanadic salt employed as the catalyst also undergoes oxidation to vanadate.<sup>2</sup> The vanadium compound here belongs to the class of catalysts known as *inductors*, and the reaction is comparable to the oxidation in aqueous solution of sodium sulphite with sodium arsenite, whereby both sodium sulphate and sodium arsenate are produced.

More recently the conversion of benzene into maleic acid in the presence of vanadium oxides as catalysts has been studied with a view to throwing light on the mechanism of such oxidations. The data obtained seem to show that the action depends on an "oscillation" between the two oxides  $V_2O_5$  and  $V_2O_4$ , the dissociation of the former supplying activated oxygen for the reaction; but it is also shown that the nature of the products of the oxidation is a function of some other property of the catalyst not yet clearly understood.<sup>3</sup>

The presence of a vanadium salt in dilute sulphuric acid solution has also been found to improve the catalytic action of platinum in the combination of hydrogen and oxygen.<sup>4</sup>

#### *The Electromotive Behaviour of Vanadium.*

Vanadium precipitates the metal from solutions of salts of gold, silver, platinum, and iridium, and reduces solutions of mercuric chloride, cupric chloride and ferric chloride to mercurous chloride, cuprous chloride, and ferrous chloride, respectively. In these reactions the vanadium passes into solution as the tetravalent ion. No precipitation or reduction ensues, however, when vanadium is added to solutions of divalent salts of zinc, cadmium, nickel, and lead. From these reactions it has been estimated that the electrolytic potential of the change, vanadium (metal)  $\rightarrow$  tetravalent ions, is about  $-0.3$  to  $-0.4$  volt, which is approximately equal to the electrolytic solution pressure of copper. This figure is a little uncertain through the difficulty of securing pure vanadium.<sup>5</sup>

When an electrolyte which is without action on vanadium at ordinary temperatures (for example, dilute solutions of mineral acids, of oxalic acid, or of potassium halides) is electrolysed with a vanadium anode, a complex tetravalent vanadium ion is produced. Similarly, electrolysis at  $100^\circ\text{C}$ . and in molten chlorides of sodium or zinc gives rise to complex tetravalent vanadium ions. The E.M.F. in each case is found to be independent of the nature of the electrolyte. When, however, solutions of caustic soda or of caustic potash are employed, the vanadium dissolves as a pentavalent ion, irrespective of variations

<sup>1</sup> Naumann, Moeser, and Lindenbaum, *J. prakt. Chem.*, 1907, [ii], 75, 146; compare Sabatier and Mailhe, *Ann. Chim. Phys.*, 1910, [viii], 20, 340.

<sup>2</sup> Luther and Rutter, *Zeitsch. anorg. Chem.*, 1907, 54, 1.

<sup>3</sup> Weiss, Downs, and Burns, *J. Ind. Eng. Chem.*, 1923, 15, 965; Senseman and Nelson, *ibid.*, 1923, 15, 524.

<sup>4</sup> Hofmann and Dolde, *Ber.*, 1924, [B], 57, 1969.

<sup>5</sup> Marino, *Zeitsch. anorg. Chem.*, 1904, 39, 152.

in concentration, temperature, or current density. The pentavalent ion is electro-negative; the tetravalent ion is strongly hydrolytic, and readily gives rise to the vanadyl ion  $[\text{VO}]^{2+}$ , which is weakly electro-positive. The trivalent vanadium ion displays more marked electro-positive properties, which again increase with the formation of divalent ions.<sup>1</sup>

In 1898, Cowper-Coles<sup>2</sup> claimed to have successfully effected the electrolytic reduction of an acid solution of vanadium pentoxide to metallic vanadium, but the product was subsequently shown by Fischer<sup>3</sup> to have been a deposit of platinum hydride. Fischer, in a series of over three hundred experiments, varied the temperature, current density, cathode material, concentration, electrolyte, addition agent, and construction of cell, but in not one instance was the formation of any metallic vanadium observed. In most cases reduction ceased at the tetravalent state (blue). At temperatures above 90° C. reduction appeared to proceed to the divalent state (lavender). The use of carbon electrodes led to the trivalent state (green), but only lead electrodes produced the trivalent state at temperatures below 90° C. Platinum electrodes reduced the electrolyte to the blue vanadyl salt below 90° C.; using a divided cell and temperatures above 90° C. the lavender salt was obtained.

Electrolytic reduction of pentavalent and tetravalent vanadium salts has frequently been employed for the preparation of vanadium compounds of lower valency.<sup>4</sup> Bleecker<sup>5</sup> has also prepared vanadium pentoxide and several vanadates electrolytically.

The passivity of vanadium is referred to on p. 23, and the electrolytic decomposition of anhydrous fused vanadium salts on p. 17.

#### VANADIUM AND HYDROGEN.

Roscoe, in 1870, found that vanadium "absorbs or combines with" up to 1.3 per cent. of its weight of hydrogen, according to the state of division of the metal, when heated in a current of the gas, and confirmed the observation in the following year.<sup>6</sup> Muthmann, Weiss, and Riedelbauch subsequently reported that the amount of hydrogen taken up by the vanadium increases with increase of temperature and duration of contact; they stated that at 1300° C. a stable hydride of vanadium was produced containing 16.1 per cent. of hydrogen. This is described as a black powder which is unaffected by air, hot water, or boiling hydrochloric acid.<sup>7</sup> Prandtl and Manz, however, were unable to obtain any compound of vanadium and hydrogen, and state that the previously observed increases in weight were due either to (a) absorption of oxygen

<sup>1</sup> Rutter has measured the E.M.F.'s associated with the successive changes,  $\text{V}^{\text{V}} \rightarrow \text{V}^{\text{IV}} \rightarrow \text{V}^{\text{III}} \rightarrow \text{V}^{\text{II}}$ , and has examined the behaviour of solutions containing these ions towards numerous oxidising and reducing agents (*Zeitsch. anorg. Chem.*, 1907, 52, 368).

<sup>2</sup> Cowper-Coles, *Institution of Mining and Metallurgy*, 1898-99, p. 198; *Chem. News*, 1899, 79, 147.

<sup>3</sup> Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 175; see also Gin, *ibid.*, 1909, 16, 439.

<sup>4</sup> Piccini, *Zeitsch. anorg. Chem.*, 1899, 19, 204; Piccini and Marino, *ibid.*, 1902, 32, 55; 1906, 50, 49; Piccini and Brizzi, *ibid.*, 1896, 11, 106; 1899, 19, 394; Stähler and Wirthwein, *Ber.*, 1905, 38, 3978; Bültemann, *Zeitsch. Elektrochem.*, 1904, 10, 141; Rutter, *ibid.*, 1906, 12, 230; Chapman and Law, *Analyst*, 1907, 32, 250.

<sup>5</sup> Bleecker, *Met. Chem. Eng.*, 1910, 8, 666; 1911, 9, 501.

<sup>6</sup> Roscoe, *J. Chem. Soc.*, 1870, 23, 358; 1871, 24, 23.

<sup>7</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 58.

and nitrogen, or (b) absorption of hydrogen by impurities in the vanadium.<sup>1</sup> More recent investigations with vanadium of 90 per cent. purity which had been preheated for one hour in a vacuum at 1100° C. have shown that the quantity of hydrogen absorbed varies with the temperature and the pressure. One gram of the metal absorbs 122.6 c.c. of hydrogen at ordinary temperatures and pressures and 2.01 c.c. at 1100° C.<sup>2</sup> It is, therefore, improbable that a definite compound is produced.<sup>3</sup>

### Vanadium and the Halogens.

The variable valency of vanadium is well displayed in its halides and oxyhalides. These are set out in the following table:—

#### HALIDES AND OXYHALIDES OF VANADIUM.

Valency.	Fluorine.	Chlorine.	Bromine.	Iodine.
Divalent	VF <sub>2</sub> *	VCl <sub>2</sub>		
Trivalent	VF <sub>3</sub> VF <sub>3</sub> .3H <sub>2</sub> O	VCl <sub>3</sub> VCl <sub>3</sub> .3H <sub>2</sub> O VOCl	VBr <sub>3</sub> VBr <sub>3</sub> .6H <sub>2</sub> O VOBr	VI <sub>3</sub> .6H <sub>2</sub> O
Tetravalent	VF <sub>4</sub> VOF <sub>2</sub>	VCl <sub>4</sub> VOCl <sub>2</sub>	VOBr <sub>2</sub>	
Pentavalent	VF <sub>5</sub> VOF <sub>3</sub> VO <sub>2</sub> F *	VOCl <sub>3</sub>	VOBr <sub>3</sub>	
Doubtful valency.		VO <sub>2</sub> Cl <sub>2</sub> .8H <sub>2</sub> O V <sub>2</sub> O <sub>2</sub> Cl <sub>4</sub> .5H <sub>2</sub> O V <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub> .4H <sub>2</sub> O	VO <sub>2</sub> Br <sub>3</sub> .5H <sub>2</sub> O	

The table shows that the stability of the halides decreases with increase in the atomic weight of the halogen. All the halides are hygroscopic and show a very strong tendency to undergo hydrolysis, a tendency which increases with the valency. The tetrabromide and tetriodide have not been isolated; VF<sub>4</sub> and VCl<sub>4</sub> can perhaps be regarded as salts of the very weak base VO<sub>2</sub>. They are easily fusible compounds, and undergo hydrolysis so readily that they evolve the gaseous halogen acid and "fume" in moist air; they are therefore comparable with the tetrahalides of titanium, germanium, tin and lead.

The preparation of the anhydrous halides of vanadium is possible only in the dry way, since attempts to remove the water from the hydrated halide result in the formation of a basic salt, as in the cases of the halides of iron, chromium, aluminium, bismuth, etc. The general methods of preparation employed are:

<sup>1</sup> Prandtl and Manz, *Zeitsch. anorg. Chem.*, 1912, 79, 209.

<sup>2</sup> Huber, Kirschfeld, and Sieverts, *Ber.*, 1926, 59, 2891.

<sup>3</sup> See also Biltz, *Zeitsch. anorg. Chem.*, 1928, 174, 42.

\* Does not exist in the free state.



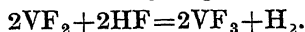
1. Halogenation of the oxides or sulphides.
2. Reduction of a higher halide either directly or by means of hydrogen.
3. Direct synthesis.

Since fluorine is difficult to prepare and manipulate, the anhydrous fluorides and oxyfluorides are prepared by the action of anhydrous hydrogen fluoride on other halides or oxyhalides of vanadium.<sup>1</sup>

#### VANADIUM AND FLUORINE.

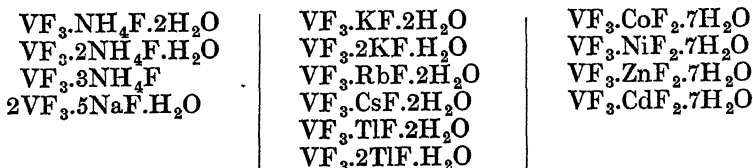
Vanadium combines directly with fluorine to produce a mixture of several fluorides, from which it is difficult to separate any in the pure state.

**Hypovanadous Fluoride, vanadium difluoride,  $\text{VF}_2$ ,** has not been isolated, but a reddish-violet solution containing it is obtained by the action of excess of hydrofluoric acid on vanadium aluminium silicide,<sup>2</sup>  $\text{V}_3\text{Al}_2\text{Si}_{13}$ , in the absence of air. In the presence of air the solution becomes green, with evolution of hydrogen :



The solution behaves generally like one of vanadium dichloride.<sup>3</sup>

**Vanadous Fluoride, vanadium trifluoride,  $\text{VF}_3$ ,** is produced when hydrogen fluoride is allowed to react with pure, dry vanadous chloride,  $\text{VCl}_3$ , at a dark red heat. It is a greenish-yellow powder, almost insoluble in water and the usual organic solvents. It sublimes at a bright red heat. Density at  $19^\circ \text{C}$ ., 3.3628.<sup>4</sup> The *trihydrate*,  $\text{VF}_3 \cdot 3\text{H}_2\text{O}$ , separates in dark green rhombohedral crystals when vanadous oxide,  $\text{V}_2\text{O}_3$ , is dissolved in aqueous hydrofluoric acid and the solution is concentrated. This fluoride has also been prepared by the electrolytic reduction of a solution of vanadyl difluoride in hydrofluoric acid.<sup>5</sup> It decomposes rapidly, with absorption of oxygen, on exposure to air or in solution. It reduces silver salts to the metal, and mercuric and cupric salts to the mercurous and cuprous state, respectively. With alkali carbonates and hydroxides it reacts to throw down a voluminous greyish-green precipitate of vanadous hydroxide,  $\text{V}(\text{OH})_3$ , which also oxidises in the air.<sup>6</sup> Vanadous fluoride possesses the property common to many fluorides<sup>7</sup> of forming a large number of easily crystallisable double salts with the fluorides of other metals and with ammonium fluoride. The following green, crystalline compounds have been prepared and described :—<sup>8</sup>



The constitution of these compounds is discussed later (see p. 39).

<sup>1</sup> Ruff and Liekfett, *Ber.*, 1911, 44, 2539.

<sup>2</sup> Manchot and Fischer, *Annalen*, 1907, 357, 129.

<sup>3</sup> Scarliarini and Airoidi, *Gazzetta*, 1925, 55, 44.

<sup>4</sup> Petersen, *J. prakt. Chem.*, 1889, [ii], 40, 47.

<sup>5</sup> See this series, Vol. VIII. (1915), pp. 45 *et seq.*

<sup>6</sup> Petersen, *ibid.*; Piccini and Giorgis, *Gazzetta*, 1888, 18, 186; 1892, 22, 55; Ephraim and Heymann, *Ber.*, 1909, 42, 4460; Costăchescu, *J. Chem. Soc., Abs.*, 1910, 98, ii, 619.

<sup>7</sup> See p. 29.

<sup>8</sup> Ruff and Liekfett, *loc. cit.*

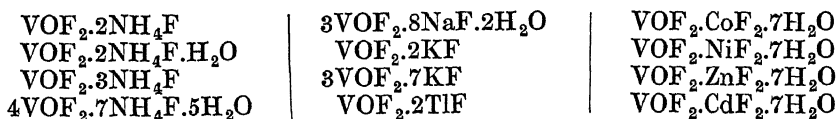
**Vanadium Tetrafluoride**, *hypovanadic fluoride*,  $\text{VF}_4$ , is produced by the action of anhydrous hydrogen fluoride on the corresponding chlorine compound,  $\text{VCl}_4$ , at temperatures from  $-28^\circ$  to  $0^\circ$  C. It is an extremely deliquescent brown powder which readily undergoes hydrolysis with water, so that it does not give rise to double salts as in the case of the trifluoride. Its density at  $23^\circ$  C. is 2.9749. It decomposes above  $325^\circ$  C., yielding a mixture of the pentafluoride and the trifluoride: <sup>1</sup>



**Vanadium Pentafluoride**, *vanadic fluoride*,  $\text{VF}_5$ , is of interest as the only pentahalide of vanadium. It cannot be prepared by the action of hydrofluoric acid on vanadium pentoxide,  $\text{V}_2\text{O}_5$ , or on sodium metavanadate,  $\text{NaVO}_3$ , because of its very strong tendency to undergo hydrolysis, with the formation of oxyfluorides. It is obtained as a white sublimate when the tetrafluoride is heated in a current of nitrogen in a platinum tube, the temperature gradually being raised from  $300^\circ$  to  $650^\circ$  C. It attacks glass and decomposes in moist air; it is therefore kept in air-tight platinum tubes. It is soluble in the common organic solvents. Density at  $19^\circ$  C., 2.1766. It boils at  $111.2^\circ$  C. under 758 mm. pressure.<sup>2</sup>

#### *Vanadium Oxyfluorides.*

**Vanadyl Difluoride**,  $\text{VOF}_2$ , is prepared by the action of anhydrous hydrogen fluoride on vanadyl dibromide,  $\text{VOBr}_2$ . It is a yellow substance. Density at  $19^\circ$  C., 3.3956.<sup>3</sup> A hydrated vanadyl difluoride,  $\text{VOF}_2 \cdot x\text{H}_2\text{O}$ , is obtained as microscopic blue crystals when hypovanadic oxide,  $\text{VO}_2$ , is dissolved in excess of hydrofluoric acid and the solution concentrated slowly over sulphuric acid.<sup>4</sup> The following double salts have been prepared, all of which are crystalline and fairly stable:—<sup>5</sup>



**Vanadium Oxytrifluoride**,  $\text{VOF}_3$ , is obtained by the action of hydrogen fluoride on the corresponding chlorine compound,  $\text{VOCl}_3$ . It is also formed when vanadous fluoride is heated to redness in oxygen. It is a yellowish-white, extremely hygroscopic substance,<sup>4</sup> readily soluble in water. Its density at  $20.5^\circ$  C. is 2.4591.<sup>6</sup> When heated to  $132^\circ$  C. it undergoes partial decomposition with formation of vanadium pentoxide. The following double salts of vanadium oxytrifluoride are known: <sup>7</sup>  $2\text{VOF}_3 \cdot 3\text{NH}_4\text{F} \cdot \text{H}_2\text{O}$ ,  $2\text{VOF}_3 \cdot 3\text{KF}$ ,  $\text{VOF}_3 \cdot 2\text{KF}$ ,  $\text{VOF}_3 \cdot \text{VF}_5$ ,  $4\text{KF}$ , and  $2\text{VOF}_3 \cdot 3\text{KF} \cdot \text{HF}$ . These double salts are white, crystalline compounds; they are stable in the air, but undergo hydrolysis in solution to form addition compounds of vanadium dioxyfluoride,  $\text{VO}_2\text{F}$ .

<sup>1</sup> Ruff and Lickfett, *Ber.*, 1911, 44, 2539.

<sup>2</sup> Ruff and Lickfett, *loc. cit.*

<sup>3</sup> Ruff and Lickfett, *loc. cit.*

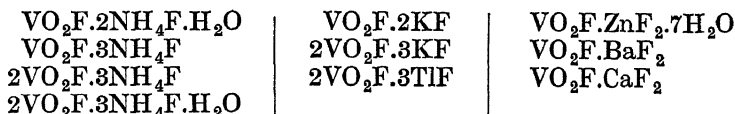
<sup>4</sup> Petersen, *J. prakt. Chem.*, 1889, [ii], 40, 194.

<sup>5</sup> Petersen, *loc. cit.*; *Ber.*, 1888, 21, 3257; Piccini and Giorgis, *loc. cit.*; Baker, *Ber.*, 1878, 11, 1722; Ephraim and Heymann, *Ber.*, 1909, 41, 4460.

<sup>6</sup> Ruff and Lickfett, *loc. cit.*

<sup>7</sup> Petersen, *J. prakt. Chem.*, 1889, [ii], 40, 271; Piccini and Giorgis, *loc. cit.*

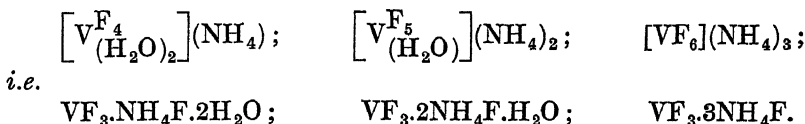
**Vanadium Dioxyfluoride**,  $\text{VO}_2\text{F}$ , has not been isolated in the free state. It combines readily with other fluorides to form a series of yellow, easily crystallisable double salts, which can be heated to  $100^\circ\text{C}$ . or even above without undergoing change. The following have been prepared :—<sup>1</sup>



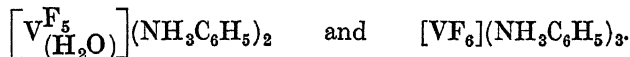
**Constitution of Vanadium Double Halides.**<sup>2</sup>

The double fluorides of vanadium and other double halogen salts in most cases can be regarded as in accordance with Werner's theory of co-ordinated compounds. The vanadium has a co-ordination number six.

The hydrated fluoride,  $\text{VF}_3 \cdot 3\text{H}_2\text{O}$ , may be regarded as an aquo-salt,  $\left[ \text{V}^{\text{F}_3}(\text{H}_2\text{O})_3 \right]$ . The gradual replacement of aquo-water by fluorine gives the following :—<sup>3</sup>



Similarly, the double potassium salt,  $\text{VF}_3 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$ , is  $\left[ \text{V}^{\text{F}_5}(\text{H}_2\text{O}) \right]\text{K}_2$ . The alkali metal can be replaced by aniline to produce salts of the same type : <sup>4</sup>



The constitution of the acid radical of the potassium salt containing one molecule of water corresponds to that of those double salts which contain seven molecules of water. It therefore follows that the acid radical in the latter is also co-ordinatively saturated. The salt  $\text{VF}_3 \cdot \text{ZnF}_2 \cdot 7\text{H}_2\text{O}$  thus becomes  $\left[ \text{V}^{\text{F}_5}(\text{H}_2\text{O}) \right][\text{Zn}(\text{H}_2\text{O})_6]$ . Replacement of the zinc atom by atoms of other metals gives the corresponding cobalt, nickel, and cadmium compounds, which have similar constitution.<sup>5</sup>

Double salts of the other vanadium halides are much less stable and therefore less numerous than those containing fluorine. They are represented on the co-ordination theory by formulæ which are analogous to those set out above. Unlike vanadium trifluoride, which forms  $\text{VF}_3 \cdot 3\text{H}_2\text{O}$ , the molecules of the corresponding hydrates of

<sup>1</sup> Piccini and Giorgis, *loc. cit.*; Baker, *J. Chem. Soc.*, 1878, 33, 388; Ephraim, *Zeitsch. anorg. Chem.*, 1903, 35, 66; Petersen, *loc. cit.*; Ephraim and Heymann, *Ber.*, 1909, 41, 4460.

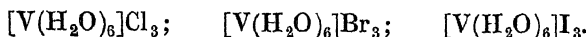
<sup>2</sup> For a general discussion of double fluorides and oxyfluorides of the metals, see this series, Vol. VIII. (1915), pp. 45 *et seq.*

<sup>3</sup> Werner, *New Ideas in Inorganic Chemistry*, translated by Hedley (Longman's, 1911), p. 120.

<sup>4</sup> Costăchescu, *J. Chem. Soc., Abs.*, 1910, 98, ii, 619.

<sup>5</sup> Werner, *loc. cit.*, 137.

the other halogen compounds are found to possess  $6\text{H}_2\text{O}$ , and are written :

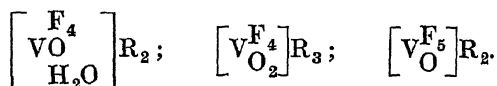


It is of interest to note that Meyer and Backa,<sup>1</sup> by treating vanadium trichloride and tribromide with liquid ammonia, have recently obtained hexammine derivatives :



These are comparable in their reactions to the hexammine of ferric chloride,  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_3$ . Hexammino-vanadium trichloride loses its chlorine on being treated with nitric acid and forms the corresponding nitrate,  $[\text{V}(\text{NH}_3)_6](\text{NO}_3)_3$ .

The double oxy-salts may be regarded as belonging to the following general series :—



Thus,  $\text{VOF}_2 \cdot 2\text{NH}_4\text{F} \cdot \text{H}_2\text{O}$  can be written  $\left[ \begin{array}{c} \text{F}_4 \\ \text{VO} \\ \text{H}_2\text{O} \end{array} \right] (\text{NH}_4)_2; \text{VOF}_2 \cdot \text{ZnF}_2 \cdot$

$7\text{H}_2\text{O}$  as  $\left[ \begin{array}{c} \text{F}_4 \\ \text{VO} \\ \text{H}_2\text{O} \end{array} \right] [\text{Zn}(\text{H}_2\text{O})_6]; \text{VO}_2\text{F} \cdot 3\text{NH}_4\text{F}$  as  $\left[ \text{VO}_2^{\text{F}_4} \right] (\text{NH}_4)_3;$

and  $\text{VO}_2\text{F} \cdot \text{ZnF}_2 \cdot 7\text{H}_2\text{O}$  as  $\left[ \begin{array}{c} \text{F}_3 \\ \text{VO}_2 \\ \text{H}_2\text{O} \end{array} \right] [\text{Zn}(\text{H}_2\text{O})_6]$ . It will be observed

that the co-ordination number six is maintained by bringing a molecule of water into the co-ordinated complex.

Ephraim has observed that the composition of the halogen double salts of vanadium and other metals appears to be dependent on the atomic weight of the second metal. This is shown by rewriting the formulæ for some of the double salts :  $2\text{VF}_3 \cdot 6\text{NH}_4\text{F}$ ,  $2\text{VF}_3 \cdot 5\text{NaF}$ , and  $2\text{VF}_3 \cdot 4\text{KF}$ . It has not been found possible to prepare double salts in which the number of molecules of alkali fluoride combined with two molecules of  $\text{VF}_3$  is greater than 6, 5, and 4 respectively. Efforts to prepare a double salt having the composition  $2\text{VF}_3 \cdot 5\text{KF}$ , for instance, were unsuccessful. Similarly, rearranging the formulæ for some double salts of vanadyl fluoride gives :<sup>2</sup>  $3\text{VOF}_2 \cdot 9\text{NH}_4\text{F}$ ,  $3\text{VOF}_2 \cdot 8\text{NaF}$ , and  $3\text{VOF}_2 \cdot 7\text{KF}$ .

#### VANADIUM AND CHLORINE.

**Hypovanadous Chloride, vanadium dichloride,  $\text{VCl}_2$ .**—Solutions of vanadium dichloride can be prepared by electrolytic reduction of higher chlorides,<sup>3</sup> or by the addition of amalgamated zinc to a hydrochloric acid solution of vanadium pentoxide.<sup>4</sup> The solution undergoes very rapid oxidation, hence the isolation of vanadium dichloride cannot

<sup>1</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

<sup>2</sup> Ephraim, *Ber.*, 1903, 36, 1177; compare Grossmann, *ibid.*, 1903, 36, 1600; Melikoff and Kasanezky, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 77.

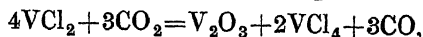
<sup>3</sup> Piccini and Marino, *Zeitsch. anorg. Chem.*, 1902, 32, 67.

<sup>4</sup> Conant and Cutter, *J. Amer. Chem. Soc.*, 1926, 48, 1023.

be effected by a wet method. It is deposited in apple-green hexagonal flakes when the vapour of vanadium tetrachloride mixed with dry hydrogen is passed through a glass tube heated to dull redness.<sup>1</sup> Vanadium trichloride undergoes decomposition to the dichloride and tetrachloride when heated to 900° C. in a stream of nitrogen or carbon dioxide. The tetrachloride produced at the same time distils away at the temperature of the reaction.<sup>2</sup> More recently, vanadium dichloride has been obtained by the action of hydrogen chloride on commercial ferrovanadium.<sup>3</sup> Its density at 18° C. is 3.23. It is a hygroscopic solid which deliquesces with oxidation to a brown liquid. In the presence of mineral acid a violet solution is formed, which, like all other solutions of divalent vanadium salts, acts as an extremely powerful reducing agent; it is, in fact, one of the strongest reducing agents known. It slowly evolves hydrogen from its aqueous or acid solutions, with formation of the trichloride; a vigorous evolution of hydrogen takes place from the acid solution in the presence of platinum foil. It bleaches litmus and indigo, precipitates the metals from solutions of salts of copper, tin, silver, gold and platinum, and has been successfully employed in the isolation of certain organic radicals, as, for example, the triphenylmethyl radical from triphenyl carbinol.<sup>4</sup> At a bright red heat it reduces carbon dioxide to the monoxide: <sup>5</sup>

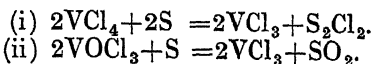


and with even stronger heating the reaction proceeds further,



pure vanadium sesquioxide being produced.

**Vanadous Chloride, vanadium trichloride,  $\text{VCl}_3$ .**—This halide is obtained by the action of hydrogen chloride on finely divided vanadium at 300° to 400° C.,<sup>6</sup> or by heating vanadium tetrachloride to 140° C. in a current of carbon dioxide, which removes the chlorine formed at the same time. It can be conveniently made also by boiling vanadium oxytrichloride,  $\text{VOCl}_3$ , vanadium tetrachloride,  $\text{VCl}_4$ , or a mixture of both, with sulphur, under reflux. The reactions involved are: <sup>7</sup>



In the former case the sulphur chloride is distilled off, and in both cases the excess of sulphur is removed by distillation in an atmosphere of carbon dioxide or nitrogen.

Anhydrous vanadium trichloride is a crystalline solid of the colour of peach blossom. It is extremely hygroscopic, deliquescing to a brown liquid. It gives green solutions in alcohol and ether. Density at 18° C., 3.00. The absorption spectrum has been studied.<sup>8</sup> On being strongly heated in hydrogen it is reduced to vanadium dichloride,  $\text{VCl}_2$ ,

<sup>1</sup> Roscoe, *J. Chem. Soc.*, 1870, 23, 344.

<sup>2</sup> Ruff and Lickfett, *Ber.*, 1911, 44, 506.

<sup>3</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

<sup>4</sup> Conant and Sloan, *J. Amer. Chem. Soc.*, 1923, 45, 2466; Conant and Lutz, *ibid.*, 1923, 45, 1047; Conant and Cutter, *ibid.*, 1926, 48, 1016.

<sup>5</sup> Ruff and Lickfett, *loc. cit.*

<sup>6</sup> Meyer and Backa, *loc. cit.*

<sup>7</sup> Ruff and Lickfett, *loc. cit.*

<sup>8</sup> Morgan and Moss, *J. Chem. Soc.*, 1913, 103, 88.

and ultimately to the metal. Tin also reduces it to the dichloride.<sup>1</sup> On being heated in a current of nitrogen to a dark red heat it is decomposed into the tetrachloride, which distils off, and the dichloride, which remains behind :



The following change also takes place :—



so that the quantity of tetrachloride produced is determined for each temperature by the partial pressure of the chlorine. If the trichloride is heated in a current of chlorine which is free from oxygen, complete conversion into the tetrachloride ensues.

The *hexahydrate*,  $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ , is prepared by dissolving vanadous hydroxide,  $\text{V}(\text{OH})_3$ , in hydrochloric acid in the absence of air,<sup>2</sup> or by the electrolytic reduction of a solution of vanadium pentoxide,  $\text{V}_2\text{O}_5$ , in hydrochloric acid.<sup>3</sup> It is a green, crystalline compound, very hygroscopic, and readily soluble in water, alcohol, or ether. On being heated it decomposes before all its water has been driven off. Its aqueous solutions are brown or yellow, according to the concentration; on addition of acid the solution assumes the green colour characteristic of solutions of trivalent vanadium salts, and as oxidation to the tetravalent state takes place the solution becomes blue. When hydrated vanadium trichloride and rubidium chloride are together dissolved in water, in the requisite proportions, and the solution is saturated with hydrochloric acid and concentrated, crystals of a double salt,  $\text{VCl}_3 \cdot 2\text{RbCl} \cdot \text{H}_2\text{O}$ , are obtained. The corresponding ammonium, potassium and caesium double salts have been prepared.<sup>4</sup> The magnesium double chloride has the composition  $\text{VCl}_3 \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$ ; <sup>5</sup> another double potassium salt,  $\text{VCl}_3 \cdot \text{KCl}$ , is known.<sup>6</sup> Addition of silver nitrate gives a precipitate which consists of a mixture of metallic silver and silver chloride; with thallium sulphate, however, a precipitate of thallium chloride is thrown down, from which it can be inferred that vanadium trichloride undergoes normal ionisation in solution, as in the case of the corresponding violet chromium chloride,  $\text{CrCl}_3$ , and ferric chloride,  $\text{FeCl}_3$ .

*Hexammino-vanadium Trichloride*,  $[\text{V}(\text{NH}_3)_6]\text{Cl}_3$ .—The similarity between the trichlorides of iron and vanadium is further shown in their behaviour towards ammonia. At ordinary temperatures ammonia reacts with vanadium trichloride to produce vanadium nitride,  $\text{VN}$ , and ammonium chloride, but if liquid ammonia is poured over vanadium trichloride, a quantitative yield of a reddish-brown salt,  $[\text{V}(\text{NH}_3)_6]\text{Cl}_3$ , is obtained, which recalls the hexammines of cobalt and chromium. The ammonia molecules are not, however, very firmly held, and the compound is, therefore, more comparable with the corresponding hexammine of ferric chloride,  $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_3$ .

Hexammino-vanadium trichloride is insoluble in water, alcohol, and

<sup>1</sup> Kremann and Noss, *Monatsh.*, 1913, 34, 54.

<sup>2</sup> Locke and Edwards, *Amer. Chem. J.*, 1898, 20, 594.

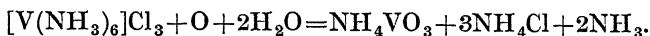
<sup>3</sup> Piccini and Brizzi, *Zeitsch. anorg. Chem.*, 1899, 19, 394.

<sup>4</sup> Stahler, *Ber.*, 1904, 37, 4411.

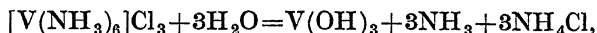
<sup>5</sup> Stähler, *loc. cit.*

<sup>6</sup> Locke and Edwards, *loc. cit.*

ether. On being exposed to dry air it decomposes slowly and becomes white :

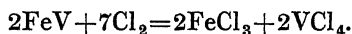


On being exposed to damp air it slowly becomes green, due to the formation of the hexa-aquo-vanadium salt,  $[\text{V}(\text{H}_2\text{O})_6]\text{Cl}_3$ . It is decomposed by boiling water,



and dissolves in dilute hydrochloric acid to give a solution which possesses the green colour characteristic of trivalent vanadium salts. By the action of nitric acid a quantitative yield of *hexammino-vanadium nitrate*,  $[\text{V}(\text{NH}_3)_6](\text{NO}_3)_3$ , is obtained.<sup>1</sup>

**Hypovanadic Chloride**, *vanadium tetrachloride*,  $\text{VCl}_4$ , can be prepared synthetically from the lower chloride,  $\text{VCl}_3$ , by heating in a stream of chlorine at 600° C. Another convenient method consists in passing dry chlorine over ferrovanadium contained in a hard glass tube heated in a combustion furnace. The reaction is expressed :



The vanadium tetrachloride distils over and is purified from any ferric chloride present either by distillation or by extraction of the product with carbon tetrachloride, in which only the vanadium halide is soluble.<sup>2</sup> Sulphuryl chloride, thionyl chloride, sulphur monochloride, and phosgene can all be used in the last reaction instead of chlorine, and the ferrovanadium also can be substituted by vanadium carbide,  $\text{V}_4\text{C}_3$ ,<sup>3</sup> nitride,  $\text{VN}$ ,<sup>4</sup> subsilicide,  $\text{V}_2\text{Si}$ ,<sup>5</sup> disilicide,  $\text{VSi}_2$ ,<sup>6</sup> or pentoxide.<sup>7</sup>

Vanadium tetrachloride is a reddish-brown, viscous liquid, which boils at 158.7° C. at 768 mm.<sup>8</sup> and melts at -109° C. Density at 0° C., 1.8584. The dielectric constant has been investigated.<sup>9</sup> The electrical conductivity is extremely low even near the boiling-point.<sup>10</sup> On being heated to 900° C. in the presence of iron it undergoes reduction to the metal.<sup>11</sup> It decomposes slowly and spontaneously in a dry atmosphere at ordinary temperatures into vanadous chloride,  $\text{VCl}_3$ , and chlorine. In moist air it undergoes slow hydrolysis with formation of hydrochloric acid, which gives rise to the usual fuming effect; on being thrown into water it is immediately hydrolysed and forms vanadyl dichloride,  $\text{VOCl}_2$ , which gives a blue solution. The tetrachloride is stable only at temperatures above about 630° C.<sup>12</sup> It is too unstable to form double salts with other chlorides. In benzene solution, however, it reacts with ammonia and its derivatives, *e.g.* aniline, to yield com-

<sup>1</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

<sup>2</sup> Mertes, *J. Amer. Chem. Soc.*, 1913, 35, 671; Meyer and Backa, *loc. cit.*

<sup>3</sup> Ruff and Lickfett, *Ber.*, 1911, 44, 506.

<sup>4</sup> Roscoe, *J. Chem. Soc.*, 1870, 23, 344.

<sup>5</sup> Moissan and Holt, *Ann. Chim. Phys.*, 1902, [vii], 27, 277.

<sup>6</sup> Meyer and Backa, *loc. cit.*

<sup>7</sup> Matignon and Bourion, *Compt. rend.*, 1904, 138, 631.

<sup>8</sup> Ruff and Lickfett, *loc. cit.*; Biltz and Keunecke (*Zeitsch. anorg. Chem.*, 1925, 147, 171) give the boiling-point as 148.5° C. at 755 mm.

<sup>9</sup> Loomis and Schlundt, *J. Physical Chem.*, 1915, 19, 734.

<sup>10</sup> Voigt and Biltz, *Zeitsch. anorg. Chem.*, 1924, 133, 277.

<sup>11</sup> Parravano and Mazzetti, *Rec. Trav. chim.*, 1923, 42, 821.

<sup>12</sup> Ruff and Friedrich, *Zeitsch. anorg. Chem.*, 1914, 89, 279.

pounds which consist of one molecule of the tetrachloride in association with from three to six molecules of ammonia or its derivative.<sup>1</sup>

### *Vanadium Oxychlorides.*

**Divanadyl Chloride**,  $V_2O_2Cl$ , is formed, together with vanadium oxymonochloride and vanadyl dichloride, when the vapour of vanadium oxytrichloride,  $VOCl_3$ , mixed with hydrogen, is passed through a glass tube heated to redness. It is an insoluble, bronze-coloured substance, similar in appearance to mosaic gold; under the microscope it is seen to consist of glistening yellow crystals. Density at  $20^\circ C.$ , 3.64. On being heated in air it forms vanadium pentoxide.<sup>2</sup> A *hydrate*,  $2V_2O_2Cl \cdot 5H_2O$ , has been obtained by the action of hydrogen sulphide on a solution of vanadium pentoxide in concentrated hydrochloric acid.<sup>3</sup> The chemical identity of divanadyl chloride is, however, a matter of doubt.

**Vanadium Oxymonochloride**,  $VOCl$ , can be obtained by heating vanadium trichloride in an atmosphere of carbon dioxide at about  $700^\circ C.$  for several hours :

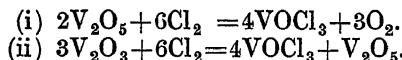


It can also be prepared by the reduction of vanadium oxytrichloride,  $VOCl_3$ , in hydrogen at a red heat. It is a flaky, brown, crystalline substance; density at  $16^\circ C.$ , 2.824; soluble with difficulty in water but readily soluble in nitric acid.<sup>4</sup>

**Vanadyl Dichloride**,  $VOCl_2$ , is produced by the partial hydrolysis of vanadium tetrachloride. It is also formed, together with small proportions of vanadium oxymonochloride,  $VOCl$ , when vanadium oxytrichloride,  $VOCl_3$ , is reduced either by means of hydrogen or by heating with metallic zinc in a sealed tube at  $400^\circ C.$ <sup>5</sup> It yields grass-green deliquescent crystals which have an unctuous feel. Density at  $13^\circ C.$ , 2.88. The dielectric constant<sup>6</sup> and absorption spectrum<sup>7</sup> have been investigated. Efforts to obtain double salts of vanadyl dichloride with chlorides of other metals, corresponding to those given by vanadyl difluoride, have not proved successful.

Two series of double salts having the general formulæ  $VOCl_2 \cdot 4R \cdot HCl \cdot xH_2O$  and  $VOCl_2 \cdot 2R \cdot HCl \cdot xH_2O$ , where  $R$  = quinoline or pyridine, are, however, known.<sup>8</sup>

**Vanadium Oxytrichloride**,  $VOCl_3$ , commonly known as "vanadyl chloride," is the easiest to prepare of all the halogen or oxyhalogen compounds of vanadium. It distils over as a yellow liquid when vanadium pentoxide is strongly heated, or when vanadium trioxide is gently heated, in a current of chlorine. Addition of charcoal accelerates the reactions :<sup>9</sup>



<sup>1</sup> Mertes and Fleck, *J. Ind. Eng. Chem.*, 1915, 7, 1037.

<sup>2</sup> Roscoe, *J. Chem. Soc.*, 1868, 21, 348.

<sup>3</sup> Crow, *ibid.*, 1876, 30, 457.

<sup>4</sup> Ruff and Lickfett, *Ber.*, 1911, 44, 506; Roscoe, *loc. cit.*

<sup>5</sup> Roscoe, *loc. cit.*

<sup>6</sup> Loomis and Schlundt, *J. Physical Chem.*, 1915, 19, 734.

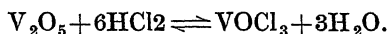
<sup>7</sup> Morgan and Moss, *J. Chem. Soc.*, 1913, 103, 88.

<sup>8</sup> Koppel, Goldmann, and Kaufmann, *Zeitsch. anorg. Chem.*, 1905, 45, 346.

<sup>9</sup> Roscoe, *J. Chem. Soc.*, 1868, 21, 342; Briscoe and Little, *ibid.*, 1914, 105, 1316.

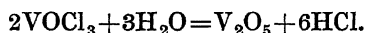


Instead of using chlorine, gaseous hydrogen chloride may be employed, provided that a strong dehydrating agent, phosphorus pentoxide or zinc chloride, is present to remove the water formed and so stop the right-to-left reaction in <sup>1</sup>



Halogenation in the presence of sulphur, or by means of sulphur halides, is also available. When chlorine is conducted into a mixture of vanadium pentoxide and sulphur, or when powdered vanadium pentoxide is treated with sulphur monochloride vapours, an immediate reaction sets in, with formation of vanadium oxytrichloride.<sup>2</sup> A quantitative yield of this compound is also obtained when vanadium trichloride is heated in oxygen at 500° to 600° C.<sup>3</sup>

Vanadium oxytrichloride is a light yellow, mobile, transparent liquid, which boils at 127·15° C at 764·5 mm.<sup>4</sup> Other determinations gave the b.pt. as 126·7° C. at 767 mm. and 124·4° C. at 723 mm.<sup>5</sup> The density has been found to be 1·8656 at 0° C.,<sup>6</sup> or 1·8362 at 15·5° C.,<sup>7</sup> compared with water at 4° C. The expansion on being heated from 0° to 130° C. has been measured.<sup>8</sup> The oxytrichloride remains a liquid at -15° C., and its vapour density at 186° C. is 6·108 (air = 1), showing it to be undecomposed. It is not decomposed on prolonged boiling with metallic sodium, potassium, or magnesium. On exposure to damp air, or on being treated with a small quantity of water, it displays the usual unstable character of the pentavalent vanadium halides in that it undergoes rapid hydrolysis and thereby becomes coated with red flakes of vanadium pentoxide :



With more water, it passes into solution; dilute solutions, which are brownish-yellow or red, according to the concentration, evolve chlorine and become blue on standing, undergoing reduction to the tetravalent state. On evaporation to dryness, all the chlorine is evolved and the residue consists of the pentoxide. Vanadium oxytrichloride is also soluble in ether and alcohol. It dissolves chlorine, bromine, iodine, yellow phosphorus, and sulphur, and is miscible with various liquid hydrocarbons and chlorinated hydrocarbons; its use as an industrial solvent has therefore been suggested.<sup>9</sup>

Addition of pyridine hydrochloride to an alcoholic solution of vanadium oxytrichloride yields an addition compound,  $\text{VOCl}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{C}_2\text{H}_5\text{OH}$ .<sup>10</sup> On being brought into reaction with cupric oxide, a dark green copper chlorovanadate is formed,  $\text{Cu}(\text{VO}_3)_2 \cdot \text{CuCl}$ ; litharge similarly yields a brick-red lead chlorovanadate,  $\text{Pb}(\text{VO}_3)_2 \cdot \text{PbCl}_2$ . From the instability of these compounds towards water it is assumed

<sup>1</sup> Ephraim, *Zeitsch. anorg. Chem.*, 1903, 35, 66.

<sup>2</sup> Matignon and Bourion, *Compt. rend.*, 1904, 138, 631.

<sup>3</sup> Ruff and Lickfett, *loc. cit.*

<sup>4</sup> Thorpe, *J. Chem. Soc.*, 1880, 37, 349.

<sup>5</sup> Prandtl and Bleyer, *Zeitsch. anorg. Chem.*, 1909, 65, 152; Roscoe, *loc. cit.*; see also L'Hote, *Compt. rend.*, 1885, 101, 1151.

<sup>6</sup> Thorpe, *loc. cit.*; see also L'Hote, *loc. cit.*

<sup>7</sup> Roscoe, *loc. cit.*; Prandtl and Bleyer, *loc. cit.*

<sup>8</sup> Thorpe, *loc. cit.*

<sup>9</sup> Brown and Snyder, *J. Amer. Chem. Soc.*, 1925, 47, 2671.

<sup>10</sup> Koppel and Kaufmann, *Zeitsch. anorg. Chem.*, 1905, 45, 355.

that the chlorine atoms are directly attached to the vanadium atom.

The copper salt is, therefore, formulated thus:  $\text{Cu} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{VOCl} \cdot \text{CuVO}_3$ .

The reaction with magnesium oxide proceeds differently and gives magnesium hexavanadate,  $\text{Mg}_2\text{V}_6\text{O}_{17} \cdot 19\text{H}_2\text{O}$ .<sup>1</sup>

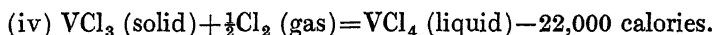
**Vanadium Oxydichloride**,  $\text{VO}_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ .—By the action of dilute aqueous hydrochloric acid on the two isomeric hydrates of hypovanadic acid, two isomeric forms of this compound have been prepared. The green hydrate gives rise to deep green crystals, and the rose hydrate to blue crystals of the same empirical composition.<sup>2</sup> Their constitutions are a matter of doubt.<sup>3</sup>

In addition to the above, two other vanadium oxychlorides have been reported:  $\text{V}_2\text{O}_2\text{Cl}_4 \cdot 5\text{H}_2\text{O}$  or  $2\text{VO}_2 \cdot 4\text{HCl} \cdot 3\text{H}_2\text{O}$ ,<sup>4</sup> and  $\text{V}_2\text{O}_3\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  or  $2\text{VO}_2 \cdot 2\text{HCl} \cdot 3\text{H}_2\text{O}$ .<sup>5</sup>

**Thermochemical Considerations.**—The heats of formation of the three anhydrous chlorides of vanadium have been determined by combustion in a bomb calorimeter and are found to be as follows:—<sup>6</sup>

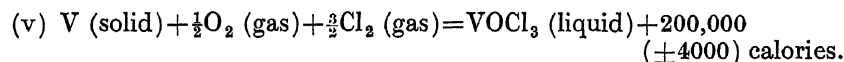
- (i)  $\text{V (solid)} + \text{Cl}_2 \text{ (gas)} = \text{VCl}_2 \text{ (solid)} + 147,000 (\pm 4000) \text{ calories.}$
- (ii)  $\text{V (solid)} + \frac{3}{2}\text{Cl}_2 \text{ (gas)} = \text{VCl}_3 \text{ (solid)} + 187,000 (\pm 8000) \text{ ,,}$
- (iii)  $\text{V (solid)} + 2\text{Cl}_2 \text{ (gas)} = \text{VCl}_4 \text{ (liquid)} + 165,000 (\pm 4000) \text{ ,,}$

It is obvious that the combustion of a molecule of vanadium with an increasing number of molecules of chlorine is not accompanied by a gradually increasing evolution of heat. The figures show that the formation of vanadium tetrachloride (liquid) from vanadium trichloride (solid) and chlorine (gas) proceeds endothermically:



Vanadium tetrachloride is, in fact, stable only at high temperatures. The last figure is, however, unreliable, since it is considerably affected by (a) the experimental errors involved in the reactions (ii) and (iii) above, and (b) the heat of liquefaction of vanadium tetrachloride, which is at present unknown.

The heat of formation of vanadium oxytrichloride is given by the equation:



#### VANADIUM AND BROMINE.

**Vanadous Bromide**, *vanadium tribromide*,  $\text{VBr}_3$ , is conveniently obtained synthetically. When powdered vanadium is gently warmed with pure, dry bromine, combination takes place readily, considerable heat is evolved and the tribromide is formed. Ferrovandium alloy gives the same product.<sup>7</sup> It is also obtained by the action of pure,

<sup>1</sup> Cuttica, Tarchi, and Alinari, *Gazzetta*, 1923, 53, [i], 189.

<sup>2</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224.

<sup>3</sup> Compare the monohydrates of Hypovanadic Oxide, p. 50.

<sup>4</sup> Crow, *J. Chem. Soc.*, 1876, 30, 453; Ferrakis, *Compt. rend.*, 1927, 184, 1430.

<sup>5</sup> Ditte, *ibid.*, 1886, 102, 1310.

<sup>6</sup> Ruff and Friedrich, *Zeitsch. anorg. Chem.*, 1914, 89, 279.

<sup>7</sup> Meyer and Backa, *ibid.*, 1924, 135, 187.

dry bromine vapour on either vanadium nitride, VN, or a mixture of vanadous oxide,  $V_2O_3$ , and charcoal,<sup>1</sup> or on pure vanadium carbide,  $V_4C_3$ .<sup>2</sup> It is a dark green or greyish-black, amorphous, deliquescent substance, which decomposes spontaneously with evolution of bromine at ordinary temperatures, giving a dark liquid. It dissolves in water without evolution of bromine to give a green solution, which possesses the same general properties as a solution of vanadium trichloride. On being gently heated in air it is rapidly converted into a mixture of vanadous oxide,  $V_2O_3$ , and vanadium pentoxide,  $V_2O_5$ .

The *hexahydrate*,  $VBr_3 \cdot 6H_2O$ , is prepared by dissolving the anhydrous tribromide in air-free water and concentrating, first on a water-bath and subsequently *in vacuo*.<sup>3</sup> It can also be prepared by dissolving vanadous hydroxide,  $V(OH)_3$ , in concentrated hydrobromic acid out of contact with air,<sup>4</sup> or by the electrolytic reduction of a solution of vanadium pentoxide,  $V_2O_5$ , in hydrobromic acid.<sup>5</sup> Hydrated vanadium tribromide is a green, hygroscopic, crystalline powder, which is less easily crystallisable and less stable than the corresponding chloride. The colour of its solution in water varies from brown to yellow according to the concentration; addition of acid gives rise to a green coloration which changes to blue as oxidation to the tetravalent state ensues.

*Hexammino-vanadium Tribromide*,  $[V(NH_3)_6]Br_3$ , is prepared by the action of liquid ammonia on vanadium tribromide. Its properties and reactions are similar to those of the corresponding chlorine compound (see p. 42).

**Hypovanadic Bromide**, *vanadium tetrabromide*,  $VBr_4$ , has not hitherto been isolated, but it is of interest to note that a double salt of composition  $VBr_4 \cdot SbBr_3 \cdot 7H_2O$  has been obtained by dissolving antimony tribromide and vanadium pentoxide in hydrobromic acid and adding bromine.<sup>6</sup>

#### *Vanadium Oxybromides.*

**Vanadium Oxymonobromide**,  $VOBr$ , is prepared by the decomposition of vanadyl dibromide,  $VOBr_2$ , *in vacuo* at  $360^\circ C$ . It forms violet, octahedral crystals, density 4.000 at  $18^\circ C$ . On being heated *in vacuo* at  $480^\circ C$ . it yields vanadium tribromide and vanadous oxide,  $V_2O_3$ . It is almost insoluble in water and the usual organic solvents.<sup>7</sup>

**Vanadyl Dibromide**,  $VOBr_2$ , is obtained by passing bromine vapour or, preferably, a mixture of sulphur bromide,  $S_2Br_2$ , and bromine over a mixture of vanadium pentoxide and sulphur at a red heat; the product is heated *in vacuo* at  $240^\circ C$ ., whereupon the vanadyl dibromide is obtained as a yellow powder.<sup>8</sup> An alternative method of preparation consists in heating vanadium oxytribromide,  $VOBr_3$ , to  $180^\circ C$ .<sup>9</sup> Vanadyl dibromide is no doubt present in the blue solution which results when hypovanadic oxide,  $VO_2$ , is dissolved in hydrobromic acid.

<sup>1</sup> Roscoe, *J. Chem. Soc.*, 1871, 24, 26.

<sup>2</sup> Ruff and Lickfett, *Ber.*, 1911, 44, 2534.

<sup>3</sup> Meyer and Backa, *loc. cit.*

<sup>4</sup> Locke and Edwards, *Amer. Chem. J.*, 1898, 20, 594.

<sup>5</sup> Piccini and Brizzi, *Zeitsch. anorg. Chem.*, 1899, 19, 394.

<sup>6</sup> Weinland and Feige, *Ber.*, 1903, 36, 260.

<sup>7</sup> Ruff and Lickfett, *loc. cit.*

<sup>8</sup> Ruff and Lickfett, *loc. cit.*

<sup>9</sup> Roscoe, *loc. cit.*

Vanadyl dibromide is a hygroscopic, unstable compound. It dissolves in water to give a blue solution. On being heated in air it forms vanadium pentoxide; *in vacuo* at 240° C. it partly sublimes and partly decomposes, with evolution of bromine and formation of a violet residue of vanadium oxymonobromide, VOBr. The dielectric constant has been investigated.<sup>1</sup>

No double salts of vanadyl dibromide have been prepared.

**Vanadium Oxytribromide**, VOBr<sub>3</sub>, is produced when pure, dry bromine is passed over vanadous oxide, V<sub>2</sub>O<sub>3</sub>, heated to redness. Yellowish-white vapours are evolved which condense to a deep red, hygroscopic liquid, density 2.9673 at 0° C. It decomposes slowly at ordinary temperatures into vanadyl dibromide and bromine, but distils without decomposition at 130° to 136° C. under 100 mm. pressure. It is much less stable than vanadyl dibromide, VOBr<sub>2</sub>.<sup>2</sup>

An oxybromide of possible constitution VO<sub>2</sub>Br<sub>3</sub>·5H<sub>2</sub>O is known, but the constitution of this compound is a matter of doubt. It is obtained by dissolving hypovanadic oxide, VO<sub>2</sub>, in dilute aqueous hydrobromic acid. Hydrochloric acid under similar conditions yields the compound VO<sub>2</sub>Cl<sub>2</sub>·8H<sub>2</sub>O.<sup>3</sup>

#### VANADIUM AND IODINE.

Iodine does not react with finely divided vanadium,<sup>4</sup> nor with the nitride, VN, or vanadous oxide, V<sub>2</sub>O<sub>3</sub>.<sup>5</sup> Anhydrous vanadium triiodide has not as yet been prepared.

**Hydrated Vanadium Tri-iodide**, VI<sub>3</sub>·6H<sub>2</sub>O, is prepared by reducing, electrolytically, a solution of vanadium pentoxide, V<sub>2</sub>O<sub>5</sub>, in hydriodic acid, until the product becomes green; more hydriodic acid is then added and the whole allowed to stand over lime and concentrated sulphuric acid at 0° C. Small green needles separate, which have the same crystalline form as the hydrated trivalent halides of titanium, iron, and chromium. These crystals are extremely hygroscopic and deliquesce in air to a brown liquid<sup>6</sup> which is extremely unstable.

*Vanadium Oxyiodides*.—No definite oxyiodides of vanadium are known, although several substances of varying composition have been obtained by the action of vanadium pentoxide on hydriodic acid.<sup>7</sup> *Vanadoiodates* and *vanadoperiodates* are described on p. 90.

#### VANADIUM AND OXYGEN.

The several oxides of vanadium have already been referred to in the section describing the general properties of vanadium compounds (see p. 30). They are set out in the table on p. 33. The thermal changes involved in their formation are discussed collectively on p. 32.

**Vanadium Suboxide**, V<sub>2</sub>O.—The existence of this oxide is extremely doubtful. It is said to be the brown substance first formed

<sup>1</sup> Loomis and Schlundt, *J. Physical Chem.*, 1915, 19, 734.

<sup>2</sup> Roscoe, *J. Chem. Soc.*, 1871, 24, 23.

<sup>3</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224.

<sup>4</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 187.

<sup>5</sup> Compare preparation of Vanadium Tribromide, p. 46.

<sup>6</sup> Piccini and Brizzi, *Zeitsch. anorg. Chem.*, 1899, 19, 399.

<sup>7</sup> Ditte, *Compt. rend.*, 1886, 102, 1310; see also Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224.

when vanadium is gently heated in the air.<sup>1</sup> Hittorf<sup>2</sup> states that it is formed when vanadium pentoxide,  $V_2O_5$ , is reduced with aluminium by the Goldschmidt process, but other investigators have found that the product so obtained is a mixture of vanadium and hypovanadous oxide,  $VO$ .<sup>3</sup>

**Hypovanadous Oxide,  $VO$ , or *vanadium dioxide*,  $V_2O_2$ ,** is the lowest definite oxide of vanadium. Vanadium surpasses uranium in its power for combining with oxygen, and, as has been previously pointed out (see p. 16), it is an extremely difficult matter to remove the last oxygen atom. Hence this oxide, in addition to enjoying a separate existence, is present also as the "vanadyl" radical in a large number of vanadium compounds. Hypovanadous oxide has been prepared in crystalline form by reduction of the pentoxide in a magnesia crucible with hydrogen at  $2500^\circ C.$  under a pressure equal to 75 atmospheres.<sup>4</sup> It is more conveniently obtained by heating vanadium oxymonochloride,  $VOCl$ , at a red heat in a stream of hydrogen until all the chlorine is removed; the product of this reaction is a black, amorphous powder.<sup>5</sup> A metallic, grey form is obtained, admixed with charcoal, when the mixed vapours of vanadium oxytrichloride,  $VOCl_3$ , and hydrogen are passed over strongly heated charcoal.<sup>6</sup> Density at  $15^\circ C.$ , 5.758.

Hypovanadous oxide resembles the metal in many of its properties. It is insoluble in water, but dissolves in acids without evolution of hydrogen to yield the lavender-coloured solutions which are characteristic of solutions of hypovanadous salts. These salts are, however, most conveniently prepared in solution by electrolytic reduction in an inert atmosphere of solutions of vanadium pentoxide in the various acids.<sup>7</sup> Hypovanadous salts are isomorphous with salts of divalent iron, chromium, and manganese. On being treated with caustic alkalis, a brown precipitate of hypovanadous hydroxide,  $V(OH)_2$ , is obtained, which rapidly oxidises to the greyish-green vanadous hydroxide,  $V(OH)_3$ .

**Vanadous Oxide, *vanadium sesquioxide*,  $V_2O_3$ ,** is obtained as a black or greyish-black powder when vanadium pentoxide,  $V_2O_5$ , or ammonium metavanadate,  $NH_4VO_3$ , is heated in a stream of hydrogen at  $900^\circ$  to  $1000^\circ C.$ <sup>8</sup> Ignition of the pentoxide in a current of pure carbon monoxide also results in the formation of vanadous oxide.<sup>9</sup> Its density at  $18^\circ C.$  is 4.870, and m.pt.  $1965^\circ C.$  The electrical resistivity of the solid has been studied by Friederich,<sup>10</sup> and the magnetic behaviour by Perrakis.<sup>11</sup> Vanadous oxide is stable in the absence of air up to temperatures approaching a white heat; it melts unchanged in hydrogen. In warm air it glows and oxidises rapidly to the pentoxide; on being exposed to air at ordinary temperatures for several months it yields indigo-blue crystals of hypovanadic oxide,  $VO_2$ .<sup>12</sup>

<sup>1</sup> Roscoe, *J. Chem. Soc.*, 1868, 21, 322.

<sup>2</sup> Hittorf, *Physikal. Zeitsch.*, 1902, 4, 196.

<sup>3</sup> Koppel and Kaufmann, *Zeitsch. anorg. Chem.*, 1905, 45, 352.

<sup>4</sup> Newbery and Pring, *Proc. Roy. Soc., A*, 1916, 92, 282.

<sup>5</sup> Wedekind and Horst, *Ber.*, 1912, 45, 262.

<sup>6</sup> Roscoe, *Phil. Trans.*, 1868, 158, 1.

<sup>7</sup> Piccini, *Zeitsch. anorg. Chem.*, 1899, 19, 204; Piccini and Marino, *ibid.*, 1902, 32, 55.

<sup>8</sup> Compare Newbery and Pring, *loc. cit.*

<sup>9</sup> Mdivani, *Ann. Chim. anal.*, 1907, 12, 305.

<sup>10</sup> Friederich, *Zeitsch. Physik*, 1925, 31, 813.

<sup>11</sup> Perrakis, *Compt. rend.*, 1925, 185, 111.

<sup>12</sup> Roscoe, *loc. cit.*; Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 145, 131.

Trituration of vanadous oxide with water results in a black, colloidal solution which is very stable in the absence of air.<sup>1</sup> The oxide reacts with ammonia at a red heat to produce vanadium nitride, VN, and is attacked by chlorine at lower temperatures to give vanadium oxytrichloride, VOCl<sub>3</sub>. The latter reaction was utilised by Briscoe and Little for the preparation of the vanadium oxytrichloride which they used for the determination of the atomic weight of vanadium (see p. 24). Vanadous oxide combines with uranium trioxide, UO<sub>3</sub>, at 600° C., forming a green, normal vanadium uranate.<sup>2</sup> The oxide is attacked by nitric acid and hydrofluoric acid, but is insoluble in other acids and alkalis. Acid solutions of the oxide are conveniently prepared either (a) by reducing acid solutions of vanadium pentoxide with metallic magnesium, or (b) by oxidising in the air solutions of hypovanadous salts. Addition of ammonium hydroxide or of hydroxides or carbonates of the alkalis to the acid solutions throws down a greyish-green flocculent precipitate of vanadous hydroxide, V(OH)<sub>3</sub>, which rapidly becomes brown as oxidation proceeds. When washed in an inert atmosphere vanadous hydroxide forms a starting material for the preparation of salts of trivalent vanadium.

**Hypovanadic Oxide, VO<sub>2</sub>, or vanadium tetroxide, V<sub>2</sub>O<sub>4</sub>.**—When vanadyl sulphate, VOSO<sub>4</sub>, or vanadyl dichloride, VOCl<sub>2</sub>, is treated in solution with an alkali hydroxide or carbonate, not in excess, a greyish-white precipitate is obtained which, after being washed in an inert atmosphere, is found to consist of an amorphous, hydrated hypovanadic oxide, VO<sub>2</sub>.xH<sub>2</sub>O. The number of molecules of water varies with the method of drying. When it is dried over concentrated sulphuric acid at room temperature its composition is expressed by the formula 2VO<sub>2</sub>.7H<sub>2</sub>O; when heated to 100° C., by 2VO<sub>2</sub>.3H<sub>2</sub>O. A compound of composition VO<sub>2</sub>.2H<sub>2</sub>O, which would correspond to V(OH)<sub>4</sub>, has not been isolated. Reduction of vanadium pentoxide with sulphur dioxide and concentration in an atmosphere of carbon dioxide yields a red, crystalline monohydrate, VO<sub>2</sub>.H<sub>2</sub>O,<sup>3</sup> which becomes green on exposure to air. The green product was originally thought to be an isomeride of the red compound,<sup>4</sup> but more recently the colour change has been shown to be due to partial oxidation.<sup>5</sup> The monohydrate loses its water when heated in an inert atmosphere at temperatures between 200° and 250° C. It dissolves in sulphuric acid to yield an azure-blue solution, with evolution of 12,620 calories of heat per gm.-mol.

Hypovanadic oxide is most conveniently obtained by heating any of the foregoing hydrates in the absence of air. It is also formed (a) from vanadium pentoxide by heating in admixture with the trioxide, carbon, or oxalic acid,<sup>6</sup> and (b) from vanadous oxide by prolonged exposure to air.<sup>7</sup>

The oxide has been variously described, according to the method of preparation, as consisting of a black or green, amorphous powder, steel-blue crystals or indigo-blue crystals. Its m.pt. is 1637° C.; density

<sup>1</sup> Wegelin, *Kolloid. Zeitsch.*, 1914, 14, 68.

<sup>2</sup> Tamman and Rosenthal, *Zeitsch. anorg. Chem.*, 1926, 156, 20; compare p. 88.

<sup>3</sup> Gain, *Compt. rend.*, 1906, 143, 823, 1154.

<sup>4</sup> Gain, *ibid.*, 1907, 146, 403.

<sup>5</sup> Parisi, *Gazzetta*, 1926, 56, 843.

<sup>6</sup> Berzelius, *Pogg. Annalen*, 1831, 22, 1; Guyard, *Bull. Soc. chim.*, 1876, [ii], 25, 351; Ditte, *Compt. rend.*, 1885, 101, 1487; Crow, *J. Chem. Soc.*, 1876, 30, 454.

<sup>7</sup> Roscoe, *ibid.*, 1868, 21, 338.

at 13° C., 4399.<sup>1</sup> Its magnetic properties have been investigated.<sup>2</sup> It is oxidised to the pentoxide on being heated in air and by nitric acid.

Hypovanadic oxide is amphoteric. It dissolves slowly in acids other than nitric acid to give solutions of vanadyl salts, as, for example, vanadyl sulphate,  $\text{VOSO}_4$ . These solutions are more conveniently prepared by the partial reduction of acid solutions of vanadium pentoxide. The reducing agent employed must, of course, be one with which reduction ceases on the formation of the tetravalent salt; sulphur dioxide, nitrous acid, phosphorous acid, the halogen acids, and, under definite conditions, sugar, and alcohol, are available for the purpose. The solutions so prepared are blue, become green after exposure to the air, and deposit blue hydrated salts on being concentrated; the anhydrous vanadyl salts are either brown or green. Vanadyl compounds undergo reoxidation to vanadic acid by the action of bromine, potassium permanganate, potassium ferricyanide or sodium peroxide in alkaline solution. Hypovanadic oxide appears to be too weakly basic to give rise to stable salts of the type  $\text{VX}_4$ , in which four acid groups are attached to a vanadium atom. The tetrafluoride and tetrachloride of vanadium,  $\text{VF}_4$  and  $\text{VCl}_4$ , have been prepared, but they undergo very ready hydrolysis to  $\text{VOF}_2$  and  $\text{VOCl}_2$  respectively. The vanadyl salts have the general formula  $\text{VOX}_2$ , and ionise in solution to give the vanadyl cation,  $[\text{VO}]^{2+}$ , which is analogous, for instance, with the uranyl cation,  $[\text{UO}_2]^{2+}$ .<sup>3</sup> Hypovanadic acid unites with many organic acids—formic, acetic, oxalic, malonic, tartaric, citric, benzoic, succinic, and salicylic—to form stable, and in most cases, crystalline compounds.<sup>4</sup>

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Hypovanadates or Vanadites.

In addition to being soluble in acids, hypovanadic oxide dissolves in excess of hot alkalis. Cooling these solutions in the absence of air gives rise to a series of crystalline hypovanadates or vanadites. Insoluble vanadites are formed by double decomposition of a metallic salt and an alkali vanadite; they usually possess the general formula  $\text{R}_2\text{V}_4\text{O}_9 \cdot x\text{H}_2\text{O}$ , and are perhaps salts of the hypothetical acid  $\text{H}_2\text{V}_4\text{O}_9$ . They are comparable to the salts produced by other weakly acid oxides, e.g. uranates, metatungstates and borates, in that the acid oxide has undergone condensation to a poly-acid.

Vanadites are either black or brown in the solid state. They become green in damp air, and in solution readily undergo oxidation to the corresponding vanadates. Addition of tannin solution produces a blue-black coloration. Lead acetate throws down a curdy, brown precipitate; silver nitrate gives a black, crystalline precipitate. According to Crow<sup>5</sup> the latter has the composition of a silver vanadite, in which there are, however, only two molecules of acid oxide in combination with one molecule of the base,  $\text{Ag}_2\text{O} \cdot 2\text{VO}_2$ ; but according to Koppel and Goldmann<sup>6</sup> the precipitate consists of a mixture of silver vanadate,

<sup>1</sup> Roscoe, *loc. cit.*; Friederich and Sittig, *loc. cit.*

<sup>2</sup> Perrakis, *Compt. rend.*, 1925, 185, 111.

<sup>3</sup> See this series, Vol. VII., Part III. (1926), p. 287.

<sup>4</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224; Berzelius, *Pogg. Annalen*, 1831, 22, 1.

<sup>5</sup> Crow, *J. Chem. Soc.*, 1876, 30, 462.

<sup>6</sup> Koppel and Goldmann, *Zeitsch. anorg. Chem.*, 1903, 36, 300.

silver vanadite, and metallic silver. The following vanadites have been prepared:—

*Ammonium Vanadite*,  $(\text{NH}_4)_2\text{V}_4\text{O}_9 \cdot 3\text{H}_2\text{O}$ .—A solution of a vanadyl salt, e.g. vanadyl dichloride,  $\text{VOCl}_2$ , is slowly added in calculated quantity to boiling concentrated ammonia solution. On cooling in the absence of air, golden-brown, glistening needles or scales are deposited, readily soluble in water but insoluble in alcohol, ether, or ammonia. The substance gradually loses ammonia on exposure to air.<sup>1</sup>

*Barium Vanadite* forms two hydrates,  $\text{BaV}_4\text{O}_9 \cdot 4\text{H}_2\text{O}$  and  $\text{BaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ , which are obtained by the action of excess of baryta water on a solution of vanadyl dichloride.<sup>2</sup> They are brown, amorphous substances, easily soluble in nitric and hydrochloric acids.

*Lead Vanadite*,  $\text{PbV}_2\text{O}_5$  or  $\text{PbO} \cdot 2\text{VO}_2$ , is obtained as a brown, curdy precipitate by the action of lead acetate on potassium vanadite.<sup>3</sup>

*Potassium Vanadite*,  $\text{K}_2\text{V}_4\text{O}_9 \cdot 4\text{H}_2\text{O}$ .—A boiling solution of a vanadyl salt is poured into an excess of a 10 per cent. solution of caustic potash and the product cooled in the absence of air. Alternatively, a solution of ammonium vanadite is warmed with caustic potash. Potassium vanadite forms a brown, pearly, glistening mass, and is similar to the ammonium salt in its general properties.<sup>4</sup> A *heptahydrate*,  $\text{K}_2\text{V}_4\text{O}_9 \cdot 7\text{H}_2\text{O}$ , has been reported.<sup>5</sup>

*Sodium Vanadite*,  $\text{Na}_2\text{V}_4\text{O}_9 \cdot 4\text{H}_2\text{O}$ , forms golden-brown needles, and is prepared similarly to the corresponding potassium salt.<sup>6</sup> Brown, crystalline scales of a *heptahydrate*,  $\text{Na}_2\text{V}_4\text{O}_9 \cdot 7\text{H}_2\text{O}$ , have also been reported.<sup>7</sup>

**Intermediate Oxides.**—Oxides which are intermediate between hypovanadic oxide,  $\text{VO}_2$ , and vanadium pentoxide,  $\text{V}_2\text{O}_5$ , are known. By the partial reduction of vanadium pentoxide, or by the partial oxidation of one of the lower oxides, there have been prepared a number of oxides which are best considered as being formed by the combination of the acidic vanadium pentoxide with a lower basic oxide in varying molecular proportions. These oxides react with alkalis, and yield a series of salts called *vanadyl vanadates*, intermediate in composition between the vanadites and the vanadates.

$2\text{VO} \cdot \text{V}_2\text{O}_5$  is produced as a dark blue, crystalline powder when either vanadium pentoxide or ammonium metavanadate is heated with excess of powdered arsenic, or when ammonium metavanadate is reduced with sulphur dioxide at a red heat. It dissolves in nitric acid to a blue solution.<sup>8</sup>

$6\text{VO}_2 \cdot \text{V}_2\text{O}_5$  is obtained as a dark blue or black powder with a metallic lustre by dissolving vanadium pentoxide in caustic potash.<sup>9</sup>

$2\text{VO}_2 \cdot \text{V}_2\text{O}_5$  also results as deep blue crystals on heating ammonium metavanadate which has previously been fused and cooled. It is stated that the fused substance does not furnish vanadium pentoxide on being decomposed.<sup>10</sup> The residue is extracted with concentrated ammonium hydroxide solution and the oxide precipitated by addition of water.

<sup>1</sup> Koppel and Goldmann, *Zeitsch. anorg. Chem.*, 1903, 36, 261; Crow, *J. Chem. Soc.*, 1876, 30, 462; Mawrow, *Zeitsch. anorg. Chem.*, 1907, 55, 147.

<sup>2</sup> Koppel and Goldmann, *loc. cit.*; Crow, *loc. cit.*

<sup>3</sup> Koppel and Goldmann, *loc. cit.*

<sup>4</sup> Koppel and Goldmann, *loc. cit.*

<sup>5</sup> Ditte, *Compt. rend.*, 1885, 101, 698, 1487.

<sup>6</sup> Manasse, *Chem. Zentr.*, 1886, 773.

<sup>7</sup> Crow, *loc. cit.*

<sup>8</sup> Crow, *loc. cit.*

<sup>9</sup> Crow, *loc. cit.*

<sup>10</sup> Compare p. 54.



The product is slightly soluble in concentrated nitric acid and is readily attacked by hydrochloric acid. It is a little doubtful if the oxide prepared in this manner is not an ammonium vanadyl vanadate.<sup>1</sup> A dark green hydrate,  $6\text{VO}_2 \cdot 3\text{V}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , has been obtained by the gentle ignition of ammonium vanadyl vanadate,  $3(\text{NH}_4)_2\text{O} \cdot 4\text{VO}_2 \cdot 4\text{V}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ .<sup>2</sup>

$\text{VO}_2 \cdot \text{V}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  results on the exposure of vanadous oxide,  $\text{V}_2\text{O}_3$ , to air for several months.<sup>3</sup>

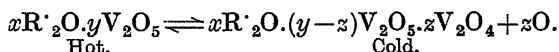
Several other purple, green, or orange intermediate oxides of doubtful composition have been reported.<sup>4</sup>

#### *Vanado-vanadates.*

These salts are made by reducing hot solutions of alkali vanadates with sulphur dioxide; after addition of acetic acid they can be salted out by addition of alkali acetate.<sup>5</sup> The following are known:—

$(\text{NH}_4)_2\text{O} \cdot 4\text{VO}_2 \cdot 2\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$	. Greenish-black crystals.
$3(\text{NH}_4)_2\text{O} \cdot 4\text{VO}_2 \cdot 4\text{V}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$	. Purple crystals with metallic lustre.
$(\text{NH}_4)_2\text{O} \cdot 2\text{VO}_2 \cdot 4\text{V}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$	. Green crystals.
$2\text{K}_2\text{O} \cdot 4\text{VO}_2 \cdot \text{V}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$	. Greenish-black crystals.
$5\text{K}_2\text{O} \cdot 4\text{VO}_2 \cdot 4\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$	. Purple crystals with metallic lustre.
$2\text{Na}_2\text{O} \cdot 4\text{VO}_2 \cdot \text{V}_2\text{O}_5 \cdot 13\text{H}_2\text{O}$	. Black, shining, hexagonal prisms.

In addition to the above, several vanado-vanadates have been prepared by fusing alkali carbonates, borates, phosphates, silicates, arsenates, etc., with vanadium pentoxide in air. The fused mass evolves oxygen during cooling, and "spitting" of the material takes place. The phenomenon recalls the behaviour of solidifying silver. On again heating in air, oxygen is re-absorbed and acid vanadates are produced. The evolution of oxygen is accompanied by reduction of a portion of the vanadium pentoxide content with formation of the vanado-vanadate. The reaction is represented:



The oxygen is liberated between the upper limit of stability of the vanado-vanadate and the point of solidification of the fused mass. The proportion of oxygen evolved is independent of the anion with which the metal is combined. The alkali salts can be substituted by thallium compounds but not by alkaline earth oxides. Investigation shows that for each base there is a definite vanadium pentoxide content for which the evolution of oxygen is a maximum.<sup>6</sup> Phase diagrams for the systems  $\text{V}_2\text{O}_5$ — $\text{Na}_2\text{O}$ ,  $\text{V}_2\text{O}_5$ — $\text{K}_2\text{O}$ ,  $\text{V}_2\text{O}_5$ — $\text{Li}_2\text{O}$ , and  $\text{V}_2\text{O}_5$ — $\text{Tl}_2\text{O}$  show that in each case three definite compounds are formed, corresponding to the *meta*-, *pyro*-, and *ortho*-vanadates. By the foregoing method the following salts have been prepared:<sup>7</sup>  $6\text{Li}_2\text{O} \cdot 2\text{VO}_2 \cdot 11\text{V}_2\text{O}_5$ ;  $4\text{Li}_2\text{O} \cdot 2\text{VO}_2 \cdot 7\text{V}_2\text{O}_5$ ;  $\text{Na}_2\text{O} \cdot 2\text{VO}_2 \cdot 5\text{V}_2\text{O}_5$ ;  $\text{Na}_2\text{O} \cdot 2\text{VO}_2 \cdot 4\text{V}_2\text{O}_5$ ;

<sup>1</sup> Ditte, *loc. cit.*

<sup>2</sup> Brierley, *J. Chem. Soc.*, 1886, 49, 30.

<sup>3</sup> Brierley, *loc. cit.*

<sup>4</sup> Berzelius, *Pogg. Annalen*, 1831, 22, 1.

<sup>5</sup> Brierley, *loc. cit.*; Gibbs, *Amer. Chem. J.*, 1886, 7, 209.

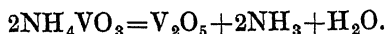
<sup>6</sup> Canneri, *Gazzetta*, 1928, 58, 6.

<sup>7</sup> Canneri, *loc. cit.*; Prandtl, *Ber.*, 1905, 38, 657; Prandtl and Murschhauser, *Zeitsch. anorg. Chem.*, 1907, 56, 173; 1908, 60, 441; Hautefeuille, *Compt. rend.*, 1880, 90, 744.

$\text{Na}_2\text{O} \cdot \text{VO}_2 \cdot 2\text{V}_2\text{O}_5$ ;  $3\text{Na}_2\text{O} \cdot 2\text{VO}_2 \cdot 5\text{V}_2\text{O}_5$ ;  $\text{K}_2\text{O} \cdot 2\text{VO}_2 \cdot 8\text{V}_2\text{O}_5$ ;  $\text{K}_2\text{O} \cdot 2\text{VO}_2 \cdot 5\text{V}_2\text{O}_5$ ;  $2\text{K}_2\text{O} \cdot 2\text{VO}_2 \cdot 9\text{V}_2\text{O}_5$ ;  $\text{K}_2\text{O} \cdot 2\text{VO}_2 \cdot 4\text{V}_2\text{O}_5$ ;  $\text{K}_2\text{O} \cdot \text{VO}_2 \cdot 2\text{V}_2\text{O}_5$ ;  $\text{Ag}_2\text{O} \cdot 2\text{VO}_2 \cdot 5\text{V}_2\text{O}_5$ .

Vanado-vanadates can also be obtained by fusing alkali vanadites with metavanadates, when no oxidation or loss of oxygen takes place. This process has furnished two salts,<sup>1</sup>  $\text{Na}_2\text{O} \cdot 2\text{VO}_2 \cdot \text{V}_2\text{O}_5$  and  $\text{K}_2\text{O} \cdot 2\text{VO}_2 \cdot \text{V}_2\text{O}_5$ .

**Vanadium Pentoxide**, *vanadic oxide*, or *vanadic anhydride*,  $\text{V}_2\text{O}_5$ .—This is one of the commonest of the compounds of vanadium, and constitutes the starting material for the preparation of many other vanadium compounds. Its manufacture on the large scale, as a stage in the industrial production of ferrovanadium and metallic vanadium, has been described on pp. 14 *et seq.* A laboratory method for its extraction from vanadium minerals is as follows: The mineral is roasted strongly with a mixture of sodium carbonate and potassium nitrate. The aqueous extract of the fused product, which contains alkali vanadates together with the alkali salts of other acids, is first neutralised with nitric acid, to precipitate silicic acid and aluminium hydroxide, and then concentrated until most of the potassium nitrate is crystallised out. The mother-liquor is heated with barium chloride and ammonium hydroxide, whereupon barium vanadate, chromate, phosphate, arsenate, molybdate, tungstate and sulphate separate out. Treatment of these barium salts with sulphuric acid liberates the free acids, which are carefully neutralised with ammonium hydroxide and concentrated. The further addition of ammonium hydroxide at this stage yields white, crystalline ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , which is purified by repeated crystallisation. On being heated in a platinum crucible with access of air, ammonium metavanadate decomposes with formation of red, amorphous vanadium pentoxide, ammonia, and water:



By dissolving the residue in caustic soda and repeating the precipitation and decomposition of ammonium metavanadate, a pure product can be obtained. It is necessary for the ammonium metavanadate to be quite free even from traces of organic matter, chlorides, phosphates, etc., as otherwise a mixture of the pentoxide and the lower oxides is obtained on ignition.

Chemically pure vanadium pentoxide is alternatively prepared by precipitating insoluble mercurous vanadate,  $\text{HgVO}_3$ , from a neutral solution of a vanadate, and distilling off the mercury, or by ignition of vanadium salts of volatile acids, for example, vanadium oxytrichloride,  $\text{VOCl}_3$ . The oxide also results from the oxidation of any of the lower oxides, or by the electrolysis of a solution of sodium vanadate or copper vanadate, using a divided cell; the last method yields a product of 98 per cent. purity.<sup>2</sup>

By addition of mineral acids to solutions of vanadates, or by the hydrolysis of vanadium oxytrichloride, a reddish-brown, gelatinous precipitate of hydrated vanadium pentoxide is obtained. This is very

<sup>1</sup> Canneri, *Gazzetta*, 1928, 58, 6.

<sup>2</sup> Bleecker, *Met. Chem. Eng.*, 1911, 9, 501; Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 175.

similar in appearance to ferric hydroxide,  $\text{Fe}(\text{OH})_3$ , and on examination is found to consist of very fine particles which cannot be washed free from the mother-liquor without undergoing peptisation to a colloidal solution. The preparation and properties of colloidal vanadium pentoxide are dealt with on p. 58.

Vanadium pentoxide can be obtained in two modifications: (a) red crystalline; (b) red or yellow amorphous.

(a) The red, crystalline variety is obtained from the amorphous form by fusing in a porcelain or platinum dish. After cooling, the mass is found to have decreased in volume and to have solidified to an intensely coloured, glistening mass of ruby-red, rhombic crystals, from 3 to 4 cm. long and from 2 to 3 mm. broad.<sup>1</sup> Bleecker describes the solid mass as consisting of needles, arranged parallel and extending inward perpendicularly to each surface; the ends of the crystals meet at  $45^\circ$ , and a vertical section has the appearance of three pyramids each with its base extending outwards.<sup>2</sup> The X-ray diffraction pattern has been examined.<sup>3</sup>

An alternative method for the preparation of crystalline vanadium pentoxide consists in heating a mixture of the amorphous oxide and calcium fluoride to red heat in an open crucible over which is suspended another crucible, inverted, to act as a receiver. The inside of the latter becomes coated with shining, needle-shaped, yellow crystals, which also become reddish-brown on being heated.<sup>4</sup>

Evaporation of the hydrochloric acid solution of the red, amorphous oxide may also give rise to crystals.<sup>5</sup>

The density of the crystalline oxide at  $20^\circ \text{C}$ . is 3.56; <sup>6</sup> other determinations gave 3.32 at  $15^\circ$  and 3.357 at  $18^\circ \text{C}$ .<sup>7</sup> The oxide is not hygroscopic even after prolonged exposure under ordinary conditions. Its saturated solution in water contains 50 mgm. per litre,<sup>8</sup> but the solubility is affected by the state of aggregation of the solid and by its tendency to form a hydrosol; trituration has given a sol which contained 910 mgm. per litre.<sup>9</sup>

(b) The red, amorphous form of vanadium pentoxide is the form most frequently met with in the laboratory. Its preparation has been described above. It melts at  $658^\circ$ <sup>10</sup> or  $675^\circ \text{C}$ .<sup>11</sup> to a dark red liquid, but is not volatile even at high temperatures; it can be vaporised only in the electric furnace.<sup>12</sup> The fused solid conducts electricity, with formation of hypovanadic oxide,  $\text{VO}_2$ ; <sup>13</sup> the electrical conductivity has been measured.<sup>14</sup> The oxide absorbs water on exposure to the air, the

<sup>1</sup> Ditte, *Compt. rend.*, 1885, 101, 698, 1487; Safarik, *Sitzungsber. K. Akad. Wiss. Wien*, 1858, 33, 1; Nordenskiöld, *Pogg. Annalen*, 1861, 112, 160; Prandtl and Bleyer, *Zeitsch. anorg. Chem.*, 1910, 67, 257.

<sup>2</sup> Bleecker, *Met. Chem. Eng.*, 1910, 8, 666; see also Thorpe, *J. Chem. Soc.*, 1880, 37, 348.

<sup>3</sup> Rinne, *Zeitsch. Kryst. Min.*, 1924, 60, 55.

<sup>4</sup> Prandtl and Manz, *Ber.*, 1911, 44, 2582.

<sup>5</sup> Bleecker, *loc. cit.*

<sup>6</sup> Safarik, *Sitzungsber. K. Akad. Wiss. Wien*, 1863, 47, 256.

<sup>7</sup> Wedekind and Horst, *Ber.*, 1912, 45, 265; Prandtl and Bleyer, *loc. cit.*

<sup>8</sup> Ditte, *loc. cit.*

<sup>9</sup> Wegelin, *Kolloid. Zeitsch.*, 1914, 14, 67.

<sup>10</sup> Carnelly, *J. Chem. Soc.*, 1878, 33, 279.

<sup>11</sup> Canneri, *Gazzetta*, 1928, 58, 6.

<sup>12</sup> Moissan and Holt, *Compt. rend.*, 1902, 135, 78, 493; compare Read, *J. Chem. Soc.*, 1894, 65, 313.

<sup>13</sup> Buff, *Annalen*, 1859, 110, 276; Bleekrode, *Wied. Annalen*, 1878, [ii], 3, 171.

<sup>14</sup> Friederich, *Zeitsch. Physik*, 1925, 31, 813.

amount taken up depending on the vapour-pressure of the surrounding atmosphere.<sup>1</sup> The water of hydration can be removed by careful heating to 300° C.<sup>2</sup> The dried oxide feels greasy to the touch and discolours the skin slightly. Its saturated solution contains between 0.90 and 1.25 gram per litre.<sup>3</sup> The density of a solution containing 0.90 gram per litre is 0.9988 at 20° C. and 0.9978 at 26° C. The adsorptive power of vanadium pentoxide for helium, oxygen, hydrogen, carbon monoxide, and carbon dioxide at different temperatures has been measured.<sup>4</sup>

The yellow, amorphous variety is unstable and its identity is a little doubtful. It is stated to be obtained sometimes from the red, amorphous form by evaporation of a solution of the latter in hydrochloric acid, and it may also result from the ignition of ammonium meta-vanadate or from the decomposition of vanadates by acids. According to Bleecker it is most conveniently prepared by the electrolytic decomposition of copper vanadate.<sup>5</sup> It becomes brick red on being heated, and is similar to the red variety in its general properties, except that it appears to be less hygroscopic and less soluble; its saturated aqueous solution contains between 300 and 400 mgm. per litre.<sup>6</sup>

Vanadium pentoxide dissolves in acids, both organic and inorganic, to form vanadyl or unstable vanadic salts,<sup>7</sup> and in alkalis to produce ortho-, pyro-, meta-, and poly-vanadates. The physico-chemical changes involved when vanadium pentoxide is heated with various basic oxides in the powder state have been investigated by Tammann.<sup>8</sup> On being digested with liquid ammonia slow absorption of ammonia takes place; the composition of the product has not been definitely established.<sup>9</sup> The oxide also dissolves in alcohols to produce esters,<sup>10</sup> and combines with methylamine and ethylamine to form compounds of the type  $2(\text{R.NH}_2).\text{V}_2\text{O}_5$ , where R represents the alkyl radical.<sup>11</sup>

Vanadium pentoxide is a powerful oxidising agent, and undergoes reduction in stages depending on the reducing agent employed and on other conditions of the process. In the absence of moisture it is reduced to hypovanadic oxide,  $\text{VO}_2$ , by sulphur dioxide, red phosphorus, and ammonia, while dry hydrogen, carbon monoxide, sulphur, and potassium cyanide, at varying temperatures and atmospheric pressure, yield vanadous oxide,  $\text{V}_2\text{O}_3$ . Hydrogen at 2500° C. and 75 atmospheres pressure yields hypovanadous oxide,  $\text{VO}$ . In acid solution reduction of vanadium pentoxide to the tetravalent state, which is characterised by the appearance of a blue colour, can be effected with quite a large number of reducing agents: sulphur dioxide, hydrogen chloride, hydrogen bromide, hydrogen iodide,<sup>12</sup> hydrogen sulphide, nitrous acid,

<sup>1</sup> Freundlich and Leonhardt, *Kolloidchem. Beihefte*, 1915, 7, 188.

<sup>2</sup> Bleecker, *loc. cit.*

<sup>3</sup> Gessner, *Kolloidchem. Beihefte*, 1924, 19, 213; Ditte (*loc. cit.*) gives 0.8 gram per litre.

<sup>4</sup> Benton, *J. Amer. Chem. Soc.*, 1923, 45, 893.

<sup>5</sup> Ditte, *loc. cit.*; Bleecker, *loc. cit.*

<sup>6</sup> Bleecker, *loc. cit.*

<sup>7</sup> Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 190.

<sup>8</sup> Tammann and Halsing, *Zeitsch. anorg. Chem.*, 1925, 149, 68; see also de Carli, *Atti R. Accad. Lincei*, 1925, [vi], 1, 533.

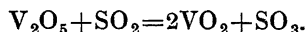
<sup>9</sup> Ephraim and Beck, *Helv. Chim. Acta*, 1926, 9, 38.

<sup>10</sup> Prandtl and Hess, *Zeitsch. anorg. Chem.*, 1913, 82, 103; Hess, *J. Soc. Chem. Ind.*, 1914, 33, 712.

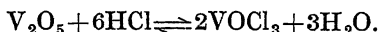
<sup>11</sup> Ditte, *Compt. rend.*, 1887, 104, 1844.

<sup>12</sup> Gooch and Curtis, *Amer. J. Sci.*, 1904, [iv], 17, 41.

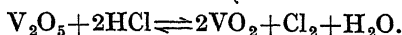
phosphorous acid, oxalic acid, tartaric acid, lactic acid, citric acid,<sup>1</sup> hydrazine, hydroxylamine, alcohol, formalin, sugar,<sup>2</sup> ferrous sulphate, sodium thiosulphate, and mercury. Sulphur dioxide is most commonly employed for the reduction; it works slowly in the cold but rapidly when the solution is heated:<sup>3</sup>



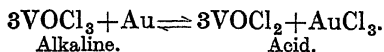
Excess of sulphur dioxide can be removed by boiling in an atmosphere of carbon dioxide. In the presence of suspended carbonaceous matter reduction may proceed to the trivalent stage. With many of the above-mentioned reagents reduction proceeds quantitatively, so that vanadium pentoxide can be employed for the estimation of the reducing agent, *e.g.* for hydroxylamine and hydrazine;<sup>4</sup> alternatively, these substances become available for the estimation of solutions of vanadium pentoxide and of vanadates. Dry hydrogen chloride in the presence of a dehydrating agent does not reduce vanadium pentoxide, but forms vanadium oxytrichloride:<sup>5</sup>



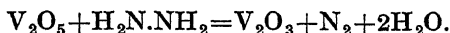
Concentrated solutions of hydrochloric acid, however, dissolve vanadium pentoxide with the production of an intense brown coloration; addition of water gives a yellow solution which evolves chlorine on being warmed, the solution becoming blue:



This reaction is reversible, so that for complete conversion to the tetravalent state the concentration of the hydrochloric acid must be maintained. Repeated evaporation of the solution to dryness gives a residue of hypovanadic oxide,  $\text{VO}_2$ .<sup>6</sup> Volatilisation of the vanadium to a small extent as oxychlorides may also take place.<sup>7</sup> Dilute hydrochloric acid has no reducing action on vanadium pentoxide. Hundeshagen<sup>8</sup> has observed that the solution of vanadium pentoxide in hydrochloric acid dissolves gold and other noble metals. If the solution is neutralised, the gold is precipitated as a greyish-violet powder, which redissolves on adding more acid. The reaction is expressed:



With hydrobromic acid and hydriodic acid reduction may proceed to the trivalent state,<sup>9</sup> and it has been shown that in the presence of acetic acid, hydrazine also produces vanadous oxide,  $\text{V}_2\text{O}_3$ , instead of hypovanadic oxide,  $\text{VO}_2$ :<sup>10</sup>



<sup>1</sup> Browning, *Zeitsch. anorg. Chem.*, 1894, 7, 158.

<sup>2</sup> Koppel and Behrendt, *ibid.*, 1903, 35, 156.

<sup>3</sup> Compare pp. 99 *et seq.*

<sup>4</sup> Hofmann and Küspert, *Ber.*, 1898, 31, 64; Knorre and Arndt, *ibid.*, 1900, 33, 30.

<sup>5</sup> Ephraim, *Zeitsch. anorg. Chem.*, 1903, 35, 66.

<sup>6</sup> Gooch and Curtis, *ibid.*, 1904, 38, 246; Auchy, *J. Ind. Eng. Chem.*, 1909, 1, 455; Edgar, *J. Amer. Chem. Soc.*, 1916, 38, 2369.

<sup>7</sup> Auerbach and Lange, *Zeitsch. angew. Chem.*, 1912, 25, 2522.

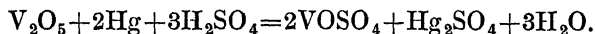
<sup>8</sup> Hundeshagen, *Chem. Zeit.*, 1905, 29, 799.

<sup>9</sup> Ditz and Bardach, *Zeitsch. anorg. Chem.*, 1915, 93, 97; Edgar, *loc. cit.*

<sup>10</sup> Meyer and Markowitz, *ibid.*, 1926, 157, 238.

Hydrogen also reduces pentavalent and tetravalent vanadium salts to the trivalent state in the presence of spongy platinum.<sup>1</sup>

With mercury the following reaction takes place:<sup>2</sup>



The equilibria for tri-, tetra-, and penta-valent vanadium in sulphuric acid solution have been studied by Auger.<sup>3</sup>

Concentrated acid solutions of vanadium pentoxide are reduced to the tetravalent state by hydrogen peroxide, the peroxides of sodium, barium, magnesium, and by persulphates of potassium and ammonium.<sup>4</sup> Acid solutions of vanadium pentoxide give rise to pervanadic acid with hydrogen peroxide.

Reduction of acid solutions of vanadium pentoxide to the tetravalent state also takes place with bismuth amalgam;<sup>5</sup> magnesium gives the trivalent salts of vanadium,<sup>6</sup> while by using zinc, zinc coated with cadmium, electrolytically deposited cadmium, or sodium amalgam in the absence of air, divalent vanadium salts are obtained in solution.<sup>7</sup> Vanadous salts and hypovanadous salts are, however, much more conveniently prepared by electrolytic reduction of acid solutions of vanadium pentoxide in an atmosphere of carbon dioxide.<sup>8</sup>

Vanadium pentoxide becomes markedly photo-sensitive when immersed in glycerol, benzaldehyde, cinnamic aldehyde, cuminol, or aqueous mannitol solution, and exposed to light. It blackens and undergoes reduction, giving rise, initially, to hypovanadic oxide,  $\text{VO}_2$ . With aqueous solutions of citric acid or tartaric acid carbon dioxide is evolved during the change.<sup>9</sup>

Molten vanadium pentoxide is a corrosive substance and attacks most containers even when made of platinum, fused silica, or graphite.<sup>10</sup>

*Colloidal Vanadium Pentoxide.*<sup>11</sup>—When a soluble vanadate is treated with mineral acids, a red, curdy form of vanadium pentoxide is precipitated, which, on being shaken with water, appears to dissolve to a red liquid. This reaction gives rise to the following usual method for making a colloidal solution: Ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , is made into a paste with 10 per cent. hydrochloric acid of 10 per cent. concentration, and the resulting gel of vanadium pentoxide is washed repeatedly on the filter with distilled water until it assumes the colloidal form, *i.e.* until it is peptised, and in consequence passes through the

<sup>1</sup> Gall and Manchot, *Ber.*, 1925, 58, [B], 482.

<sup>2</sup> McCay and Anderson, *J. Amer. Chem. Soc.*, 1922, 44, 1018.

<sup>3</sup> Auger, *Compt. rend.*, 1921, 173, 306.

<sup>4</sup> Auger, *ibid.*, 1921, 172, 1355; Cain and Hostetter, *J. Amer. Chem. Soc.*, 1912, 34, 274.

<sup>5</sup> Someya, *Zeitsch. anorg. Chem.*, 1926, 152, 368.

<sup>6</sup> Roscoe, *J. Chem. Soc.*, 1868, 21, 322; Gooch and Gilbert, *Zeitsch. anorg. Chem.*, 1903, 35, 420; Glassmann, *Ber.*, 1905, 38, 600, 605; but compare Gooch and Edgar, *Amer. J. Sci.*, 1908, [iv], 25, 233.

<sup>7</sup> Chapman and Law, *Analyst*, 1907, 32, 250; Treadwell, *Helv. Chim. Acta*, 1921, 4, 563; 1922, 5, 739.

<sup>8</sup> Piccini and Brizzi, *Zeitsch. anorg. Chem.*, 1899, 19, 394; Bultemann, *Zeitsch. Elektrochem.*, 1904, 10, 141; Renschler, *ibid.*, 1912, 18, 137; Piccini, *Zeitsch. anorg. Chem.*, 1899, 19, 204; Piccini and Marino, *ibid.*, 1902, 32, 55; see also p. 34 (this volume).

<sup>9</sup> Renz, *Helv. Chim. Acta*, 1921, 4, 961; Gibbons, *Chem. News*, 1874, 30, 267.

<sup>10</sup> Bleecker, *Met. Chem. Eng.*, 1910, 8, 666; Mdivani, *Ann. Chim. anal.*, 1907, 12, 305.

<sup>11</sup> A review of the history and preparation of colloidal vanadium pentoxide is given by Gessner, *Kolloidchem. Beihfte*, 1924, 19, 213.

filter. On shaking the residue at this stage with a large quantity of water, a beautiful, clear red hydrosol is obtained.<sup>1</sup> Vanadium pentoxide hydrosols have been prepared also: (a) By hydrolysing the organic esters of vanadic acid;<sup>2</sup> (b) by pouring fused vanadium pentoxide into water;<sup>3</sup> (c) by passing the vapours of vanadium oxytrichloride,  $\text{VOCl}_3$ , into boiling water. The flakes of vanadium pentoxide produced are treated with a large quantity of distilled water.<sup>4</sup> Sols prepared by these methods vary in colour from blood red to reddish-brown, but Wegelin also prepared a canary-yellow sol by prolonged trituration of the reddish-brown crystals of vanadium pentoxide obtained by slow cooling from the molten state.<sup>5</sup>

Vanadium pentoxide sols may contain up to 1.25 gram of vanadium pentoxide per litre.<sup>6</sup> They do not undergo change on being boiled with water, and are not precipitated by addition of alcohol. The particles are negatively charged, and on being electrolysed move towards the anode; the hydrosol behaves like solutions of vanadates and vanadium pentoxide in that it yields the ions of polyvanadic acids.<sup>7</sup> The sol is very sensitive to the action of electrolytes, relatively low concentrations of which are sufficient to produce clouding within a few minutes. The flocculation value<sup>8</sup> as a rule is lower the greater the value of the precipitating ion. Addition of several drops of mineral acid or of other electrolyte is followed by immediate adsorption of the positive ion with formation of vanadium pentoxide gel. If nitric acid has been added the gel can be reconverted into the sol with water—that is, the gelation is reversible; if sodium chloride or calcium chloride has been used the gel cannot be re-solated. When treated with suitable concentrations of electrolytes a vanadium pentoxide sol sets to a stiff jelly. In these sols there is always a small amount of the oxide in molecular solution. This portion is not thrown down by electrolytes, and passes through a dialysing membrane. The relative flocculation values with some inorganic salts have been determined,<sup>9</sup> and the cataphoresis at small electrolyte concentrations has been measured.<sup>10</sup> Stiff, transparent gels of vanadium pentoxide have been prepared from its hydrosols by coagulation with a suitable electrolyte, or by dialysis;<sup>11</sup> hydrosols of the vanadates of manganese, iron, aluminium and zinc can also be used.

Vanadium pentoxide sols can be employed to bring about coagulation of positively charged colloids; for example, ferric hydroxide and aluminium hydroxide. The amount necessary for the coagulation of a given quantity of the positive colloid is very small in comparison with the required quantities of arsenic trisulphide, antimony trisulphide, and other negative colloids. It appears, therefore, that the colloidal

<sup>1</sup> Biltz, *Ber.*, 1904, 37, 1098.

<sup>2</sup> Riedel, *Chem. Zentr.*, 1914, [1], 1738.

<sup>3</sup> Muller, *Kolloid. Zeitsch.*, 1911, 8, 302.

<sup>4</sup> Wegelin, *Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 25.

<sup>5</sup> Wegelin, *Kolloid. Zeitsch.*, 1914, 14, 65.

<sup>6</sup> Gessner, *loc. cit.*; compare Wegelin, *loc. cit.*

<sup>7</sup> Dumanski, *Kolloid. Zeitsch.*, 1923, 33, 147; Osterman, *Chem. Zentr.*, 1923, 1, 396.

<sup>8</sup> The flocculation value is the minimum concentration required for turbidity in a definite time.

<sup>9</sup> Freundlich and Leonhardt, *Kolloidchem. Beihefte*, 1915, 7, 195; Ghosh and Dhar, *J. Physical Chem.*, 1927, 31, 187, 649.

<sup>10</sup> Ivanitskii and Proskurnin, *Kolloid. Zeitsch.*, 1926, 39, 15.

<sup>11</sup> Ghosh, Chakravarti, and Dhar, *Zeitsch. anorg. Chem.*, 1926, 152, 399.

particles of vanadium pentoxide carry a relatively much larger electrical charge.<sup>1</sup> The pentoxide sols on being treated with reducing agents furnish the sols of lower oxides of vanadium, which are also found to be negatively charged.<sup>2</sup> The viscosity of vanadium pentoxide sols has been investigated.<sup>3</sup>

Vanadium pentoxide sols display peculiar optical phenomena. A freshly prepared sol is quite clear; after ageing, however, the sol, on being stirred and observed by reflected light, appears to be filled with yellow, shining streaks, as though fine crystals were floating in it. When viewed by transmitted light the aged sol appears to be clear, although peculiar dark streaks can be clearly seen. On being further examined between crossed Nicols, the aged sol exhibits the striking property of double refraction; the field remains dark so long as the sol is not disturbed, but stirring, or placing the sol in a magnetic or an electric field, causes it to become bright at once.<sup>4</sup> The double refraction produced is so strong that if a concentrated sol is caused to flow through a tube of triangular cross-section which is used as a prism, it is able to split up spectral lines; the red hydrogen line, for instance, is resolved in this manner into two oppositely polarised lines.<sup>5</sup> Plates showing the appearance of vanadium pentoxide sols under the ultramicroscope and in polarised light are given by Zocher.<sup>6</sup>

A possible explanation of the cause of the double refraction is afforded by examination of the freshly prepared and aged sols under the ultramicroscope. The freshly prepared sol contains only sub-microns below the limits of ultramicroscopic visibility; on ageing, however, the concentration of the molecularly dispersed vanadium pentoxide decreases, and there begin to grow in the sol elongated, rod-like needles the length of which is approximately thirty times the diameter. These new particles are unquestionably crystalline, and possess slow Brownian movement, but their formation is not the ordinary process of crystallisation, because the ageing of the sol is also accompanied by changes in the dielectric constant,<sup>7</sup> the specific inductive capacity,<sup>8</sup> the electrical conductivity,<sup>9</sup> the sensitivity towards electrolytes, and the viscosity.<sup>10</sup> The growth of the rods is due to the aggregation of non-spherical primary particles in parallel layers.<sup>11</sup> With further ageing the red colour of the sol finally changes to yellow, and yellow solutions are devoid of colloidal particles. It is generally thought that the phenomenon of double refraction is due to the appearance of these ultramicroscopic needles, the longitudinal axes of which become orientated so as to be coincident with the optical axes when the sol is

<sup>1</sup> Freundlich and Leonhardt, *loc. cit.*

<sup>2</sup> Dumanski, *Kolloid. Zeitsch.*, 1923, 23, 147.

<sup>3</sup> Gessner, *Kolloidchem. Beihefte*, 1924, 19, 213; Chakravarti and Dhar, *Zeitsch. anorg. Chem.*, 1926, 152, 393.

<sup>4</sup> Freundlich, *Zeitsch. Elektrochem.*, 1916, 22, 27.

<sup>5</sup> Freundlich, *Physikal. Zeitsch.*, 1915, 16, 419.

<sup>6</sup> Zocher, *Zeitsch. anorg. Chem.*, 1925, 147, 108; see also Joachims, *Kolloid. Zeitsch.*, 1927, 41, 215; Zocher and Jacobsohn, *ibid.*, 1927, 41, 220.

<sup>7</sup> Bikerman, *Physikal. Zeitsch.*, 1926, 27, 769; Furth and Bluh, *Kolloid. Zeitsch.*, 1924, 34, 259.

<sup>8</sup> Errera, *Bull. Soc. chim. Belg.*, 1924, 33, 422, 432.

<sup>9</sup> Dumanski, *J. Russ. Phys. Chem. Soc.*, 1924, 54, 703.

<sup>10</sup> Gessner, *Kolloidchem. Beihefte*, 1924, 19, 213.

<sup>11</sup> Zocher, *Zeitsch. physikal. Chem.*, 1921, 98, 293; compare Reinders and Van der Lee, *Rec. Trav. chim.*, 1928, 47, 193.



disturbed. A similar bi-refringence in sols of several slightly soluble substances which ordinarily form microscopic crystals, *e.g.* mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ , and lead iodide,  $\text{PbI}_2$ , has been demonstrated by Reinders.<sup>1</sup> Freundlich does not agree, however, that these rod-like structures are necessarily responsible for the double refraction; he attributes the chief cause to the presence of aggregates of amicronic non-spherical particles, not discernible under the ultramicroscope and separated from one another by amicronic distances.<sup>2</sup> It is adduced in support of this view that double refraction can be produced in and removed from sols of benzopurpurin without any change being visible in the ultramicroscope. Double refraction is also shown, although not so strongly, by aged ferric hydroxide sols, aluminium hydroxide sols,<sup>3</sup> clay suspensions, soap solutions, alizarin, aniline-blue, *p*-azoxyanisole, *p*-azoxyphenetole.<sup>4</sup> Red gold sols and silver sols also become doubly refracting under the influence of an alternating current.<sup>5</sup>

*Hydrates of Vanadium Pentoxide.*—Several hydrates of vanadium pentoxide have been obtained by the action of mineral acids on solutions of alkali vanadates. In many cases their composition agrees with that of one of the free acids corresponding to the vanadates, but it has been shown that they are not true acids;<sup>6</sup> the amount of water present depends only on the conditions of drying. Von Hauer<sup>7</sup> and Fritzsche<sup>8</sup> both obtained an insoluble *dihydrate*,  $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , which was supposed to be free pyrovanadic acid,  $\text{H}_4\text{V}_2\text{O}_7$ . By continuing the drying of this hydrate over concentrated sulphuric acid von Hauer<sup>9</sup> obtained the *monohydrate*,  $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , which similarly was supposed to be free metavanadic acid,  $\text{HVO}_3$ . Ditte<sup>10</sup> obtained several other hydrates,  $\text{V}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , the composition of which also depended on the vapour-pressure of the atmosphere. A hydrate corresponding to orthovanadic acid,  $\text{H}_3\text{VO}_4$  or  $\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , has not been obtained.

When hydrated vanadium pentoxide is precipitated under special conditions it forms a yellow or orange substance known as *vanadium bronze*. Boiling a solution of sulphur dioxide with copper vanadate gives scales of a golden or orange colour.<sup>11</sup> The precipitate obtained may, however, be a partial reduction product of the vanadate, in which case its composition would be analogous to that of the tungsten bronzes.<sup>12</sup> A vanadium bronze is also obtained when a solution of ammonium metavanadate is added to a solution of copper sulphate in excess of ammonium chloride until a permanent precipitate forms, the suspension then being heated to 75° C. The more slowly the precipitation takes

<sup>1</sup> Reinders, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 19, 189.

<sup>2</sup> Freundlich, *Colloid and Capillary Chemistry*, translated by Hatfield (Methuen, London, 1926), p. 823.

<sup>3</sup> Aschenbrenner, *Zeitsch. physikal. Chem.*, 1927, 127, 415.

<sup>4</sup> Zocher, *loc. cit.*; Freundlich, Schuster, and Zocher, *Zeitsch. physical. Chem.*, 1923, 105, 119.

<sup>5</sup> Bergholm and Björnsthål, *Physikal. Zeitsch.*, 1920, 21, 137; *Phil. Mag.*, 1921, [vi], 42, 352.

<sup>6</sup> Düllberg, *Zeitsch. physikal. Chem.*, 1903, 45, 175.

<sup>7</sup> von Hauer, *J. prakt. Chem.*, 1860, 80, 324.

<sup>8</sup> Fritzsche, *ibid.*, 1851, 53, 93.

<sup>9</sup> See also Manasse, *Chem. Zentr.*, 1886, 773.

<sup>10</sup> Ditte, *Compt. rend.*, 1885, 101, 698.

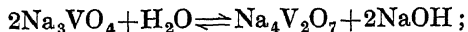
<sup>11</sup> Gerland, *J. prakt. Chem.*, 1871, [ii], 4, 139; *Bull. Soc. chim.*, 1873, [ii], 19, 501; *Ber.*, 1877, 10, 1515.

<sup>12</sup> See this series, Vol. VII., Part III. (1926), p. 243.

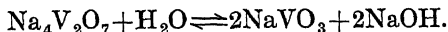
place the more brilliant is the colour of the bronze. Guyard<sup>1</sup> states that the bronze is not a hydrate of vanadium pentoxide, but an acid ammonium vanadate.

#### THE VANADATES.

**General.**—It seems certain that the free acids corresponding to these salts do not exist in the solid state, and that, with the possible exception of hexavanadic acid, mentioned below, they are also incapable of existing in solution, although salts of all the acids are known. The most stable class of salts is the metavanadates, the next in order of stability being the pyrovanadates, while the orthovanadates are few in number and undergo rapid hydrolysis even in the cold, to give the pyro-salts :

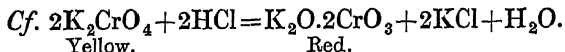
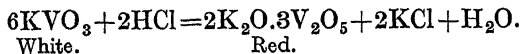


the pyro-salt is converted into the meta-salt on boiling the solution :



These reactions are reversible, and removal of the caustic alkali by addition of acids effects the immediate conversion of ortho- or pyro-salts into the meta-salts. On the other hand, the presence of a large excess of caustic alkali favours the formation of the ortho- and pyro-salts. The order of stability is the reverse of that which applies to the ortho-, pyro-, and meta-phosphates. Orthophosphates are prepared from the other two classes either by boiling or by addition of weak acids.

Metavanadates of the alkalis are white or colourless, and give colourless aqueous solutions which rapidly become yellow, and, on addition of acids, red or orange. These coloured solutions contain polyvanadates, the formation of which is comparable to that of the polychromates and other salts formed by condensation of weakly acid oxides of metals, *e.g.* molybdates and borates. Thus, under definite conditions of temperature and concentration, potassium metavanadate is converted into the acid salt  $2\text{K}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ , in accordance with the equation :

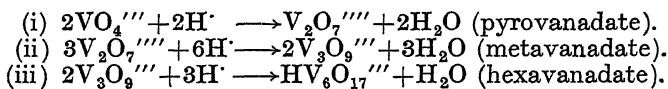


Polyvanadates produced in this manner are much more numerous than the polychromates, and have the general composition  $\text{R}'_2\text{O} \cdot n\text{V}_2\text{O}_5$ , where  $n$  is greater than one. Solutions of polyvanadates contain equilibrium mixtures the compositions of which vary considerably with the acidity, the temperature, and the concentration of the solution. Thus, by acidifying a solution of lithium metavanadate with acetic acid, crystals having the composition  $3\text{Li}_2\text{O} \cdot 4\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$  are obtained, the mother-liquor from which, on being boiled, gives the compound  $3\text{Li}_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ . Again, by treating a solution of potassium metavanadate with acetic acid under different conditions of temperature and concentration, a series of salts has been obtained in which  $n = \frac{3}{2}, \frac{5}{3}, 2, \frac{5}{2},$  and 3. In several salts the molecular proportions of vanadium pentoxide and basic oxide are not so simple, for example in the com-

<sup>1</sup> Guyard, *Bull. Soc. chim.*, 1876, [ii], 25, 356.

pound  $22\text{K}_2\text{O}\cdot 0.24\text{V}_2\text{O}_5\cdot 7\text{H}_2\text{O}$ , and it is noteworthy that in several instances efforts to repeat the preparation of one particular compound have failed under apparently identical conditions. The acid vanadates on the whole have not been accurately investigated by physico-chemical methods, and their composition is sufficiently varied to suggest that, as in the case of the double vanadates and heteropoly-acids, they may be isomorphous mixtures of simple substances in varying proportions, despite the facts (1) that they are easily crystallisable compounds, and (2) that from their analytical data definite formulæ can be written down for them.

*Hexavanadic Acid.*—The acids corresponding to these various salts have not been isolated, but according to Düllberg<sup>1</sup> many of the polyvanadates can be looked upon as being derived from hexavanadic acid,  $\text{H}_4\text{V}_6\text{O}_{17}$  or  $2\text{H}_2\text{O}\cdot 3\text{V}_2\text{O}_5$ , the existence of which in solution is indicated by the changes in electrical conductivity that ensue when alkali vanadates are gradually neutralised. When sodium orthovanadate,  $\text{Na}_3\text{VO}_4$ , is treated with increasing quantities of hydrochloric acid, it is found that the ions finally present in solution are  $\text{Na}^+$  and  $[\text{HV}_6\text{O}_{17}]'''$ . The fourth hydrogen atom in hexavanadic acid is not easily replaceable by a metal. The change takes place in the following sequence, commencing with the  $\text{VO}_4'''$  ion supplied by solution of the orthovanadate :—



Hexavanadic acid is also stated to be formed in solution by the decomposition of pervanadic acid,<sup>2</sup> which is produced when vanadium pentoxide is treated with hydrogen peroxide, but more recently the properties of the solution have been attributed to the formation of peroxyorthovanadic acid,  $\text{HVO}_4\cdot\text{H}_2\text{O}$  (see p. 91). According to Düllberg the compound which has the composition  $\text{Na}_2\text{O}\cdot 2\text{V}_2\text{O}_5\cdot 9\text{H}_2\text{O}$  should be formulated as the trisodium salt of hexavanadic acid,  $\text{Na}_3\text{HV}_6\text{O}_{17}\cdot 13\text{H}_2\text{O}$ ; similarly the compound which has the composition  $\text{Na}_2\text{O}\cdot 3\text{V}_2\text{O}_5\cdot 3\text{H}_2\text{O}$  should be formulated as the disodium salt of hexavanadic acid,  $\text{Na}_2\text{H}_2\text{V}_6\text{O}_{17}\cdot 2\text{H}_2\text{O}$ . It is of some interest to note that many of the heteropoly-acid compounds which contain vanadium can also be written as being derived from hexavanadic acid,<sup>3</sup> although this theory of their constitution is not now held.<sup>4</sup> The hexavanadic acid theory does not exclude the possibility of the existence of other more highly condensed acids. Many of the alkali polyvanadates can be prepared in two crystalline forms: (a) Orange, transparent crystals, and (b) golden, scaly masses, with a metallic lustre. It is suggested that the latter are derived from the more highly condensed acids.

All the vanadates are powerful oxidising agents and undergo reduction in acid solution in the manner already described for vanadium pentoxide. The alkali vanadates are usually easily soluble in water, and are white or pale yellow, crystalline compounds, and frequently

<sup>1</sup> Düllberg, *Zeitsch. physikal. Chem.*, 1903, 45, 175; compare Rosenheim and Yang, *Zeitsch. anorg. Chem.*, 1923, 129, 181.

<sup>2</sup> Pissarjewsky, *Zeitsch. physikal. Chem.*, 1903, 43, 173.

<sup>3</sup> Prandtl, *Zeitsch. anorg. Chem.*, 1911, 73, 223; 1915, 92, 198.

<sup>4</sup> Meyer and Pawletta, *Zeitsch. anal. Chem.*, 1926, 69, 15.

dimorphous. They are insoluble in alcohol, which is often employed to throw them out from solution. When ammonia gas is passed over the vanadates of the heavy metals, or when the latter are digested in liquid ammonia, slow absorption ensues with formation of *hexamine addition compounds*; usually six molecules of ammonia are taken up for each atom of metal present.<sup>1</sup>

**Orthovanadates**,  $R_3VO_4$  or  $3R_2O.V_2O_5$ .—The alkali orthovanadates can be prepared by fusing a mixture of vanadium pentoxide with the calculated quantity of alkali carbonate. The best known is the sodium salt  $Na_3VO_4.12H_2O$ . Ammonium orthovanadate does not appear to exist. Ditte<sup>2</sup> obtained a number of vanadates by fusing a mixture of vanadium pentoxide, sodium halide, and the halide of the desired metal, and this method has furnished several orthovanadates. Copper, lead and silver orthovanadates have been prepared by double decomposition in solution, but addition of metallic salts to a soluble orthovanadate most often yields variously coloured precipitates of uncertain composition; because of their strong tendency to undergo hydrolysis the ortho-salts give rise to the corresponding pyro- and meta-vanadates, or to a mixture of them; the hydroxide of the metal may also be produced, and in the case of ferrous sulphate and other reducing agents oxidation takes place.

Silver orthovanadate reacts with alkyl halides to give *esters* of vanadic acid. These are yellow liquids of general formula  $Alk_3VO_4$ , in which Alk. represents the alkyl radical. Esters of orthovanadic acid are more stable than those of pyro- and meta-vanadic acids; that is, the order of stability is the reverse of that which applies to the inorganic salts.<sup>3</sup> The following orthovanadates have been prepared:—

*Bismuth Orthovanadate*,  $BiVO_4$ , is a bright yellow compound obtained by the double decomposition of bismuth nitrate with an alkali vanadate.<sup>4</sup>

*Cerous Orthovanadate*,  $CeVO_4$ , has been prepared as dark red needles by fusing sodium metavanadate with cerous chloride.<sup>5</sup>

*Copper Orthovanadate*,  $Cu_3(VO_4)_2$ .—When treated with solutions of copper salts, solutions of orthovanadates yield a greenish-yellow precipitate which consists mainly of copper orthovanadate with excess of vanadium pentoxide.<sup>6</sup>

*Lead Orthovanadate*,  $Pb_3(VO_4)_2$ , is precipitated as a white powder when sodium orthovanadate is treated with lead acetate solution.<sup>7</sup>

*Lithium Orthovanadate*,  $Li_3VO_4$ .—The yellow, anhydrous salt results on fusing a mixture of lithium carbonate and vanadium pentoxide in the requisite proportions.<sup>8</sup> Crystals of the *hexahydrate*,  $Li_3VO_4.6H_2O$ , have been obtained by concentrating the mother-liquor left from crystallisation of lithium pyrovanadate.<sup>9</sup> Two other lithium vanadates,  $4Li_2O.V_2O_5.H_2O$  and  $4Li_2O.V_2O_5.14H_2O$ , have also been prepared.<sup>10</sup>

*Nickel Orthovanadate*,  $Ni_3(VO_4)_2$ , yields green, prismatic needles

<sup>1</sup> Ephraim and Beck, *Helv. Chim. Acta*, 1926, 9, 38.

<sup>2</sup> Ditte, *Compt. rend.*, 1883, 96, 1048.

<sup>3</sup> Hall, *J. Chem. Soc.*, 1887, 51, 751; Hess, *J. Soc. Chem. Ind.*, 1914, 33, 712.

<sup>4</sup> Carnot, *Compt. rend.*, 1887, 105, 119; Frenzel, *Jahrb. Miner.*, 1875, 680.

<sup>5</sup> Abegg, *Handbuch der anorganischen Chemie* (Leipzig), 1906, 3, i, 208.

<sup>6</sup> Gerland, *Ber.*, 1876, 9, 873.

<sup>7</sup> Roscoe, *J. Chem. Soc.*, 1871, 24, 23; Amadori, *ibid.*, *Ab.*, 1919, 116, ii, 413.

<sup>8</sup> Rammelsberg, *Wed. Annalen*, 1883, [ii], 20, 928.

<sup>9</sup> Ditte, *Compt. rend.*, 1887, 104, 1168.

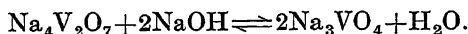
<sup>10</sup> Ditte, *loc. cit.*

when a fused mixture of vanadium pentoxide, sodium bromide and a small proportion of nickel bromide is extracted with dilute nitric acid and the solution concentrated.<sup>1</sup>

*Potassium Orthovanadate*,  $K_3VO_4$ , forms as a pale yellow, crystalline mass when vanadium pentoxide and potassium carbonate are fused together in the necessary molecular proportions.<sup>2</sup> It melts at a temperature above  $1000^\circ C$ .<sup>3</sup> A solution of vanadium pentoxide in three equivalent proportions of caustic potash yields colourless, transparent, deliquescent crystals of two hydrates,  $2K_3VO_4 \cdot 9H_2O$  and  $K_3VO_4 \cdot 6H_2O$  respectively, according to the temperature of crystallisation.<sup>4</sup> If a large excess of caustic potash is employed the compound obtained is  $4K_2O \cdot V_2O_5 \cdot 20H_2O$ .<sup>5</sup>

*Silver Orthovanadate*,  $Ag_3VO_4$ , is precipitated as a deep orange powder when a freshly prepared solution of sodium orthovanadate is treated with a carefully neutralised solution of silver nitrate.<sup>6</sup> It melts between  $403^\circ$  and  $565^\circ C$ .<sup>7</sup> and is soluble in nitric acid and in ammonium hydroxide; the latter solution yields yellow hexagonal crystals of the composition  $3AgVO_3 \cdot 2NH_3 \cdot H_2O$ .<sup>8</sup>

*Sodium Orthovanadate*,  $Na_3VO_4 \cdot 12H_2O$ , is the orthovanadate most frequently met with. It is readily obtained by adding excess of caustic soda to a solution of sodium pyrovanadate :



It can be conveniently crystallised from caustic soda solutions, in which it is less soluble than in water. It forms hexagonal prisms isomorphous with the corresponding phosphate and arsenate,  $Na_3PO_4 \cdot 12H_2O$  and  $Na_3AsO_4 \cdot 12H_2O$ . The *decahydrates*,  $Na_3VO_4 \cdot 10H_2O$ ,  $Na_3AsO_4 \cdot 10H_2O$ , and  $Na_3PO_4 \cdot 10H_2O$ , are also isomorphous.<sup>9</sup> In consequence of the reversible nature of the above reaction, solutions of sodium orthovanadate are strongly alkaline; their electrical conductivity has been studied by Düllberg.<sup>10</sup> The anhydrous salt,  $Na_3VO_4$ , melts at  $866^\circ$ <sup>11</sup> or  $850^\circ C$ .<sup>12</sup> It can be prepared by fusing sodium carbonate and vanadium pentoxide in the required molecular proportions. Extraction of the product with water and precipitation with alcohol gives colourless needle-shaped crystals of a hydrate containing sixteen molecules of water,  $Na_3VO_4 \cdot 16H_2O$ .<sup>13</sup> The *hepta-* and *octa-hydrates*,  $Na_3VO_4 \cdot 7H_2O$  and  $Na_3VO_4 \cdot 8H_2O$ , have also been prepared.<sup>14</sup>

By dissolving vanadium pentoxide in a large excess of caustic soda, Ditte<sup>15</sup> obtained two crystalline vanadates which contained a larger proportion of the basic oxide than is present in the orthovanadate, and to which he gave the formulæ  $4Na_2O \cdot V_2O_5 \cdot 30H_2O$  and  $4Na_2O \cdot V_2O_5 \cdot 26H_2O$ .

*Strontium Orthovanadate*,  $Sr_3(VO_4)_2$ , is obtained in transparent, pale yellow leaves by heating together a mixture of vanadium pentoxide, sodium iodide, and strontium iodide.<sup>16</sup>

*Thallium Orthovanadate*,  $Tl_3VO_4$ , is a light brown substance obtained by carefully fusing three molecular proportions of thallium carbonate

<sup>1</sup> Ditte, *Compt. rend.*, 1883, 96, 1048.

<sup>3</sup> Canneri, *Gazzetta*, 1928, 58, 6.

<sup>6</sup> Ditte, *loc. cit.*      <sup>6</sup> Roscoe, *loc. cit.*

<sup>8</sup> Ditte, *Compt. rend.*, 1887, 104, 1705.

<sup>10</sup> Düllberg, *Zeitsch. physikal. Chem.*, 1903, 45, 129; Rosenheim and Yang, *loc. cit.*

<sup>11</sup> Carnelly, *loc. cit.*

<sup>12</sup> Canneri, *loc. cit.*

<sup>13</sup> Roscoe, *loc. cit.*

<sup>14</sup> Baker, *loc. cit.*; cf. Hall, *J. Chem. Soc.*, 1887, 51, 94.

<sup>15</sup> Ditte, *Compt. rend.*, 1887, 104, 902, 1061.

<sup>2</sup> Rammelsberg, *loc. cit.*

<sup>4</sup> Ditte, *Compt. rend.*, 1887, 104, 902, 1061.

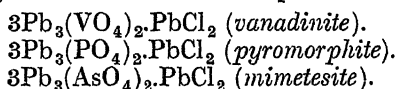
<sup>7</sup> Carnelly, *J. Chem. Soc.*, 1878, 33, 273.

<sup>9</sup> Baker, *J. Chem. Soc.*, 1885, 47, 357.

<sup>16</sup> Ditte, *ibid.*, 1883, 96, 1048.

with one molecular proportion of vanadium pentoxide. Its density is 8.6. One gram dissolves in a litre of water at 15° C.<sup>1</sup> M.pt. 566°<sup>2</sup> or 555° C.<sup>3</sup>

*Double Compounds of Orthovanadates and Halogen Salts.*—Although the orthovanadates of divalent metals are not very stable compounds, they form very stable double salts with certain metallic halides. These double salts are of interest in that isomorphous analogues are frequently given by orthophosphates and orthoarsenates. The following naturally occurring double salts are isomorphous:—<sup>4</sup>



They are isomorphous also with the calcium compounds  $\text{Ca}_3(\text{VO}_4)_2 \cdot \text{CaCl}_2$  and  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$ .<sup>5</sup> The discovery of isomorphism among these double salts led Roscoe to transfer vanadium from the chromium family, in which it had been previously placed, to Group V. (see p. 24).

The general method of preparation of these double salts consists in fusing vanadium pentoxide with excess of the halide of the metal. Except in the case of the sodium compound, the residue is simply washed with water, in which the double salts are insoluble. The following have been described:—

$2\text{Na}_3\text{VO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$ . Limpid octahedra, isomorphous with the corresponding phosphorus and arsenic compounds.<sup>6</sup>

$3\text{Ba}_3(\text{VO}_4)_2 \cdot \text{BaBr}_2$  . Hexagonal, transparent plates.<sup>7</sup>  
 $3\text{Ba}_3(\text{VO}_4)_2 \cdot \text{BaI}_2$  . Hexagonal, brown, transparent prisms.<sup>8</sup>  
 $3\text{Cd}_3(\text{VO}_4)_2 \cdot \text{CdCl}_2$  . Hexagonal prisms; density 5.264.  
 $3\text{Cd}_3(\text{VO}_4)_2 \cdot \text{CdBr}_2$  . Hexagonal prisms; density 5.456.

(The corresponding cadmium iodide has not been isolated.<sup>9</sup>)

$\text{Ca}_3(\text{VO}_4)_2 \cdot \text{CaCl}_2$  . Glistening, rhombic crystals.<sup>10</sup>  
 $\text{Ca}_3(\text{VO}_4)_2 \cdot \text{CaBr}_2$  . Glistening, thin leaves.<sup>11</sup>  
 $3\text{Ca}_3(\text{VO}_4)_2 \cdot \text{CaBr}_2$  . White, glistening crystals.<sup>12</sup>  
 $3\text{Ca}_3(\text{VO}_4)_2 \cdot \text{CaI}_2$  . Hexagonal, colourless, transparent crystals.<sup>13</sup>  
 $3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2$  . Reddish-brown, transparent, hexagonal prisms.<sup>14</sup>

(This lead salt is the artificial form of the important natural ore *vanadinite*.)

$3\text{Sr}_3(\text{VO}_4)_2 \cdot \text{SrBr}_2$  . Hexagonal plates.<sup>15</sup>  
 $3\text{Sr}_3(\text{VO}_4)_2 \cdot \text{SrI}_2$ .<sup>16</sup>

<sup>1</sup> Carnelly, *J. Chem. Soc.*, 1873, 26, 325.

<sup>2</sup> Carnelly, *ibid.*, 1878, 33, 273.

<sup>3</sup> Canneri, *loc. cit.*

<sup>4</sup> Roscoe, *J. Chem. Soc.*, 1868, 21, 322. The refractive indices of these ores have been measured by Bowman (*Min. Mag.*, 1903, 13, 324).

<sup>5</sup> Hautefeuille, *Compt. rend.*, 1873, 77, 896.

<sup>6</sup> Baker, *J. Chem. Soc.*, 1885, 47, 358; Travers, *Bull. Soc. chim.*, 1923, [iv], 33, 297.

<sup>7</sup> Ditte, *Compt. rend.*, 1883, 96, 575, 846; *Ber.*, 1883, 16, 1097.

<sup>8</sup> Ditte, *loc. cit.*

<sup>9</sup> de Schulten, *Bull. Soc. chim.*, 1900, [iii], 23, 159.

<sup>10</sup> Hautefeuille, *loc. cit.*

<sup>11</sup> Ditte, *Compt. rend.*, 1883, 96, 575.

<sup>12</sup> Ditte, *ibid.*, 1882, 94, 1592; 1883, 96, 575, 846, 1226.

<sup>13</sup> Ditte, *loc. cit.*

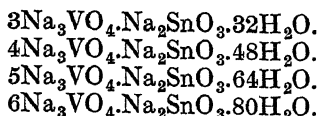
<sup>14</sup> Hautefeuille, *loc. cit.*; Roscoe, *J. Chem. Soc.*, 1871, 24, 23; Carobbi and Restaino, *Gazzetta*, 1926, 56, 59.

<sup>15</sup> Ditte, *Compt. rend.*, 1883, 96, 575, 1846.

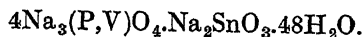
<sup>16</sup> Ditte, *loc. cit.*

*Chlororthovanadates of beryllium and zirconium*,<sup>1</sup> and *chlormetavanadates of lead and copper* (see p. 45), have also been prepared.

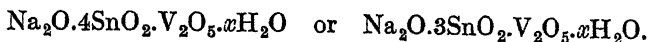
**Sodium Stannovanadates or Vanadostannates.**—By crystallising mixed solutions of sodium stannate and sodium orthovanadate, a series of sodium stannovanadates has been prepared, the salts having the following compositions :—



The constant difference between each member is  $\text{Na}_3\text{VO}_4 \cdot 16\text{H}_2\text{O}$ . The particular member obtained depends on the concentration of the constituents and on the temperature. The same compounds can be prepared by fusing together stannic oxide,  $\text{SnO}_2$ , vanadium pentoxide and caustic soda, and crystallising the fused mass. They are all isomorphous, and form doubly refracting, transparent, rhombic needles. The use of sodium orthoarsenate and sodium orthophosphate instead of the vanadate gives rise to two analogous series of stannophosphates and stannoarsenates. A mixed salt having the composition of both the phosphate and arsenate has also been isolated :



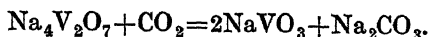
When a solution containing sodium orthovanadate and stannous chloride is carefully neutralised with caustic soda, an amorphous yellow substance is obtained which has the composition



This compound is considered to be a complex salt of a heteropoly-acid formed from stannic oxide and vanadium pentoxide, and it is therefore comparable with the vanadoselenites and vanadotellurites.<sup>2</sup>

**Pyrovanadates,  $\text{R}_4\text{V}_2\text{O}_7$ , or  $2\text{R}'_2\text{O} \cdot \text{V}_2\text{O}_5$ .**—The alkali pyrovanadates are prepared by dissolving the equivalent quantity of vanadium pentoxide in solutions of alkalis, or by the spontaneous decomposition in solution of the alkali orthovanadates. Pyrovanadates of other metals are obtained by fusing vanadium pentoxide with the salts or hydroxides of the metals in molecular proportions, or, when they are sufficiently insoluble, by double decomposition between an alkali pyrovanadate and a salt of the metal required.

Pyrovanadates are more stable than orthovanadates, but, in consequence of the weakly acid character of pyrovanadic acid, they undergo easy conversion into the metavanadates. Sodium pyrovanadate in solution is thus converted by carbon dioxide into the metavanadate :

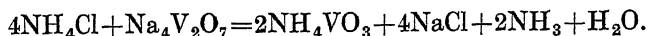


Ammonium pyrovanadate does not appear to exist; addition of

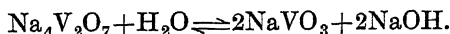
<sup>1</sup> Tanatar and Kurowski, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 813.

<sup>2</sup> Prandtl and Rosenthal, *Ber.*, 1907, 40, 2125.

ammonium chloride to a solution of a pyrovanadate precipitates ammonium metavanadate :



These reactions suggest that sodium pyrovanadate undergoes partial hydrolysis in solution :



The introduction of carbon dioxide into the solution removes the caustic soda (or, from the point of view of the ionic theory, the OH' ions), so that the equilibrium is disturbed and the reaction then proceeds completely from left to right. Similarly, addition of ionised ammonium chloride suppresses the concentration of the OH' ions already present in solution; more of the pyrovanadate therefore undergoes hydrolysis, in order that the equilibrium concentrations of ions shall be maintained, until all the pyrovanadate is converted into metavanadate.

The weakly acid nature of pyrovanadic acid is also shown by the fact that solutions of pyrovanadates react alkaline to phenolphthalein. The solutions have been shown to contain the colourless ( $\text{V}_2\text{O}_7$ )'''' ion.<sup>1</sup>

Silver pyrovanadate gives esters of pyrovanadic acid only with the higher alkyl halides, e.g. *amyl pyrovanadate*,  $(\text{C}_5\text{H}_{11})_4\text{V}_2\text{O}_7$ .<sup>2</sup>

The following pyrovanadates have been prepared :—

*Barium Pyrovanadate*,  $\text{Ba}_2\text{V}_2\text{O}_7$ , is precipitated on addition of barium chloride to a solution of sodium pyrovanadate or of other vanadates in the presence of ammonia.<sup>3</sup> It has more recently been prepared by the action of barium peroxide on vanadium pentoxide.<sup>4</sup> It is a white, amorphous powder which melts above 863° C.<sup>5</sup>

*Calcium Pyrovanadate*,  $2\text{Ca}_2\text{V}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ , is formed by adding calcium chloride to a solution of sodium pyrovanadate and drying the precipitate at 100° C.<sup>6</sup> The *dihydrate*,  $\text{Ca}_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , has been obtained in transparent needles by adding calcium chloride to ammonium metavanadate solution and then excess of ammonium hydroxide.<sup>7</sup>

*Copper Pyrovanadate*,  $\text{Cu}_2\text{V}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , has been obtained in greenish-yellow, transparent, rhombohedral plates by the action of copper sulphate on ammonium metavanadate.<sup>8</sup> The anhydrous salt has also been prepared by saturating a solution of vanadium pentoxide and a copper salt with ammonia.<sup>9</sup> According to Radau,<sup>10</sup> addition of copper sulphate to solutions of pyrovanadates gives rise to precipitates the composition of which approximates to the formula  $8\text{CuO} \cdot 3\text{V}_2\text{O}_5$ .

*Lead Pyrovanadate*,  $\text{Pb}_2\text{V}_2\text{O}_7$ .—This salt is of interest in that it is the artificial form of *desclouite*, one of the important natural ores of vanadium. It is obtained by boiling mixed solutions of lead nitrate and ammonium metavanadate in the presence of acetic acid.<sup>11</sup> A pale yellow basic pyrovanadate of lead,  $2\text{Pb}_2\text{V}_2\text{O}_7 \cdot \text{PbO}$ , is obtained by

<sup>1</sup> Dullberg, *Zeitsch. physikal. Chem.*, 1903, 45, 129.

<sup>2</sup> Hall, *J. Chem. Soc.*, 1887, 51, 751.

<sup>3</sup> Roscoe, *ibid.*, 1871, 24, 23; Carnot, *Compt. rend.*, 1887, 104, 1803, 1850.

<sup>4</sup> Hedvall and Zweigbergk, *Zeitsch. anorg. Chem.*, 1919, 108, 119.

<sup>5</sup> Carnelly, *J. Chem. Soc.*, 1878, 33, 273.

<sup>6</sup> Roscoe, *loc. cit.*

<sup>7</sup> Ditte, *Compt. rend.*, 1887, 104, 1705.

<sup>8</sup> Ditte, *loc. cit.*

<sup>9</sup> Carnot, *Compt. rend.*, 1887, 105, 121.

<sup>10</sup> Radau, *Dissertation* (Berlin, 1888).

<sup>11</sup> Ditte, *loc. cit.*



the addition of lead acetate to a solution of a vanadate. The composition of the compound produced in this manner is, however, not constant.<sup>1</sup>

*Lithium Pyrovanadate*,  $\text{Li}_4\text{V}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ .—When a solution of sodium metavanadate is made strongly alkaline with lithium hydroxide and concentrated *in vacuo*, white, silky needles of the *hexahydrate* are obtained, which leave a white, nacreous mass of the *anhydrous* salt,  $\text{Li}_4\text{V}_2\text{O}_7$ , on being heated.<sup>2</sup> The *tetrahydrate*,  $\text{Li}_4\text{V}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ , has been obtained by fusing vanadium pentoxide with lithium nitrate and extracting the melt with water, in which it is readily soluble.<sup>3</sup>

*Manganese Pyrovanadate*,  $\text{Mn}_3\text{V}_2\text{O}_7$ , is obtained in large, brilliant brown needles by fusing together a mixture of vanadium pentoxide, sodium bromide and manganese bromide.<sup>4</sup>

*Potassium Pyrovanadate*,  $\text{K}_4\text{V}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ , separates out in colourless, transparent crystals when one molecular proportion of vanadium pentoxide is dissolved in two molecular proportions of potassium hydroxide. These lose water when heated, melt, and leave a crystalline mass of the *anhydrous* salt  $\text{K}_4\text{V}_2\text{O}_7$ ,<sup>5</sup> which is deliquescent and melts at  $910^\circ \text{C}$ .<sup>6</sup> A white, crystalline, readily soluble *trihydrate*,  $\text{K}_4\text{V}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , has also been prepared.<sup>7</sup>

*Silver Pyrovanadate*,  $\text{Ag}_4\text{V}_2\text{O}_7$ , is obtained as a dense yellow precipitate by the addition of neutral silver nitrate to sodium pyrovanadate solution.<sup>8</sup> It has also been obtained as brilliant yellow, transparent plates.<sup>9</sup> M.pt.  $383^\circ \text{C}$ .<sup>10</sup>

*Sodium Pyrovanadate*,  $\text{Na}_4\text{V}_2\text{O}_7 \cdot 18\text{H}_2\text{O}$ , is prepared by fusing vanadium pentoxide (1 mol.) with sodium carbonate (2 mols.) and extracting the melt with water. Alternatively, the vanadium pentoxide is dissolved in caustic soda solution, using the same molecular proportions. It forms long, six-sided plates, or pearly, glistening needles which are efflorescent and readily soluble in water. At  $100^\circ \text{C}$ . it loses seventeen molecules of water, the last molecule being evolved at  $140^\circ \text{C}$ . The anhydrous salt melts at  $654^\circ$ <sup>11</sup> or  $632^\circ \text{C}$ .<sup>12</sup> By partial dehydration, and crystallisation from a mixture of alcohol and water, an *octahydrate*,  $\text{Na}_4\text{V}_2\text{O}_7 \cdot 8\text{H}_2\text{O}$ , has been obtained.<sup>13</sup>

*Thallium Pyrovanadate*,  $\text{Tl}_4\text{V}_2\text{O}_7$ , is precipitated as a light yellow powder by the addition of thallium sulphate to a cold, saturated solution of sodium orthovanadate. It also results on fusing a mixture of vanadium pentoxide and thallium carbonate.<sup>14</sup> It melts at  $454^\circ$ <sup>15</sup> or  $416^\circ \text{C}$ .<sup>16</sup> and is soluble in about 5000 parts of water at  $14^\circ \text{C}$ .

<sup>1</sup> Roscoe, *loc. cit.*; Descloizeaux, *Ann. Chim. Phys.*, 1854, [iii], 41, 78; Amadori, *J. Chem. Soc., Abs.*, 1919, 116, ii, 413.

<sup>2</sup> Ditte, *Compt. rend.*, 1887, 104, 1168.

<sup>3</sup> Rammelsberg, *Wied. Annalen*, 1883, [ii], 20, 928.

<sup>4</sup> Ditte, *Compt. rend.*, 1883, 96, 1048.

<sup>5</sup> Ditte, *ibid.*, 1887, 104, 902.

<sup>6</sup> Canneri, *Gazzetta*, 1928, 58, 6.

<sup>7</sup> Rammelsberg, *loc. cit.*

<sup>8</sup> Roscoe, *loc. cit.*

<sup>9</sup> Ditte, *Compt. rend.*, 1887, 104, 1705.

<sup>10</sup> Carnelly, *J. Chem. Soc.*, 1878, 33, 273.

<sup>11</sup> Carnelly, *loc. cit.*

<sup>12</sup> Canneri, *loc. cit.*

<sup>13</sup> Ditte, *Compt. rend.*, 1887, 104, 1061.

<sup>14</sup> Carnelly, *J. Chem. Soc.*, 1873, 26, 323.

<sup>15</sup> Carnelly, *ibid.*, 1878, 33, 273.

<sup>16</sup> Canneri, *loc. cit.*

*Thorium Pyrovanadate*,  $\text{Th}_2\text{V}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ , is greenish-yellow, and is obtained by the action of thorium chloride in dilute solution on ammonium metavanadate.<sup>1</sup>

*Zinc Pyrovanadate*,  $\text{Zn}_2\text{V}_2\text{O}_7$ , forms orange-red prisms when vanadium pentoxide is fused with a mixture of sodium bromide and zinc bromide.<sup>2</sup> It is appreciably soluble in water.

Several vanadates are known the compositions of which are intermediate between that of the pyrovanadates,  $2\text{R}'\text{O} \cdot \text{V}_2\text{O}_5$ , and that of the metavanadates,  $\text{R}'\text{O} \cdot \text{V}_2\text{O}_5$ . They can be looked upon as **basic metavanadates**. The following have been described:—

*Basic Lithium Metavanadate*,  $3\text{Li}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$  or  $\text{Li}_2\text{O} \cdot 4\text{LiVO}_3 \cdot 15\text{H}_2\text{O}$ , is obtained by crystallising lithium orthovanadate from dilute nitric acid.<sup>3</sup>

*Basic Potassium Metavanadate*,  $5\text{K}_2\text{O} \cdot 4\text{V}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$  or  $\text{K}_2\text{O} \cdot 8\text{KVO}_3 \cdot 7\text{H}_2\text{O}$ , separates in white crystals when a solution of potassium pyrovanadate,  $\text{K}_4\text{V}_2\text{O}_7$ , is acidified with acetic acid and concentrated.<sup>4</sup>

*Basic Sodium Metavanadate*,  $3\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  or  $\text{Na}_2\text{O} \cdot 4\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ , and the hexahydrate,  $\text{Na}_2\text{O} \cdot 4\text{NaVO}_3 \cdot 6\text{H}_2\text{O}$ , have both been prepared by fusing sodium carbonate (3 mols.) with vanadium pentoxide (2 mols.).<sup>5</sup> They are not readily soluble in water.

*Basic Thallium Metavanadates*,  $3\text{Tl}_2\text{O} \cdot 2\text{V}_2\text{O}_5$  or  $\text{Tl}_2\text{O} \cdot 4\text{TlVO}_3$ , is obtained as a sparingly soluble, yellow powder by the action of thallium sulphate on the corresponding sodium compound.<sup>6</sup>

$6\text{Tl}_2\text{O} \cdot 5\text{V}_2\text{O}_5$  or  $\text{Tl}_2\text{O} \cdot 10\text{TlVO}_3$  is prepared by the action of thallium sulphate on sodium pyrovanadate,  $\text{Na}_4\text{V}_2\text{O}_7$ , in the presence of excess of vanadium pentoxide.<sup>7</sup> It dissolves in 9372 parts of water at 11° C. and in 3366 parts of water at 100° C.

*Basic Silver Metavanadate*,  $3\text{Ag}_2\text{O} \cdot 2\text{V}_2\text{O}_5$  or  $\text{Ag}_2\text{O} \cdot 4\text{AgVO}_3$ , is prepared by the action of silver nitrate on the corresponding sodium salt. It is a dark yellow compound, almost insoluble in water.<sup>8</sup>

*Basic Lead Metavanadate*,  $3\text{PbO} \cdot 2\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  or  $\text{PbO} \cdot 2\text{Pb}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ , is obtained as a yellow powder by the action of lead nitrate on an acid manganese vanadate.<sup>9</sup>

*Basic Strontium Metavanadate*,  $3\text{SrO} \cdot 2\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  or  $\text{SrO} \cdot 2\text{Sr}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ , has also been prepared.<sup>10</sup>

**Metavanadates**,  $\text{R}'\text{VO}_3$  or  $\text{R}'\text{O} \cdot \text{V}_2\text{O}_5$ .—These salts are more stable than either the ortho- or pyrovanadates. Solutions of the latter yield metavanadates on being evaporated or by treatment with carbon dioxide. The alkali metavanadates are prepared directly by dissolving vanadium pentoxide in the calculated quantity of alkali hydroxide. The metavanadates of other metals are prepared by fusing vanadium pentoxide with the oxide or carbonate of the metal in calculated quantity,<sup>11</sup> or by the action of a soluble salt of the metal

<sup>1</sup> Volck, *Zeitsch. anorg. Chem.*, 1894, 6, 161.

<sup>2</sup> Ditte, *Compt. rend.*, 1883, 96, 1048; cf. Radau, *Annalen*, 1889, 251, 114.

<sup>3</sup> Rammelsberg, *Wied. Annalen*, 1883, [ii], 20, 938.

<sup>4</sup> Rammelsberg, *loc. cit.*

<sup>5</sup> Carnelly, *Annalen*, 1873, 166, 155.

<sup>6</sup> Carnelly, *J. Chem. Soc.*, 1873, 26, 330.

<sup>7</sup> Carnelly, *loc. cit.*

<sup>8</sup> Carnelly, *loc. cit.*

<sup>9</sup> Ephraim and Beck, *Helv. Chim. Acta*, 1926, 9, 38.

<sup>10</sup> Ephraim and Beck, *loc. cit.*

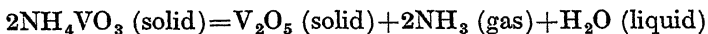
<sup>11</sup> de Carli, *Atti R. Accad. Lincei*, 1925, [vi], 1, 533.

on a neutral solution of alkali metavanadate. The alkali and alkaline earth metavanadates are white or pale yellow; metavanadates of the heavy metals are deep yellow, brown, or red. Most of the alkali metavanadates are soluble in water; vanadates of the heavy metals are almost insoluble in water or dilute acetic acid. According to Bleecker,<sup>1</sup> all the vanadates of the metals seem to be soluble in water to some extent, but become insoluble in the presence of small quantities of the precipitating agent. They show a tendency to precipitate in the colloidal state; especially is this the case with the vanadates of iron, copper, zinc and aluminium. The vanadates of mercury, lead, copper and iron fuse at about 600° C., but the vanadates of aluminium, calcium, zinc and tungsten do not fuse at much higher temperatures. The fused vanadates of iron and copper are extremely hard and are good conductors of electricity. On being treated with mineral acid, vanadates decompose with the formation of red colloidal vanadium pentoxide.

The following metavanadates have been prepared:—

*Aluminium Metavanadate*,  $\text{Al}(\text{VO}_3)_3$ , may be prepared electrolytically or by the addition of an aluminium salt in solution to an alkali vanadate.<sup>2</sup>

*Ammonium Metavanadate*,  $\text{NH}_4\text{VO}_3$ , is one of the commonest compounds of vanadium, and forms the starting material for the preparation of a large number of vanadium salts. Its preparation from a vanadium ore has been described on p. 54. It is obtained in the laboratory by dissolving vanadium pentoxide in excess of ammonium hydroxide and concentrating, or, instead of concentrating, alcohol may be added, in which the salt is insoluble. Recrystallisation from dilute ammonium hydroxide gives a pure product.<sup>3</sup> Ammonium metavanadate is also insoluble in a saturated solution of ammonium chloride, and it is quantitatively precipitated by the addition of an excess of solid ammonium chloride to a neutral solution of sodium metavanadate or pyrovanadate.<sup>4</sup> It is a white powder which can be obtained in colourless, granular crystals, isomorphous with potassium metavanadate. Its density is 2.826. One hundred parts of water dissolve 5.18 parts at 15° C. and 10.4 parts at 32° C.<sup>5</sup> On being gently heated in air ammonium metavanadate becomes yellow, red, and then brown, with loss of ammonia: <sup>6</sup>



—43,600 calories.

At temperatures above 210° C. the salt undergoes reduction and leaves a residue of the lower oxides of vanadium, and may also give some nitride.<sup>7</sup>

*Barium Metavanadate*,  $\text{Ba}(\text{VO}_3)_2 \cdot \text{H}_2\text{O}$ , is obtained in white or yellow microscopic crystals by the action of barium chloride on

<sup>1</sup> Bleecker, *Met. Chem. Eng.*, 1910, 8, 666.

<sup>2</sup> Bleecker, *ibid.*, 1911, 9, 501.

<sup>3</sup> Lachartre, *Bull. Soc. chim.*, 1924, [iv], 35, 321.

<sup>4</sup> Gooch and Gilbert, *Zeitsch. anorg. Chem.*, 1902, 32, 174; Rosenheim, *ibid.*, 1902, 32, 181; Campagne, *Ber.*, 1903, 36, 3164.

<sup>5</sup> Lachartre, *loc. cit.*; compare, however, Ditte, *Compt. rend.*, 1886, 102, 918; Meyer, *Zeitsch. Elektrochem.*, 1909, 15, 266.

<sup>6</sup> Matignon, *Chem. Zeit.*, 1905, 29, 987.

<sup>7</sup> Roscoe, *Annalen, Suppl.*, 1868, 6, 104; Ditte, *Compt. rend.*, 1885, 101, 698.

potassium metavanadate.<sup>1</sup> It undergoes dehydration between 190° and 200° C. The anhydrous salt has also been prepared by the action of barium peroxide on vanadium pentoxide.<sup>2</sup>

*Beryllium Metavanadate*,  $\text{Be}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ .—Addition of solutions of beryllium salts to alkali vanadates gives rise to basic vanadates of indefinite composition. The pure salt is obtained by boiling beryllium hydroxide and vanadium pentoxide in water in the required proportions. The solution is filtered, concentrated to a syrup and poured into alcohol, whereupon isometric cubes, modified by an octahedron, are obtained. The larger crystals polarise light. Density, 2.273. One gram dissolves in a litre of water at 25° C.<sup>3</sup>

*Cadmium Metavanadate*,  $\text{Cd}(\text{VO}_3)_2$ , is obtained as brilliant, transparent, slender, yellowish needles by fusing a mixture of vanadium pentoxide, sodium bromide and cadmium bromide.<sup>4</sup>

*Cæsium Metavanadate*,  $\text{CsVO}_3$ , has been obtained by boiling vanadium pentoxide with cæsium carbonate solution.<sup>5</sup>

*Calcium Metavanadate*,  $\text{Ca}(\text{VO}_3)_2 \cdot 3\text{H}_2\text{O}$ , gives rise to bright yellow needles when a solution of ammonium metavanadate is boiled with calcium chloride solution and precipitated with alcohol.<sup>6</sup> The *tetrahydrate*,  $\text{Ca}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ , is prepared by allowing a mixture of potassium metavanadate and calcium chloride to evaporate for several days.<sup>7</sup> Anhydrous calcium metavanadate is a white, porous substance, which is unaffected by strong heating, but is readily decomposed by acids to yield vanadium pentoxide.<sup>8</sup> It is much more soluble in water than strontium metavanadate.

*Cobalt Metavanadate*,  $\text{Co}(\text{VO}_3)_2 \cdot 3\text{H}_2\text{O}$ , separates out on boiling a solution of ammonium vanadate with excess of cobalt nitrate which has been feebly acidified with nitric acid.<sup>9</sup> It is easily soluble in water.

*Copper Metavanadate*.—Addition of copper sulphate solution to sodium metavanadate throws down a precipitate which consists mainly of copper metavanadate, which is light yellow. The precipitate may, however, be green or blue, because its composition varies considerably. Copper metavanadate can also be produced electrolytically. On being fused at a high temperature in a graphite crucible it forms copper and vanadium carbide.<sup>10</sup>

“*Didymium*” *Metavanadate*, “*Di*” $\text{VO}_3$ , is thrown down as a fine, grey precipitate when ammonium metavanadate is treated with “*didymium*” nitrate.<sup>11</sup>

*Indium Metavanadate*,  $\text{In}(\text{VO}_3)_3 \cdot 2\text{H}_2\text{O}$ , is a yellow substance produced by the action of sodium metavanadate on indium chloride solution.<sup>12</sup>

<sup>1</sup> Manasse, *Annalen*, 1887, 240, 23.

<sup>2</sup> Hedvall and Zweigbergk, *Zeitsch. anorg. Chem.*, 1919, 108, 119.

<sup>3</sup> Brinton, *J. Amer. Chem. Soc.*, 1916, 38, 2361; Tanatar and Kurowski, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 813.

<sup>4</sup> Ditte, *Compt. rend.*, 1883, 96, 1048.

<sup>5</sup> Chabrie, *Ann. Chim. Phys.*, 1902, [vii], 26, 228.

<sup>6</sup> Scheuer, *Zeitsch. anorg. Chem.*, 1898, 16, 284.

<sup>7</sup> Manasse, *Annalen*, 1887, 240, 44.

<sup>8</sup> Bleecker, *Met. Chem. Eng.*, 1910, 8, 666.

<sup>9</sup> Ditte, *Compt. rend.*, 1887, 104, 1705; cf. Carnot, *ibid.*, 1887, 105, 119, and Hedvall, *Zeitsch. anorg. Chem.*, 1915, 93, 313.

<sup>10</sup> Bleecker, *Met. Chem. Eng.*, 1910, 8, 666; 1911, 9, 501.

<sup>11</sup> Cleve, *Bull. Soc. chim.*, 1885, 43, 359. “*Didymium*” is now known to consist of two elements, namely, *praseodymium* and *neodymium*; see Auer v. Welsbach, *Monatsh.*, 1885, 6, 477.

<sup>12</sup> Renz, *Dissertation* (Breslau, 1902).

*Iron Vanadate* is, metallurgically, the most important vanadate. Precipitation of a solution of a vanadate with ferrous sulphate gives rise to a precipitate of indefinite composition, ortho-, pyro-, meta-, and perhaps a poly-vanadate being present, as well as ferric or ferrous oxide. Reduction of the vanadate to a vanadyl salt may also ensue. The precipitate is usually colloidal and carries down with it some sodium vanadate. The dried powder may be either green, yellow, brown, or red; the more nearly the precipitate approximates to a red colour the lower is its vanadium content. An iron vanadate has also been prepared by electrolysis of a solution of sodium vanadate between iron poles.<sup>1</sup>

*Lead Metavanadate*,  $\text{Pb}(\text{VO}_3)_2$ .—Acid solutions of vanadates on being treated with lead salts give rise to yellow basic vanadates the composition of which varies with the conditions. The precipitation of normal lead vanadate is, therefore, difficult. It has been accomplished by the addition of lead acetate to ammonium metavanadate solution in the presence of acetic acid.<sup>2</sup> The lead precipitates contain all the vanadic acid originally present in solution, and precipitation of vanadates with lead salts has, therefore, been employed for the quantitative estimation of vanadium.<sup>3</sup> The mineral *deschenite* consists chiefly of lead metavanadate; a portion of the lead is, however, frequently replaced by zinc.<sup>4</sup>

*Lithium Metavanadate*,  $\text{LiVO}_3 \cdot 2\text{H}_2\text{O}$ , forms brilliant, silky needles when lithium carbonate (1 mol.) and vanadium pentoxide (1 mol.) are boiled together in water and the product concentrated in a vacuum.<sup>5</sup> It melts at  $618^\circ \text{C}$ .<sup>6</sup> and is readily soluble in water.

*Magnesium Metavanadate*,  $\text{Mg}(\text{VO}_3)_2 \cdot 6\text{H}_2\text{O}$ , is obtained as transparent crystals by boiling an excess of basic magnesium carbonate with vanadium pentoxide and concentrating the filtered solution in a vacuum.<sup>7</sup> It is easily soluble in water.

*Manganese Metavanadate*,  $\text{Mn}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ , is a sparingly soluble, dark red powder, obtained by interaction between manganese sulphate and ammonium metavanadate in solution. When the powder is boiled in the precipitating solution, reddish-brown six-sided plates of the anhydrous metavanadate,  $\text{Mn}(\text{VO}_3)_2$ , are produced.<sup>8</sup>

*Mercurous Metavanadate*,  $\text{HgVO}_3$ , is thrown down as an orange precipitate when mercurous nitrate is added to a solution of a vanadate. If the solutions are carefully neutralised the precipitation is complete, and it is used for the gravimetric estimation of vanadium, the mercurous vanadate being ignited and the residue weighed as vanadium pentoxide. In the presence of a slight excess of ammonia, a grey or black precipitate of complex composition is produced. Addition of mercuric chloride to a neutral solution of a vanadate produces a white precipitate, soluble in acids; in the presence of ammonia a yellow compound is thrown down.<sup>9</sup>

<sup>1</sup> Bleecker, *loc. cit.*

<sup>2</sup> Bleecker, *loc. cit.*

<sup>3</sup> Roscoe, *Annalen, Suppl.*, 1872, 8, 102.

<sup>4</sup> Bergemann, *Pogg. Annalen*, 1850, 80, 393.

<sup>5</sup> Ditte, *Compt. rend.*, 1887, 104, 1168; Rammelsberg, *Wied. Annalen*, 1883, [ii], 20, 938.

<sup>6</sup> Canneri, *Gazzetta*, 1928, 58, 6.

<sup>7</sup> Ditte, *Compt. rend.*, 1887, 104, 1705; Manasse, *Annalen*, 1887, 240, 48.

<sup>8</sup> Radau, *Chem. Zentr.*, 1888, 1378; Scheuer, *Zeitsch. anorg. Chem.*, 1898, 16, 284.

<sup>9</sup> Carnot, *loc. cit.*

*Nickel Metavanadate*,  $\text{Ni}(\text{VO}_3)_2$ , separates as greenish-yellow, transparent prisms when a solution of ammonium metavanadate is boiled with excess of nickel nitrate solution feebly acidified with nitric acid.<sup>1</sup>

*Potassium Metavanadate*,  $\text{KVO}_3$ , is obtained as white or colourless crystals by dissolving vanadium pentoxide in hot, strong caustic potash solution. By varying the concentrations several hydrates have also been prepared:  $2\text{KVO}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{KVO}_3 \cdot 2\text{H}_2\text{O}$ ;  $2\text{KVO}_3 \cdot 5\text{H}_2\text{O}$ ;  $\text{KVO}_3 \cdot 3\text{H}_2\text{O}$ .<sup>2</sup> On being heated, all these hydrates lose their water and leave a white, nacreous mass of the anhydrous salt, which melts at  $495^\circ \text{C}$ .<sup>3</sup> Two other hydrates were prepared by Rammelsberg:  $4\text{KVO}_3 \cdot \text{H}_2\text{O}$  and  $\text{KVO}_3 \cdot 7\text{H}_2\text{O}$ .

*Silver Metavanadate*,  $\text{AgVO}_3$ , is a yellow, gelatinous substance obtained by interaction between silver nitrate and a metavanadate in neutral solution. It is soluble in nitric acid and in ammonia.<sup>5</sup>

*Sodium Metavanadate*,  $\text{NaVO}_3$ , is manufactured industrially by decomposing commercial iron vanadate with sodium carbonate or sodium hydroxide, or by dissolving vanadium pentoxide in solutions of these sodium compounds. It was prepared in the pure state by McAdam,<sup>6</sup> to determine the atomic weight of vanadium. Its electrolytic production has been studied.<sup>7</sup> Ditte<sup>8</sup> reported the existence of several hydrates:  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ ;  $\text{NaVO}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ;  $\text{NaVO}_3 \cdot 3\text{H}_2\text{O}$  or  $4\text{H}_2\text{O}$ ; but solubility experiments<sup>9</sup> indicate the existence in solution of only the *dihydrate*,  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ . Cryoscopic measurements show that the anhydrous salt associates in solution to give  $\text{Na}_3\text{V}_3\text{O}_9$ .<sup>10</sup> One hundred grams of water dissolve 21.1 grams of anhydrous sodium metavanadate at  $25^\circ \text{C}$ . and 38.8 grams at  $70^\circ \text{C}$ . The salt possesses such powerful colouring properties that 1 part of it imparts a yellow tint to 200,000 parts of water. The hydrated salt is efflorescent, and melts at  $562^\circ \text{C}$ . to a dark red, amorphous mass.<sup>11</sup> The m.pt. of the anhydrous salt is also given as  $630^\circ \text{C}$ .<sup>12</sup> It is decomposed by mineral acids in the cold to give colloidal vanadium pentoxide; when a current of hydrogen chloride gas is passed over sodium metavanadate at  $440^\circ \text{C}$ ., the whole of the vanadic acid is volatilised and sodium chloride is left. The volatile product condenses as a semi-opaque, reddish-brown, oily liquid, which is probably  $2\text{VO}_2 \cdot 4\text{HCl} \cdot 3\text{H}_2\text{O}$ .<sup>13</sup>

*Strontium Metavanadate*,  $\text{Sr}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ , is obtained as colourless, monoclinic prisms by the action of strontium chloride on potassium metavanadate. It is only sparingly soluble in water and undergoes dehydration at  $280^\circ \text{C}$ .<sup>14</sup>

*Thallium Metavanadate*,  $\text{TlVO}_3$ , is prepared by fusing thallium

<sup>1</sup> Ditte, *Compt. rend.*, 1887, 104, 1705; cf. Carnot, *ibid.*, 1887, 105, 119.

<sup>2</sup> Ditte, *ibid.*, 1887, 104, 902.

<sup>3</sup> Canneri, *loc. cit.*

<sup>4</sup> Rammelsberg, *loc. cit.*

<sup>5</sup> Bleecker, *loc. cit.*; Browning and Palmer, *Amer. J. Sci.*, 1910, [iv], 30, 220.

<sup>6</sup> McAdam, *J. Amer. Chem. Soc.*, 1910, 32, 1603; see also McAdam and Pierle, *ibid.*, 1912, 34, 604.

<sup>7</sup> Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 194.

<sup>8</sup> Ditte, *Compt. rend.*, 1887, 104, 1061.

<sup>9</sup> McAdam and Pierle, *loc. cit.*

<sup>10</sup> Düllberg, *Zeitsch. physikal. Chem.*, 1903, 45, 129; but compare Canneri, *Gazzetta*, 1923, 56, ii, 779.

<sup>11</sup> Carnelly, *J. Chem. Soc.*, 1878, 33, 273.

<sup>12</sup> Canneri, *loc. cit.*

<sup>13</sup> Smith and Hibbs, *Zeitsch. anorg. Chem.*, 1894, 7, 41.

<sup>14</sup> Manasse, *Annalen*, 1887, 240, 33.

carbonate with vanadium pentoxide in molecular proportions.<sup>1</sup> It forms dark, laminated crystals, which are almost insoluble in water. Its sp. gr. is 6.019 at 17° C.; m.pt. 424°<sup>2</sup> or 391° C.<sup>3</sup>

*Zinc Metavanadate*,  $\text{Zn}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ , forms brilliant, pale yellow, cubic or rhombic crystals when zinc nitrate is added to a neutral solution of ammonium metavanadate and the mixture is concentrated.<sup>4</sup> It has also been obtained electrolytically.<sup>5</sup>

*Chlormetavanadates of lead and of copper* have also been prepared (see p. 45).

Metavanadic acid yields *addition compounds* with *hydroxylamine* and *ammonia*.<sup>6</sup> When hydroxylamine hydrochloride and ammonium metavanadate are added to a cold saturated solution of ammonia and the whole kept at 0° C. until precipitation takes place, rosettes of lemon-yellow crystals having the composition  $\text{HVO}_3 \cdot 2\text{NH}_2\text{OH} \cdot 2\text{NH}_3$  or  $\text{VO}_5\text{N}_4\text{H}_{13}$ , are formed. These are stable in the presence of ammonia, but are decomposed by water, dilute caustic soda, air, and carbon dioxide. On addition of hydrochloric or sulphuric acid, evolution of nitrous oxide takes place. By decreasing the proportion of ammonium metavanadate added to the saturated ammonia solution, yellow crystals of composition  $\text{HVO}_3 \cdot 3\text{NH}_2\text{OH} \cdot 2\text{NH}_3$  or  $\text{VO}_6\text{N}_5\text{H}_{16}$  separate out. An extremely unstable compound,  $\text{HVO}_3 \cdot 3\text{NH}_2\text{OH}$  or  $\text{VO}_6\text{N}_3\text{H}_{10}$ , has also been prepared. Addition compounds with hydroxylamine are also given by arsenic acid and phosphoric acid, and by tungstates, uranates, and molybdates.<sup>7</sup>

A reaction which is very comparable to that which takes place with hydroxylamine consists in the formation of *amine vanadates* by the action of vanadium pentoxide on the alkylamines. The simplest of those that have been prepared are :<sup>8</sup>

*Methylamine vanadate*,  $\text{CH}_3\text{NH}_2 \cdot \text{HVO}_3$ .

*Dimethylamine vanadate*,  $(\text{CH}_3)_2\text{NH} \cdot \text{HVO}_3$ .

*Ethylamine vanadate*,  $(\text{C}_2\text{H}_5)\text{NH}_2 \cdot \text{HVO}_3$ .

*Tetraethylamine vanadate*,  $(\text{C}_2\text{H}_5)_4\text{N} \cdot \text{VO}_3$ .

**Polyvanadates or Acid Vanadates.**—In addition to the salts of vanadium pentoxide which have been described, there exists a large number of polyvanadates in which the molecular proportion of vanadium pentoxide to basic oxide is greater than in the case of the metavanadates. The constitution of these acid salts has been discussed on p. 62. A general method for preparing the alkali polyvanadates consists in adding acetic acid to a solution of the ortho-, pyro-, or meta-vanadate, and concentrating. Usually several compounds of varying composition can be isolated. The polyvanadates of the heavy metals can sometimes be prepared by double decomposition of alkali vanadates with solutions of salts of these metals, but more usually complex salts containing both the heavy metal and the alkali (double vanadates) are precipitated. By precipitating a

<sup>1</sup> Carnelly, *J. Chem. Soc.*, 1873, 26, 323.

<sup>2</sup> Carnelly, *ibid.*, 1878, 33, 273.

<sup>3</sup> Ditte, *Compt. rend.*, 1887, 104, 1705.

<sup>4</sup> Bleecker, *loc. cit.*

<sup>5</sup> Hofmann and Kohlschütter, *Zeitsch. anorg. Chem.*, 1898, 16, 463.

<sup>6</sup> Kohlschütter and Hofmann, *Annalen*, 1899, 307, 314; Hofmann, *Zeitsch. anorg. Chem.*, 1897, 15, 75.

<sup>7</sup> Bailey, *J. Chem. Soc.*, 1884, 45, 690; Ditte, *Compt. rend.*, 1887, 104, 1844.

<sup>8</sup> Canneri, *loc. cit.*

solution of acid barium vanadate,  $2\text{BaO} \cdot 3\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ , with salts of various heavy metals, Ephraim and Beck<sup>1</sup> have recently prepared a series of acid vanadates of general formula  $2\text{R} \cdot \text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 12$  or  $15\text{H}_2\text{O}$ , or, less frequently,  $3\text{R} \cdot \text{O} \cdot 5\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . These lose their water of crystallisation largely or completely at  $220^\circ \text{C}$ ., with decomposition in the case of the oxidisable heavy metals. The acid vanadates are unstable towards weak acids, and are frequently decomposed even by boiling water. They are intensely coloured, usually red. The following polyvanadates are known:—

*Ammonium Polyvanadates.*—The compound  $(\text{NH}_4)_2\text{O} \cdot 3\text{V}_2\text{O}_5$  appears to be the most stable of the acid ammonium vanadates. It is formed by addition of a 10 per cent. solution of acetic acid to a solution of ammonium metavanadate, or by boiling an aqueous solution of any other ammonium polyvanadate. It forms thin, transparent, yellow, octagonal plates, or golden, microscopic, rhombic plates which become temporarily vermilion on being heated, and which are only slightly soluble in water. It has also been obtained combined with two, five, or six molecules of water, according to the temperature of crystallisation or extent of dehydration.<sup>2</sup>

$2(\text{NH}_4)_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  can be looked upon as *ammonium hexavanadate*,  $(\text{NH}_4)_4\text{V}_6\text{O}_{17} \cdot 4\text{H}_2\text{O}$  (see p. 63). It is obtained as transparent, ruby-red, monoclinic crystals when a solution of ammonium oxalate, saturated at  $30^\circ \text{C}$ ., is treated with vanadium pentoxide and evaporated in a vacuum. Crystals containing  $6\text{H}_2\text{O}$  can also be obtained.<sup>3</sup> It is very soluble in water.

By the action of small quantities of acetic acid of varying concentration on hot, saturated solutions of ammonium metavanadate, other complexes have been obtained:  $(\text{NH}_4)_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ,  $2\text{H}_2\text{O}$ , or  $3\text{H}_2\text{O}$ ; <sup>4</sup>  $3(\text{NH}_4)_2\text{O} \cdot 7\text{V}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ ;  $2(\text{NH}_4)_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ .<sup>5</sup>

*Barium Polyvanadates.*—*Barium hexavanadate*,  $2\text{BaO} \cdot 3\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ , is prepared by the addition of barium chloride to an acid solution of calcium vanadate under definite conditions of concentration and acidity.<sup>6</sup> Another hydrate,  $2\text{BaO} \cdot 3\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$  or  $\text{Ba}_2\text{V}_6\text{O}_{17} \cdot 14\text{H}_2\text{O}$ , is obtained as red, rhombic crystals when barium nitrate is added to a boiling solution of sodium metavanadate acidified with acetic acid.<sup>7</sup> Addition of barium chloride to a solution of potassium pyrovanadate in the presence of a large excess of acetic acid yields red crystals having the composition  $3\text{BaO} \cdot 5\text{V}_2\text{O}_5 \cdot 19\text{H}_2\text{O}$ . These are soluble in about 5000 parts of water; <sup>8</sup> the mother-liquor, after crystallisation of the foregoing salt, gives the compound  $4\text{BaO} \cdot 5\text{V}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$ .<sup>9</sup>

*Beryllium Polyvanadate*,  $2\text{BeO} \cdot 3\text{V}_2\text{O}_5 \cdot 11\text{H}_2\text{O}$ , forms dark red, hygroscopic crystals which are obtained by the action of beryllium sulphate on barium hexavanadate.<sup>10</sup>

<sup>1</sup> Ephraim and Beck, *Helv. Chim. Acta*, 1926, 9, 38.

<sup>2</sup> Ditte, *Compt. rend.*, 1886, 102, 918, 1019; Lachartre, *Bull. Soc. chim.*, 1924, [iv], 35, 321.

<sup>3</sup> Ditte, *loc. cit.*

<sup>4</sup> Ditte, *loc. cit.*; Lachartre, *loc. cit.*; Guyard, *Bull. Soc. chim.*, 1876, [ii], 25, 351.

<sup>5</sup> Rammelsberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1883, 87, 3.

<sup>6</sup> Ephraim and Beck, *Helv. Chim. Acta*, 1926, 9, 38.

<sup>7</sup> Ditte, *Compt. rend.*, 1887, 104, 1705.

<sup>8</sup> Manasse, *Chem. Zentr.*, 1886, 773; von Hauer, *Sitzungsber. K. Akad. Wiss. Wien*, 1856, 21, 358; 1860, 39, 451.

<sup>9</sup> Norblad, *Dissertation* (Upsala University, 1873).

<sup>10</sup> Ephraim and Beck, *loc. cit.*



*Cadmium Polyvanadates.*—Two are known,  $2\text{CdO} \cdot 3\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$  and  $\text{CdO} \cdot 3\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ . The former is obtained by the action of cadmium sulphate on the corresponding barium salt,<sup>1</sup> and the latter by the action of cadmium nitrate on ammonium metavanadate in the presence of acetic acid.<sup>2</sup>

*Calcium Polyvanadates.*—Addition of calcium chloride to a solution of potassium pyrovanadate in the presence of acetic acid has furnished  $3\text{CaO} \cdot 4\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$ ;  $\text{CaO} \cdot 2\text{V}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ ;  $\text{CaO} \cdot 2\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ ;  $3\text{CaO} \cdot 7\text{V}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ ;  $2\text{CaO} \cdot 5\text{V}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ ;  $3\text{CaO} \cdot 8\text{V}_2\text{O}_5 \cdot 26\text{H}_2\text{O}$ , according to the concentration, temperature, and acidity of the mixture.<sup>3</sup> Addition of calcium nitrate to excess of ammonium metavanadate solution in the presence of nitric acid has given the compound  $\text{CaO} \cdot 3\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ ,<sup>4</sup> which is readily soluble in water.

*Cerous Polyvanadate*,  $\text{Ce}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 27\text{H}_2\text{O}$ , has been prepared by evaporating a solution containing ammonium metavanadate and cerous sulphate.<sup>5</sup>

*Cobalt Polyvanadate*,  $2\text{CoO} \cdot 3\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$ , forms large, six-sided brown leaves which effloresce readily in air. It is obtained by the action of cobalt sulphate on the corresponding barium salt.<sup>6</sup>

*Copper Polyvanadate*,  $3\text{CuO} \cdot 5\text{V}_2\text{O}_5 \cdot 22\text{H}_2\text{O}$ , is prepared by the action of copper sulphate on barium hexavanadate.<sup>7</sup> It forms thin, iridescent spangles.

*"Didymium" Polyvanadate*, " $\text{Di}$ "<sub>2</sub> $\text{O}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 28\text{H}_2\text{O}$ , is obtained by mixing solutions of "didymium" nitrate and the acid sodium salt,  $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5$ .<sup>8</sup>

*Gadolinium Polyvanadate*,  $\text{Gd}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 26\text{H}_2\text{O}$ ,<sup>9</sup> and *Lanthanum Vanadate*<sup>10</sup> are known.

*Lead Polyvanadate*,  $\text{PbO} \cdot 2\text{V}_2\text{O}_5$ , can be obtained as yellow, transparent needles by fusing a mixture of vanadium pentoxide, sodium iodide, and lead iodide.<sup>11</sup>

*Lithium Polyvanadate*,  $5\text{Li}_2\text{O} \cdot 6\text{V}_2\text{O}_5 \cdot 30\text{H}_2\text{O}$ , has been prepared as red, transparent prisms by the addition of acetic acid to the mother-liquor left from the crystallisation of lithium metavanadate.<sup>12</sup> If the acetic acid is added directly to a solution of lithium metavanadate or orthovanadate, the compound obtained has the composition  $3\text{Li}_2\text{O} \cdot 4\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ . The same process has also yielded  $2\text{Li}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$  or  $16\text{H}_2\text{O}$ ,  $\text{Li}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ,  $9\text{H}_2\text{O}$  or  $12\text{H}_2\text{O}$ ,<sup>13</sup> according to the acidity, temperature, and concentration. Evaporation of the mother-liquor from the crystallisation of the compound  $3\text{Li}_2\text{O} \cdot 4\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$  has given the sparingly soluble compound  $3\text{Li}_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$  or  $12\text{H}_2\text{O}$ .<sup>14</sup>

*Magnesium Polyvanadates.*—Addition of a slight excess of magnesium

<sup>1</sup> Ephraim and Beck, *loc. cit.*

<sup>2</sup> Ditte, *loc. cit.*

<sup>3</sup> Manasse, *loc. cit.*; also *Annalen*, 1887, 240, 44; Ephraim and Beck, *loc. cit.*

<sup>4</sup> Ditte, *loc. cit.*

<sup>5</sup> Abegg, *Handbuch der anorganischen Chemie* (Leipzig, 1906), 3, i, 208.

<sup>6</sup> Ephraim and Beck, *loc. cit.*; see also Carnot, *Compt. rend.*, 1889, 109, 148.

<sup>7</sup> Ephraim and Beck, *loc. cit.*

<sup>8</sup> Cleve, *Bull. Soc. chim.*, 1885, 43, 359; see footnote, p. 72.

<sup>9</sup> Benedicks, *Zeitsch. anorg. Chem.*, 1900, 20, 393.

<sup>10</sup> Carobbi and Restaino, *Gazzetta*, 1926, 56, 59.

<sup>11</sup> Ditte, *Compt. rend.*, 1883, 96, 1048.

<sup>12</sup> Rammelsberg, *Wied. Annalen*, 1883, [ii], 20, 938.

<sup>13</sup> Ditte, *Compt. rend.*, 1887, 104, 1168.

<sup>14</sup> Rammelsberg, *loc. cit.*

sulphate to a hot solution of potassium pyrovanadate gives red crystals which have the composition  $4\text{MgO} \cdot 6\text{V}_2\text{O}_5 \cdot 19\text{H}_2\text{O}$ . They are only slightly soluble in water and undergo dehydration at  $200^\circ \text{C}$ .<sup>1</sup> When magnesium oxide is boiled with vanadium pentoxide in solution and excess of acetic acid is added, a dimorphous, soluble polyvanadate having the composition  $3\text{MgO} \cdot 5\text{V}_2\text{O}_5 \cdot 28\text{H}_2\text{O}$  is formed.<sup>2</sup> Decomposition of a hot, saturated solution of ammonium metavanadate with excess of magnesium chloride and acetic acid gives another compound,  $\text{MgO} \cdot 2\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$  or  $8\text{H}_2\text{O}$ ;<sup>3</sup> and a *hexavanadate*,  $2\text{MgO} \cdot 3\text{V}_2\text{O}_5 \cdot 19\text{H}_2\text{O}$ , has been prepared by the action of magnesium oxide on vanadium oxytrichloride.<sup>4</sup>

*Manganese Polyvanadates*.—The action of manganese sulphate on acid barium vanadate has given the salt  $2\text{MnO} \cdot 3\text{V}_2\text{O}_5 \cdot 11\text{H}_2\text{O}$ .<sup>5</sup> A compound  $5\text{MnO}_2 \cdot \text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$  has also been prepared.<sup>6</sup> This can be looked upon as a vanadic manganite.

*Nickel Polyvanadates*.— $\text{NiO} \cdot 2\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  is obtained as greenish-brown crystals from the mother-liquor left after crystallisation of nickel metavanadate. The compound  $3\text{NiO} \cdot 5\text{V}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$  has been prepared in two crystalline forms.<sup>7</sup>

*Potassium Polyvanadates*.—By the action of acetic acid on solutions of potassium metavanadate at different temperatures and concentrations, soluble acid vanadates of the following compositions have been prepared:  $3\text{K}_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ ;  $\text{K}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ ;  $2\text{K}_2\text{O} \cdot 4\text{V}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ ; <sup>8</sup>  $2\text{K}_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ .<sup>9</sup> By dissolving excess of vanadium pentoxide in potassium carbonate solution and then adding acetic acid, Ditte<sup>10</sup> also isolated the compounds  $\text{K}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  or  $8\text{H}_2\text{O}$  or  $10\text{H}_2\text{O}$ , and  $\text{K}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$  or  $5\text{H}_2\text{O}$  or  $6\text{H}_2\text{O}$ .<sup>11</sup> The anhydrous compound  $\text{K}_2\text{O} \cdot 3\text{V}_2\text{O}_5$  is almost insoluble in water.

*Potassium Hexavanadate*,  $2\text{K}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$  or  $\text{K}_4\text{V}_6\text{O}_{17} \cdot 6\text{H}_2\text{O}$ , is obtained as orange plates by concentration of the mother-liquor from the salt  $\text{K}_2\text{O} \cdot 2\text{V}_2\text{O}_5$ .<sup>12</sup> The *heptahydrate*,  $\text{K}_4\text{V}_6\text{O}_{17} \cdot 7\text{H}_2\text{O}$ , has also been prepared.<sup>13</sup> When vanadium pentoxide is fused with potassium chloride and the product extracted with water, the following are obtained:  $22\text{K}_2\text{O} \cdot 24\text{V}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ ;  $\text{K}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  or  $6\text{H}_2\text{O}$ ; and the insoluble residue is found to contain the compound  $2\text{K}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ . Substitution of potassium fluoride for the chloride in this reaction gives a vanadate which contains the highest proportion of vanadium pentoxide in the series, namely,  $2\text{K}_2\text{O} \cdot 9\text{V}_2\text{O}_5$ .<sup>14</sup>

*Samarium Polyvanadates*.—Addition of a neutral samarium salt to a solution of a metavanadate throws down a yellow, amorphous precipitate which consists mainly of samarium orthovanadate. Two acid

<sup>1</sup> Manasse, *Annalen*, 1887, 240, 49.

<sup>2</sup> Manasse, *loc. cit.*; Sugiura and Baker, *J. Chem. Soc.*, 1879, 35, 715.

<sup>3</sup> von Hauer, *loc. cit.*

<sup>4</sup> Cuttica, Tarohi, and Alinari, *Gazzetta*, 1923, 53, 189.

<sup>5</sup> Ephraim and Beck, *loc. cit.*

<sup>6</sup> Sarker and Dhar, *Zeitsch. anorg. Chem.*, 1922, 121, 135.

<sup>7</sup> Ephraim and Beck, *loc. cit.*

<sup>8</sup> Radau, *Annalen*, 1889, 251, 114; Norblad, *Dissertation* (Upsala University, 1873).

<sup>9</sup> Manasse, *Annalen*, 1887, 240, 23.

<sup>10</sup> Ditte, *Compt. rend.*, 1887, 104, 902.

<sup>11</sup> Norblad, *loc. cit.*

<sup>12</sup> Ditte, *loc. cit.*

<sup>13</sup> Friedheim, *Ber.*, 1890, 23, 1526.

<sup>14</sup> Ephraim, *Zeitsch. anorg. Chem.*, 1903, 35, 66.

samarium vanadates, namely,  $\text{Sm}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 28\text{H}_2\text{O}$  and  $\text{Sm}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$ , have been isolated from the mother-liquors.<sup>1</sup>

*Sodium Polyvanadates.*—*Sodium hexavanadate*,  $\text{Na}_4\text{V}_6\text{O}_{17}$  or  $2\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ , is prepared by acidifying a solution of sodium metavanadate. It has been obtained combined with  $18\text{H}_2\text{O}$ ,  $16\text{H}_2\text{O}$ ,<sup>2</sup>  $10\text{H}_2\text{O}$ ,<sup>3</sup> and  $9\text{H}_2\text{O}$ .<sup>4</sup> The anhydrous salt is almost insoluble in water. From electrical conductivity data under different conditions, Düllberg<sup>5</sup> was able to show the existence in solution of *hexavanadic acid*,  $\text{H}_4\text{V}_6\text{O}_{17}$ , which gives rise also to the following acid salts:  $\text{Na}_3\text{HV}_6\text{O}_{17} \cdot 13\text{H}_2\text{O}$  and  $\text{Na}_2\text{H}_2\text{V}_6\text{O}_{17} \cdot 2\text{H}_2\text{O}$ . It is by no means certain, however, that these acid salts are derivatives of hexavanadic acid; they can be alternatively formulated as  $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$  and  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  respectively. The former has been prepared by the action of acetic acid on sodium metavanadate; <sup>6</sup> its *pentahydrate*,  $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , and *decahydrate*,  $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ , are also known,<sup>7</sup> both of which undergo dehydration at about  $200^\circ\text{C}$ .; the residue melts at  $581^\circ\text{C}$ .<sup>8</sup> The compound  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  has been made by the action of caustic soda on excess of vanadium pentoxide.<sup>9</sup> Its *pentahydrate*,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , and *nonahydrate*,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ , are also known.<sup>10</sup> All these sodium salts are red, easily crystallisable substances.

Slight variations in the method of preparation have yielded several further polyvanadates of sodium:  $5\text{Na}_2\text{O} \cdot 8\text{V}_2\text{O}_5 \cdot 39\text{H}_2\text{O}$ ;  $4\text{Na}_2\text{O} \cdot 7\text{V}_2\text{O}_5 \cdot 33\text{H}_2\text{O}$ ; <sup>11</sup>  $3\text{Na}_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 22\text{H}_2\text{O}$  or  $23\text{H}_2\text{O}$ ; <sup>12</sup>  $4\text{Na}_2\text{O} \cdot 7\text{V}_2\text{O}_5 \cdot 35\text{H}_2\text{O}$ ; <sup>13</sup>  $3\text{Na}_2\text{O} \cdot 7\text{V}_2\text{O}_5 \cdot 33\text{H}_2\text{O}$ ;  $2\text{Na}_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 28\text{H}_2\text{O}$ ; <sup>14</sup>  $4\text{Na}_2\text{O} \cdot 10\text{V}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ ; <sup>15</sup>  $2\text{Na}_2\text{O} \cdot 8\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$  or  $17\text{H}_2\text{O}$ .<sup>16</sup>

*Strontium Polyvanadates.*—By the action of strontium chloride on potassium metavanadate solution in the presence of acetic acid, the following compounds have been isolated:  $3\text{SrO} \cdot 4\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ ; <sup>17</sup>  $4\text{SrO} \cdot 7\text{V}_2\text{O}_5 \cdot 30\text{H}_2\text{O}$ ;  $\text{SrO} \cdot 2\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ .<sup>18</sup> The last-mentioned salt has also been obtained from the mother-liquors left after the separation of strontium pervanadate.<sup>19</sup> Using the compound  $\text{K}_2\text{O} \cdot 2\text{V}_2\text{O}_5$  in place of the metavanadate yields the more acid salt,  $2\text{SrO} \cdot 6\text{V}_2\text{O}_5 \cdot 27\text{H}_2\text{O}$ .<sup>20</sup> A polyvanadate containing four molecules of vanadium pentoxide, viz.  $\text{SrO} \cdot 4\text{V}_2\text{O}_5 \cdot 11\text{H}_2\text{O}$ , has also been prepared.<sup>21</sup>

*Thallium Polyvanadate.*—By treating ammonium metavanadate with

<sup>1</sup> Cleve, *Bull. Soc. chim.*, 1885, 43, 162.

<sup>2</sup> Rammelsberg, *Wied. Annalen*, 1883, [ii], 20, 934; Ditte, *Compt. rend.*, 1887, 104, 1061.

<sup>3</sup> Norblad, *loc. cit.*

<sup>4</sup> Düllberg, *Zeitsch. physikal. Chem.*, 1903, 45, 175.

<sup>5</sup> Düllberg, *loc. cit.*; but compare Canneri, *Gazzetta*, 1923, 56, ii, 779.

<sup>6</sup> von Hauer, *loc. cit.*

<sup>7</sup> Ditte, *loc. cit.*

<sup>8</sup> Carnelly, *J. Chem. Soc.*, 1878, 33, 273.

<sup>9</sup> Ditte, *loc. cit.*

<sup>10</sup> Norblad, *loc. cit.*; Prandtl and Lustig, *Zeitsch. anorg. Chem.*, 1907, 53, 393.

<sup>11</sup> Friedheim and Michaelis, *ibid.*, 1893, 5, 441.

<sup>12</sup> Prandtl and Lustig, *loc. cit.*; von Rex, *Dissertation* (Bern, 1901).

<sup>13</sup> Schmitz-Dumont, *ibid.* (Berlin, 1891).

<sup>14</sup> Rothenbach, *ibid.*

<sup>15</sup> Rammelsberg, *loc. cit.*

<sup>16</sup> Baragiola, *Dissertation* (Bern, 1902).

<sup>17</sup> Manasse, *Annalen*, 1887, 240, 43.

<sup>18</sup> von Hauer, *loc. cit.*

<sup>19</sup> Scheuer, *Zeitsch. anorg. Chem.*, 1898, 16, 284.

<sup>20</sup> Manasse, *loc. cit.*; von Hauer, *J. prakt. Chem.*, 1859, 76, 156.

<sup>21</sup> Manasse, *loc. cit.*

thallium sulphate, a red acid salt of composition  $6\text{Ti}_2\text{O}_3 \cdot 7\text{V}_2\text{O}_5$  has been obtained.<sup>1</sup> It melts at  $408^\circ \text{C}$ .<sup>2</sup> A *hexavanadate*,  $\text{Ti}_2\text{O}_3 \cdot 3\text{V}_2\text{O}_5$ , has also been prepared.<sup>3</sup>

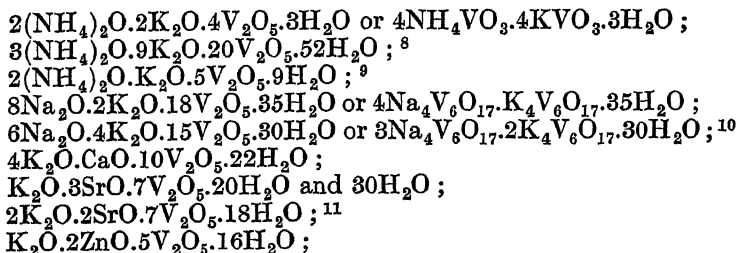
*Thorium Polyvanadate*,  $\text{ThO}_2 \cdot 6\text{V}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ ,<sup>4</sup> is known.

*Ytterbium Polyvanadates*,  $3\text{Yb}_2\text{O}_3 \cdot 5\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and  $\text{Yb}_2\text{O}_3 \cdot 15\text{V}_2\text{O}_5$ , are known.<sup>5</sup>

*Zinc Polyvanadate*,  $2\text{ZnO} \cdot 3\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$ , is obtained as well-defined crystals by the action of zinc sulphate on acid barium vanadate.<sup>6</sup>

**Double Vanadates.**—Vanadium pentoxide exhibits a strong tendency to combine with two or more bases to produce well-crystallised double salts. Their general method of preparation consists in adding a solution of a salt of the required metal to a solution of an alkali vanadate; concentration of the mother-liquor after precipitation of the simple vanadate gives rise to a vanadate which is found to contain both the alkali base and the metallic base. Frequently from the same two bases and vanadic acid a series of such double vanadates can be prepared in which the relative proportions of basic oxides and vanadic acid vary. The decomposition of ammonium metavanadate with acetic acid in the presence of sodium silicate yields glistening red crystals of the composition  $2(\text{NH}_4)_2\text{O} \cdot \text{Na}_2\text{O} \cdot 5\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$ . The molecular proportions in this compound are simple, but a large number of double vanadates have been prepared in which the molecular proportions are by no means simple. Thus, by the action of two molecular proportions of ammonium chloride on a boiling, concentrated solution of one molecular proportion of sodium metavanadate, yellowish-red prisms of composition  $4[(\text{NH}_4)_{1\frac{2}{3}} \cdot \text{Na}_{1\frac{1}{3}}] \text{O} \cdot 7\text{V}_2\text{O}_5 \cdot 17\frac{1}{2}\text{H}_2\text{O}$  are obtained.<sup>7</sup> It is a matter of some doubt whether these complex double salts should be looked upon as definite compounds, each having independent existence, or whether each series is not more correctly regarded as composed of isomorphous mixtures of variable composition. The problem is similar to that of the constitution of the salts of the heteropoly-acids, in which vanadium pentoxide is combined with other acid anhydrides.

Other double vanadates which have been prepared are :



<sup>1</sup> Carnelly, *J. Chem. Soc.*, 1873, 26, 323.

<sup>2</sup> Carnelly, *ibid.*, 1878, 33, 273.

<sup>3</sup> Cuttica, Tarchi, and Alinari, *Gazzetta*, 1923, 53, 189.

<sup>4</sup> Cleve, *Jahresber.*, 1874, 261.

<sup>5</sup> Cleve, *Zeitsch. anorg. Chem.*, 1902, 32, 129.

<sup>6</sup> Ephraim and Beck, *loc. cit.*

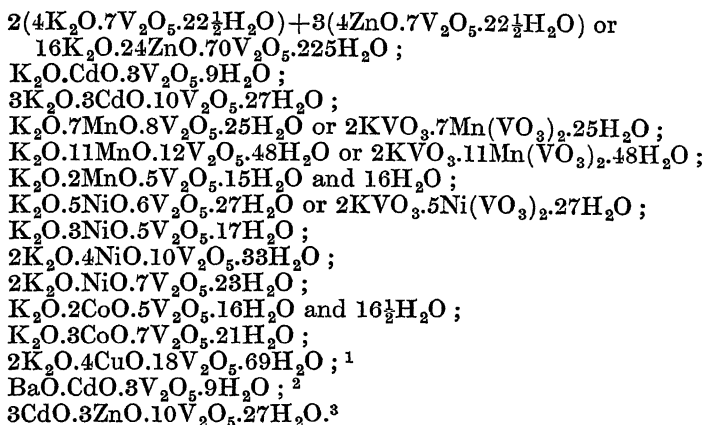
<sup>7</sup> Baragiola, *Dissertation* (Bern, 1902).

<sup>8</sup> Baragiola, *loc. cit.*

<sup>9</sup> Ditte, *Compt. rend.*, 1887, 104, 1844.

<sup>10</sup> Friedheim and Michaelis, *Zeitsch. anorg. Chem.*, 1894, 5, 441.

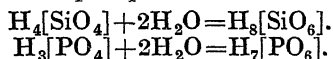
<sup>11</sup> Manasse, *Annalen*, 1887, 240, 46.



Many of the naturally occurring ores of vanadium have also the composition of double vanadates (see table on p. 11).

#### HETEROPOLY-ACIDS CONTAINING VANADIUM.

**General.**—Vanadium possesses the property of entering into the composition of a large number of compounds which contain it as a constituent of a complex anion. Light has been thrown on the nature and constitution of these compounds by investigations into other heteropoly-acids, which are now found to be most satisfactorily formulated by the application of a modification of Werner's co-ordination theory first suggested by Miolati,<sup>4</sup> and extended by Rosenheim and his co-workers.<sup>5</sup> According to this theory the heteropoly-acids are produced by hydration of acids having the general formula  $H_{8-n}[R^nO_4]$ , where  $n$  represents the valency of the metal R. Thus, for example, in the cases of silicon and phosphorus the following schemes obtain :—



Or, generally,



It will be observed that the basicity of each of these acids is determined by deducting the valency of the central atom in the complex anion from 12. The greatest number of oxygen atoms or other divalent radicals that can be co-ordinated with the central atom is 6; and this number usually holds good in a true compound, but not always. For example, the co-ordination number of the acid  $H[P^{(VO_3)_2}O_2]$  is only 4.

Substitution of the co-ordinated oxygen atoms by divalent radicals yields the various heteropoly-acids. The *vanado-phosphates*, for instance, are derivatives of the hypothetical phosphato-acid  $H_7[PO_6]$ ,

<sup>1</sup> Radau, *Chem. Zentr.*, 1888, 1378; *Annalen*, 1889, 251, 114. Other double salts of potassium and manganese have been prepared.

<sup>2</sup> Weinland and Feige, *Ber.*, 1903, 36, 260.

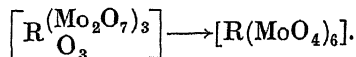
<sup>3</sup> Radau, *loc. cit.*

<sup>4</sup> Miolati, *J. prakt. Chem.*, 1908, 77, 439.

<sup>5</sup> See Rosenheim and Jänicke (*Zeitsch. anorg. Chem.*, 1917, 100, 304) for a comprehensive review of the subject.

in which one or more of the oxygen atoms have been replaced by divalent  $(V_2O_6)''$  radicals. The compound to which the formula  $7(NH_4)_2O.P_2O_5.12V_2O_5.26H_2O$  has been ascribed from its analytical data thus becomes  $(NH_4)_7[P(V_2O_6)_6].13H_2O$ . If some of the oxygen atoms in the complex anion are replaced by  $(V_2O_6)''$  radicals and others by  $(Mo_2O_7)''$  radicals, the *molybdovanado-phosphates* are produced, e.g.  $(NH_4)_7\left[P\left(\frac{V_2O_6}{(Mo_2O_7)_3}\right)_3\right].16H_2O$  and  $K_5H_2\left[P\left(\frac{V_2O_6}{(Mo_2O_7)_5}\right)_5\right].51H_2O$ . Similarly, substitution by both  $(V_2O_6)''$  and  $(W_2O_7)''$  radicals gives rise to the *tungstovanado-phosphates*. The *heteropolyvanado-arsenates* are derived from the hypothetical arseno-acid  $H_7[AsO_6]$ . It has recently been shown that the arsenic in these compounds may undergo partial substitution by phosphorus to give rise to series of mixed crystals which are called *heteropolyvanado-arsenophosphates* or *heteropolyvanado-phosphoarsenates*.<sup>1</sup> The *heteropolyvanado-silicates* are derived from the acid  $H_8[SiO_6]$ .

The existence of such associated radicals as  $(V_2O_6)''$ ,  $(Mo_2O_7)''$ , and  $(W_2O_7)''$  has been assumed in order to explain the very frequent occurrence of twelve  $(\frac{1}{2}V_2O_5)$ ,  $MoO_3$ , or  $WO_3$  radicals in the complex anions of compounds the co-ordination number of which is six. A greater number than twelve has never been observed. As a rule only four of the oxygen atoms can undergo substitution by these associated radicals; thereafter an isomeric change appears to take place, thus :



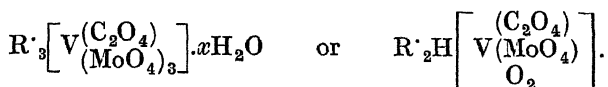
Compounds are said to be *saturated* when all the oxygen atoms of the parent anion are replaced by metallic acid anions; *unsaturated* compounds contain some replaceable oxygen.

The decision as to which element forms the central atom of the complex anion depends on the fact that in any particular series of compounds the atomic proportions of the metals in the place of the co-ordinated oxygen will show very considerable variation when calculated for one atomic weight of the element which constitutes the central atom. Among the *molybdo-vanadophosphates* many are known which contain varying amounts of molybdenum and vanadium in combination with one gram-atom of phosphorus. Hydrogen also provides the nuclear atoms in some series, which are best viewed as derivatives of a hypothetical co-ordinated hexa-aquo-acid,  $H_{10}[H_2O_6]$ .<sup>2</sup> The *vanado-tungstates* (or *tungsto-vanadates*) are, for instance, represented by the general formula  $H_{10}\left[H_2\left(\frac{V_2O_6}{(W_2O_7)_{6-x}}\right)_x\right]$ . Compounds of this type contain water of constitution.

It should be noted that vanadium does not as a rule form the central atom of the complex anion in the heteropoly-compounds. The *oxalo-vanadates*, however, most probably contain the anion  $\left[V\left(\frac{C_2O_4}{O_2}\right)_2\right]'''$ , which is obtained by substituting two oxygen atoms in the anion of orthovanadic acid, i.e. the  $[VO_4]'''$  ion by two  $(C_2O_4)''$  groups. Substitution by  $(MoO_4)''$  groups gives rise to the *oxalo-molybdovanadates* of the general formula :

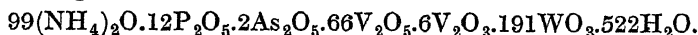
<sup>1</sup> Canneri, *Gazzetta*, 1926, 56, 871.

<sup>2</sup> Copaux, *Ann. Chim. Phys.*, 1906, 7, 118; 1909, 17, 217; 1912, 26, 22.



*Uranyl-vanadates*, which are probably derived from *uranyl-vanadic acid*,  $H \left[ V \begin{matrix} UO_3 \\ O_3 \end{matrix} \right]$ , have also recently been prepared.

The constitution of many of the heteropoly-acids and of their salts may thus be explained, although direct proof of the correctness of some of these formulæ is lacking. Some of the heteropoly-compounds of vanadium are, however, very complex, and cannot be represented by application of the foregoing scheme. To take an extreme instance, Rogers<sup>1</sup> prepared a black, crystalline compound to which he ascribed the following formula:—



The composition of these substances is necessarily a matter of doubt, because of the difficulty of conducting exact analyses of compounds of very high molecular weight; a small difference in the analytical data makes a large difference in the number of molecules. Further, the heteropoly-compounds are characterised by the ease with which they undergo hydrolysis; even the process of recrystallisation frequently produces a different complex.

In many cases the salts of any one series which have been analysed are not true compounds, but consist of isomorphous mixtures of simple chemical compounds; the composition of the mixtures varies with the composition, temperature, and acidity of the media from which they separate. This has been shown to apply to the *molybdo-vanadates* (or *vanado-molybdates*),<sup>2</sup> *molybdo-vanadophosphates*,<sup>3</sup> *vanado-selenous acid* and the *vanado-selenites*,<sup>4</sup> as well as to telluric acid and its salts.<sup>5</sup> Recently, Canneri<sup>6</sup> has succeeded in preparing a large number of mixed crystals of salts, and in some cases of the free acids, which belong to different series; for example, mixed crystals of *tungsto-vanadophosphates* and *tungsto-vanadoarsenates*, of *tungsto-vanadophosphates* and *molybdo-vanadophosphates*, of *tungsto-vanadoarsenates* and *molybdo-vanadoarsenates*; and, finally, mixed crystals of members of all the four series mentioned have been obtained. The mixed crystals have the same crystalline habit as that of their components, and complete isomorphism exists between any two series which mix in all proportions to form continuous series of mixed crystals containing four or five different oxygenated acid radicals. The crystallographic data of a number of ammonium *tungsto-vanadoarsenates* have also recently been independently determined, and it has been shown that the crystal form is unaffected when the arsenic is substituted by phosphorus, or when the  $(W_2O_7)''$  radicals are partially substituted by  $(Mo_2O_7)''$ .<sup>7</sup>

It appears probable that adsorption of uncombined radicals by molecules which contain a large number of these radicals, but which

<sup>1</sup> Rogers, *J. Amer. Chem. Soc.*, 1903, 25, 298.

<sup>2</sup> See *infra*.

<sup>3</sup> Cain and Hostetter, *J. Amer. Chem. Soc.*, 1921, 43, 2552; Wherry, *J. Franklin Inst.*, 1910, 169, 486.

<sup>4</sup> Rosenheim and Krause, *Zeitsch. anorg. Chem.*, 1921, 118, 177.

<sup>5</sup> Rosenheim and Jander, *Kolloid. Zeitsch.*, 1918, 22, 23.

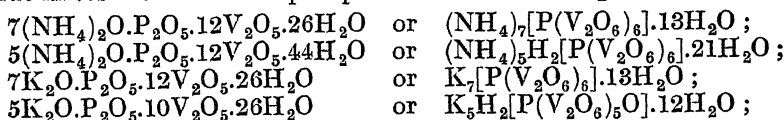
<sup>6</sup> Canneri, *Gazzetta*, 1926, 56, 871.

<sup>7</sup> Rodolico, *Atti R. Accad. Lincei*, 1926, [vi], 4, 471.

are not saturated, takes place, and that the only true chemical individuals are the maximum co-ordinated compounds. It has been shown that vanadium pentoxide forms a colloidal solution, in which state it is readily adsorbed.<sup>1</sup>

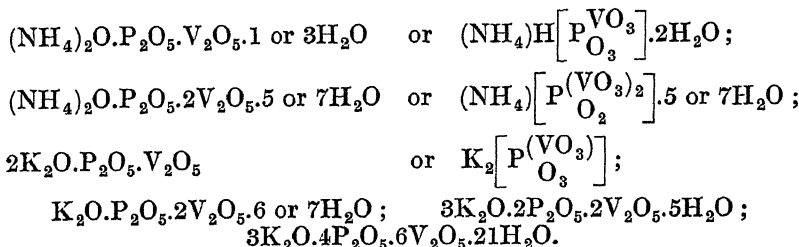
**Vanado-phosphates.**—Alkali vanado-phosphates are numerous, and contain from one to twelve molecules of vanadium pentoxide in combination with one molecule of phosphorus pentoxide. Those with high vanadium pentoxide content are red, crystalline substances, and are called *purpureo*-compounds; those with low vanadium pentoxide content form yellow crystals, and are styled *luteo*-compounds.<sup>2</sup>

**Purpureo Series.**—These are prepared by dissolving vanadium pentoxide in solutions of alkali phosphates. The following are known:—<sup>3</sup>

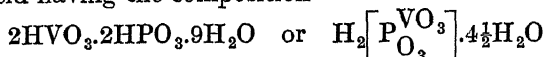


together with caesium and rubidium compounds analogous to the last member of the above.

**Luteo Series.**—These are prepared by adding excess of phosphoric acid to solutions of alkali vanadates. The following are known:—<sup>4</sup>



A free acid having the composition



has been obtained in golden-yellow leaves by the action of vanadium pentoxide on syrupy phosphoric acid.

**Molybdo-vanadophosphates.**—These are derived from the hypothetical acid  $\text{H}_7[\text{PO}_6]$ , in which the co-ordinated oxygen atoms have been partly replaced by one or more  $(\text{V}_2\text{O}_6)''$  radicals and partly by  $(\text{Mo}_2\text{O}_7)''$  radicals. The relative proportions of these radicals present may undergo variation with constant phosphorus content, so that a phosphorus atom must form the central atom of the complex anion. As the phosphorus content also varies, it is obvious that a very large number of acids becomes possible. These are usually *heptabasic*, *hexabasic*, or *pentabasic*, and the ammonium, potassium, and barium salts, as well as the barium-ammonium and barium-potassium double salts of many of them are known. Their general method of preparation consists in acidifying solutions containing molybdates, vanadates, and

<sup>1</sup> Gessner, *Kolloidchem. Beihefte*, 1924, 19, 213.

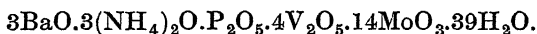
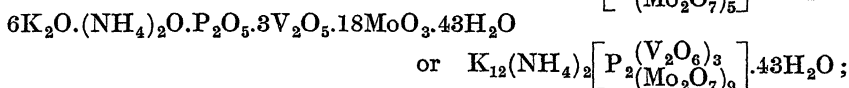
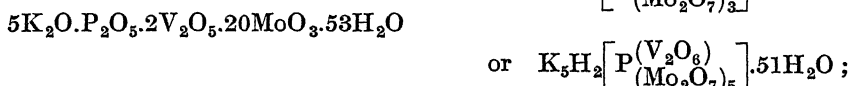
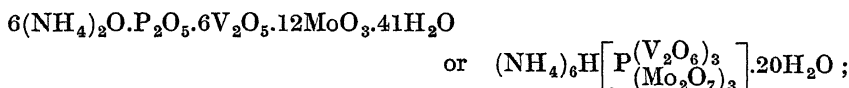
<sup>2</sup> Friedheim and Szamatolski, *Ber.*, 1890, 23, 1530, 2600; Rosenheim and Pieck, *Zeitsch. anorg. Chem.*, 1916, 98, 225; Rosenheim and Yang, *ibid.*, 1923, 129, 181.

<sup>3</sup> See also Friedheim and Michaelis, *ibid.*, 1894, 5, 446.

<sup>4</sup> See also Friedheim and Michaelis, *loc. cit.*; Gibbs, *Amer. Chem. J.*, 1885, 7, 209; Ditte, *Compt. rend.*, 1886, 102, 1019.

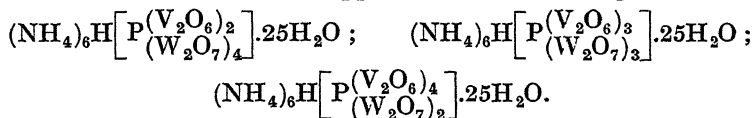


phosphates. They form isomorphous, beautiful orange-red to brown, octahedral crystals, which undergo hydrolysis very readily, so that it is frequently impossible to state the experimental directions whereby a salt of definite composition can be produced. A few examples only of these compounds are here set out. For the exhaustive list of those hitherto prepared and analysed, the references cited should be consulted.<sup>1</sup>



Many of the compounds in this class cannot be represented by co-ordinative formulæ.

**Tungsto-vanadophosphates.**—These are analogous to the molybdo-vanadophosphates, only differing from them in that the place of the  $(\text{Mo}_2\text{O}_7)''$  radical in the complex anion is now taken by the  $(\text{W}_2\text{O}_7)''$  radical. Thus, an *ammonium tungsto-vanadophosphate* which, from its analytical data, has the formula  $6(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 4\text{V}_2\text{O}_5 \cdot 16\text{WO}_3 \cdot 21\text{H}_2\text{O}$ , is written  $(\text{NH}_4)_6\text{H} \left[ \text{P} \left( \frac{\text{V}_2\text{O}_6}{\text{W}_2\text{O}_7} \right)_4 \right] \cdot 20\text{H}_2\text{O}$ , and a barium salt which has the composition  $18\text{BaO} \cdot 3\text{P}_2\text{O}_5 \cdot 2\text{V}_2\text{O}_5 \cdot 60\text{WO}_3 \cdot 144\text{H}_2\text{O}$  becomes  $9\text{BaH}_3 \left[ \text{P}_3 \left( \frac{\text{V}_2\text{O}_6}{\text{W}_2\text{O}_7} \right)_{15} \right] \cdot 141\text{H}_2\text{O}$ . A number of ammonium, potassium and barium salts have been prepared. The ammonium salts in some cases approach to the following series:—<sup>2</sup>



By the action of dilute sulphuric acid on the barium salts several free *tungsto-vanadophosphoric acids* have been isolated.<sup>3</sup>

**Vanado-arsenates.**—The salts of this class which have hitherto been prepared are all of low vanadium pentoxide content compared with the amount of arsenic pentoxide present. They correspond, therefore, to the *luteo* vanado-phosphates. Three series are known. The

first has the general formula  $\text{R}'' \cdot \text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  or  $\text{R}'' \cdot \left[ \text{As} \frac{\text{VO}_3}{\text{O}_3} \right] \cdot x\text{H}_2\text{O}$ ,

where  $\text{R}''$  may be Mg, Zn, Cu, or Co. They form yellow crystals which are obtained by the addition of arsenic pentoxide to solutions

<sup>1</sup> Gmelin-Kraut, *Handbuch der anorganischen Chemie* (Heidelberg), 1908, 3, ii, 205–213, 1095–1104.

<sup>2</sup> Gmelin-Kraut, *ibid.*, pp. 187–188; Rodolico, *Atti R. Accad. Lincei*, 1926, [vi], 4, 471; Canneri, *Gazzetta*, 1926, 56, 642.

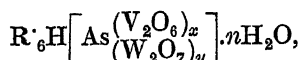
<sup>3</sup> Canneri, *ibid.*, 1926, 56, 871.

of the respective vanadates, or by the action of the carbonate of the metal on the free vanado-phosphoric acid (see below). Of the second series only the *ammonium* and *potassium* salts are known, viz.  $(\text{NH}_4)_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  or  $(\text{NH}_4)[\text{As}(\text{VO}_3)_2] \cdot 5\text{H}_2\text{O}$ , and  $\text{K}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  or  $\text{K}[\text{As}(\text{VO}_3)_2] \cdot 5\text{H}_2\text{O}$ . These also give rise to yellow crystals. The third series has the general formula  $2\text{R} \cdot \text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 3\text{As}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ , where  $\text{R} \cdot 2$  may be  $(\text{NH}_4)_2$ , Ca, Sr, Mg, Zn, Mn, Co, Ni. They result from the action of arsenic pentoxide on solutions of vanadates, and form red crystals which, however, are unstable, and are readily converted by water into compounds of the first series.<sup>1</sup>

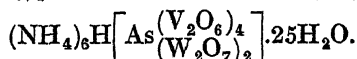
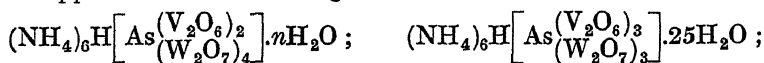
The free acid of the first series has been obtained in yellow plates by boiling vanadium pentoxide with a solution of arsenic acid. Its composition is  $\text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$  or  $\text{H}_2[\text{As}(\text{VO}_3)] \cdot 4\text{H}_2\text{O}$ . Recrystallisation of this hydrate from concentrated nitric acid gives a *dihydrate*,  $\text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , which can be looked upon as the acid  $\text{H}_2[\text{As}(\text{VO}_3)]$ . The *anhydride*,  $\text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5$ , is obtained by heating the dihydrate to  $440^\circ \text{C}$ .

**Molybdo-vanadoarsenates.**—A number of compounds have been described which are analogous to the molybdo-vanadophosphates described above, and which contain arsenic for the nuclear atom of the complex anion. In many cases these compounds approximate to the general formula  $\text{R}'_6\text{H}[\text{As}(\frac{\text{V}_2\text{O}_6}{\text{Mo}_2\text{O}_7})_x] \cdot n\text{H}_2\text{O}$ , where  $x+y=6$ ;  $x$  and  $y$  are not necessarily whole numbers, because of the tendency shown by these heteropoly-acid salts to form isomorphous mixtures of simple compounds. *Ammonium*, *barium* and *thallium* salts have been prepared.<sup>2</sup>

**Tungsto-vanadoarsenates.**—These are comparable to the molybdo-vanadoarsenates, and can be represented generally,



where  $x+y=6$ , although  $x$  and  $y$  are not necessarily whole numbers. Canneri found a definite relation to exist between the composition of the salt obtained and that of the solution from which it separates, from which it is inferred that a condition of equilibrium exists between various salts in solution or between their ions; this equilibrium for fixed concentrations is remarkably sensitive to changes in temperature or acidity. Among other salts three series of ammonium salts have been obtained which approach to the following formulæ:—



<sup>1</sup> Gibbs, *Amer. Chem. J.*, 1886, 7, 209; Friedheim, *Ber.*, 1890, 23, 1530, 2600; *Zeitsch. anorg. Chem.*, 1892, 2, 319; Schmitz-Dumont, *Dissertation* (Berlin, 1891); Fernandez, *Ber.*, 1884, 17, 1632; Ditte, *Compt. rend.*, 1886, 102, 757, 1019.

<sup>2</sup> Canneri, *Gazzetta*, 1923, 53, 773; 1926, 56, 871.

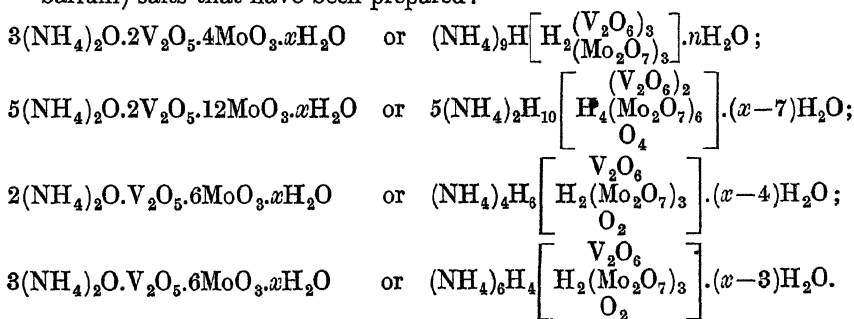
*Barium* and *thallium* salts have also been described, and some of the free acids have been isolated.<sup>1</sup>

*Tungsto-vanadoarsenophosphates*.—Several ammonium salts have been prepared, which are most probably isomorphous mixtures of arsenates and phosphates.<sup>2</sup>

*Vanado-tungstomolybdoarsenophosphates* have been described; these are also isomorphous mixtures of simple compounds.<sup>3</sup>

**Molybdo-vanadates** or **Vanado-molybdates**.—These are obtained in red crystals, rich in vanadium, or yellow powders, poor in vanadium, by dissolving molybdic anhydride,  $\text{MoO}_3$ , in solutions of alkali meta-vanadates, or by acidifying mixed solutions of molybdates and vanadates. A large number of salts have been prepared, which vary considerably in their analytical data. Repetition of the same process of preparation often gives crystals of different composition, so that a definite compound cannot easily be prepared. The salts are usually unstable, and undergo change even on being recrystallised. The same solution may give rise to different salts according to the temperature. Thus, one portion of a solution divided into two parts gave crystals of  $2(\text{NH}_4)_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 5\text{MoO}_3 \cdot 10\text{H}_2\text{O}$  at  $10^\circ \text{C}$ ., while at  $30^\circ \text{C}$ . the other portion gave crystals of  $4(\text{NH}_4)_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 5\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ . From a study of the systems  $\text{NH}_4\text{VO}_3$ ,  $\text{MoO}_3$ ;  $\text{KVO}_3$ ,  $\text{MoO}_3$ ;  $\text{NaVO}_3$ ,  $\text{MoO}_3$ , it has been concluded that solutions of alkali molybdo-vanadates of fixed concentration and at a definite temperature contain definite compounds which are in equilibrium with isomorphous mixtures of polyvanadates and polymolybdates. The yellow powders poor in vanadium are presumed to be definite compounds because they resist fractionation, while the red crystals consist of isomorphous mixtures.<sup>4</sup>

Comparison with other heteropoly-acids strongly suggests that the molybdo-vanadates do not contain either vanadium or molybdenum as the central atom of the complex anion. They are therefore written as derivatives of the hypothetical hexa-aquo-acid,  $\text{H}_{10}[\text{H}_2\text{O}_6]$ , in which the oxygen atoms in the anion have undergone complete or partial replacement by  $(\text{V}_2\text{O}_6)''$  radicals and by  $(\text{Mo}_2\text{O}_7)''$  or  $(\text{MoO}_4)''$  radicals. The following examples are typical of series of alkali (and in some cases barium) salts that have been prepared:—<sup>5</sup>



<sup>1</sup> Gibbs, *loc. cit.*; Rogers, *J. Amer. Chem. Soc.*, 1903, 25, 298; Canneri, *Gazzetta*, 1923, 53, 773, 779; 1925, 55, 883; 1926, 56, 871; Rodolico, *loc. cit.*

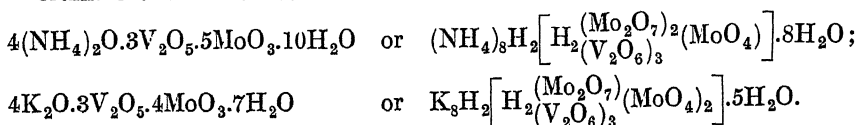
<sup>2</sup> Rogers, *loc. cit.*; Rodolico, *loc. cit.*; Canneri, *loc. cit.*

<sup>3</sup> Rogers, *J. Amer. Chem. Soc.*, 1903, 25, 312; Rodolico, *loc. cit.*; Canneri, *loc. cit.*

<sup>4</sup> Canneri, *Gazzetta*, 1923, 53, 779; 1925, 55, 390.

<sup>5</sup> Gmelin-Kraut, *Handbuch der anorganischen Chemie* (Heidelberg), 1908, 3, ii, 191-204, 1092-1094; Abegg and Auerbach, *ibid.* (Leipzig), 1921, 4, i (second half), 1052; Canneri, *loc. cit.*

The following are also known, as well as many others for which coordinative formulæ cannot be written :—

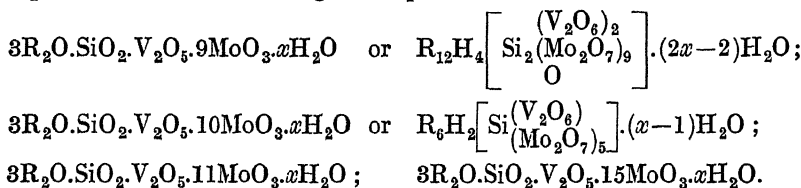


**Tungsto-vanadates** or **Vanado-tungstates**.—Three well-defined series of complex salts containing tungsten and vanadium have been obtained, which are comparable to the molybdo-vanadates in that they probably do not contain either vanadium or tungsten as the nuclear atom of the complex anion. They are obtained (1) by saturation of a solution of a paratungstate with vanadium pentoxide, (2) by the action of acetic acid on solutions of mixed alkali tungstates and vanadates, or (3) by the addition of a paratungstate to a metavanadate. The salts are characteristically coloured and all contain water of constitution. The dichromate-coloured series has the composition  $5\text{R} \cdot 2\text{O}$ .

$3\text{V}_2\text{O}_5 \cdot 6\text{WO}_3 \cdot x\text{H}_2\text{O}$  or  $\text{R} \cdot 5\text{H}_2 \left[ \text{H}_2 \left( \text{VO}_3 \right)_3 \right] \cdot (x-4)\text{H}_2\text{O}$ , where R· may be  $\text{NH}_4$ , K, or Na. The yellowish-red salts have the composition  $2\text{R} \cdot 2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 4\text{WO}_3 \cdot x\text{H}_2\text{O}$ , and salts of the *alkali metals*, *alkaline earth metals*, and *silver* have been prepared. The salts of both these series have properties similar to the paratungstates. The salts of the third series are deep red in colour, have the composition  $5\text{R} \cdot 2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 14\text{WO}_3 \cdot x\text{H}_2\text{O}$ , and resemble the metatungstates. The *ammonium*, *potassium*, *caesium*, and *barium* salts have been prepared.<sup>1</sup>

**Uranyl-vanadates**.—By adding uranic anhydride to fused potassium or sodium metavanadate, microscopic, rectangular, fluorescent plates of the compositions  $\text{K}(\text{UO}_2)\text{VO}_4$  and  $\text{Na}(\text{UO}_2)\text{VO}_4$  are obtained. These are probably derivatives of a relatively stable *uranyl-vanadic acid*,  $\text{H} \left[ \text{V} \left( \text{UO}_3 \right) \right]$ , and are analogous to the uranyl-phosphates which occur naturally.<sup>2</sup>

**Molybdo-vanadosilicates**.—The simple vanado-silicates do not appear to be stable, but a number of molybdo-vanadosilicates have been obtained either by acidifying solutions which contain molybdates, vanadates and silicates, or by addition of vanadium pentoxide to the molybdo-silicates. They form heavy, yellowish-red to brownish-red crystals, which are very easily hydrolysed and are, therefore, not always reproducible. The following isomorphous series has been recognised :—



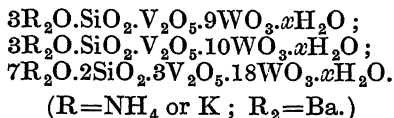
(R =  $\text{NH}_4$  or K;  $\text{R}_2 = \text{Ba}$ .)

<sup>1</sup> Gmelin-Kraut, *loc. cit.*, pp. 179–188; Prandtl and Humbert, *Zeitsch. anorg. Chem.*, 1911, 73, 223; Prandtl and Hecht, *ibid.*, 1915, 92, 198; Sweeney, *J. Amer. Chem. Soc.*, 1916, 38, 2377; Rosenheim and Pieck, *Zeitsch. anorg. Chem.*, 1916, 98, 223.

<sup>2</sup> Canneri and Pestelli, *Gazzetta*, 1924, 54, 641; compare *Carnotite* (see p. 10).

*Potassium-ammonium double salts* have also been prepared. The first two series can be looked upon as derivatives of the co-ordinated silico-acid,  $H_8[Si^{IV}O_6]$ ; the last two series cannot be formulated in accordance with Werner's theory.<sup>1</sup>

**Tungsto-vanadosilicates.**—These complexes are analogous to the molybdo-vanadosilicates, and are prepared as yellowish-red to red crystals by the action of vanadates on the silico-tungstates, or by the action of hydrofluosilicic acid on the tungsto-vanadates. The following series has been recognised :—



Double salts have also been isolated.<sup>2</sup>

Several of the natural ores of vanadium consist of complex silicates, e.g. *ardennite* and *roscoelite*.

**Vanado-selenites.**—Three series of alkali vanado-selenites are known, the members of which are all prepared by treating solutions of alkali vanadates with selenous acid in varying proportions, or by acidifying mixed solutions of vanadates and selenites with acetic acid. The members of the first series are yellow, and have the composition  $R'_2O \cdot V_2O_5 \cdot 2SeO_2 \cdot xH_2O$ . The second series of salts is orange, and includes types of varying composition:  $R'_2O \cdot 3V_2O_5 \cdot 4SeO_2 \cdot xH_2O$ ,  $R'_2O \cdot 6V_2O_5 \cdot 8SeO_2 \cdot xH_2O$ , as well as other types which contain greater proportions of  $SeO_2$ . The salts belonging to the third series are red, and have the composition  $4R'_2O \cdot 6V_2O_5 \cdot 5SeO_2 \cdot xH_2O$ . All these vanado-selenites lose selenous oxide on being boiled with water. It has been shown that when the same amount of ammonium metavanadate is boiled with selenous acid solutions of gradually increasing concentration, the yellow crystals obtained contain gradually increasing proportions of selenous oxide. It appears, therefore, that the large number of vanado-selenites known, and their complexity, are due to their semi-colloidal character, in consequence of which they adsorb constituents from solutions.<sup>3</sup> As might be expected, only a few of them can be represented by co-ordinative formulæ. According to Prandtl, the second and third series above are derivatives of *hexavanadic acid*,  $H_4V_6O_{17}$ .<sup>4</sup>

By the action of vanadium pentoxide on selenous acid solutions, or by reduction of a solution of vanadium pentoxide in selenic acid, red crystals of a free vanado-selenous acid have been obtained, the composition of which is  $3V_2O_5 \cdot 4SeO_2 \cdot 4H_2O \cdot x aq$ . It contains four molecules of water of constitution, and, according to Prandtl, should be formulated  $H_4V_6O_{17} \cdot 4H_2SeO_3 \cdot (x-2) aq$ .

**Vanado-tellurites.**—These compounds are of interest in that they are the only heteropoly-acid compounds containing tetravalent tellurium. They are prepared by mixing hydrochloric acid solutions of tellurium dioxide with solutions of vanadium pentoxide in caustic soda and then neutralising with more hydrochloric acid, or by mixing strongly alkaline

<sup>1</sup> Friedheim and Castendyck, *Ber.*, 1900, 33, 1612.

<sup>2</sup> Friedheim and Henderson, *ibid.*, 1902, 35, 3243.

<sup>3</sup> Rosenheim and Krause, *Zeitsch. anorg. Chem.*, 1921, 118, 177.

<sup>4</sup> Prandtl and Lustig, *Ber.*, 1905, 38, 1307; *Zeitsch. anorg. Chem.*, 1907, 53, 393; 1911, 73, 223; compare Canneri, *Gazzetta*, 1923, 53, 779; Rosenheim, *Zeitsch. anorg. Chem.*, 1915, 93, 273.

solutions of tellurium dioxide (in excess) and vanadium pentoxide. The former method gives rise to yellow powders which readily hydrolyse and become colloidal with water. Their composition is  $\text{Na}_2\text{O} \cdot n\text{TeO}_2 \cdot 2\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ , where  $n=5, 6$  or  $10$ , according to the composition of the precipitating medium. The latter method is remarkable because all other heteropoly-acid salts are prepared either in acid or neutral solution; it gives rise to white needles, the composition of which again varies with the relative proportions of oxides used. The products lose some of their tellurium dioxide content on being recrystallised, and are probably not true compounds.<sup>1</sup>

No vanado-tellurates have been prepared, although molybdo-, tungsto-, phospho-, and other heteropoly-tellurates are known.

**Vanado-iodates.**—When vanadium pentoxide is dissolved in hot solutions of iodic acid,  $\text{HIO}_3$ , orange-yellow crystals of a sparingly soluble substance having the composition  $\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  are obtained. The four molecules of water are a factor in the constitution of the acid, since they cannot be removed without decomposition taking place. Several other similarly constituted compounds have been prepared,<sup>2</sup> viz.  $\text{V}_2\text{O}_5 \cdot 2\text{I}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ ;  $\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ ;  $2\text{V}_2\text{O}_5 \cdot 3\text{I}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$ . These all undergo hydrolysis with precipitation of vanadium pentoxide on being boiled with water. By the action of ammonium hydrogen iodate,  $\text{NH}_4\text{H}(\text{IO}_3)_2$ , and potassium hydrogen iodate,  $\text{KH}(\text{IO}_3)_2$ , on the acid  $\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , salts have been prepared which have the following compositions:  $(\text{NH}_4)_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{I}_2\text{O}_5$  and  $\text{K}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{I}_2\text{O}_5$ . The vanado-iodic acids are probably derivatives of "ortho-iodic acid,"  $\text{I}(\text{OH})_5$ . The compound  $\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , therefore, has the following probable

constitution<sup>3</sup>:  $\text{I} \begin{cases} \text{VO}_3 \\ (\text{OH})_4 \end{cases}$ .

**Vanado-periodates.**—Vanadium pentoxide dissolves in boiling solutions of the alkali periodates to produce yellow or red, crystalline vanado-periodates, the compositions of which approximate to the following:  $5\text{Na}_2\text{O} \cdot 0.5\text{V}_2\text{O}_5 \cdot 2\text{I}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  and  $5\text{K}_2\text{O} \cdot 0.5\text{V}_2\text{O}_5 \cdot 2\text{I}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ . By altering the relative acidity of the solution, various other complexes have been obtained,<sup>4</sup> e.g.  $5\text{Na}_2\text{O} \cdot 0.7\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_7 \cdot 27\text{H}_2\text{O}$ ;  $6\text{Na}_2\text{O} \cdot 0.9\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_7 \cdot 48\text{H}_2\text{O}$ ;  $3\text{Na}_2\text{O} \cdot 0.2\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$ ;  $3\text{K}_2\text{O} \cdot 0.2\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_7 \cdot 17\frac{1}{2}\text{H}_2\text{O}$ ; and  $3(\text{NH}_4)_2\text{O} \cdot 0.2\text{V}_2\text{O}_5 \cdot \text{I}_2\text{O}_7 \cdot 6\frac{1}{2}\text{H}_2\text{O}$ . The water in the last three compounds has been shown not to be water of constitution, and the salts can be regarded as tribasic vanado-periodates of the general formula  $\text{R}_3 \left[ \text{I} \begin{smallmatrix} \text{VO}_3 \\ \text{O}_4 \end{smallmatrix} \right]_2 \cdot x\text{H}_2\text{O}$ ; two oxygen atoms in the periodate ion  $[\text{IO}_6]^\vee$  have been replaced by  $(\text{VO}_3)'$  radicals.<sup>5</sup>

**Oxalo-vanadates.**—These compounds are obtained in large yellow prisms (side by side with red polyvanadates) by the action of vanadium pentoxide on boiling solutions of alkali oxalates, or by the action of normal alkali vanadates on acid oxalates. They have the general formula  $3\text{R}'_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 4\text{C}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  or  $\text{R}_3 \left[ \text{V} \begin{smallmatrix} (\text{C}_2\text{O}_4) \\ \text{O}_2 \end{smallmatrix} \right]_2 \cdot n\text{H}_2\text{O}$ , i.e.

<sup>1</sup> Jena, *Dissertation* (Giessen, 1907); Abegg and Auerbach, *Handbuch der anorganischen Chemie* (Leipzig), 1921, 4, i (second half), 1012.

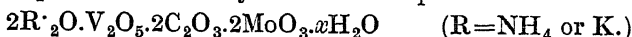
<sup>2</sup> Ditto, *Compt. rend.*, 1886, 102, 756, 1019, 1115.

<sup>3</sup> Rosenheim and Yang, *Zeitsch. anorg. Chem.*, 1923, 129, 181.

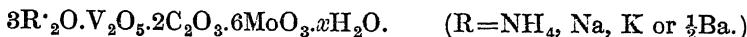
<sup>4</sup> Butzback, *Dissertation* (Bern, 1905).

<sup>5</sup> Rosenheim and Yang, *loc. cit.*

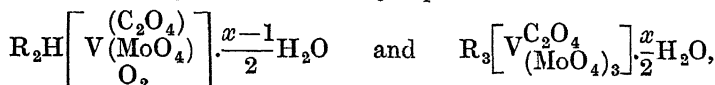
they can be looked upon as derivatives of orthovanadic acid,  $H_3VO_4$ . The *ammonium*, *sodium*, *potassium* and *barium salts* have been prepared.<sup>1</sup> On being boiled with vanadium pentoxide these salts give rise to the *oxalo-molybdovanadates*, which also form bright yellow crystals.<sup>2</sup> Those which separate most easily have the compositions:



and



These are most probably derivatives of the oxalo-vanadates in which co-ordinative oxygen atoms have undergone substitution by  $(MoO_4)''$  groups. Hence they are alternatively represented as



respectively.

**Vanado-stannates** are referred to on p. 67.

All the foregoing heteropoly-compounds contain vanadium pentoxide. A large number of other compounds have been prepared which, from their analytical data, appear to contain one of the lower oxides in varying proportions together with the pentoxide, e.g. *vanadous-vanadophosphates*,<sup>3</sup> *vanadous-vanadoarsenates*,<sup>4</sup> *vanadous-vanadomolybdates*,<sup>5</sup> *vanadous-vanadotungstates*.<sup>6</sup> The constitutions of these have not been established.

#### PERVANADIC ACID AND THE PERVANADATES.

**Pervanadic Acid** has not been definitely isolated in the solid state. When vanadium pentoxide is dissolved in hydrogen peroxide solution which also contains sulphuric acid, a red solution is formed from which on concentration *in vacuo* greyish-yellow crystals, which are assumed to have the composition  $HVO_4$ , pervanadic acid, are deposited. They give the reactions of a per-acid, but are difficult to analyse in consequence of their unstable character.<sup>7</sup> The preparation of the crystals is best carried out at low temperatures, because at ordinary temperatures vigorous evolution of oxygen takes place in consequence of the catalytic decomposition of the hydrogen peroxide by the vanadium pentoxide. A similarly coloured solution with similar properties is also obtained by the action of sulphuric acid on barium pervanadate.<sup>8</sup> According to Meyer and Pawletta,<sup>9</sup> the red solution contains the compound  $(VO_2)_2(SO_4)_3$ , which undergoes hydrolysis in the following manner:—

<sup>1</sup> Rosenheim, *Ber.*, 1893, 26, 1191; *Zeitsch. anorg. Chem.*, 1893, 4, 368; 1896, 11, 225; Rosenheim, Itzig, and Koppel, *ibid.*, 1899, 21, 1; Ditte, *Compt. rend.*, 1886, 102, 1019.

<sup>2</sup> Abegg and Auerbach, *loc. cit.*, p. 1040; Gmelin-Kraut, *Handbuch* (Heidelberg), 1908, 3, ii, 204–205, 1094–1095.

<sup>3</sup> Gmelin-Kraut, *loc. cit.*, pp. 127–128, 148.

<sup>4</sup> *Ibid.*, pp. 629–630, 632–633.

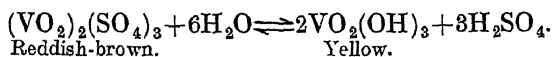
<sup>5</sup> *Ibid.*, pp. 203–204.

<sup>6</sup> *Ibid.*, pp. 186–188, 634.

<sup>7</sup> Scheuer, *Zeitsch. anorg. Chem.*, 1898, 16, 284.

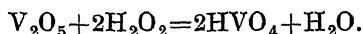
<sup>8</sup> Pissarjewsky, *Zeitsch. physikal. Chem.*, 1903, 43, 160, 173; *J. Russ. Phys. Chem. Soc.*, 1902, 34, 210, 472; 1903, 35, 42.

<sup>9</sup> Meyer and Pawletta, *Zeitsch. anal. Chem.*, 1926, 69, 15; *Zeitsch. angew. Chem.*, 1926, 39, 1284; Hothersall, *J. Soc. Chem. Ind.*, 1924, 43, 270.



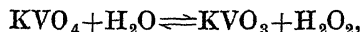
The yellow compound  $\text{VO}_2(\text{OH})_3$  thus formed can be looked upon as a *hydrated pervanadic acid*,  $\text{HVO}_4 \cdot \text{H}_2\text{O}$ , or as *peroxyorthovanadic acid*,<sup>1</sup>  $\text{H}_3\left[\text{V}\left(\begin{smallmatrix} \text{O}_2 \\ \text{O}_3 \end{smallmatrix}\right)\right]$ . It decomposes slowly at ordinary temperatures, and more rapidly on being warmed, with evolution of oxygen and reprecipitation of vanadium pentoxide.

It has been shown that in the formation of the red compound in solution each molecule of vanadium pentoxide reacts with two molecules of hydrogen peroxide :



Pervanadic acid appears, therefore, to be formed from metavanadic acid,  $\text{HVO}_3$ . This view of the reaction and the formula for pervanadic acid are further supported by titrating the red solution with caustic soda, when it is found that two molecules of caustic soda are required for each molecule of vanadium pentoxide. The monobasicity of the acid is confirmed by measuring the equivalent conductivities of solutions of potassium pervanadate.

A solution of pervanadic acid evolves a mixture of oxygen and chlorine on the addition of hydrochloric acid ; it evolves oxygen slowly on standing, more rapidly on warming, and leaves a residue of vanadium pentoxide. Decomposition of the solution is accelerated by the presence of dilute sulphuric acid.<sup>2</sup> Pervanadates of the alkali metals have been prepared by the action of hydrogen peroxide on the alkali metavanadates ; pervanadates of several heavy metals have also been isolated by double decomposition with ammonium pervanadate. These salts vary from bright yellow to deep orange in colour, and are amorphous or micro-crystalline. They undergo hydrolysis in dilute solution, *e.g.*



and evolve oxygen when platinised asbestos is introduced into their concentrated solutions. The following *metapervanadates* have been prepared :<sup>3</sup> *Ammonium pervanadate*,  $\text{NH}_4\text{VO}_4$  ; *barium pervanadate*,  $\text{Ba}(\text{VO}_4)_2$  ; *cadmium pervanadate*,  $\text{Cd}(\text{VO}_4)_2$  ; *calcium pervanadate*,  $\text{Ca}(\text{VO}_4)_2$  ; *lead pervanadate*,  $\text{Pb}(\text{VO}_4)_2$  ; *lithium pervanadate*,  $\text{LiVO}_4$  ; *potassium pervanadate*,  $\text{KVO}_4$  ; *silver pervanadate*,  $\text{AgVO}_4$  ; *sodium pervanadate*,  $\text{NaVO}_4$  ; and *strontium pervanadate*,  $\text{Sr}(\text{VO}_4)_2$ . Scheuer was unable to prepare the pervanadates of aluminium, cobalt, copper, magnesium, manganese, and nickel.

**Pyropervanadates.**—Pyropervanadic acid has not been isolated, but ammonium and potassium salts derived from it are known.<sup>4</sup> The *ammonium salt* has the composition  $(\text{NH}_4)_2\text{V}_2\text{O}_{11}$ , and is prepared by dissolving ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , in an aqueous solution of hydrogen peroxide, adding ammonium hydroxide until the solution smells of ammonia, and then precipitating the salt with alcohol. The reaction is thought to take the following course : Ammonium meta-

<sup>1</sup> Meyer, *Zeitsch. anorg. Chem.*, 1927, 161, 321.

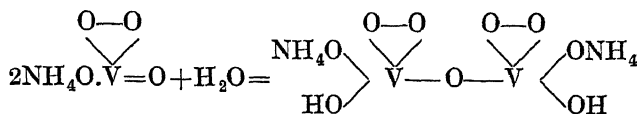
<sup>2</sup> Auger, *Compt. rend.*, 1921, 172, 1355.

<sup>3</sup> Scheuer, *loc. cit.* ; Pissarjewsky, *loc. cit.* ; *Zeitsch. anorg. Chem.*, 1902, 32, 341.

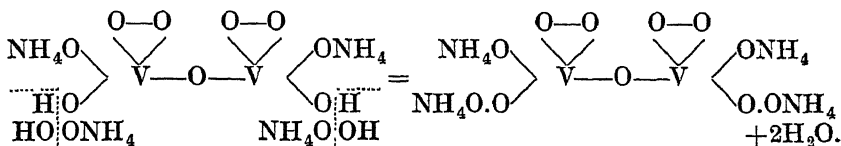
<sup>4</sup> Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1899, 19, 405.



pervanadate,  $\text{NH}_4\text{VO}_4$ , is first formed, and this reacts with water to yield ammonium pyropervanadate,  $(\text{NH}_4)_2\text{H}_2\text{V}_2\text{O}_9$ , in solution :



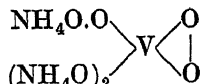
This substance undergoes further change with ammonium hydroperoxide,  $\text{NH}_4\text{O} \cdot \text{OH}$ , which is also formed in solution at the same time, to yield the compound  $(\text{NH}_4)_4\text{V}_2\text{O}_{11}$  :



Ammonium pyropervanadate crystallises in minute, slender, yellow, rhombic prisms, remaining undecomposed for some time when dry, then slowly decomposing with evolution of oxygen. With concentrated sulphuric acid it yields ozonised oxygen, and with dilute sulphuric acid hydrogen peroxide.

The ammonium and potassium salts of *orthopervanadic acid* have also been prepared.<sup>1</sup>

**Orthopervanadates.**—The *ammonium salt*,  $(\text{NH}_4)_3\text{VO}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , is obtained by dissolving ammonium metavanadate in excess of concentrated ammonia solution, cooling to  $0^\circ \text{C}$ ., adding 30 per cent. hydrogen peroxide, and then precipitating with alcohol. The product, after washing with ether and drying, is pale blue, and probably has the constitution



With large excess of hydrogen peroxide an indigo-blue salt which contains more oxygen, probably  $\text{VO}_2(\text{OH})(\text{O} \cdot \text{ONH}_4)_2$ , is obtained.

*Potassium Orthopervanadate*,  $\text{K}_3\text{VO}_6 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , is also blue, and is prepared similarly to the ammonium salt.

Vanadium oxyfluorides also react with hydrogen peroxide to yield complex compounds.<sup>2</sup> These are not so well defined as in the case of the peroxyfluorides of niobium and tantalum.

#### VANADIUM AND SULPHUR.

**Vanadium Monosulphide, VS.**—The lowest oxide of vanadium which can be obtained by the reducing action of hydrogen is vanadium trioxide,  $\text{V}_2\text{O}_3$ . In the case of the sulphides, however, the reducing action of hydrogen appears to proceed still further, notwithstanding the fact that hydrogen sulphide is a much less stable compound at a red heat than water-vapour. By passing hydrogen over heated vanadium trisulphide,  $\text{V}_2\text{S}_3$ , at  $1100^\circ$  to  $1200^\circ \text{C}$ . for from four to eight

<sup>1</sup> Melikoff and Jelhechanoff, *Ber.*, 1909, 42, 2291.

<sup>2</sup> Abegg, *Handbuch der anorganischen Chemie* (Leipzig), 1907, 3, iii, 745, 781.

days, the monosulphide, VS, has been obtained.<sup>1</sup> Wedekind and Horst,<sup>2</sup> however, were unable to obtain any of the sulphide by this method, but found that it resulted, more or less impure, from the action of hydrogen sulphide on hypovanadous oxide, VO. Vanadium monosulphide forms either glistening, black scales, of density 4.2, or a brownish-black, amorphous powder, density 4.4. Its magnetic susceptibility has been studied.<sup>3</sup> On being heated in air it absorbs oxygen readily with formation of vanadium pentoxide and evolution of sulphur dioxide. It is attacked only very slightly by boiling hydrochloric acid, both strong and dilute, and boiling dilute sulphuric acid; hot concentrated sulphuric acid dissolves it slowly, while nitric acid, strong or dilute, attacks it readily. It is soluble in colourless ammonium sulphide, giving a purple solution, and in yellow ammonium sulphide, yielding a wine-red solution. Caustic soda and ammonium hydroxide have a slight solvent action on the sulphide.

**Vanadium Trisulphide,  $V_2S_3$ .**—The most convenient method for the preparation of vanadium trisulphide in quantity consists in drawing the vapour of carbon disulphide for several hours over vanadium pentoxide heated to redness.<sup>4</sup> It also results from the action of hydrogen sulphide gas on vanadous oxide,  $V_2O_3$ , or on the higher oxides of vanadium, or from the action of hydrogen sulphide at a red heat on any chloride or oxychloride of vanadium. Vanadium trisulphide has been obtained in black, glistening scales, of density 3.7, or as a black, amorphous powder, of density 4.0, according to the initial material. On being heated in air this sulphide evolves sulphur dioxide and forms vanadium pentoxide, but the reaction proceeds much less readily than in the case of the lower sulphide. The behaviour towards acids, colourless ammonium sulphide, yellow ammonium sulphide, caustic soda, and ammonium hydroxide is like that with the lower sulphide.

**Vanadium Pentasulphide,  $V_2S_5$ .**—Vanadium pentasulphide is prepared by heating vanadium trisulphide with slight excess over the calculated quantity of sulphur at 400° C. for several hours; excess of sulphur is finally removed with carbon disulphide. This reaction is reversible, for on being heated in the absence of air the pentasulphide loses sulphur and re-forms the trisulphide. Heated in air it forms vanadium pentoxide. It is a black powder, of density 3.0. It does not differ from the lower sulphides in its behaviour towards acids; colourless ammonium sulphide also dissolves it to give the purple solution given by the other sulphides, but yellow ammonium sulphide produces a brownish-red solution. It differs markedly from the other sulphides in being readily dissolved by caustic soda, especially on warming, and in this respect acts in a manner comparable to vanadium pentoxide. Several *thiovanadates* analogous to the vanadates are known.<sup>5</sup>

The order of stability of the sulphides of vanadium is not the same as that of the oxides; for whilst in the oxygen series the penta-compound is stable at a red heat, in the sulphur series the penta-compound is converted into the trisulphide at this temperature. Again, the trioxide is permanent in hydrogen at intense redness, whilst the trisulphide is reduced to the monosulphide under similar conditions.

<sup>1</sup> Kay, *J. Chem. Soc.*, 1880, 37, 734.

<sup>2</sup> Wedekind and Horst, *Ber.*, 1912, 45, 262.

<sup>3</sup> Wedekind, *Zeitsch. angew. Chem.*, 1924, 37, 87.

<sup>4</sup> Kay, *loc. cit.*

<sup>5</sup> Kay, *loc. cit.*

A sulphide in which the vanadium is tetravalent, corresponding to the oxide  $\text{VO}_2$ , has not hitherto been prepared.

**Vanadium Oxysulphides.**—No vanadium oxysulphides of definite composition have been prepared. By the action of acids on solutions of vanadium pentoxide in ammonium sulphide, or on solutions of alkali vanadates which have been saturated with hydrogen sulphide, brown precipitates are obtained which consist of oxysulphides of variable composition.<sup>1</sup>

**Hypovanadous Sulphate**,  $\text{VSO}_4 \cdot 7\text{H}_2\text{O}$ , is obtained in solution when vanadium pentoxide is dissolved in sulphuric acid and reduced in the absence of air with sodium-amalgam, zinc, or cadmium. The separation of the hydrate is effected by first reducing the pentoxide in acid solution with sulphur dioxide to the blue tetravalent state, and then continuing the reduction electrolytically in an atmosphere of carbon dioxide until the colour of the solution changes to violet.<sup>2</sup> Concentration *in vacuo* deposits transparent, reddish-violet crystals, which become bluish-violet even with traces of oxygen. The crystals are monoclinic, and isomorphous with crystals of ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . They undergo oxidation rapidly on exposure to air and are readily soluble in water; dilute aqueous solutions in the absence of oxygen evolve hydrogen, while concentrated solutions also yield hydrogen sulphide.<sup>3</sup> When brought into contact with other compounds the sulphate exerts the same reducing action as hypovanadous chloride. Its solutions have the property common to solutions of ferrous sulphate and chromous sulphate of absorbing nitric oxide.

Hypovanadous sulphate gives rise to double sulphates with the sulphates of ammonium, potassium, and rubidium. *Hypovanadous ammonium sulphate*,  $\text{VSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , is formed when ammonium vanadate is electrolytically reduced in the presence of sulphuric acid. *Hypovanadous potassium sulphate*,  $\text{VSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , is made by electrolytically reducing vanadium pentoxide in sulphuric acid solution, then adding potassium sulphate and continuing the reduction. In the same way *hypovanadous rubidium sulphate* has been prepared, but it has not been found possible to obtain it free from vanadium rubidium alum. These double sulphates form violet, monoclinic crystals, which are not stable in air; they are not so rapidly oxidised as the simple hypovanadous salt, however; they are less soluble in water than the simple salt, and give yellow or brownish-yellow solutions which may contain complex ions. Hypovanadous sulphate also has the property of forming mixed crystals with magnesium, ferrous and chromous sulphates; these have the formulæ:  $(\text{V.Mg})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ;  $(\text{V.Fe})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ;  $(\text{V.Cr})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ .<sup>4</sup>

**Vanadous Sulphate** or **vanadium sesquisulphate**,  $\text{V}_2(\text{SO}_4)_3$ , is readily obtained in solution by reducing a solution of vanadium pentoxide in sulphuric acid either by means of magnesium or electrolytically.<sup>5</sup> The solid has been obtained by slowly heating to  $180^\circ \text{C}$ . in an atmosphere of carbon dioxide a solution of green acid vanadous sulphate,  $\text{V}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$  (see next page), in water which has been slightly acidified with sulphuric acid. Ammonium vanadous sulphate,  $(\text{NH}_4)\text{V}(\text{SO}_4)_2$ , can

<sup>1</sup> Berzelius, *Pogg. Annalen*, 1831, 22, 1; Kay, *loc. cit.*

<sup>2</sup> Conant and Cutter, *J. Amer. Chem. Soc.*, 1926, 48, 1019.

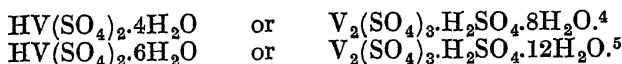
<sup>3</sup> Rutter, *Dissertation* (Leipzig, 1906).

<sup>4</sup> Piccini, *Zeitsch. anorg. Chem.*, 1899, 19, 204; Piccini and Marino, *ibid.*, 1902, 32, 55.

<sup>5</sup> Rutter, *Zeitsch. Elektrochem.*, 1906, 12, 130.

also be used.<sup>1</sup> Vanadous sulphate forms a micro-crystalline, yellow powder, which is insoluble in water; it decomposes on being heated in air with formation of vanadium pentoxide.<sup>2</sup> By the action of concentrated sulphuric acid on vanadic acetate several green or yellowish-green hydrates of vanadous sulphate have recently been prepared:<sup>3</sup>  $V_2(SO_4)_3 \cdot 3H_2O$ ;  $V_2(SO_4)_3 \cdot 4H_2O$ ;  $V_2(SO_4)_3 \cdot 9H_2O$ ;  $V_2(SO_4)_3 \cdot 10-11H_2O$ ; of these the tri- and tetra-hydrates appear to correspond in general behaviour to the green tri- and tetra-hydrates of chromium sulphate.

*Acid Vanadous Sulphates and double vanadous sulphates.*—Electrolytic reduction of solutions of vanadyl sulphate,  $VOSO_4$ , has given two green, crystalline, acid vanadous sulphates, according to the amount of sulphuric acid also added:



By electrolysis a solution of ammonium metavanadate in sulphuric acid instead of vanadyl sulphate, the ammonium salts of these acid sulphates are obtained, viz.  $NH_4V(SO_4)_2 \cdot 4H_2O$  and  $NH_4V(SO_4)_2 \cdot 6H_2O$ . The latter is referred to again below. These acids (and their salts) differ from one another in their general properties, for instance in the acidity of their solutions, in the electrical conductivity of their solutions, and in the ease with which they undergo oxidation. From a study of their analogy with the corresponding compounds of chromium, the constitution  $[V(SO_4)(H_2O)_4]SO_3H$  has been ascribed to the *tetrahydrate acid*, and the constitution  $[V(SO_4)_2(H_2O)_2]H \cdot 4H_2O$  to the *hexahydrate acid*.<sup>6</sup> By the action of sulphuric acid in varying quantity on solutions of vanadic acetate in glacial acetic acid, compounds having the compositions  $HV(SO_4)_2 \cdot 5H_2O$  and  $HV(SO_4)_2 \cdot 8H_2O$  have been prepared; dehydration of these gives rise to  $HV(SO_4)_2 \cdot 2H_2O$  and  $HV(SO_4)_2$ . The ammonium salt of the *pentahydrate acid*,  $NH_4V(SO_4)_2 \cdot 5H_2O$  or  $[V(H_2O)_4](SO_4)(SO_4NH_4) \cdot H_2O$ , has also been isolated.

When the reduction of the vanadyl sulphate is allowed to proceed in the presence of the sulphates of the alkali metals or of thallium, two series of double salts are obtained, the composition of which again varies with the amount of sulphuric acid present and with the other conditions.

*Series I.* has the general formula  $RV(SO_4)_2 \cdot 12H_2O$  or  $R_2SO_4 \cdot V_2(SO_4)_3 \cdot 24H_2O$ , which corresponds to the composition of the alums formed by the metals of Group III. and other groups. The *vanadium alums* are very similar in their behaviour to ferric, chromium and aluminium alums. They crystallise in regular, pentagonal hemihedra, varying in colour, with increase in atomic weight of the alkali metal, from the violet of the ammonium alum to the ruby-red of the caesium alum. The following table includes those alums which have hitherto been prepared:—<sup>7</sup>

<sup>1</sup> Auger, *Compt. rend.*, 1921, 173, 306.

<sup>2</sup> Stähler and Wirthwein, *Ber.*, 1905, 38, 3978.

<sup>3</sup> Meyer and Markowitz, *Zeitsch. anorg. Chem.*, 1926, 157, 211.

<sup>4</sup> Brierley, *J. Chem. Soc.*, 1886, 49, 823; compare Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 191.

<sup>5</sup> Stähler and Wirthwein, *loc. cit.*

<sup>6</sup> Meyer and Markowitz, *loc. cit.*

<sup>7</sup> Piccini, *Zeitsch. anorg. Chem.*, 1896, 11, 106; 1897, 13, 441; Locke, *Amer. Chem. J.*, 1901, 26, 166; Auger, *loc. cit.*; Eichner, *Compt. rend.*, 1927, 185, 1200.

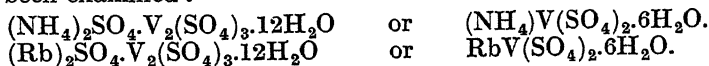
## VANADIUM ALUMS.

Formula.	Solubility in 2 litres of Water at 25° C. (gram-mols.).	Temperature at which Crystals Melt in their Water of Crystallisation.	Colour.	Density.
$V_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$	1.210	20° C.	Violet	1.687
$V_2(SO_4)_3 \cdot Na_2SO_4 \cdot 24H_2O$	..	45° C.	..	..
$V_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$	3.480 <sup>1</sup>	9° C.	Greenish-violet	1.782
$V_2(SO_4)_3 \cdot Rb_2SO_4 \cdot 24H_2O$	0.177	64° C.	Bluish-violet	1.915
$V_2(SO_4)_3 \cdot Cs_2SO_4 \cdot 24H_2O$	0.020	82° C.	Ruby-red	2.033
$V_2(SO_4)_3 \cdot Tl_2SO_4 \cdot 24H_2O$	0.573	48° C.	Reddish-violet	2.342

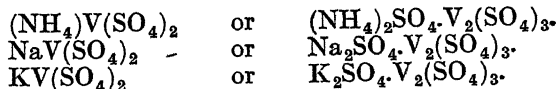
Bültemann<sup>2</sup> observed that vanadium ammonium alum separates out in blue crystals from a solution containing sulphuric acid, but from solutions containing a weak acid, or from neutral solutions, red crystals are obtained. (The chromium alums can also be prepared in differently coloured modifications.) The analytical data, melting-point, electrical conductivity, rate of efflorescence, and general behaviour of both kinds of crystals are identical, so that it is difficult to ascribe different constitutions to them. Meyer and Markowitz<sup>3</sup> have shown that both forms separate out when the molecular proportion of sulphuric acid in the solution is less than that theoretically required, and attribute the red colour to the presence of traces of vanadous oxide,  $V_2O_3$ , or its hydroxide,  $V(OH)_3$ . Vanadium rubidium and vanadium caesium alums behave in the same way. A *vanadium guanidine alum* has also been prepared.<sup>4</sup>

The general constitutional formula for the vanadium alums is  $[V(H_4O_2)_6](SO_4)(SO_4R)$ , which differs from the formulæ for other double vanadium sulphates in that the sulphato groups are not attached to the nuclear vanadium atom.

*Series II.*—This appears to comprise the salts of the acid  $HV(SO_4)_2 \cdot 6H_2O$  mentioned above, since they can be obtained by boiling this acid with the respective alkali sulphates. Only two members of the class have been examined :



By heating the alkali vanadyl sulphates, compounds have been obtained which can be looked upon either as the dehydrated forms of members of this series, or as salts of the acid sulphate,  $HV(SO_4)_2$ , mentioned above :<sup>5</sup>



These have the general formula  $[V(SO_4)_2]R$ .

<sup>1</sup> At 10° C.

<sup>2</sup> Bültemann, *Zeitsch. Elektrochem.*, 1904, 10, 141.

<sup>3</sup> Meyer and Markowitz, *loc. cit.*

<sup>4</sup> Canneri, *Gazzetta*, 1925, 55, 611.

<sup>5</sup> Rosenheim and Mong, *Zeitsch. anorg. Chem.*, 1925, 148, 78.

It is of some interest to note that iron and aluminium also give rise to double sulphates in which the number of molecules of water is less than in the alums.

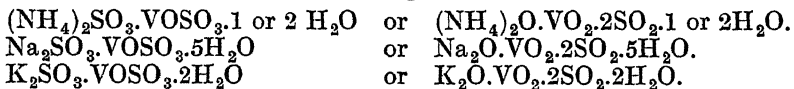
**Vanadyl Sulphites.**—Normal sulphites containing tetravalent vanadium have not hitherto been prepared in consequence of the readiness with which hydrolysis takes place. A considerable number of vanadyl sulphites are, however, known, as well as their double salts, which, no doubt, are *heteropoly-acid compounds*.

When a mixture of the oxides  $V_2O_3$  and  $V_2O_4$ , resulting from the decomposition of ammonium metavanadate, is treated in boiling aqueous solution with sulphur dioxide, a blue liquid is obtained from which under suitable conditions the following blue, crystalline hydrates of vanadyl sulphite,  $VOSO_3$ , can be isolated:  $VOSO_3 \cdot 3H_2O$ ;  $VOSO_3 \cdot 4H_2O$ ;  $VOSO_3 \cdot 8H_2O$ . The liquid also gives rise to an amorphous, green, hydrated, basic vanadyl sulphite,  $VO_2 \cdot VOSO_3 \cdot 4\frac{1}{2}H_2O$  or  $2VO_2 \cdot SO_2 \cdot 4\frac{1}{2}H_2O$ .<sup>1</sup> Another blue, crystalline complex sulphite, having the composition  $4VO_2 \cdot 3SO_2 \cdot 10H_2O$ , has been prepared by a similar process,<sup>2</sup> and by reducing barium metavanadate in aqueous suspension, the blue, crystalline compound  $3VO_2 \cdot 2SO_2 \cdot 4\frac{1}{2}H_2O$  results.<sup>3</sup>

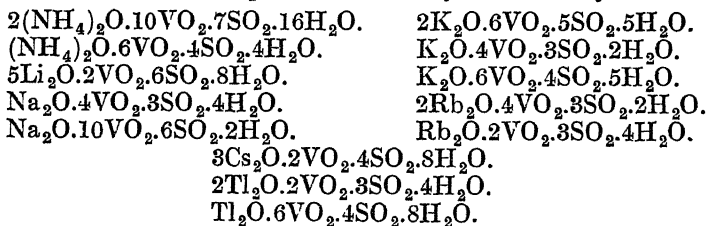
*Double Salts of Vanadyl Sulphite.*—By the action of sulphur dioxide on vanadates in the presence of varying molecular proportions of alkali sulphites, two series of alkali vanadyl sulphites have been obtained.

*Series I.*—This consists of blue compounds having the general formula  $R_2O \cdot 3VO_2 \cdot 2SO_2 \cdot xH_2O$ , which can be regarded as derivatives of the vanadyl sulphite,  $3VO_2 \cdot 2SO_2 \cdot 4\frac{1}{2}H_2O$ , which can be alternatively written,  $H_2O \cdot 3VO_2 \cdot 2SO_2 \cdot 3\frac{1}{2}H_2O$ . The following have been prepared:  $(NH_4)_2O \cdot 3VO_2 \cdot 2SO_2 \cdot H_2O$ ;  $Na_2O \cdot 3VO_2 \cdot 2SO_2 \cdot 3H_2O$ ;  $K_2O \cdot 3VO_2 \cdot 2SO_2$ ; and  $ZnO \cdot 3VO_2 \cdot 2SO_2$ .

*Series II.*—This comprises green substances which are generally less stable than the members of former series, and have the general formula  $R_2O \cdot VO_2 \cdot 2SO_2 \cdot xH_2O$ . The following are known:—



In addition to the foregoing, Gain<sup>4</sup> has prepared a large number of alkali vanadyl sulphites in which the proportions of basic oxide, vanadium dioxide, and sulphur dioxide vary considerably:



It is improbable that these are all true individual chemical compounds.

**Vanadyl Sulphates.**—By treating hypovanadic oxide,  $VO_2$ , with sulphuric acid at about  $200^\circ C$ ., or by reducing a sulphuric acid solution

<sup>1</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224.

<sup>2</sup> Gain, *Compt. rend.*, 1906, 143, 823.

<sup>3</sup> Koppel and Behrendt, *Zeitsch. anorg. Chem.*, 1903, 35, 154; *Ber.*, 1901, 34, 3929.

<sup>4</sup> Gain, *loc. cit.*

of vanadium pentoxide,  $V_2O_5$ , with sulphur dioxide, two distinct compounds are obtainable, according to the quantity of sulphuric acid present :

- (a) Neutral vanadyl sulphate,  $VOSO_4$ .  
 (b) Acid vanadyl sulphate,  $2VOSO_4 \cdot H_2SO_4 \cdot xH_2O$ .

*Vanadyl Sulphate*,  $VOSO_4$ , exists in two modifications, *insoluble* and *soluble*. The insoluble variety is best obtained by heating any of the acid vanadyl sulphates to  $260^\circ C$ . It is a greyish-green, micro-crystalline powder, which is insoluble both in hot water and in hot dilute acids. It is readily decomposed by alkalis to form brown, hydrated hypovanadic oxide. On being heated at  $130^\circ C$ . in a sealed tube with a little water, it undergoes conversion into the soluble form, which can also be obtained by evaporation of a solution of the hydrate,  $2VOSO_4 \cdot 7H_2O$ , to dryness,<sup>1</sup> or by evaporation of a solution of vanadium pentoxide in sulphuric acid in the presence of alcohol.<sup>2</sup> This modification is a blue, amorphous, gummy mass, completely soluble in water, giving a blue solution which becomes green in air and slowly deposits the green oxide,  $VO_2$ . On being heated in the absence of air it again forms hypovanadic oxide; in the presence of air the pentoxide,  $V_2O_5$ , is produced.<sup>3</sup>

Several blue, crystalline hydrates of vanadyl sulphate<sup>4</sup> have been prepared from hypovanadic oxide,  $VO_2$ :  $VOSO_4 \cdot 2H_2O$ ;  $VOSO_4 \cdot 2\frac{1}{2}H_2O$ ;  $VOSO_4 \cdot 3H_2O$ ;  $VOSO_4 \cdot 3\frac{1}{2}H_2O$ ;  $VOSO_4 \cdot 5H_2O$ ;  $VOSO_4 \cdot 6\frac{1}{2}H_2O$ ;  $VOSO_4 \cdot 7H_2O$ . The *dihydrate*,  $VOSO_4 \cdot 2H_2O$ , has been prepared electrolytically.<sup>5</sup> Most of these give a greyish-green *monohydrate*,  $VOSO_4 \cdot H_2O$ , on being heated to  $150^\circ C$ ., and all of them undergo dehydration to form insoluble vanadyl sulphate at  $260^\circ C$ . It is doubtful if these are all individual chemical compounds; they may be mixtures of hydrates. They are, however, characterised by their crystalline forms, and in that they can, in several cases, be prepared by different methods.

*Acid Vanadyl Sulphates*, of general formula  $2VOSO_4 \cdot H_2SO_4 \cdot xH_2O$ , are prepared by reducing solutions of vanadium pentoxide in sulphuric acid of such concentration that there are more than three molecules of sulphuric acid per molecule of vanadium pentoxide.<sup>6</sup> Evaporation on the water-bath yields the *pentahydrate*,  $2VOSO_4 \cdot H_2SO_4 \cdot 5H_2O$ , which, on being heated to  $200^\circ C$ ., undergoes dehydration and forms the compound  $2VOSO_4 \cdot SO_3$  or  $2VO_2 \cdot 3SO_3$ . By treatment at intermediate temperatures the following hydrates have also been prepared:  $2VOSO_4 \cdot H_2SO_4 \cdot 3H_2O$ ;  $2VOSO_4 \cdot H_2SO_4 \cdot 2H_2O$ ;  $4VOSO_4 \cdot 2H_2SO_4 \cdot H_2O$ . Gain<sup>7</sup> has shown that hypovanadic oxide combines with sulphur trioxide to produce various other complexes all of which are blue, crystalline, fairly stable substances. They have the general formula  $4VO_2 \cdot xSO_3 \cdot yH_2O$ , in which  $x$  varies between 4 and 10.

*Double Salts of Vanadyl Sulphate*.—Two series of double salts of

<sup>1</sup> Crow, *J. Chem. Soc.*, 1876, 30, 457.

<sup>2</sup> Guyard, *Bull. Soc. chim.*, 1876, [ii], 25, 352.

<sup>3</sup> Gerlandt, *Ber.*, 1876, 9, 869; 1877, 10, 2109; Koppel and Behrendt, *Zeitsch. anorg. Chem.*, 1903, 35, 170.

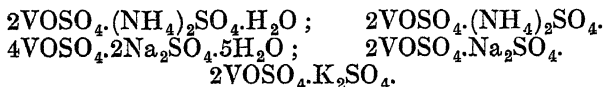
<sup>4</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224.

<sup>5</sup> Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 193.

<sup>6</sup> Compare Auger, *Compt. rend.*, 1921, 173, 306.

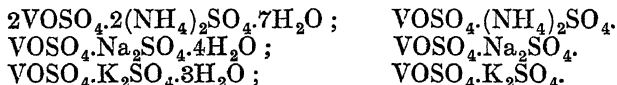
<sup>7</sup> Gain, *loc. cit.*; *Compt. rend.*, 1906, 143, 1154.

vanadyl sulphate and alkali sulphates are known.<sup>1</sup> The members of the first series have the general formula  $2\text{VOSO}_4 \cdot \text{R}'_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ , and are obtained by reducing solutions of the alkali metavanadates in sulphuric acid with sulphur dioxide and then adding excess of the particular alkali sulphate desired. They form blue, crystalline compounds which undergo dehydration at  $175^\circ\text{C}$ . The following have been prepared :—



Fischer,<sup>2</sup> by the same method, prepared the double sulphates with calcium, magnesium and aluminium sulphates.

The members of the second series possess the general formula  $\text{VOSO}_4 \cdot \text{R}'_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ , and thus contain a smaller molecular proportion of vanadyl sulphate than the members of the preceding series, from which they are prepared by the prolonged action of alcohol on neutral solutions. They also yield dark blue, crystalline compounds, which undergo dehydration at  $175^\circ\text{C}$ . The following are known :—



The general compositions of these two series of double salts correspond to the compositions of the double sulphates of divalent metals, e.g.  $2\text{ZnSO}_4 \cdot \text{K}_2\text{SO}_4$  and  $\text{ZnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .<sup>3</sup>

**Vanadic Sulphates.**—Two of these are known, viz.  $\text{V}_2\text{O}_5 \cdot 3\text{SO}_3$  and  $\text{V}_2\text{O}_5 \cdot 2\text{SO}_3$ . The former has been prepared in ruby-red, transparent octahedra by boiling vanadium pentoxide with excess of sulphuric acid ; if the boiling is continued for some time, golden-yellow needles separate out. The crystals absorb water rapidly and simultaneous formation of vanadyl sulphate takes place, so that analysis is difficult.<sup>4</sup> Münzing<sup>5</sup> doubts the existence of  $\text{V}_2\text{O}_5 \cdot 3\text{SO}_3$ , because by the same process he obtained the substance  $\text{V}_2\text{O}_5 \cdot 2\text{SO}_3$ , which is also extremely deliquescent, and exists either as a red, crystalline mass or as a yellow powder. If the sulphuric acid solution is strongly heated, a dark-brown modification is obtained which changes slowly into the red variety. It has recently been shown that when heated in sulphuric acid solution, tetravalent vanadium is partially oxidised and pentavalent vanadium partially reduced to an equilibrium mixture.<sup>6</sup> A crystalline form of the compound  $\text{V}_2\text{O}_5 \cdot 2\text{SO}_3$ , with rather different properties, has been obtained by the decomposition of alkali vanadyl sulphates.<sup>7</sup> The action of concentrated sulphuric acid on vanadium pentoxide has also given a hydrate,  $\text{V}_2\text{O}_5 \cdot 3\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , in either yellow or red, deliquescent crystals.<sup>8</sup> This hydrate can be alternatively written  $\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{SO}_4$ , but no corresponding salts are known, although by addition of the respective alkali

<sup>1</sup> Koppel and Behrendt, *loc. cit.*

<sup>2</sup> Fischer, *Trans. Amer. Electrochem. Soc.*, 1916, 30, 187.

<sup>3</sup> Rosenheim and Mong, *Zeitsch. anorg. Chem.*, 1925, 148, 26.

<sup>4</sup> Gerland, *Ber.*, 1878, 11, 99.

<sup>5</sup> Münzing, *Chem. Zentr.*, 1889, ii, 908.

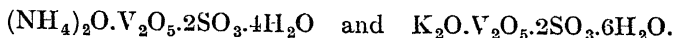
<sup>6</sup> Eichner, *Compt. rend.*, 1927, 185, 1200.

<sup>7</sup> Rosenheim and Mong, *loc. cit.*

<sup>8</sup> Ditte, *Compt. rend.*, 1886, 102, 757.



sulphate to its solutions two complex salts have been prepared, which can be looked upon as double sulphates of  $V_2O_5 \cdot SO_3$ , namely,



A compound intermediate in composition between vanadic sulphate and vanadyl sulphate has been obtained by reducing a solution of a vanadic salt in sulphuric acid with sulphur dioxide, or by mixing solutions of the pentoxide and the dioxide in sulphuric acid.<sup>1</sup>

**Vanadyl Dithionate**,  $VOS_2O_6$ , is prepared by treating a solution of vanadyl sulphate with barium dithionate. It decomposes on standing, with evolution of sulphur dioxide.<sup>2</sup>

*Thiovanadates and Oxythiovanadates.*—A series of crystalline salts is known which resemble the ortho- and pyro-vanadates in composition, except that the oxygen is either wholly or partially replaced by sulphur. *Copper orthothiovanadate*,  $Cu_3(VS_4)_2$ , occurs naturally as *sulvanite* (see p. 11). The following thio- and oxythio-compounds have been prepared.<sup>3</sup>

**Ammonium Orthothiovanadate**,  $(NH_4)_3VS_4$ , is obtained in rhombic crystals by the action of ammonium hydrosulphide on potassium metavanadate or sodium pyrovanadate solution. It also separates out slowly from an ice-cold saturated solution of ammonium metavanadate in concentrated ammonium hydroxide which has been previously treated with hydrogen sulphide.

**Ammonium Pyroxyhexathiovanadate**,  $(NH_4)_4V_2S_6O$ , is deposited in red crystals when hydrogen sulphide is passed into a solution of ammonium metavanadate in ammonium hydroxide of higher specific gravity than 0.898 and the mixture kept for several months at a low temperature. The corresponding *potassium salts*,  $K_4V_2S_6O \cdot 3H_2O$  and  $K_4V_2S_6O \cdot 1\frac{1}{2}H_2O$ , are prepared in a similar manner. The normal potassium orthothiovanadate,  $K_3VS_4$ , has not been separately isolated, although mixtures which most probably contain it, together with the normal ammonium salt, have been prepared.

**Sodium Orthoxytrithiovanadate**,  $Na_3VS_3O \cdot 5H_2O$ , is obtained in dark, reddish-brown, deliquescent crystals by the action of sodium hydrosulphide on sodium pyrovanadate. The anhydrous salt is formed when vanadium pentoxide, sulphur and sodium carbonate are fused together,<sup>4</sup> or by the action of hydrogen sulphide on sodium orthovanadate at  $500^\circ$  to  $700^\circ$  C.<sup>5</sup>

**Sodium Orthoxymonothiovanadate**,  $Na_3VSO_3 \cdot 10H_2O$ , has been obtained in orange-yellow crystals by the action of sodium hydrosulphide on sodium pyrovanadate.

The action of hydrogen sulphide at high temperatures on sodium pyrovanadate gives rise to **sodium pentathiopyrovanadate**,  $Na_4V_2S_5O_2$ , which is a hygroscopic substance very similar in its colour and lustre to potassium permanganate.

Thiovanadates of the heavy metals have proved difficult to isolate; addition of solutions of salts of zinc, manganese, copper and silver to a solution of ammonium thiovanadate gives precipitates which consist

<sup>1</sup> Auger and Eichner, *Compt. rend.*, 1927, 185, 208.

<sup>2</sup> Bevan, *Chem. News*, 1878, 38, 294.

<sup>3</sup> Kruss and Ohnmais, *Ber.*, 1890, 23, 2547; *Annalen*, 1891, 263, 39.

<sup>4</sup> Krüss, *Zeitsch. anorg. Chem.*, 1893, 3, 264.

<sup>5</sup> Locke, *Amer. Chem. J.*, 1898, 20, 373.

of sulphides or thiovanadates of the metals, or mixtures of both. A black, crystalline lead salt of the probable composition  $\text{Pb}_2\text{V}_2\text{S}_2\text{O}_5$ , *lead dithiopyrovanadate*, has, however, been obtained.<sup>1</sup>

#### VANADIUM AND SELENIUM.

**Vanadium Selenides.**—The preparation of the following selenides of vanadium has been claimed in an American patent,<sup>2</sup> but no details or analytical data are given:  $\text{V}_2\text{Se}$  (white),  $\text{V}_2\text{Se}_2$  (yellow),  $\text{V}_2\text{Se}_3$  (red),  $\text{V}_2\text{Se}_4$  (dark blue),  $\text{V}_2\text{Se}_5$  (green),  $\text{V}_2\text{Se}_8$ .

**Vanadyl Selenite**,  $\text{VO}_2\cdot\text{SeO}_2\cdot 2\text{H}_2\text{O}$ , is obtained in blue, microscopic crystals when the hydrate of hypovanadic oxide,  $\text{VO}_2\cdot 2\text{H}_2\text{O}$ , is dissolved in an aqueous solution of selenous acid and the solution evaporated.<sup>3</sup> Efforts to prepare normal selenates and selenate alums of trivalent vanadium were unsuccessful, but several *hydrated acetoselenates* of trivalent vanadium have been isolated.<sup>4</sup>

**Vanadyl Selenates.**—Two blue, deliquescent, crystalline vanadyl selenates, having the compositions  $4\text{VO}_2\cdot 7\text{SeO}_3\cdot 14\text{H}_2\text{O}$  and  $2\text{VO}_2\cdot 5\text{SeO}_3\cdot 10\text{H}_2\text{O}$ , have been obtained by very slow evaporation of a solution of hydrated hypovanadic oxide,  $\text{VO}_2\cdot 2\text{H}_2\text{O}$ , in selenic acid.<sup>5</sup>

Vanadium pentoxide and selenous acid condense together to form a large number of complex *vanadoselenites* which are described on p. 89.

#### VANADIUM AND CHROMIUM.

Normal chromates of vanadium have not been prepared. An *ammonium vanadochromate*,  $2(\text{NH}_4)_2\text{O}\cdot\text{V}_2\text{O}_5\cdot 2\text{CrO}_3\cdot 7\text{H}_2\text{O}$ , has been prepared in red crystals by dissolving vanadium pentoxide in ammonium chromate solution and evaporating at ordinary temperatures *in vacuo*.<sup>6</sup>

#### VANADIUM AND NITROGEN.

Vanadium combines slowly with nitrogen when heated in the gas to high temperatures. A substance having the empirical formula  $\text{V}_2\text{N}$  was obtained at a red heat,<sup>7</sup> but the existence of this compound must be regarded as doubtful, because the mononitride,  $\text{VN}$ , is formed at a white heat.<sup>8</sup> The temperature at which combination takes place is also somewhat uncertain. Pure vanadium does not absorb nitrogen below  $1250^\circ\text{C}$ .,<sup>9</sup> but with a ferrovandium alloy it was found that absorption of nitrogen by the vanadium takes place at an increasing rate from  $800^\circ$  to  $1200^\circ\text{C}$ ., when a maximum absorption of 8 per cent. of nitrogen is reached; at higher temperatures the nitrogen content decreases rapidly.<sup>10</sup>

<sup>1</sup> Locke, *loc. cit.*

<sup>2</sup> von Oefele, *U.S. Pat.* 1154949 (1915).

<sup>3</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224.

<sup>4</sup> Meyer and Markowitz, *Zeitsch. anorg. Chem.*, 1926, 157, 211.

<sup>5</sup> Gain, *loc. cit.*; also *Compt. rend.*, 1907, 144, 1271.

<sup>6</sup> Ditte, *Compt. rend.*, 1886, 102, 1019, 1105.

<sup>7</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 58.

<sup>8</sup> Whitehouse, *J. Soc. Chem. Ind.*, 1907, 26, 738.

<sup>9</sup> Shukoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 457; *J. Chem. Soc., Abs.*, 1908, [ii], 94, 484.

<sup>10</sup> Tchigevsky and Blinow, *Rev. Soc. russe de Métall.*, 1914, 1, 636; *J. Soc. Chem. Ind., Abs.*, 1916, 35, 893; compare also Tammann, *Zeitsch. anorg. Chem.*, 1922, 124, 25.

**Vanadium Subnitride**,  $V_2N$ , is described as a black powder which is not attacked by hydrochloric acid or caustic potash solution. It is soluble in concentrated nitric and sulphuric acids, and evolves ammonia on being heated with solid caustic potash.

**Vanadium Mononitride**,  $VN$ , can be prepared synthetically, but it is more conveniently prepared by calcining ammonium metavanadate,  $NH_4VO_3$ , in air, and heating the black residue to a white heat in a current of dry ammonia.<sup>1</sup> It has also been obtained by the action of dry ammonia gas on vanadium oxytrichloride,  $VOCl_3$ ,<sup>2</sup> and by heating a mixture of vanadous oxide,  $V_2O_3$ , and carbon at  $1200^\circ C$ . in an atmosphere of nitrogen.<sup>3</sup> It is a greyish-brown powder which melts with decomposition at  $2050^\circ C$ . Its density is 5.91. The electrical conductivity, magnetic susceptibility, and crystal structure have been investigated,<sup>4</sup> and the dissociation pressures and calculated heat of formation are given by Slade and Higson.<sup>5</sup> Vanadium mononitride is a very stable compound; it yields vanadium pentoxide only on being very strongly heated in air. It evolves ammonia on being treated with steam at  $400^\circ C$ ,<sup>6</sup> when heated with soda-lime or when boiled with caustic potash solution. Nitric acid dissolves it, but hydrochloric acid and sulphuric acid are without action.

**Vanadium Dinitride**,  $VN_2$ , is obtained as a black powder by passing ammonia gas over vanadium oxytrichloride,  $VOCl_3$ , heated in a glass tube (to expel the ammonium chloride formed), washing with ammonium hydroxide, and drying *in vacuo* over sulphuric acid. It undergoes oxidation and evolves ammonia on being exposed to air; on being heated it evolves nitrogen and forms the mononitride,  $VN$ ; it is readily attacked by molten caustic potash and hot nitric acid.<sup>7</sup>

**Alkali Vanadyl Nitrites**.—By dissolving hypovanadic oxide,  $VO_2$ , in aqueous solutions of vanadyl nitrites the following alkali vanadyl nitrites have been prepared:—



The corresponding sodium salt is very unstable.<sup>8</sup>

**Vanadium Nitrates**.—No nitrates of vanadium have been isolated. When hypovanadic oxide is dissolved in nitric acid the blue solution which results probably contains vanadyl nitrate,  $VO(NO_3)_2$ , but on evaporation oxidation ensues and hydrated vanadium pentoxide is obtained. Blue solutions of vanadyl nitrate are more conveniently obtained by precipitating vanadyl chloride with silver nitrate or vanadyl sulphate with barium nitrate.<sup>9</sup> Addition of nitric acid to hexammino-vanadium trichloride yields *hexammino-vanadium nitrate*,<sup>10</sup>  $[V(NH_3)_6](NO_3)_3$ .

<sup>1</sup> Roscoe, *J. Chem. Soc.*, 1870, 23, 344, 358.

<sup>2</sup> Roscoe, *ibid.*, 1868, 21, 349.

<sup>3</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 143, 303.

<sup>4</sup> Wedekind and Horst, *Ber.*, 1912, 45, 268; Friederich, *Zeitsch. Physik*, 1925, 31, 813; Becker and Ebert, *ibid.*, 1925, 31, 268.

<sup>5</sup> Slade and Higson, *B.A. Reports*, 1913, 451; *J. Chem. Soc.*, 1919, 115, 215.

<sup>6</sup> Whitehouse, *loc. cit.*

<sup>7</sup> Roscoe, *J. Chem. Soc.*, 1868, 21, 349; Uhrlaub, *Pogg. Annalen*, 1858, 103, 134.

<sup>8</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224.

<sup>9</sup> Guyard, *Bull. Soc. chim.*, 1876, [ii], 25, 352.

<sup>10</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

## VANADIUM AND PHOSPHORUS.

**Vanadyl Hypophosphite**,  $\text{VO}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ , is a bluish-green, sparingly soluble, crystalline substance, obtained by heating solutions of vanadium pentoxide and hypophosphorous acid.<sup>1</sup>

**Vanadyl Phosphates**,  $\text{VO}_2 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and  $2\text{VO}_2 \cdot 3\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ , are prepared in blue needles by the action of hypovanadic oxide on phosphoric acid.<sup>2</sup>

**Vanadous Pyrophosphate**,  $\text{V}_4(\text{P}_2\text{O}_7)_3 \cdot 30\text{H}_2\text{O}$ , is obtained as a green, flocculent precipitate when vanadium ammonium alum is added to a solution of an alkaline pyrophosphate.<sup>3</sup>

The *vanadophosphates*, *molybdovanadophosphates*, and *tungstovanadophosphates* have been described on pp. 84 and 85.

## VANADIUM AND ARSENIC.

**Vanadyl Arsenates**.—Two of these have been prepared by the action of hydrated hypovanadic oxide on solutions of arsenic acid:  $2\text{VO}_2 \cdot 2\text{As}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and  $2\text{VO}_2 \cdot 3\text{As}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ . They are both sky-blue, crystalline compounds, and the latter rapidly becomes green on exposure to air.<sup>4</sup>

The *heteropoly-acid salts* of vanadium and arsenic have been dealt with on pp. 85 and 86.

## VANADIUM AND CARBON.

When either vanadium trioxide,  $\text{V}_2\text{O}_3$ , or vanadium pentoxide,  $\text{V}_2\text{O}_5$ , is reduced with carbon in the electric furnace, the product contains carbon in proportions varying from 4 per cent. to 25 per cent., depending on the temperature attained and other conditions.<sup>5</sup> If a mixture of the pentoxide and sugar charcoal is heated in the carbon tube of the electric furnace for ten minutes, a definite carbide having the formula VC is obtained. More recently this compound has been prepared by heating a mixture of vanadium trioxide and carbon in an atmosphere of hydrogen at  $1100^\circ \text{C}$ .<sup>6</sup>

**Vanadium Carbide**, VC, forms silvery-white crystals which are harder than quartz; density 5.25 to 5.40; m.pt. approximately  $2750^\circ \text{C}$ . Vanadium carbide is not attacked by water, hydrochloric acid, or hydrogen sulphide, even at a red heat. Nitric acid dissolves it in the cold. It burns at  $800^\circ \text{C}$ . in chlorine with incandescence, and at a red heat it reacts with oxygen, nitrogen, ammonia, potassium nitrate, and potassium chlorate. On being fused with vanadium trioxide,  $\text{V}_2\text{O}_3$ , in a crucible provided with a refractory lining, the carbon burns away and a product containing 98.11 per cent. of vanadium is obtained.<sup>7</sup> The dissociation pressures,<sup>8</sup> electrical conductivity, and crystal structure for this carbide<sup>9</sup> have been measured.

<sup>1</sup> Mawrow, *Zeitsch. anorg. Chem.*, 1907, 55, 147.

<sup>2</sup> Gain, *Compt. rend.*, 1907, 144, 1271.

<sup>3</sup> Rosenheim and Triantaphyllides, *Ber.*, 1915, 48, 582.

<sup>4</sup> Berzelius, *Pogg. Annalen*, 1831, 22, 1; Friedheim and Schmitz-Dumont, *Ber.*, 1890, 23, 2600; Gain, *Compt. rend.*, 1907, 144, 1271.

<sup>5</sup> Moissan, *ibid.*, 1893, 116, 1225; 1896, 122, 1297; Ruff and Martin, *Zeitsch. angew. Chem.*, 1912, 25, 49; compare p. 18.

<sup>6</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1924, 144, 172.

<sup>7</sup> Ruff and Martin, *loc. cit.*

<sup>8</sup> Slade and Higson, *J. Chem. Soc.*, 1919, 115, 210.

<sup>9</sup> Friederich, *Zeitsch. Physik*, 1925, 31, 813; Becker and Ebert, *ibid.*, 1925, 31, 268.

Moissan reported the existence of several other vanadium carbides,  $V_3C$ ,  $V_3C_2$ ,  $V_2C_2$ ,  $V_2C_3$ , and some of these have received attention in connection with the investigation of the constitution of vanadium steels. Arnold and Reed isolated a double carbide of iron and vanadium having the formula  $2Fe_3C.V_4C_3$ , but  $V_4C_3$  may be a mixture of several other carbides.<sup>1</sup> The action of various etching agents on vanadium carbide has been investigated with a view to distinguishing it from other carbides in metallographic work.<sup>2</sup>

A carbide of vanadium is also obtained by the action of carbon monoxide on the metal at  $500^\circ$  to  $800^\circ$  C. The finely divided metal catalyses the reaction,  $2CO=CO_2+C$ , and the carbon thereby isolated is taken up by the vanadium.<sup>3</sup>

*Normal carbonates* of vanadium are unknown. An unstable ammonium vanadyl carbonate, of composition  $3(NH_4)_2CO_3.7VO_2.5CO_2.16H_2O$ , has been obtained in small, violet crystals by the addition of ammonium carbonate to a neutral solution of vanadyl sulphate.<sup>4</sup>

#### VANADIUM AND CYANOGEN.

**Vanadyl Cyanide.**—Berzelius<sup>5</sup> obtained vanadyl cyanide by the action of hydrocyanic acid on hydrated hypovanadic oxide in the absence of air. The product was not, however, analysed.

**Potassium Vanadocyanide**,  $K_4[V(CN)_6].3H_2O$ , is obtained by reduction of a solution of vanadous oxide,  $V_2O_3$ , in acetic acid by means of potassium amalgam in the absence of air, the product being treated with potassium cyanide.<sup>6</sup> Its aqueous solution is red, and addition of alcohol to it precipitates brownish-yellow, apparently tetragonal crystals which rapidly become dark blue in moist air. It reduces silver salts to metallic silver, mercuric chloride to mercurous chloride, and is analogous to the corresponding potassium ferro-, potassium manganous-, and potassium cobalto-double cyanides.

**Potassium Vanadicyanide**,  $K_3[V(CN)_6]$ , is prepared by the addition of excess of concentrated potassium cyanide solution to a concentrated solution of vanadous chloride,  $VCl_3$ ; precipitation in the cold with alcohol gives rise to small rhombohedral plates. The solution is not very stable and rapidly becomes turbid, while addition of an acid produces the green colour which is characteristic of the  $V^{++}$  ion. The complex ion  $[V(CN)_6]^{4-}$  appears, therefore, to be unstable, unlike the corresponding  $[Fe(CN)_6]^{4-}$ ,  $[Cr(CN)_6]^{3-}$ , and  $[Co(CN)_6]^{3-}$  complex ions. The solution reacts with salts of heavy metals to yield variously coloured precipitates of double cyanides.<sup>7</sup>

An unstable double salt of potassium pyrovanadate and potassium cyanide,  $K_4V_2O_7.4KCN.14H_2O$ , has been prepared,<sup>8</sup> as well as a complex addition compound of sodium vanadyl cyanide and hexamethylenetetramine,  $Na_3VO(CN)_5.2C_6H_{12}N_4.5H_2O$ .<sup>9</sup>

<sup>1</sup> Arnold and Reed, *J. Iron Steel Inst.*, 1912, 85, 215.

<sup>2</sup> Groesbeck, *Proc. Amer. Soc. for Testing Materials*, 1926, 26, i, 569.

<sup>3</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

<sup>4</sup> Koppel, Goldmann, and Kaufmann, *ibid.*, 1905, 45, 349.

<sup>5</sup> Berzelius, *Pogg. Annalen*, 1831, 22, 1.

<sup>6</sup> Petersen, *Ber.*, 1903, 36, 1911; *Zeitsch. anorg. Chem.*, 1904, 38, 342.

<sup>7</sup> Locke and Edwards, *Amer. Chem. J.*, 1898, 20, 594.

<sup>8</sup> Petersen, *loc. cit.*

<sup>9</sup> Barbieri and Parisi, *Ber.*, 1927, 60, [B], 2418.

**Vanadium Ferrocyanides.**—Solutions of vanadates, when treated with potassium ferrocyanide, yield a precipitate of doubtful composition.<sup>1</sup> The compound is insoluble in mineral acids of high concentration, and a method involving its precipitation has recently been suggested for the estimation of vanadium in steels.<sup>2</sup>

*Double Salts of Vanadous Thiocyanate.*—When vanadous sulphate,  $V_2(SO_4)_3$ , in solution, is treated with barium thiocyanate, a green solution<sup>3</sup> is obtained which is believed to contain vanadous thiocyanate,  $V(SCN)_3$ , but attempts to isolate this compound have not met with success. Its double salts with the alkali thiocyanates have, however, been obtained in well-defined crystals when an alkali thiocyanate is substituted for the barium salt. The following are known :—

*Ammonium vanadous thiocyanate*,  $3NH_4SCN.V(SCN)_3.4H_2O$ ; dark green crystals.

*Sodium vanadous thiocyanate*,  $3NaSCN.V(SCN)_3.12H_2O$ ; red tablets or leaflets.

*Potassium vanadous thiocyanate*,  $3KSCN.V(SCN)_3.4H_2O$ ; bright red crystals.

These compounds probably do not contain a complex  $[V(SCN)_6]$  anion; if they do, it must be extremely unstable in dilute solution, because (a) their aqueous solutions, which are brown at first, assume the green colour due to the  $V^{+++}$  ion; (b) addition of an alkali precipitates vanadous hydroxide,  $V(OH)_3$ ; (c) acidified solutions on the addition of ferric salts give the blood-red colour characteristic of the  $(SCN)'$  ion; (d) depression of freezing-point data bear out the foregoing facts.<sup>4</sup> *Hexa-methylenetetramine aquo-vanadous pentathiocyanate*,  $(C_6H_{12}N_4.H)_2[V(SCN)_5.(OH)_2].H_2O$ , and a *basic pyridine vanadous tetrathiocyanate*,  $(C_5H_5N.H)_3.[V(SCN)_4(OH)_2]$ , have, however, been prepared from ammonium vanadous thiocyanate.<sup>5</sup>

**Ammonium Vanadyl Thiocyanate.**—This compound and the corresponding *potassium vanadyl thiocyanate* are obtained in blue, isomorphous, rhombic crystals by the addition of ammonium or potassium thiocyanate, as the case may be, to a neutral solution of vanadyl sulphate,  $VOSO_4$ . Their compositions are  $2NH_4SCN.VO(SCN)_2.5H_2O$  and  $2KSCN.VO(SCN)_2.5H_2O$ . Neither the corresponding sodium compound nor the free vanadyl thiocyanate,  $VO(CNS)_2$ , has been isolated,<sup>6</sup> but a violet-red *bismuth vanadyl thiocyanate*,  $2Bi(SCN)_3.3VO(SCN)_2.7H_2O$  or  $(VO)_3[Bi(SCN)_6]_2.7H_2O$ , has recently been prepared.<sup>7</sup>

Among other organic compounds of vanadium the following are known: *Vanadous acetate*,<sup>8</sup> *vanadous acetylacetonate*, *vanadous benzoyl-acetonate*,<sup>9</sup> *vanadous carbanides*,<sup>10</sup> *vanadyl acetates*,<sup>11</sup> *vanadyl acetate*,

<sup>1</sup> Wyruboff, *Ann. Chim. Phys.*, 1876, [v], 8, 444; compare Atterberg, *Ber.*, 1876, 9, 1475.

<sup>2</sup> Evans and Clarke, *Analyst*, 1928, 53, 475.

<sup>3</sup> Compare Bongiovanni, *Bolletino chimico farmaceutico*, 1910, 49, 467; *J. Chem. Soc.*, A, 1910, 98, [i], 721.

<sup>4</sup> Locke and Edwards, *loc. cit.*; Cioci, *Zeitsch. anorg. Chem.*, 1899, 19, 308.

<sup>5</sup> Scagliarini and Tartarini, *Gazzetta*, 1923, 53, 139, 876.

<sup>6</sup> Koppel and Goldmann, *Zeitsch. anorg. Chem.*, 1903, 36, 381.

<sup>7</sup> Paciello and Foa, *Gazzetta*, 1923, 53, 526.

<sup>8</sup> Meyer and Markowitz, *Zeitsch. anorg. Chem.*, 1926, 157, 211.

<sup>9</sup> Morgan and Moss, *J. Chem. Soc.*, 1913, 103, 85.

<sup>10</sup> Barbieri, *Atti R. Accad. Lincei*, 1915, [v], 24, 435.

<sup>11</sup> Morgan and Moss, *loc. cit.*; Parisi, *Gazzetta*, 1927, 57, 859.

*vanadyl oxalate, vanadyl malonates, vanadyl succinate, vanadyl salicylate,*<sup>1</sup> *alkali vanadous oxalates,*<sup>2</sup> *alkali vanadyl oxalates,*<sup>3</sup> *alkali vanadyl tartrates, alkali vanadyl salicylates,*<sup>4</sup> *alkali vanadyl citrates,*<sup>5</sup> *oxalo-vanadates,*<sup>6</sup> *citro-vanadates,*<sup>7</sup> *complex cinnamates and camphorates,*<sup>8</sup> *aceto-selenates.*<sup>9</sup>

#### VANADIUM AND SILICON.

Vanadium and silicon are miscible in all proportions in the liquid state up to 60 per cent. vanadium. The eutectic point is at 1411° C. near to the silicon end of the series, while the composition at the maximum approximates to the composition of the disilicide,  $\text{VSi}_2$ .<sup>10</sup> Two compounds of vanadium and silicon,  $\text{V}_2\text{Si}$  and  $\text{VSi}_2$ , have been prepared in the electric furnace.

**Vanadium Subsilicide,  $\text{V}_2\text{Si}$ ,** is obtained by fusing a mixture of vanadium trioxide,  $\text{V}_2\text{O}_3$ , and silicon, with the addition of either a large excess of vanadium or carbon or copper. The carbide or copper alloy produced is decomposed at the temperature employed.<sup>11</sup> The silicide forms metallic prisms, of density 5.48 at 17° C., the m.pt. of which is higher than in the case of the disilicide. It is attacked by the halogens, hydrogen chloride gas, and fused sodium or copper, but hydrochloric acid, nitric acid and sulphuric acid are without action.

**Vanadium Disilicide,  $\text{VSi}_2$ ,** is prepared by reducing a mixture of vanadium trioxide and silicon with magnesium; vanadium pentoxide can also be employed with the addition of fluorspar to the mixture.<sup>12</sup> Gin used a mixture of the pentoxide, silica, and coke.<sup>13</sup> Vanadium disilicide is a very stable compound; it forms metallic prisms which melt at 1655° C., have a specific gravity of 4.42, and are hard enough to scratch glass. It is attacked by hydrofluoric acid, hydrogen chloride gas, and fused alkalis.

Hypovanadic oxide,  $\text{VO}_2$ , and vanadium pentoxide,  $\text{V}_2\text{O}_5$ , both dissolve in hydrofluosilicic acid to yield a *vanadyl fluosilicate* and a *vanadium fluosilicate*, both of doubtful composition.<sup>14</sup>

A compound of vanadium, aluminium, and silicon is referred to on p. 28. The *molybdovanadosilicates* and *tungstovanadosilicates* are described on pp. 88 and 89.

#### VANADIUM AND BORON.

**Vanadium Boride, VB,** is prepared by fusing a mixture of the elements *in vacuo* at the temperature of the electric furnace. It is a

<sup>1</sup> Gain, *Ann. Chim. Phys.*, 1908, [viii], 14, 224; Schramm, *Zeitsch. anorg. Chem.*, 1927, 161, 231; see also Berzelius, *Pogg. Annalen*, 1831, 22, 1.

<sup>2</sup> Piccini and Brizzi, *Zeitsch. anorg. Chem.*, 1899, 19, 394; Bultemann, *Zeitsch. Elektrochem.*, 1904, 10, 141.

<sup>3</sup> Koppel and Goldmann, *Zeitsch. anorg. Chem.*, 1903, 36, 381.

<sup>4</sup> Barbieri, *Atti R. Accad. Lincei*, 1914, 23, 47, 408; Rosenheim and Mong, *Zeitsch. anorg. Chem.*, 1925, 148, 131.

<sup>5</sup> Canneri, *Gazzetta*, 1926, 56, 637, 901.

<sup>6</sup> See p. 90.

<sup>7</sup> Barbieri, *Atti R. Accad. Lincei*, 1915, [v], 24, 724.

<sup>8</sup> Scarliarini and Airoidi, *Gazzetta*, 1925, 55, 44.

<sup>9</sup> Meyer and Markowitz, *Zeitsch. anorg. Chem.*, 1926, 157, 211.

<sup>10</sup> Giebelhausen, *ibid.*, 1915, 91, 251.

<sup>11</sup> Moissan and Holt, *Ann. Chim. Phys.*, 1902, [vii], 27, 277.

<sup>12</sup> Meyer and Backa, *Zeitsch. anorg. Chem.*, 1924, 135, 177.

<sup>13</sup> Gin, *Electrochem. Met. Ind.*, 1909, 7, 264.

<sup>14</sup> Berzelius, *Pogg. Annalen*, 1824, 1, 169; 1824, 2, 210; Guyard, *Bull. Soc. chim.*, 1876, [ii], 25, 352.

hard, metallic substance, which is attacked by nitric acid, hydrofluoric acid, and fused alkali.<sup>1</sup>

A *vanadium borate* of uncertain composition is obtained by fusing a mixture of vanadium pentoxide and boric anhydride. It forms green or yellowish-green crystals which, however, undergo hydrolysis readily.<sup>2</sup> A *vanadyl borate* is also obtained by the action of borax on vanadyl sulphate solution,<sup>3</sup> and a complex *vanadium borotungstate* has been prepared.

<sup>1</sup> Wedekind, *Ber.*, 1913, 46, 1198.

<sup>2</sup> Guyard, *Bull. Soc. chim.*, 1876, [ii], 25, 350.

<sup>3</sup> Berzelius, *Pogg. Annalen*, 1831, 22, 1.



## CHAPTER IV.

### THE DETECTION AND ESTIMATION OF VANADIUM.

**Detection.**—Apart from naturally occurring ores of vanadium, vanadium steels, and ferrovanadium, the commonest compounds of vanadium are those which contain the element in the pentavalent state, viz. the pentoxide and the various vanadates. The analytical reactions usually employed are, therefore, those which apply to vanadates. Most vanadium ores can be prepared for the application of these reactions by digesting with mineral acids or by alkaline fusion with the addition of an oxidising agent. When the silica content is high, preliminary treatment with hydrofluoric acid is recommended. Vanadium steels and bronzes, and ferrovanadium, are decomposed by the methods used for other steels; the drillings are, for instance, dissolved in sulphuric acid and any insoluble carbides then taken up in nitric acid, or they are filtered off and submitted to an alkaline fusion. Compounds of lower valency are readily converted into vanadates by oxidation with bromine water, sodium peroxide, or potassium permanganate.

*Wet Tests.*—(a) When rendered faintly acid, colourless solutions of vanadates become yellow, and, with the addition of more acid, orange-red, in consequence of the formation of polyvanadates.

(b) Hydrogen sulphide, on being passed through an acidified solution of a vanadate, does not give rise to a precipitate, but a blue solution results in consequence of the formation of a vanadyl salt. Blue solutions are obtained also by the action of other reducing agents (see p. 57). This reaction is not peculiar to vanadium compounds, since salts of molybdenum also give blue solutions on being reduced. In the case of vanadium, however, by the use of zinc, cadmium or aluminium, reduction can be made to proceed still further, with the formation of a green, and finally a lavender, solution.

(c) Ammonium sulphide, on being added to a neutral solution of a vanadate, gives rise to a brownish-red solution which contains a thiovanadate. Ammonium sulphide cannot, however, be employed to separate those metals normally precipitated by this reagent, since vanadates of zinc, manganese and nickel are thrown down when the solution is rendered alkaline. When the thiovanadate solution is acidified, partial precipitation of the vanadium takes place in the form of sulphides or oxysulphides.

(d) Ammonium chloride solution has no action on the alkali vanadates, but if sufficient of the solid is added to form a saturated solution, colourless ammonium metavanadate is precipitated.

(e) Ammonium hydroxide is similarly without action on acid solutions of alkali vanadates, but if added to a vanadate solution which

contains cations of ferric iron, aluminium, chromium, uranium, barium, etc., vanadates of these metals may be precipitated. In the ordinary process of group analysis, the vanadyl salt which is present in the filtrate from the hydrogen sulphide group may undergo reoxidation to the vanadate when this filtrate is warmed with nitric acid previous to adding ammonium hydroxide for the precipitation of the hydroxides of iron, aluminium, and chromium. This oxidation can be carried to completion by boiling with hydrogen peroxide solution. For the separation of vanadium from iron and aluminium, the precipitate first produced on addition of ammonium hydroxide is redissolved in nitric acid, and the precipitation is repeated two or three times. If the precipitate is boiled with ammonium phosphate, the vanadium passes into solution and leaves the iron and aluminium in the residue. Iron can also be separated from vanadium by the addition of excess of sodium carbonate and sodium peroxide to an acidified solution of the salts, whereupon the iron is thrown out as ferric hydroxide and the vanadium remains in the filtrate as vanadate. Traces of vanadium occluded in the precipitate can be removed by dissolving the latter in the minimum quantity of nitric acid and repeating the precipitation. An alternative method for the separation of aluminium from vanadium depends on the fact that a boiling dilute solution of sodium aluminate and sodium vanadate precipitates aluminium hydroxide when it is treated with a large excess of ammonium nitrate in small quantities at a time; addition of barium chloride to the filtrate precipitates barium metavanadate.<sup>1</sup> If chromium is present it will have been oxidised to chromate by the hydrogen peroxide or sodium peroxide treatment, and will be left in solution with the vanadate after removal of iron and aluminium. In order to separate the chromium and vanadium, the acidified chromate-vanadate solution is reduced with sulphur dioxide, warmed with bromine water (which oxidises the vanadyl salt back to the vanadate without affecting the chromium salt), and then poured into a 10 per cent. solution of caustic soda. Chromium hydroxide is precipitated, while the vanadate remains in solution.<sup>2</sup> An alternative method for the separation of chromium and vanadium consists in precipitating with lead acetate; acetic acid and hydrogen peroxide are added to the vanadate-chromate solution, whereby the chromate is reduced to the chromic salt; addition of lead acetate at this stage throws down lead vanadate, the chromium salt remaining in solution.

(f) The colour change produced by the addition of hydrogen peroxide to a strongly acid solution of a vanadate constitutes the commonest qualitative test for the presence of vanadium. High concentrations of vanadium give rise to an intense reddish-brown coloration (see p. 91), while very low concentrations give a faint rose-red tint. The reaction is sufficiently delicate to detect 1 part of vanadium in 160,000.<sup>3</sup> In applying the test it is necessary to remember that chromium, titanium and iron also produce comparable colorations. In the case of chromium, however, the further addition of ether gives a blue colour, whereas the colour due to vanadium is unaffected; <sup>4</sup> addition of hydrofluoric acid

<sup>1</sup> Wenger and Vogelsson, *Helv. Chim. Acta*, 1919, 2, 550.

<sup>2</sup> Browning, *J. Amer. Chem. Soc.*, 1921, 43, 114.

<sup>3</sup> Meyer and Pawletta, *Zeitsch. anal. Chem.*, 1926, 69, 15.

<sup>4</sup> Reichard, *ibid.*, 1901, 40, 577.

or of ammonium fluoride destroys the colour due to titanium, and any yellow colour due to the presence of iron is removed by addition of phosphoric acid.

(g) Tannin yields a rich blue coloration with vanadates in concentrations down to 2 mgm. of vanadium pentoxide per litre. Gallic acid and pyrogallol also give a blue colour. Commercial ethers, which contain vinyl alcohol, give rise to a rose coloration in concentrations down to 0.1 mgm. of vanadium pentoxide per litre, or even as low as 0.02 mgm. per litre if the proportion of vinyl alcohol is increased.<sup>1</sup> "Cupferron" produces a red coloration with weak solutions of vanadium salts even when the dilution is  $10^{-6}$  mgm. per c.c.<sup>2</sup> A 0.2 per cent. aqueous solution of diphenylamine in the presence of hydrochloric acid gives a violet coloration with aqueous solutions of vanadium compounds; this colour is not affected by the presence of nitrates, titanates, or iron, and detects vanadium in a solution which contains 0.0002 per cent.<sup>3</sup> Addition of an extremely dilute solution of potassium thiocyanate and a trace of sulphuric acid gives a yellow coloration which becomes blue with further addition of sulphuric acid; this reaction is sensitive to 1 part of vanadium pentoxide in 5000.<sup>4</sup> Vanadates also give colour changes with resorcinol,<sup>5</sup> quinine,<sup>6</sup> morphine,<sup>7</sup> strychnine, phenol,<sup>8</sup> aniline,<sup>9</sup> etc., and have, therefore, been employed from time to time as analytical reagents for these organic compounds.<sup>10</sup>

(h) Solutions of vanadates which are neutral or faintly acid with acetic acid readily yield precipitates of vanadates of the heavy metals. Silver nitrate, with a carefully neutralised solution, produces a curdy, reddish-brown precipitate, soluble both in ammonium hydroxide and in nitric acid. Mercurous nitrate throws down a yellow precipitate of mercurous vanadate, which is soluble in nitric acid. Lead acetate gives a yellow precipitate, which dissolves in nitric acid and becomes white on standing. Orthovanadates can be distinguished from metavanadates by the colours of the copper salts which they throw down on the addition of copper sulphate; metavanadates yield a yellow, crystalline precipitate, while orthovanadates yield an apple-green precipitate.<sup>11</sup> These colours vary, however, with the acidity of the solution.

(i) Solutions of pyrocatechol acetate and aniline, or pyrocatechol acetate and piperazine, are sensitive micro-reagents for vanadium.<sup>12</sup>

*Dry Tests.*—(a) When strongly heated in a borax bead vanadium compounds impart a yellow coloration to the oxidising flame and a light green coloration to the reducing flame. (b) When heated in a bead of microcosmic salt in the oxidising flame, vanadium compounds impart a brownish-red coloration to the bead, which becomes orange on cooling; in the reducing flame a brownish-green colour is produced. (c) Vanadium compounds do not colour the ordinary flame.

<sup>1</sup> Matignon, *Compt. rend.*, 1904, 138, 82.

<sup>2</sup> Rodeja, *Anal. Fis. Quim.*, 1914, 12, 305.

<sup>3</sup> Meaurio, *Anal. Soc. Quim. Argentina*, 1917, 5, 185.

<sup>4</sup> Ellram, *Chem. Zentr.*, 1896, [ii], 211.

<sup>5</sup> Lévy, *Compt. rend.*, 1886, 103, 1195.

<sup>6</sup> von Klecki, *Zeitsch. anorg. Chem.*, 1894, 5, 374.

<sup>7</sup> Reichard, *Zeitsch. anal. Chem.*, 1903, 42, 95, 293.

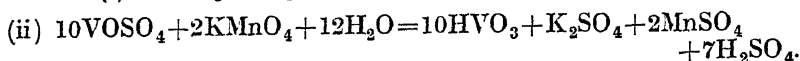
<sup>8</sup> Truchot, *Ann. Chim. anal.*, 1902, 7, 167.

<sup>9</sup> Laar, *Ber.*, 1882, 15, 2086.

<sup>10</sup> Mandelin, *Zeitsch. anal. Chem.*, 1884, 23, 235; Dragendorff and Johannson, *Jahresber.*, 1884, 1646; Reichard, *loc. cit.*

<sup>11</sup> Roscoe, *J. Chem. Soc.*, 1871, 24, 31. <sup>12</sup> Martini, *British Chem. Abs.*, A, 1926, 1244.

**Estimation of Vanadium.**<sup>1</sup>—*Volumetric Methods.*—The most convenient and the usual method for the estimation of vanadium is a volumetric process. The vanadium is first obtained in acid solution as vanadate, and reduced to the tetravalent state by one of several reducing agents which are available. The solution is then titrated in the presence of sulphuric acid with hot potassium permanganate solution, which quantitatively oxidises the lower vanadium salt to the vanadate. Using sulphur dioxide to effect the reduction, the following reactions take place :—



Excess of sulphur dioxide is removed before the titration by boiling the reduced solution in an atmosphere of carbon dioxide.<sup>2</sup> Hydrogen sulphide can be used in place of sulphur dioxide and gives slightly higher results; excess is removed in the same manner by boiling, and the precipitated sulphur is removed before titrating.<sup>3</sup> Hydrogen peroxide, when added in small proportions to a concentrated sulphuric acid solution of a pentavalent vanadium salt, also brings about reduction to the tetravalent state; excess of the hydrogen peroxide is decomposed catalytically by the vanadyl sulphate formed.<sup>4</sup> Other reducing agents which have been employed are bismuth amalgam,<sup>5</sup> mercury,<sup>6</sup> sodium thiosulphate,<sup>7</sup> concentrated hydrochloric acid,<sup>8</sup> and electrolytic methods.<sup>9</sup> The use of hydrochloric acid has not always given good results in the hands of different chemists, since reduction has a tendency to proceed lower than the tetravalent stage;<sup>10</sup> the use of alcohol and hydrochloric acid has been recommended.<sup>11</sup>

The estimation of a vanadate solution by direct titration with ferrous sulphate or ferrous ammonium sulphate solution has been worked out, and is found to be specially applicable to the analysis of vanadium alloys. The vanadate is again reduced to the tetravalent state by the ferrous salt, the end point being obtained by the use of potassium ferricyanide as internal indicator; alternatively, a known excess of the ferrous salt solution is added to the vanadate, the amount unused

<sup>1</sup> The bibliography on the estimation of vanadium up to the year 1901 is given by Brearley, *Chem. News*, 1901, 83, 163.

<sup>2</sup> Gerland, *Ber.*, 1877, 10, 1513, 1516; Holverscheid, *Dissertation* (Berlin, 1890); Hillebrand, *J. Amer. Chem. Soc.*, 1898, 20, 461; Cain, *J. Ind. Eng. Chem.*, 1911, 3, 476.

<sup>3</sup> Koenig, *Stahl und Eisen*, 1914, 34, 405; Lundell and Knowles, *J. Amer. Chem. Soc.*, 1921, 43, 1560.

<sup>4</sup> Cain and Hostetter, *ibid.*, 1912, 34, 274; Hothersall, *J. Soc. Chem. Ind.*, 1924, 43, 270.

<sup>5</sup> Someya, *Zeitsch. anorg. Chem.*, 1926, 152, 368.

<sup>6</sup> McCay and Anderson, *J. Amer. Chem. Soc.*, 1922, 44, 1018.

<sup>7</sup> Oberhelman, *Amer. J. Sci.*, 1915, [iv], 39, 530.

<sup>8</sup> Gooch and Stookey, *ibid.*, 1902, [iv], 14, 369; Campagne, *Ber.*, 1903, 36, 3164; Cain, *J. Ind. Eng. Chem.*, 1911, 3, 476.

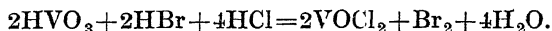
<sup>9</sup> Bleecker, *Met. Chem. Eng.*, 1911, 9, 211; Gooch and Scott, *Amer. J. Sci.*, 1918, [iv], 46, 427.

<sup>10</sup> Compare Rosenheim, *Annalen*, 1889, 251, 197; Holverscheid, *loc. cit.*; Auchy, *J. Ind. Eng. Chem.*, 1909, 1, 455; Wilms and Fischbach, *Stahl und Eisen*, 1914, 34, 417; Hartmann, *Zeitsch. anal. Chem.*, 1925, 66, 16.

<sup>11</sup> Müller and Diefenthaler, *Zeitsch. anorg. Chem.*, 1911, 71, 243; Wegelin, *Zeitsch. anal. Chem.*, 1914, 53, 81.

being titrated with potassium dichromate.<sup>1</sup> This method facilitates the rapid estimation of vanadium in the presence of chromium. Knop's indicator (diphenylamine in sulphuric acid) has recently been successfully employed.<sup>2</sup>

Vanadium lends itself also to *iodometric methods* of determination. The vanadate solution is reduced with hydrobromic acid, excess of potassium iodide is added, and the iodine thereupon liberated is estimated with sodium thiosulphate solution. The reaction is :<sup>3</sup>



This method is also available for the estimation of vanadium and chromium together in solution.<sup>4</sup> The use of hydriodic acid as the reducing agent gives rise to inconsistent results, as reduction does not stop at the tetravalent stage, but may proceed also to the trivalent stage, according to the experimental conditions.<sup>5</sup> The care necessary in the application of iodometric methods renders it unlikely that they will come into general use.<sup>6</sup>

Treadwell<sup>7</sup> has recently shown that vanadium in acid solution is reduced quantitatively to the divalent state by electrolytically deposited cadmium, zinc amalgam, or lead amalgam, if air is carefully excluded; the reduced solution is run into excess of potassium permanganate and titrated with oxalic acid, or it may be oxidised to the tetravalent state by the addition of excess of copper sulphate solution and then titrated with potassium dichromate, using diphenylamine as indicator. A modification of this procedure consists in running the acidified vanadate solution through a Jones reductor which contains amalgamated zinc into an excess of ferric alum solution; the quantity of ferric salt thereby reduced is determined by back titration with potassium permanganate.<sup>8</sup>

Other volumetric processes which have been worked out include the use of potassium ferrocyanide,<sup>9</sup> potassium ferricyanide,<sup>10</sup> titanous chloride,<sup>11</sup> and stannous chloride.<sup>12</sup> According to Rosenheim and Yang,<sup>13</sup> vanadium pentoxide is best determined in solution by addition of excess of caustic soda and back titration with sulphuric acid at 100° C., using  $\alpha$ -naphthophthalein as indicator.

The application of any of the foregoing processes involves the previous

<sup>1</sup> Williams, *J. Soc. Chem. Ind.*, 1902, 21, 389; Clark, *Met. Chem. Eng.*, 1913, 11, 195; Etheridge, *Analyst*, 1923, 48, 588.

<sup>2</sup> Someya, *Zeitsch. anorg. Chem.*, 1924, 139, 237; Russell, *J. Soc. Chem. Ind.*, 1926, 45, 57.

<sup>3</sup> Gooch and Curtis, *Amer. J. Sci.*, 1904, [iv], 17, 41.

<sup>4</sup> Edgar, *ibid.*, 1908, [iv], 26, 333.

<sup>5</sup> Ditte, *Compt. rend.*, 1886, 102, 1310; Gooch and Curtis, *loc. cit.*; Edgar, *J. Amer. Chem. Soc.*, 1916, 38, 2369; Wegelin, *Zeitsch. anal. Chem.*, 1914, 53, 80; Ditz and Bardach, *Zeitsch. anorg. Chem.*, 1915, 93, 97; Stoppel, Sidener, and Brinton, *J. Amer. Chem. Soc.*, 1924, 46, 2448; Heczko, *Zeitsch. anal. Chem.*, 1926, 68, 461.

<sup>6</sup> Compare Heczko, *loc. cit.*; Ramsey, *J. Amer. Chem. Soc.*, 1927, 49, 1138.

<sup>7</sup> Treadwell, *Helv. Chim. Acta*, 1921, 4, 563; 1922, 5, 739.

<sup>8</sup> Nakazono, *J. Chem. Soc. Japan*, 1921, 42, 761; see also Someya, *Zeitsch. anorg. Chem.*, 1927, 163, 206.

<sup>9</sup> Müller and Diefenthaler, *Zeitsch. anal. Chem.*, 1912, 51, 21.

<sup>10</sup> Palmer, *Amer. J. Sci.*, 1910, [iv], 30, 141.

<sup>11</sup> Atack, *Analyst*, 1913, 38, 99.

<sup>12</sup> Warinski and Mdivani, *Bull. Soc. chim.*, 1908, [iv], 3, 626.

<sup>13</sup> Rosenheim and Yang, *Zeitsch. anorg. Chem.*, 1923, 129, 181.

separation of other elements which may interfere. For details of these the reader is referred to standard works on analysis.<sup>1</sup>

*Electrometric Methods* have been applied for the estimation of vanadium alone and alloyed with other metals, e.g. iron, chromium, uranium. The reduced solution is either gradually oxidised by means of a suitable oxidising agent (potassium permanganate, ammonium persulphate, nitric acid), or the vanadate solution is gradually reduced with ferrous sulphate solution; the changes in the E.M.F. of a suitable cell indicate the end point.<sup>2</sup>

*Colorimetric Methods* are used only for the estimation of very small percentages of vanadium, e.g. in vanadium steels and alloys. The most important depend on the intensity of the reddish-brown colour produced by the action of hydrogen peroxide on an acid vanadate solution.<sup>3</sup> If chromium is present, an equal amount must be introduced into the standard vanadium solution under the same conditions of temperature, acid concentration, etc. Phosphoric acid is added to destroy any yellow colour due to ferric iron, and either hydrofluoric acid or ammonium fluoride to destroy any colour produced by titanium.<sup>4</sup> A colorimetric method for the simultaneous estimation of small quantities of titanium and vanadium has also been worked out.<sup>5</sup> Other colorimetric processes are based on (a) the formation of a yellow to black coloration, due to aniline black, in the presence of aniline hydrochloride and potassium chlorate or other oxidising agent,<sup>6</sup> and (b) the orange coloration finally produced when an acid solution of a vanadate is brought into contact with strychnine sulphate.<sup>7</sup>

*Electrolytic Method.*—Truchot<sup>8</sup> has developed an electrolytic process for the estimation of small quantities of vanadium in solution as vanadate; the solution is rendered faintly alkaline with ammonium hydroxide, and on passing the electric current a lower oxide is deposited, which is collected, converted to the pentoxide by heating in air, and weighed.

*Arc Spectrum.*—Vanadium has been estimated in ores with fair accuracy by comparative measurement of the intensity of the lines in the arc spectrum.<sup>9</sup>

*Gravimetric Methods.*—The vanadium compound is converted into sodium vanadate by fusion or other method, and after separation from other salts (e.g. arsenate, molybdate, phosphate, chromate, tungstate) is precipitated from nearly neutral solution either as (a) mercurous vanadate or (b) basic lead vanadate. In (a), mercurous

<sup>1</sup> See also, for a particularly good account, *Analytical Methods for Certain Metals*, Bulletin 212, 1923, Bureau of Mines, Washington.

<sup>2</sup> Kelley and Conant, *J. Amer. Chem. Soc.*, 1916, 38, 341; Kelley, Wiley, Bohn, and Wright, *J. Ind. Eng. Chem.*, 1921, 13, 939; Gustavson and Knudson, *J. Amer. Chem. Soc.*, 1922, 44, 2756; Müller and Just, *Zeitsch. anorg. Chem.*, 1922, 125, 155; Muller and Flath, *Zeitsch. Elektrochem.*, 1923, 29, 500; Willard and Fenwick, *J. Amer. Chem. Soc.*, 1923, 45, 84; Kolthoff and Tomicek, *Rec. Trav. chim.*, 1924, 43, 447.

<sup>3</sup> Meyer and Pawletta, *Zeitsch. anal. Chem.*, 1926, 69, 15.

<sup>4</sup> Slavik, *Chem. Zeit.*, 1910, 34, 648; Pickard, *Chem. World*, 1914, 2, 341; Fenner, *Chem. Zeit.*, 1918, 42, 403; McCabe, *Chem. News*, 1911, 104, 194; *J. Ind. Eng. Chem.*, 1913, 5, 736; Georges, *Bull. de Belg.*, 1922, 31, 123; Kropf, *Zeitsch. angew. Chem.*, 1922, 35, 366; Meyer and Pawletta, *Zeitsch. anal. Chem.*, 1926, 69, 15.

<sup>5</sup> Mellor, *Trans. Eng. Ceram. Soc.*, 1913, [i], 12, 33.

<sup>6</sup> Witz and Osmond, *Bull. Soc. chim.*, 1886, [ii], 45, 309; McAdam, *J. Amer. Chem. Soc.*, 1910, 32, 1611.

<sup>7</sup> Gregory, *Chem. News*, 1909, 100, 221. <sup>8</sup> Truchot, *Ann. Chim. anal.*, 1902, 7, 165.

<sup>9</sup> Porlezza and Donati, *ibid.*, 1926, 16, 519; 1927, 17, 3.

nitrate solution is added to the vanadate solution drop by drop until no further precipitation takes place; the mercurous vanadate so obtained is heated under a hood, whereupon the mercury is volatilised; the residue of pure vanadium pentoxide is weighed; hydrochloric acid should not be present.<sup>1</sup> The results have a tendency to be high.<sup>2</sup> In (b), lead acetate solution is added to a solution of the vanadate rendered faintly acid with acetic acid, whereupon all the vanadium is precipitated as a basic lead vanadate of variable composition. The precipitate is dissolved in nitric acid, the lead removed by boiling with sulphuric acid, and the filtrate, which contains vanadic acid, is then either evaporated to dryness and the residue weighed as  $V_2O_5$ , or the vanadic acid in it is estimated by a volumetric process.<sup>3</sup> For the application of either of these methods, the removal of arsenic is effected by reducing the acidified solution of vanadate and arsenate with sulphur dioxide; the arsenic is then precipitated as sulphide with hydrogen sulphide, and the vanadium which remains in solution as the vanadyl salt is reoxidised to the vanadate for estimation. Molybdenum is separated by a similar process, except that the hydrogen sulphide is used under pressure.<sup>4</sup> For the estimation of vanadium in the presence of a phosphate, mercury vanadate and phosphate are precipitated together, ignited, and the residue of vanadium pentoxide, after being weighed, converted into sodium vanadate and phosphate by fusion with sodium carbonate. The vanadate is converted into the vanadyl salt by reduction with sulphur dioxide and the phosphate determined by means of ammonium molybdate. Deduction of the equivalent quantity of phosphorus pentoxide from the weight of mixed oxides gives the vanadium content.

A general method for the separation of vanadium from arsenic, molybdenum, phosphorus, chromium, uranium, tungsten, and silicon, consists in precipitating these metals as their respective lead salts and digesting the precipitate with potassium carbonate, whereupon all the lead salts are decomposed with the exception of the lead vanadate.<sup>5</sup>

The gravimetric estimation of vanadium in alkaline vanadate solutions has also been effected by precipitating as ammonium metavanadate in the presence of ammonium chloride.<sup>6</sup> Precipitation is incomplete, however, unless the solution is quite saturated with ammonium chloride;<sup>7</sup> the addition of alcohol is recommended.<sup>8</sup> Other gravimetric processes which have been investigated include the precipitation of barium pyrovanadate,<sup>9</sup> precipitation of silver metavanadate,<sup>10</sup> precipitation of manganese pyrovanadate,<sup>11</sup> and the use of cupferron.<sup>12</sup>

<sup>1</sup> Auerbach and Lange, *Zeitsch. angew. Chem.*, 1912, 25, 2522.

<sup>2</sup> Bleecker, *Met. Chem. Eng.*, 1911, 9, 213.

<sup>3</sup> Roscoe, *Annalen, Suppl.*, 1872, 3, 102; Cormimbœuf, *Ann. Chim. anal.*, 1902, 7, 258.

<sup>4</sup> Stoppel, Sidener, and Brinton, *Chem. News*, 1925, 130, 353.

<sup>5</sup> Fischer, *Dissertation* (Rostock, 1894).

<sup>6</sup> von Hauer, *J. prakt. Chem.*, 1856, 69, 388; Ditte, *Compt. rend.*, 1887, 104, 982; Rosenheim, *Zeitsch. anorg. Chem.*, 1902, 32, 181.

<sup>7</sup> Gooch and Gilbert, *Amer. J. Sci.*, 1902, [iv], 14, 205.

<sup>8</sup> Beard, *Ann. Chim. anal.*, 1905, 10, 41.

<sup>9</sup> Carnot, *Compt. rend.*, 1887, 104, 1803.

<sup>10</sup> Browning and Palmer, *Amer. J. Sci.*, 1910, [iv], 30, 220.

<sup>11</sup> Carnot, *Compt. rend.*, 1887, 104, 1844.

<sup>12</sup> Turner, *Amer. J. Sci.*, 1916, 42, 109; Rolla and Nuti, *J. Chem. Soc., Abs.*, 1921, 20, [ii], 597; Clarke, *Analyst*, 1927, 52, 466.

The analysis of vanadium steels is effected by the application of one of the foregoing methods. Blank determinations on a steel free from vanadium but otherwise of the same approximate composition are used as a control. Iron and molybdenum are removed from hydrochloric acid solution by Rothe's ether separation method;<sup>1</sup> chromium, nickel, copper, etc., are then precipitated as hydroxides by caustic soda, the filtrate containing the vanadium as vanadate.<sup>2</sup> The method is modified for the simultaneous estimation of both vanadium and chromium in a vanadium-chromium steel.<sup>3</sup>

<sup>1</sup> Rothe, *Zeitsch. anal. Chem.*, 1901, 40, 809; Deiss and Leysakt, *Chem. Zett.*, 1911, 35, 869, 878.

<sup>2</sup> Blair, *J. Amer. Chem. Soc.*, 1908, 30, 1229; compare Dougherty, *J. Ind. Eng. Chem.*, 1915, 7, 419; Demorest, *ibid.*, 1912, 4, 249.

<sup>3</sup> Campagne, *Bull. Soc. chim.*, 1904, 31, 962; Edgar, *Amer. J. Sci.*, 1908, [iv], 26, 333; Palmer, *ibid.*, 1910, [iv], 30, 141; Cain, *J. Ind. Eng. Chem.*, 1911, 3, 476.



## CHAPTER V.

### NIOBIUM<sup>1</sup> AND TANTALUM.

#### THEIR OCCURRENCE, HISTORY, EXTRACTION, ESTIMATION, AND DETECTION.

**Occurrence.**—Niobium is almost always associated with tantalum in its natural ores, so that it will be convenient to consider the occurrence of both these elements together. There are very few niobium-bearing minerals which are free from tantalum and *vice versa*.

Niobium and tantalum do not occur naturally in the free state to any extent; native tantalum containing small amounts of nickel has, however, been found in the gold washings from the Ural and Altai Mountains.<sup>2</sup> The metals are found mainly as negative radicals in minerals in which the oxides of iron, manganese, calcium, and various rare earth metals, for example yttrium, thorium, lanthanum, cerium and uranium, form the bases. Titanium, zirconium and tin, as well as other rare earth metals, are also frequently present. The minerals are numerous, and are very generally distributed in small quantities over the earth—niobium in apparently greater quantity than tantalum. The largest deposits have been found in North America, Greenland, Finland, Sweden, the Ural Mountains, Bavaria, and Australia.

The most important ores are described below, and tables showing typical analyses are appended.<sup>3</sup>

*Niobites (or Columbites) and Tantalites.*—These are mainly ferrous salts of metaniobic acid and metatantallic acid in which the iron is more or less replaced by manganese. They can be generally formulated  $\text{Fe}(\text{Mn})(\text{NbO}_3)_2$  and  $\text{Fe}(\text{Mn})(\text{TaO}_3)_2$ , *i.e.* the salts present are *niobates* and *tantalates* (see pp. 160 and 200). If the niobium is in excess they are called *niobites* (or *columbites*), and if the tantalum is in excess they are called *tantalites*. There is no definite line of demarcation between the two classes. *Tapiolite* contains only iron salts. Tin and tungsten are also frequently present in small amounts, and some samples of *niobites* have recently been found to contain the two higher homologues of man-

<sup>1</sup> Niobium is also known as *columbium*. The latter name has always been preferred in America, and is retained, no doubt, out of patriotism. In England the name *columbium* was employed by the Chemical Society from 1904 to 1923 inclusive; in 1924 the name *niobium* was readopted. On the Continent the element has been more consistently referred to by the various translations of *niobium*.

<sup>2</sup> Dana, *Text Book of Mineralogy*, 3rd ed. (New York, 1850), p. 350; Walther, *Nature*, 1909, 81, 335; von John, *ibid.*, 1910, 83, 398.

<sup>3</sup> Schilling, *Zeitsch. angew. Chem.*, 1905, 18, 883. All analyses of minerals containing tantalum previously published are here collected by Schilling. The densities, percentages of niobium and tantalum present, the localities in which the minerals occur, and the references to the literature, are tabulated.

## ANALYSES OF NIOBITES OR COLUMBITES.

SOURCE . .	Norway.	Massachusetts.	Greenland.	South Dakota.
DENSITY .	5.32	6.15	5.395	5.201
AUTHORITY .	Brögger. <sup>1</sup>	Blomstrand. <sup>2</sup>	Blomstrand. <sup>2</sup>	Headdden. <sup>3</sup>
	Per cent.	Per cent.	Per cent.	Per cent.
Nb <sub>2</sub> O <sub>5</sub>	72.37	51.53	77.97	68.00
Ta <sub>2</sub> O <sub>5</sub>	5.26	28.55	..	9.88
WO <sub>3</sub>	..	0.76	0.13	} 0.88
SnO <sub>2</sub>	0.67	0.34	0.73	
FeO	15.04	13.54	17.33	5.45
MnO	5.97	4.55	3.28	14.79
ZrO <sub>2</sub>	..	0.34	0.13	TiO <sub>2</sub> :—0.53
MgO	..	0.42	0.23	..
CaO	0.58	..	PbO :—0.12	..
H <sub>2</sub> O	..	0.16	..	..
Totals	99.89 <sup>4</sup>	100.19 <sup>4</sup>	99.92 <sup>4</sup>	99.53

ganese, *masurium* and *rhenium*.<sup>5</sup> Niobites and tantalites are usually found in igneous rocks, and are not uncommon as constituents of cassiterite-bearing *pegmatite* veins. Their chief localities are the Black Hills of South Dakota, U.S.A., Greenbushes and Wodgina in Western Australia, and on the Finnis River near Port Darwin in Northern Australia, from all of which regions tantalites for industrial use have been obtained, although, in consequence of the restricted demand, the total output has been small and irregular. Single masses of niobite weighing up to 2000 lb. have been discovered in the granite veins in the Black Hills of South Dakota, while at Wodgina the tantalite occurs in crystalline masses weighing up to about 550 lb. It is collected from the surface soil of the neighbouring alluvial deposits or by quarrying the *pegmatite*. Most native niobites and tantalites offer considerable resistance to chemical change, and as they are both hard and tough, they occur frequently in detrital deposits. These are, however, usually overlooked unless they happen to be worked for gold or tin.<sup>6</sup>

Other places where ores are known to occur are Greenland, Bavaria, Finland, Miask in the Ural Mountains, Chanteloube near Limoges in France, California, and Colorado. For recent observations of their occurrence in the British Empire see the references cited.<sup>7</sup>

<sup>1</sup> Brögger, *J. Chem. Soc., Abs.*, 1907, ii, 92, 885.

<sup>2</sup> Blomstrand, *J. prakt. Chem.*, 1866, 99, 44.

<sup>3</sup> Headdden, *Amer. J. Sci.*, 1922, [v], 3, 296; see also *J. Chem. Soc., Abs.*, 1906, [ii], 90, 37.

<sup>4</sup> The absence of titanium from these ores is remarkable.

<sup>5</sup> Noddack and Tacke, *Oesterr. Chem. Zeit.*, 1925, 28, 127; Noddack and Noddack, *Zeitsch. physikal. Chem.*, 1927, 125, 264.

<sup>6</sup> Simpson, *Chem. News*, 1909, 99, 49.

<sup>7</sup> Rhodesia: Zealley, *Nature*, 1918, 101, 174. South Africa: Rogers, *Trans. Geol. Soc. S. Africa*, 1916, 18, 5; Reuning, *Zeitsch. Kryst. Min.*, 1923, 58, 455. India: Tipper, *Rec. Geol. Survey India*, 1919, 50, 255. Canada: Ellsworth, *Can. Dept. Mines, Summary Report*, 1923, C, 1, 6. Australia: Simpson, *loc. cit.*

ANALYSES OF TANTALITES.

SOURCE .	Australia.		America.	Sweden.	South Dakota.
DENSITY .	7.03	..	..	6.08	7.190
AUTHORITY	Simpson. <sup>1</sup>	Weiss and Landecker. <sup>2</sup>	Weiss and Landecker. <sup>2</sup>	Rammelsberg. <sup>3</sup>	Headden. <sup>4</sup>
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Ta <sub>2</sub> O <sub>5</sub>	68.65	65.67	49.57	42.15	77.23
Nb <sub>2</sub> O <sub>5</sub>	15.11	9.15	20.12	40.21	5.18
TiO <sub>2</sub>	0.40	6.20	6.53	..	1.38
SnO <sub>2</sub>	0.48	0.17	0.37	0.18	0.32
MnO	14.15	4.78	19.86	1.07	0.42
FeO	1.63	12.32	3.11	16.00	14.84
MgO	0.15	..	Al <sub>2</sub> O <sub>3</sub> :—1.65	..	..
CaO	trace	1.32	1.47	trace	..
Totals	100.57	99.61	102.68	99.61 <sup>5</sup>	99.37

The natural niobites and tantalites are usually black, and form isomorphous, prismatic crystals, belonging to the rhombic system. They are easily fusible and very brittle, presenting an uneven fracture. Their density increases from 5.2 to 8.2 with increase in tantalum content.<sup>6</sup> When heated to redness *in vacuo* they evolve small quantities of gas, which consists of carbon dioxide, nitrogen and oxygen.<sup>7</sup> Small quantities of helium have also been found occluded in them.

*Pyrochlore*.—This is a crude calcium niobate which may also contain appreciable quantities of titanium, thorium and cerium, together with smaller quantities of iron, magnesium, the alkali metals, and fluorine. It does not contain chlorine, and it is of interest in that some specimens are remarkably free from tantalum. It occurs in Norway and near Miask in the Ural Mountains. The ore is brown, forms regular octa-

<sup>1</sup> Simpson, *Chem. News*, 1909, 99, 77. This ore occurs at Wodgina in the Pilbara Goldfield in the north of Western Australia, and is shipped to Europe in the quantities required for the extraction of its tantalum.

<sup>2</sup> Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 65; *Chem. News*, 1910, 101, 28.

<sup>3</sup> Rammelsberg, *Pogg. Annalen*, 1871, 144, 65; *Chem. News*, 1871, 23, 60, 71, 286; 1871, 24, 275.

<sup>4</sup> Headden, *Amer. J. Sci.*, 1922, [v], 3, 296; see also Shibata and Kimura, *J. Chem. Soc. Japan*, 1921, 42, 957; *J. Chem. Soc., Abs.*, 1922, 122, ii, 220.

<sup>5</sup> The absence of titanium from this ore is remarkable.

<sup>6</sup> Mügge, *Centr. Min.*, 1924, 417; Walker and Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1923, No. 16; *Zeitsch. Kryst. Min.*, 1925, 61, 353; Headden, *Amer. J. Sci.*, 1922, [v], 3, 393; Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 65; *Chem. News*, 1910, 101, 28; Foote and Langley, *Amer. J. Sci.*, 1910, [iv.], 30, 393; Weinland and Herz, *Zeitsch. anorg. Chem.*, 1907, 54, 230; Brögger, *loc. cit.*; Hall and Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 177; *Chem. News*, 1905, 92, 220; Hall, *J. Amer. Chem. Soc.*, 1904, 26, 1235; Tschernik, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 684; *J. Chem. Soc., Abs.*, 1903, ii, 84, 157; Dana, *A System of Mineralogy* (Chapman and Hall, London), 1899, 6th ed., pp. 731 *et seq.*

<sup>7</sup> Chabrié and Levallois, *Compt. rend.*, 1906, 143, 680.

hedra, is brittle, and presents a conchoidal fracture. Its density varies from 4.2 to 4.5.<sup>1</sup>

*Niobates and Tantalates of the Rare Earth Metals.*—These are of importance for their rare earth content rather than for their niobium and tantalum. Examples are :

*Yttrotantalite*, which is found at Ytterby and other parts of Sweden, and in Norway. It is richer in tantalum than in niobium, and contains considerable proportions of yttrium, erbium, cerium, and uranium, together with calcium, iron, etc.<sup>2</sup> Tungstates and stannates are also present.

*Fergusonite*.—This ore is also found at Ytterby (Sweden), and in Norway, Greenland, Texas, South Africa and Ceylon. Its composition is comparable to that of yttrotantalite, except that the niobium content is usually greater than that of the tantalum, and lanthanum is also found in the basic portion. According to Rammelsberg,<sup>3</sup> fergusonite from Greenland consists of isomorphous mixtures of yttrium meta-niobate,  $Y_2O_3 \cdot Nb_2O_5$ , and yttrium metatantalate,  $Y_2O_3 \cdot Ta_2O_5$ . It forms brown or black tetragonal crystals, the density of which varies from 4.3 to 5.8.<sup>4</sup> It is radioactive, and glows suddenly with evolution of helium when heated from 500° to 600° C.

*Samarските* occurs in the Ural Mountains, Mitchell County (North Carolina, U.S.A.), Canada, and India. The tantalum content is often small, sometimes *nil*, and the rare earth oxides, chiefly yttria and ceria, are usually present in considerable number and proportions. The ore is radioactive and contains helium. It forms black, orthorhombic crystals. The density varies from 4.2 to 6.2.<sup>5</sup> It has been suggested that the niobium and tantalum are disintegration products of compounds of yttrium and cerium with the two higher homologues of manganese,<sup>6</sup> *masurium*, and *rhenium*.

*Euaxenite*, *aceschynite*,<sup>7</sup> and *polycrase* are found in Norway, and differ in composition from samarskite in that they usually contain considerable quantities of titanium. Tantalum is not always present.<sup>8</sup>

*Wöhlerite* is a niobate of calcium, iron, manganese, sodium, etc., associated with considerable quantities of zirconia and silica. It is found in Norway.<sup>9</sup> Other silicates which contain niobium or tantalum are *strüverite*<sup>10</sup> and *ilmenorutile*.<sup>11</sup>

Tin and tungsten minerals frequently contain small proportions of

<sup>1</sup> Rammelsberg, *Pogg. Annalen*, 1871, 144, 191; 1873, 150, 198; Weidmann, *Jahrb. Miner.*, 1909, [i], 226; Tschernik, *Zeitsch. Kryst. Min.*, 1904, 39, 624; *J. Russ. Phys. Chem. Soc.*, 1904, 36, 712.

<sup>2</sup> Rammelsberg, *loc. cit.*; *Chem. News*, 1872, 26, 265; Tschernik, *J. Chem. Soc., Abs.*, 1913, ii, 104, 970.

<sup>3</sup> Rammelsberg, *Pogg. Annalen*, 1873, 150, 198.

<sup>4</sup> Schilling, *Zeitsch. angew. Chem.*, 1905, 18, 883; Lacroix, *Zeitsch. Kryst. Min.*, 1911, 49, 316; Krusch, *J. prakt. Geol.*, 1911, 19, 83.

<sup>5</sup> Dana, *loc. cit.*, p. 738; Tschernik, *Zeitsch. Kryst. Min.*, 1904, 39, 627; Smith, *Chem. News*, 1883, 48, 13, 29; Lacroix, *Compt. rend.*, 1911, 152, 559.

<sup>6</sup> von Oefele, *Pharmaceutische Zentralhalle*, 1916, 57, 83.

<sup>7</sup> Tschernik, *J. Chem. Soc., Abs.*, 1908, ii, 94, 399.

<sup>8</sup> Miller and Knight, *Amer. J. Sci.*, 1917, [iv], 44, 243; Hofmann, *Ber.*, 1910, 43, 2632; Hauser and Wirth, *ibid.*, 1909, 42, 4443; 1910, 43, 1807; Lange, *Zeitsch. Naturwiss. Halle*, 1910, 82; *J. Chem. Soc., Abs.*, 1911, ii, 100, 499; Lacroix, *Bull. Soc. franç. Min.*, 1910, 33, 321; 1913, 35, 233; Brogger, *loc. cit.*; Dana, *loc. cit.*, p. 742.

<sup>9</sup> Tschernik, *J. Chem. Soc., Abs.*, 1909, ii, 96, 1028; Dana, *loc. cit.*, p. 376.

<sup>10</sup> Hess and Wells, *Amer. J. Sci.*, 1911, [iv], 31, 432; Crook and Johnstone, *Min. Mag.*, 1912, 16, 224; Zambonini and Prior, *ibid.*, 1908, 15, 78; *J. Chem. Soc., Abs.*, 1908, ii, 94, 398; 1907, ii, 92, 364.

<sup>11</sup> Zambonini and Prior, *loc. cit.*; *Jahrb. Miner.*, 1909, [i], 175; Brogger, *loc. cit.*

niobium and tantalum, which are also occasionally associated naturally with *cryolite* and *pitchblende*.

ANALYSES OF PYROCHLORE, YTTROTANTALITE, FERGUSONITE, AND SAMARSKITE.

	Pyrochlore.	Pyrochlore.	Yttrotantalite	Fergusonite.	Samarskite.
SOURCE .	Scandinavia.	Scandinavia.	Norway.	Norway.	Madagascar.
DENSITY .	4.23	4.955	5.92	4.97	4.20
AUTHORITY	Rammelsberg. <sup>1</sup>	Tschernik. <sup>2</sup>	Brögger. <sup>3</sup>	Brögger. <sup>4</sup>	Lacroix. <sup>5</sup>
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Nb <sub>2</sub> O <sub>5</sub>	47.13	30.70	20.38	39.30	43.60
Ta <sub>2</sub> O <sub>5</sub>	..	33.03	39.53	6.25	11.15
WO <sub>3</sub>	..	..	0.66	..	..
SiO <sub>2</sub>	..	..	0.96	1.44	..
TiO <sub>2</sub>	13.52	9.11	1.67	..	1.42
SnO <sub>2</sub>	..	..	1.20	0.98	..
ZrO <sub>2</sub>	..	4.65	0.57	trace	..
ThO <sub>2</sub>	..	trace	0.67	2.51	1.05
UO <sub>2</sub>	..	..	3.85	4.68	8.70
Cc <sub>2</sub> O <sub>3</sub>	7.30	5.90	0.42	0.72	..
"Di" <sub>2</sub> O <sub>3</sub>	..	..	..	..	..
La <sub>2</sub> O <sub>3</sub>	..	..	1.71	2.25	4.05
Y <sub>2</sub> O <sub>3</sub>	..	0.46	12.48	..	..
Er <sub>2</sub> O <sub>3</sub>	..	..	3.58	35.03	9.50
Al <sub>2</sub> O <sub>3</sub>	..	..	..	..	0.80
FeO	10.03	..	7.48	0.78	5.40
MnO	..	..	1.85	0.15	..
MgO	0.19	trace	0.15	0.05	..
BeO	..	..	0.35	0.40	..
CaO	15.94	10.62	1.28	1.23	2.43
Na <sub>2</sub> O	3.12	2.35	0.57	..	..
H <sub>2</sub> O	..	1.37	0.51	4.00	11.14
F	2.90	2.17	..	..	..
Totals	100.13	100.36	99.87	99.77	99.24

<sup>1</sup> Rammelsberg, *Pogg. Annalen*, 1871, 144, 191; 1873, 150, 198; *Chem. News*, 1872, 26, 265.

<sup>2</sup> Tschernik, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 712; *J. Chem. Soc., Abs.*, 1904, ii, 86, 620; see also Tschernik, *ibid.*, 1909, ii, 96, 411.

<sup>3</sup> Brögger, *ibid.*, 1907, ii, 92, 884; see also Rammelsberg, *loc. cit.*

<sup>4</sup> Brögger, *loc. cit.*; see also Rammelsberg, *loc. cit.*; Tschernik, *Zeitsch. Kryst. Min.*, 1904, 39, 625; Shibata and Kimura, *J. Chem. Soc., Abs.*, 1921, ii, 120, 269; Sató, *ibid.*, 1926, A, 934; Kimura, *ibid.*, 1926, A, 144.

<sup>5</sup> Lacroix, *Compt. rend.*, 1911, 152, 559; see also Brögger, *loc. cit.*; J. L. Smith, *Amer. J. Sci.*, 1877, 13, 360; *Chem. News*, 1883, 48, 13, 29; 1885, 51, 289, 304; Donald, *ibid.*, 1884, 49, 259; Roscoe, *J. Chem. Soc.*, 1882, 41, 277; Gibbs, *Amer. Chem. J.*, 1893, 15, 546.

**History.**—The discovery of niobium is intimately connected with that of tantalum, firstly because these metals are consistently associated together in their natural ores, and secondly, because their separation from one another has proved an extremely difficult matter. Indeed, the chemistry of these elements is so closely parallel that considerable time elapsed before their separate identities were definitely established.

In 1801 Hatchett,<sup>1</sup> an English chemist, while working on some chromium minerals in the British Museum, examined a black mineral which had been found in the Connecticut valley and had been sent to the then president of the Royal Society. Hatchett reported the existence in the mineral of a new element, for which he suggested the name columbium, because the ore had come from America. The mineral itself became known as *columbite*. In the following year Ekeberg<sup>2</sup> found what he thought was another new element in two other minerals, what is now known as *tantalite*, from Kimito (Finland), and *yttrotantalite*, from Ytterby (Sweden). This new element was named tantalum, partly because mythological names were then common for new elements, and partly because of the tantalising difficulty that was experienced in dissolving the oxide of the new metal in excess of acids. Wollaston<sup>3</sup> subsequently compared the properties of the two new elements by re-examining their ores, and endeavoured to show that they were identical. It is now known that what was then looked upon as the pure oxide must have been tantalum pentoxide mixed with small proportions of niobium pentoxide, and the new "element" was therefore impure tantalum.

In 1839 Wöhler<sup>4</sup> investigated some peculiar properties of an acid oxide (now known to be a mixture of niobic acid and titanitic acid) present in the mineral *pyrochlore* and in some Bavarian *tantalites*. Rose<sup>5</sup> followed up the observation that many *columbites* and *tantalites*, as well as the acids obtained from them, displayed widely varying densities, and, after close investigation into their composition, he announced in 1844 that the columbites from Bodenmais in Bavaria contained, in addition to tantalic acid, the acid oxide of a metal which was not present in columbites from Sweden and Finland. The new metal was named niobium after Niobe, a daughter of Tantalus. In 1846 Rose thought that he had discovered the acid oxide of still another metal, to which he gave the name pelopium,<sup>6</sup> but later he decided that this new acid was merely hyponiobic acid.<sup>7</sup> In 1856-57 Hermann showed that both tantalum and niobium occur in the various natural *tantalites* and *columbites*.

From a consideration of the composition of the halides, and because of the supposed isomorphism of tantalic acid and stannic acid, Rose gave the formulæ  $\text{NbO}_2$  and  $\text{TaO}_2$  to anhydrous niobic acid and tantalic acid respectively, but in so doing he repeated an error that had previously been made by Berzelius with regard to vanadium compounds, and overlooked the presence in the halides of an oxygen atom (see p. 24). Blomstrand<sup>8</sup>

<sup>1</sup> Hatchett, *Proc. Roy. Soc.*, 1802, 92, 49.

<sup>2</sup> Ekeberg, *Öfvers. K. Vet.-Akad. Förh.*, 1802, 23, 180; *Ann. Chim.*, 1802, 43, 76.

<sup>3</sup> Wollaston, *Phil. Trans.*, 1809, 99, 246; see also Berzelius, *Pogg. Annalen*, 1825, 4, 6; *Öfvers. K. Vet.-Akad. Förh.*, 1824, 2; *Ann. Chim. Phys.*, 1825, [ii], 29, 300.

<sup>4</sup> Wöhler, *Pogg. Annalen*, 1839, 48, 91.

<sup>5</sup> Rose, *ibid.*, 1844, 63, 307, 693.

<sup>6</sup> Rose, *ibid.*, 1846, 69, 118.

<sup>7</sup> Rose, *ibid.*, 1853, 90, 471.

<sup>8</sup> Blomstrand, *J. prakt. Chem.*, 1866, 97, 37.

and Marignac<sup>1</sup> subsequently analysed a large number of chlorides of different origin, and investigated the constitution of the fluorides and double fluorides of niobium. A "hyponiobic fluoride" was found to contain three atoms of fluorine for one atom of oxygen, and its double fluorides with the fluorides of other metals were shown to be isomorphous with similar double fluorides given by titanium tetrafluoride,  $TiF_4$ , tin tetrafluoride,  $SnF_4$ , and tungsten oxydifluoride,  $WO_2F_2$ . Furthermore, a comparison of the oxyfluorides of tungsten with the fluorides of titanium, tin, silicon and zinc had previously shown that an atom of fluorine in these compounds could be replaced by an atom of oxygen without disturbing the isomorphism. The formula for "hyponiobic fluoride" thereupon became  $NbOF_3$ , and in consequence, niobic anhydride became  $Nb_2O_5$ . The formula for tantalalic anhydride was established as  $Ta_2O_5$  at the same time, because tantalalic acid occurs in isomorphous mixtures with niobic acid in several minerals, from which isomorphous double fluorides, such as potassium tantalum fluoride,  $K_2TaF_7$ , and potassium niobium fluoride,  $K_2NbF_7$ , were also obtained. These conclusions were confirmed by determinations of the vapour densities of niobium pentachloride,  $NbCl_5$ , tantalum pentachloride,  $TaCl_5$ , and niobium oxytrichloride,  $NbOCl_3$ , by Deville and Troost in 1865.<sup>2</sup>

Marignac<sup>3</sup> also showed that previous methods for the separation of niobium and tantalum were far from perfect, and for the first time he succeeded in preparing pure niobium and tantalum compounds. His methods are still in use to some extent, and his analyses provided the first reliable values for the atomic weights of these elements. It should be stated, too, that Rose's earlier researches, which extended over a period of nearly twenty years, have provided a valuable source of information for the chemistry of niobium and tantalum.<sup>4</sup> His calculations and formulæ were revised by Rammelsberg<sup>5</sup> in the light of subsequent discoveries.

During the years 1860 to 1871 the presence of various other elements in columbites and tantalites was reported. Hermann<sup>6</sup> defended the original formulæ of Rose for niobium and tantalum compounds, and announced the existence of another element, which he styled ilmenium, in *ytthro-ilmenite*, *samarските*, and other niobium-bearing minerals, but ilmenium was shown by Marignac to be a mixture of niobium and titanium. Hermann also claimed<sup>7</sup> the discovery of still another metal, which he called neptunium, but Blomstrand and Larsson<sup>8</sup> independently showed it to be identical with niobium, and Smith<sup>9</sup> was unable to confirm Hermann's preparation. Kobell<sup>10</sup> came to the conclusion that niobites from Bodenmais in Bavaria contained the acid oxide of a metal which he named dianium, and which was not present in niobites from North America and Greenland; but the identity of dianium and

<sup>1</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 5, 49; 1866, 9, 249.

<sup>2</sup> Deville and Troost, *Compt. rend.*, 1865, 60, 1221.

<sup>3</sup> Marignac, *ibid.*, 1865, 60, 234.

<sup>4</sup> Rose, *Pogg. Annalen*, 1844-63, 63-118.

<sup>5</sup> Rammelsberg, *ibid.*, 1869, 136, 177, 362.

<sup>6</sup> Hermann, *J. prakt. Chem.*, 1846, 38, 91; 1870, 2, 108; 1871, 3, 373; 1871, 4, 178; *Chem. News*, 1871, 24, 73; 1872, 26, 194; 1873, 27, 59.

<sup>7</sup> Hermann, *Zeitsch. anal. Chem.*, 1871, 10, 344; *Chem. News*, 1877, 35, 197.

<sup>8</sup> Larsson, *Zeitsch. anorg. Chem.*, 1896, 12, 189.

<sup>9</sup> E. F. Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 151; *Chem. News*, 1905, 92, 209.

<sup>10</sup> Kobell, *J. prakt. Chem.*, 1860, 79, 291; 1861, 83, 193, 449; *Chem. News*, 1862, 5, 41.

niobium was also soon established.<sup>1</sup> Krüss and Nilson,<sup>2</sup> on spectroscopic evidence, assumed the existence of still another element in *fergusonite*, but the assumption became untenable.<sup>3</sup> A re-investigation of American niobites and tantalites carried out in 1905<sup>4</sup> failed to bring to light any new elements other than niobium and tantalum; this result was confirmed by spectroscopic examination of several samples of niobium pentoxide which had been prepared from various minerals.<sup>5</sup>

Niobium and tantalum suddenly received considerable attention about the year 1905 as possible materials for the filaments of incandescent electric lamps in place of the carbon filament then in use. The metals were then prepared in the pure state for the first time by Dr Werner von Bolton,<sup>6</sup> and their properties were examined. Niobium was found to be unsuitable for the purpose in view, but tantalum proved to be satisfactory. Tantalum lamps were manufactured in large quantities between the years 1905 and 1911, when the metal was displaced by the electrically more efficient tungsten.

**Extraction.**—The method of extraction of niobium and tantalum compounds from their natural ores does not differ from the process followed in the quantitative examination of the ores, and consists, briefly, in fusing the material with an alkali or alkali salt, extracting the fused mixture of niobates and tantalates with water, and hydrolysing the solution by boiling, whereupon a comparatively insoluble mixture of niobic and tantalic acids or their anhydrides is obtained, which yields the pentoxides,  $Nb_2O_5$  and  $Ta_2O_5$ , on being ignited. Only those metals which give rise to acid oxides demand special separation.<sup>7</sup>

The more detailed description of the extraction is conveniently divided into three stages:

- I. Preparation of a mixture free from tin, antimony, iron, manganese, etc.
- II. Removal of titanium from the mixture.
- III. Separation of niobium from tantalum in the product.

#### *I. Preparation of a Mixture Free from Tin, Antimony, Iron, Manganese, Etc.*

The finely powdered niobite or tantalite, which should contain as little titanium as possible, is fused for several hours with a large excess of potassium hydrogen sulphate or sodium hydrogen sulphate in a silica or platinum crucible; the cooled mass is thoroughly extracted by boiling with water, and the precipitate, which consists mainly of niobic and tantalic acids together with some of the sulphates,<sup>8</sup> is digested with ammonium sulphide to remove tin, antimony and tungsten, and to convert any iron or manganese into sulphide, which

<sup>1</sup> Deville and Troost, *Compt. rend.*, 1861, 53, 1044.

<sup>2</sup> Kruss and Nilson, *Ber.*, 1887, 20, 2134; *Chem. News*, 1887, 56, 86.

<sup>3</sup> Larsson, *loc. cit.*

<sup>4</sup> E. F. Smith, *loc. cit.*; Hall and Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 177; *Chem. News*, 1905, 92, 220, 232, 242, 252, 262, 276; Hall, *J. Amer. Chem. Soc.*, 1904, 26, 1235.

<sup>5</sup> Barr, *ibid.*, 1908, 30, 1668; Hildebrand, *ibid.*, 1908, 30, 1672.

<sup>6</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45, 722; 1907, 13, 145; see also Siemens, *Chem. News*, 1909, 100, 223.

<sup>7</sup> For a scheme for the complete analysis of an ore, see Schoeller and Powell, *The Analysis of Minerals and Ores of the Rarer Elements* (Griffin, London), 1919, 141.

<sup>8</sup> Todd, *Univ. Toronto Studies, Geol. Ser.*, 1923, No. 16, pp. 40–45; *J. Chem. Soc., Abs.*, 1924, ii, 126, 207; Giles, *Chem. News*, 1909, 99, 3.



is removed with hydrochloric acid.<sup>1</sup> Some of the niobic and tantalonic acids may also be dissolved by the hydrochloric acid, however.<sup>2</sup> Separation of silica is effected in the usual way by evaporation of the hydrofluoric acid solution of the residue in a platinum dish with addition of sulphuric acid. In order to remove silica without loss of niobium and tantalum through possible vaporisation of the pentafluorides,  $NbF_5$  and  $TaF_5$ , extraction of the niobic and tantalonic acids with caustic soda or caustic potash has been recommended.<sup>3</sup>

Treatment of the fused ore with ammonium sulphide, as described above for the removal of tin, antimony and tungsten, does not proceed quantitatively; better separation is claimed to result on fusing the mixed niobic and tantalonic acids with a large excess of a mixture of sodium carbonate and sulphur and then extracting with water, several refusions being necessary.<sup>4</sup> An alternative method for the removal of tungsten consists in boiling the alkaline aqueous extract of the fused ore with ammonium nitrate, the mixed niobic and tantalonic acids being precipitated, while ammonium tungstate is left in solution.<sup>5</sup> In a more recent method the mixed niobic and tantalonic acids are fused with potassium carbonate and the aqueous extract treated with sodium chloride; the mixed acids are thereupon precipitated, the tungsten being left in the filtrate as tungstic acid.<sup>6</sup>

Instead of lixiviating with water, the pyrosulphate fusion is followed in a recent process<sup>7</sup> by extraction with tartaric acid solution; the insoluble residue contains silica, tin, and lead, and the solution, after being saturated with hydrogen sulphide for the precipitation of copper, antimony, etc., contains the hydroxides of niobium and tantalum as well as tungsten, titanium, zirconium, rare earth metals, etc.

In addition to potassium hydrogen sulphate and sodium hydrogen sulphate<sup>8</sup> for opening up the ore, potassium carbonate,<sup>9</sup> sodium peroxide, and alkali hydroxides<sup>10</sup> have been employed. The use of potassium hydroxide is preferred in the case of a high-grade ore of low titanium content;<sup>11</sup> it has the advantage over sodium hydroxide that potassium tantalates are soluble in solutions which contain excess of the alkali, whereas sodium tantalates are insoluble.

For minerals in which the titanium content is high it has been found preferable to attack the ore with potassium hydrogen fluoride,  $KHF_2$ , or concentrated hydrofluoric acid.<sup>12</sup> In one such process the powdered

<sup>1</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 62; Rammelsberg, *J. prakt. Chem.*, 1869, 107, 343; *Pogg. Annalen*, 1871, 144, 64; Weinland and Storz, *Zeitsch. anorg. Chem.*, 1907, 54, 230; Chesneau, *Compt. rend.*, 1909, 149, 1132.

<sup>2</sup> Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 65; *Chem. News*, 1910, 101, 3.

<sup>3</sup> von John, *Chem. News*, 1909, 100, 154; compare Schoeller and Powell, *Analyst*, 1928, 53, 258.

<sup>4</sup> Compare, however, Schoeller and Jahn, *ibid.*, 1927, 52, 504; Giles, *loc. cit.* E. F. Smith, *Chem. News*, 1905, 92, 209; Hall, *J. Amer. Chem. Soc.*, 1904, 26, 1235; Bedford, *ibid.*, 1905, 27, 1216.

<sup>5</sup> Bullheimer, *Chem. Zeit.*, 1900, 24, 870; *Chem. News*, 1902, 85, 184; compare Schoeller and Jahn, *loc. cit.*

<sup>6</sup> Schoeller and Jahn, *loc. cit.*

<sup>7</sup> Powell and Schoeller, *J. Chem. Soc.*, 1921, 119, 1927.

<sup>8</sup> Sears, *J. Amer. Chem. Soc.*, 1926, 48, 343; 1929, 51, 122.

<sup>9</sup> Russ, *Zeitsch. anorg. Chem.*, 1902, 31, 50; Giles, *Chem. News*, 1909, 99, 1, 25.

<sup>10</sup> Moir, *ibid.*, 1916, 113, 256; Balke, *J. Amer. Chem. Soc.*, 1910, 32, 1129; Rose, *Pogg. Annalen*, 1861, 113, 301.

<sup>11</sup> Simpson, *Chem. News*, 1909, 99, 243; Balke, *Industrial and Engineering Chemistry*, 1923, 15, 560.

<sup>12</sup> Smith, *Compt. rend.*, 1878, 87, 146; *Chem. News*, 1883, 48, 13, 29.

niobite is evaporated almost to dryness with a solution of potassium hydrogen fluoride, and the residue fused and dissolved in hydrofluoric acid, from which crystals of potassium tantalum fluoride,  $K_2TaF_7$ , and of potassium niobium oxyfluoride,  $K_2NbOF_5 \cdot H_2O$ , are obtained on evaporating and cooling. These are freed from iron and manganese either by recrystallising, or better, by previous treatment in solution with hydrogen sulphide.<sup>1</sup>

Older methods of opening up the ore, now only of historical interest, consisted in heating it for several hours with a mixture of sugar charcoal and sodium carbonate in a carbon crucible, whereupon the niobium, tantalum and titanium formed their carbides and nitrides. The product was treated with boiling concentrated hydrochloric acid and dilute hydrofluoric acid, which removed the tin, iron, calcium, and some of the yttrium. The dried residue was carefully heated in a stream of chlorine; the more volatile chlorides of titanium and silicon were thereby removed, and there was left in the tube a mixture of the chlorides of niobium and tantalum, together with small proportions of ferric chloride and tungsten oxychloride. The product was extracted with dilute hydrochloric acid, and the niobium and tantalum chlorides hydrolysed by boiling water to the pentoxides.<sup>2</sup> Moissan<sup>3</sup> obtained a mixture of niobic and tantalic acids very conveniently by heating a powdered niobite with sugar charcoal in the electric oven. Most of the manganese and the greater portion of the iron and silicon were volatilised; the residue, which consisted of the carbides of niobium and tantalum, was dissolved in hydrofluoric acid to which a small quantity of nitric acid had been added. The iron was removed with ammonium sulphide, and potassium fluoride added, whereupon concentration and cooling gave a mixture of potassium tantalum fluoride,  $K_2TaF_7$ , and potassium niobium oxyfluoride,  $K_2NbOF_5 \cdot H_2O$ .

Zirconium can be removed from the mixed precipitated acids by fusing them with potassium carbonate and extracting the melt with cold water. The niobium and tantalum pass into solution as niobate and tantalate of potassium respectively, while the zirconium remains undissolved as the dioxide,  $ZrO_2$ .<sup>4</sup> The method is more suited for the removal of zirconium from niobates than from tantalates.<sup>5</sup>

## II. Removal of Titanium.

The removal of titanium from mixed niobic and tantalic acids is a difficult matter. Although titanium and niobium compounds display considerable differences in their general behaviour, when the two elements occur together they appear to undergo a change, in consequence of which they become difficult to separate. Niobic acid, for instance, is precipitated from a much more concentrated boiling sulphuric acid solution than is titanous acid; but when the two acids are dissolved

<sup>1</sup> Gibbs, *Amer. J. Sci.*, 1864, [ii], 37, 355; Pennington, *J. Amer. Chem. Soc.*, 1896, 18, 40; Barr, *ibid.*, 1908, 30, 1669; Foote and Langley, *Amer. J. Sci.*, 1910, [iv], 30, 393.

<sup>2</sup> Joly, *Annales Scientifiques de l'École Normale Supérieure, Paris*, 1877, [ii], 6, 138.

<sup>3</sup> Moissan, *Bull. Soc. chim.*, 1902, [iii], 27, 430; *Compt. rend.*, 1901, 133, 20.

<sup>4</sup> Noyes and Bray, *Qualitative Analysis for the Rare Elements* (Macmillan, London), 1927, 79, 103; see also Bailey, *J. Chem. Soc.*, 1886, 49, 149, 481; Morozewitz, *Chem. Zentr.*, 1909, [i], 1965; Headden, *Amer. Chem., Abs.*, 1917, 11, 2311; Marden and Rich, *U.S. Bureau of Mines, Bulletin* 186 (1921).

<sup>5</sup> Schoeller and Powell, *J. Chem. Soc.*, 1921, 119, 1927; see also Schoeller and Waterhouse, *Analyst*, 1928, 53, 467.

together in sulphuric acid the precipitation of the niobic acid does not take place unless the solution has been diluted considerably, *i.e.* the hydrolysis of the niobium salt is impeded by the presence of titanium.<sup>1</sup> (On the other hand, the hydrolysis of the niobium salt is accelerated by the presence of a small quantity of tantalum.) Again, when titanitic acid is fused with potassium carbonate and the melt is extracted with boiling water, only about 1 per cent. of the titanitic acid is dissolved; in the presence of niobic acid, however, the greater proportion of the titanitic acid passes into solution on the same treatment, and some of the niobic acid remains in the residue. These modifications in the properties of niobium in the presence of titanium were in part responsible for the erroneous assumption of the existence of various new elements in niobium and tantalum ores (see p. 123). More recently it has also been shown that the solubilities of niobic acid, tantalic acid and titanitic acid in acidified hydrogen peroxide solution, are affected by the presence of each other, according to the conditions.<sup>2</sup>

A completely satisfactory process for the quantitative separation of titanium from niobium and tantalum has not yet been evolved; <sup>3</sup> nearly all the methods that have been suggested from time to time have subsequently received adverse criticism. One that suffers least in this respect consists in boiling the mixed precipitated acids for several hours with excess of a dilute solution of salicylic acid. The titanitic acid is dissolved; the residue is ignited and the process repeated several times, when all the niobium and tantalum are contained in the residue, while the salicylate filtrates contain all the titanium, which is subsequently precipitated with ammonia and estimated as titanium dioxide,  $TiO_2$ .<sup>4</sup> Another process of separation, which is stated to be available in the presence of appreciable amounts of titanium, consists in fusing the mixed acids (after removal of tin, antimony, tungsten) with sodium nitrate, or with an alkali and an oxidising agent, which is claimed to prevent the formation of soluble compounds of titanium with niobium or tantalum.<sup>5</sup> After extracting the fused product with water only a very little titanium remains in solution, and this is removed by hydrogen sulphide.<sup>6</sup> The filtrate is boiled until free from hydrogen sulphide, acidified with sulphuric acid, and boiled with sulphurous acid, which precipitates only niobic and tantalic acids.<sup>7</sup> Alternatively, the mixed precipitated acids may be dissolved in acidified hydrogen peroxide and boiled with sulphurous acid; the precipitate contains only a small amount of titanium, and repetition of the process is stated to yield a titanium-free product.<sup>8</sup> Fusion of the mixed acids with a mixture

<sup>1</sup> Schoeller and Waterhouse, *Analyst*, 1928, 53, 467; Marignac, *Ann. Chim. Phys.*, 1868, [iv], 13, 7.

<sup>2</sup> Hahn and Gille, *Zeitsch. anorg. Chem.*, 1920, 112, 283; Giles, *Chem. News*, 1907, 95, 37.

<sup>3</sup> Schoeller and Deering, *Analyst*, 1927, 52, 625.

<sup>4</sup> Muller, *J. Amer. Chem. Soc.*, 1911, 33, 1506; Noyes and Bray, *Qualitative Analysis for the Rare Elements* (Macmillan, London), 1927, 77; Dittrich and Freund, *Zeitsch. anorg. Chem.*, 1907, 56, 344, 346.

<sup>5</sup> Compare, however, Hauser and Lewite, *Zeitsch. angew. Chem.*, 1912, 25, 100; Meimberg and Winzer, *ibid.*, 1913, 26, 157.

<sup>6</sup> Ruff and Schiller (*Zeitsch. anorg. Chem.*, 1911, 72, 329) deny this.

<sup>7</sup> Weiss and Landecker, *ibid.*, 1909, 64, 65; *Chem. News*, 1910, 101, 14; compare Ott, *Dissertation* (Munich, 1911); Wedekind and Maas, *Zeitsch. angew. Chem.*, 1910, 23, 2315.

<sup>8</sup> Weiss and Landecker, *loc. cit.*; Hahn and Gille (*loc. cit.*) were unable to obtain satisfactory separation by this method.

of caustic potash and potassium cyanide has also been recommended for the quantitative separation of titanium; the melt is extracted with hot water, all the titanium remaining in the residue.<sup>1</sup>

In 1905 Hall and Smith<sup>2</sup> investigated all the then known methods for the removal of titanium, and tried various other processes; they were unable, however, to improve on Marignac's method of fractional recrystallisation of the double potassium fluorides.<sup>3</sup> This method has the disadvantage that in the case of the niobium salt protracted and tedious repetition is necessary before it is obtained free from titanium, and the method becomes impossible with small quantities of material.<sup>4</sup>

### III. Separation of Niobium and Tantalum.

The close similarity in the chemical behaviour of the compounds of these two elements has rendered their separation extremely difficult. Although many processes have been investigated, the method most in use appears to be that evolved by Marignac as long ago as 1866, or a modification of it.<sup>5</sup> This depends, firstly, on the difference in the solubilities of potassium niobium oxyfluoride,  $K_2NbOF_5 \cdot H_2O$  (1 part in 12 to 13 parts of water between 17° and 21° C.), and potassium tantalum fluoride,  $K_2TaF_7$  (1 part in 150 to 160 parts of water containing a small quantity of hydrofluoric acid, at the same temperature); and, secondly, on the fact that these two compounds are not isomorphous, and mixed crystals or solid solutions are therefore not produced. For the separation, the mixture of niobic acid and tantalic acid is dissolved in concentrated hydrofluoric acid, potassium fluoride is added in correct quantity, and the whole is carefully concentrated.<sup>6</sup> The double potassium tantalum fluoride is first precipitated in acicular, rhombic needles; the filtrate, on being concentrated, with further addition of hydrofluoric acid and potassium fluoride, yields white, semi-transparent, granular plates of potassium niobium oxyfluoride mixed with the needles of potassium tantalum fluoride, which are separated by recrystallisation. In a modification of this process, potassium chloride is added to the hydrofluoric acid solution of the niobic and tantalic acids instead of potassium fluoride; the double potassium niobium fluoride,  $K_2NbF_7$ , remains dissolved and the tantalum salt is precipitated.<sup>7</sup>

Ruff and Schiller<sup>8</sup> determined the solubilities of the double fluorides of niobium and tantalum,  $K_2NbF_7$  and  $K_2TaF_7$ , in varying quantities of hydrofluoric acid and potassium fluoride, and based a method of fractional separation on the results, which showed that the solubility of both fluorides diminishes with increasing concentration of potassium fluoride and decreasing concentration of hydrofluoric acid; the solubility increases rapidly with rising temperature, and is always

<sup>1</sup> Weiss and Landecker, *loc. cit.*; Moir, *loc. cit.*

<sup>2</sup> Hall and Smith, *Chem. News*, 1905, 92, 232.

<sup>3</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 5, 49, 68.

<sup>4</sup> Kruss and Nilson, *Ber.*, 1887, 20, 1684; Smith, *Chem. News*, 1905, 92, 209.

<sup>5</sup> Marignac, *loc. cit.*; see also Ruff and Schiller, *Zeitsch. anorg. Chem.*, 1911, 72, 239; Meimberg, *Zeitsch. angew. Chem.*, 1913, 26, 83; Levy, *Analyst*, 1915, 40, 204.

<sup>6</sup> For practical details see Mellor, *A Treatise on Quantitative Inorganic Analysis* (Griffin, London), 1913, 421; also Schoeller and Powell, *The Analysis of Minerals and Ores of the Rarer Elements* (Griffin, London), 1919, 133.

<sup>7</sup> Meimberg and Winzer, *Zeitsch. angew. Chem.*, 1913, 26, 157.

<sup>8</sup> Ruff and Schiller, *loc. cit.*

greater for the niobium than for the tantalum salt. The tantalum may also be precipitated and removed partly<sup>1</sup> or completely<sup>2</sup> as potassium tantalum oxyfluoride, while the niobium remains in solution.<sup>3</sup>

Conversion of the separated fluorides into the corresponding oxides is effected by boiling with concentrated sulphuric acid until free from fluorine, and then hydrolysing the product by boiling with water. Alternatively, the hydrated acids are precipitated by the addition of ammonia to the solutions of the double fluorides.<sup>4</sup> Niobium pentoxide, Nb<sub>2</sub>O<sub>5</sub>, or tantalum pentoxide, Ta<sub>2</sub>O<sub>5</sub>, is obtained on ignition of the precipitated hydrate.

A method of separation which avoids the preparation of the double fluorides consists in fusing the mixed niobic and tantallic acids with sodium carbonate and nitrate; the product is digested with warm water and a current of carbon dioxide is passed through the solution. It is claimed that only tantallic acid is precipitated.<sup>5</sup> This process has, however, been the subject of adverse criticism.<sup>6</sup> Partial separation of niobium from tantalum can be effected by warming the mixed, freshly precipitated, hydrated oxides with a mixture of hydrogen peroxide and hydrochloric acid; the niobium dissolves readily, while the tantalum dissolves only sparingly.<sup>7</sup>

A more recent process, which avoids the difficulties associated with Marignac's method, is based on the solubility of niobium pentoxide and the comparative insolubility of tantalum pentoxide in a mixture of equal volumes of selenium oxychloride, SeOCl<sub>2</sub>, and concentrated sulphuric acid.<sup>8</sup> The tantalum pentoxide is left in the residue, and hydrolysis of the extract after dilution yields niobic acid.

### Estimation of Niobium and Tantalum.

The various methods in use for opening up the natural ores, and the separation of other metals from niobium and tantalum, have already been described in dealing with the extraction of these elements (see p. 124); similar methods apply to quantitative processes. The quantitative determination of either niobium or tantalum is best effected by converting the niobium or tantalum compound into the pentoxide and weighing as such. In the case of the fluorides, oxyfluorides, or double fluorides with the alkali metals, and the niobates and tantalates, the conversion is effected either by digesting with concentrated sulphuric acid or by fusing with potassium hydrogen sulphate; the residue, after extraction with water, is ignited in the presence of ammonium carbonate.<sup>9</sup> In technical practice the product will usually contain both niobium pentoxide and tantalum pentoxide.

<sup>1</sup> Hall and Smith, *Chem. News*, 1905, 92, 221.      <sup>2</sup> von John, *ibid.*, 1909, 100, 154.

<sup>3</sup> Noyes and Bray, *loc. cit.*

<sup>4</sup> Balke, *Chem. Met. Eng.*, 1922, 26, 1272.

<sup>5</sup> Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 65; *Chem. News*, 1910, 101, 2, 13, 26.

<sup>6</sup> Wedekind and Maas, *Zeitsch. angew. Chem.*, 1910, 23, 2314; Hauser and Lewite, *ibid.*, 1912, 25, 100; Foote and Langley, *Amer. J. Sci.*, 1910, [iv], 30, 401; Meimberg and Winzer, *loc. cit.*; compare also Headden, *loc. cit.*

<sup>7</sup> Weiss and Landecker, *loc. cit.*

<sup>8</sup> Lenher, *J. Amer. Chem. Soc.*, 1921, 43, 21; Merrill, *ibid.*, 1921, 43, 2378.

<sup>9</sup> Wöhler, *Pogg. Annalen*, 1839, 48, 92; Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 63; Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 66.

*Estimation of Niobium and Tantalum when Present Together.*

(a) **Gravimetric Methods.**—The mixture of pentoxides of niobium and tantalum is redissolved in concentrated hydrofluoric acid and separated by Marignac's process (see p. 128); the potassium tantalum fluoride and potassium niobium oxyfluoride are then separately converted into the pentoxides as described above, and weighed.<sup>1</sup> This method has several disadvantages: (1) The ratio of the solubilities of the two compounds on which the separation is based is only approximately 10 : 1, and the process is, therefore, necessarily inaccurate; even when the recrystallisation is repeated to a tedious extent the error approaches 1 per cent. (2) The concentration of the hydrofluoric acid and of the potassium fluoride must be carefully controlled; if the acidity is too low, an oxyfluoride of tantalum is precipitated; if the acidity is too great, a normal fluoride of niobium is obtained. (3) Several platinum dishes are necessary.

An entirely different method of separation, which avoids the disadvantages of Marignac's process, is based on the differential hydrolytic dissociation of oxalo-niobic acid and oxalo-tantallic acid in the presence of tannin in slightly acid solution. The colour of the tantalum precipitate (sulphur yellow) is much paler than that of the niobium precipitate (vermilion).<sup>2</sup> The presence of titanium interferes with the precipitation.<sup>3</sup> Extraction of niobium pentoxide in a mixture of equal volumes of selenium oxychloride and concentrated sulphuric acid, in which tantalum pentoxide is insoluble, also provides a convenient quantitative separation.<sup>4</sup> In another recent process the niobium pentoxide is determined in the presence of tantalum by reducing it to the dioxide, NbO<sub>2</sub>, in a stream of hydrogen, and noting the gain in weight on reoxidising it in air at a red heat.<sup>5</sup> A rough method for the estimation of niobium pentoxide and tantalum pentoxide depends on the considerable difference in their densities; the ordinary specific gravity bottle is used, and the composition of the mixture ascertained by reference to a table.<sup>6</sup>

The analysis of ferrotantalum alloys and of tantalum steels also involves the conversion of the tantalum present into the pentoxide. The material is dissolved in hydrofluoric acid and nitric acid, evaporated to dryness, and the residue fused with potassium hydrogen sulphate; extraction with dilute hydrochloric acid and hydrolysis yield a precipitate of hydrated tantallic pentoxide, the iron remaining in solution.<sup>7</sup>

Cupferron can be employed for the estimation of niobium and tantalum together, but does not differentiate between them; any titanium present is also simultaneously precipitated.<sup>8</sup>

(b) **Volumetric Methods.**—Pentavalent niobium compounds differ

<sup>1</sup> Compare Tighe, *J. Soc. Chem. Ind.*, 1906, 25, 681.

<sup>2</sup> Powell and Schoeller, *Analyst*, 1925, 50, 485.

<sup>3</sup> Schoeller and Powell, *ibid.*, 1928, 53, 258.

<sup>4</sup> Merrill, *J. Amer. Chem. Soc.*, 1921, 43, 2378.

<sup>5</sup> Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1926, 156, 213.

<sup>6</sup> Foote and Langley, *Chem. News*, 1911, 103, 53; Levy, *Analyst*, 1915, 40, 216; compare, however, remarks on the variation of the specific gravities of these oxides with heat treatment, pp. 155 and 197.

<sup>7</sup> Arnold and Ibbotson, *Steel Works Analysis* (Pitman, London), 1919, 212, 265; Travers, *Compt. rend.*, 1918, 166, 494; Kelly, Myers, and Illingworth, *J. Ind. Eng. Chem.*, 1917, 9, 852.

<sup>8</sup> Pied, *Compt. rend.*, 1924, 179, 897.

from pentavalent tantalum compounds in that they can be reduced by nascent hydrogen in hot acid solution approximately to the trivalent state, and can then be titrated back with potassium permanganate solution, the tantalum compound remaining unaltered. The final stage of the reduction has been variously reported as being equivalent to  $Nb_8O_{13}$ ,<sup>1</sup>  $Nb_{10}O_{17}$ ,<sup>2</sup>  $Nb_2O_{3-107}$ ,<sup>3</sup> and appears to depend on the quality of the reagents, the degree of dispersion of the niobic acid, and on other conditions concerning which insufficient is known at present to render the method accurate.<sup>4</sup> Treadwell<sup>5</sup> recommends reduction with cadmium amalgam in the presence of ammonium vanadate, ammonium molybdate, or titanium sulphate, and electrometric titration of the trivalent solution so obtained with potassium permanganate.

(c) **Colorimetric Method.**—A colorimetric method for the estimation of small quantities of niobium in tantalum compounds has been worked out by Meimberg.<sup>6</sup> This takes advantage of the colour change that is produced when a pentavalent niobium salt in acid solution is reduced with tin; a tantalum salt remains unaffected under the same conditions.

The estimation of small quantities of tantalum in niobium compounds is more difficult, and cannot be carried out colorimetrically. The usual method is to convert the material into the potassium double fluoride, and then to take advantage of the fact that a white precipitate of potassium tantalum oxyfluoride,  $K_4Ta_4O_5F_{14}$  (see p. 132), is thrown down when a solution of potassium tantalum fluoride,  $K_2TaF_7$ , is boiled.<sup>7</sup> Powell and Schoeller<sup>8</sup> find this test imperfect, and have modified the procedure (based on the differential hydrolytic dissociation of oxaloniobic acid and oxalo-tantallic acid in the presence of tannin in slightly acid solution) for the detection and estimation of traces of tantalum in niobium compounds.

The determination of tantalum by ordinary methods of spectroscopy<sup>9</sup> and by means of X-ray spectra<sup>10</sup> also appears to be possible.

### Detection of Niobium and Tantalum.

The detection of niobium and tantalum depends almost entirely on the reactions given by niobic acid and tantalic acid. All the common niobium and tantalum compounds are hydrolysed on being boiled in acid solutions, and yield precipitates of the respective acids. Natural minerals are previously fused with potassium hydrogen sulphate, and the aqueous extract of the melt usually precipitates the mixed acids

<sup>1</sup> Osborne, *Chem. News*, 1886, 53, 43; compare Warren, *ibid.*, 1906, 94, 298.

<sup>2</sup> Levy, *loc. cit.*

<sup>3</sup> Metzger and Taylor, *Chem. News*, 1909, 100, 257, 270; Giles, *ibid.*, 1909, 99, 1; Todd, *Univ. Toronto Studies, Geol. Ser.*, 1923, No. 16, pp. 40-45; *J. Chem. Soc., Abs.*, 1924, 126, [ii], 207.

<sup>4</sup> Schoeller and Waterhouse, *Analyst*, 1924, 49, 215; compare Kiehl and Hart, *J. Amer. Chem. Soc.*, 1928, 50, 1608.

<sup>5</sup> Treadwell, *Helv. Chim. Acta*, 1922, 5, 732, 806.

<sup>6</sup> Meimberg, *Zeitsch. angew. Chem.*, 1913, 26, 83.

<sup>7</sup> Hall, *J. Amer. Chem. Soc.*, 1904, 26, 1239.

<sup>8</sup> Powell and Schoeller, *Analyst*, 1925, 50, 485.

<sup>9</sup> Powell and Schoeller, *loc. cit.*

<sup>10</sup> Hevesy and Böhm, *Zeitsch. anorg. Chem.*, 1927, 164, 69.

<sup>11</sup> Weiss and Landecker, *ibid.*, 1909, 64, 100; *Chem. News*, 1910, 101, 28; Moir, *ibid.*, 1916, 113, 256; Pennington, *J. Amer. Chem. Soc.*, 1896, 18, 52; *Chem. News*, 1897, 75, 31.

spontaneously; removal of other metals is effected by the methods described on p. 124 *et seq.*

**A. Wet Reactions.**—(1) Both niobic acid and tantalic acid dissolve readily in hydrofluoric acid, but only very slightly in concentrated hydrochloric acid and in hot concentrated sulphuric acid. The residue from the hydrochloric acid solution of niobic acid, however, readily forms a hydrosol on being triturated with water. The sulphuric acid solution of niobic acid remains clear on being diluted with water, whereas the sulphuric acid solution of tantalic acid becomes turbid on being diluted, and reprecipitates the acid.

(2) The hydrofluoric acid solution of niobic acid does not yield a precipitate on the addition of *potassium fluoride* (potassium niobium fluoride,  $K_2NbF_7$ , which is formed, being soluble in about 12.5 parts of water), whereas the hydrofluoric acid solution of tantalic acid yields colourless, rhombic needles of potassium tantalum fluoride,  $K_2TaF_7$  (which is soluble in about 150 parts of water under the same conditions), when treated with a saturated solution of potassium fluoride, carefully evaporated and cooled slowly. After removal of the tantalum, and with further concentration, any niobium present separates in plates of potassium niobium oxyfluoride,  $K_2NbOF_5 \cdot H_2O$ , if the hydrofluoric acid is not in excess, and in needles of potassium niobium fluoride,  $K_2NbF_7$ , if the hydrofluoric acid is in excess.

The potassium tantalum fluoride first precipitated is a fusible substance. Its aqueous solutions on being boiled precipitate a very insoluble potassium tantalum oxyfluoride,  $4KF \cdot Ta_2O_5 \cdot 2TaF_5$  or  $K_4Ta_4O_5F_{14}$ , as a white powder. This reaction is stated to constitute a sensitive test for tantalum.<sup>1</sup>

(3) Hydrochloric acid solutions of pentavalent niobium compounds which are free from hydrofluoric acid, on being reduced with zinc, first become blue, and with further action of the reducing agent, olive-green or dark brown, according to the concentration of the acid and other conditions. The blue stage is not difficult to attain; the brown stage is best attained by passing the solution through a zinc reductor several times. The reduced solution precipitates white mercurous chloride from solutions of mercuric chloride. This reaction is given by 1 mgm. of niobium.

Tantalum compounds in solution do not give a colour change on being reduced with zinc, and this test also serves to establish niobium in the presence of titanium, which produces a violet coloration.<sup>2</sup> Vanadium, molybdenum, and tungsten solutions, however, behave similarly to niobium, and these metals must, therefore, be previously removed.

(4) When a solution of niobic acid in concentrated hydrochloric acid (2 : 1) is boiled with *tin* for some time, a deep sapphire-blue coloration is obtained, which fades on standing and is regenerated by boiling.

(5) Addition of excess of *potassium thiocyanate* to an alkaline solution of a niobate, followed by *zinc* and *concentrated hydrochloric acid*, produces a golden-brown colour which may be almost red in the presence of larger quantities of niobium. It is stated that neither tantalum nor titanium gives any coloration under the same conditions.<sup>3</sup> Addition of

<sup>1</sup> Compare Powell and Schoeller, *Analyst*, 1925, 50, 495.

<sup>2</sup> Compare Moir, *loc. cit.*

<sup>3</sup> Pennington, *loc. cit.*



potassium thiocyanate to a hydrochloric acid solution of tantallic acid or niobic acid gives a colourless solution.

(6) *Potassium ferrocyanide* yields a yellow or reddish-brown precipitate with a hot solution of tantallic acid in hydrochloric acid; niobic acid gives a reddish-brown<sup>1</sup> or greyish-green<sup>2</sup> precipitate.

(7) *Tannin* produces an orange-red or chocolate-red precipitate with an acid solution of niobic acid, and a yellow or light brown precipitate with acid solutions of tantallic acid. *Pyrogallol* and other *polyhydroxy derivatives of benzene* behave similarly.

(8) Addition of *ammonium hydroxide* or *ammonium sulphide* to solutions of niobic acid and tantallic acid in mineral acids reprecipitates the niobic and tantallic acids, which may, however, retain some of the ammonia. This test does not distinguish between niobium and tantalum, and it does not proceed in the presence of tartaric acid.

**B. Dry Reactions.**—When heated in the reducing flame a *bead of microcosmic salt* assumes a blue, violet, or brown colour with increasing quantities of niobic acid; the heated bead becomes red on the addition of ferrous sulphate. With tantallic acid under these conditions the bead remains colourless.

Borax beads do not produce colorations either with niobium or tantalum.

<sup>1</sup> Moir, *loc. cit.*

<sup>2</sup> Weiss and Landecker, *loc. cit.*; compare also Pennington (*loc. cit.*) on effect of presence of fluorides.

## CHAPTER VI.

### NIOBIUM AND ITS ALLOYS.

Symbol, Nb. Atomic Weight, 93·8 (O=16).

**Preparation of Metallic Niobium.**—The preparation of metallic niobium is not carried out industrially, as there is no demand for the metal. Its laboratory preparation depends on the reduction of the pentoxide. This is effected with difficulty, firstly, because of the tendency for partially reduced products to be formed,<sup>1</sup> and secondly, because of the tendency of the reducing agent, for example carbon<sup>2</sup> or aluminium,<sup>3</sup> to combine or alloy with any niobium formed.

One method of preparation consists in a modification of the Goldschmidt process. Niobium pentoxide is mixed with an alloy of the rare earths, called *mixed metal*, obtained in the manufacture of thorium nitrate, and consisting roughly of 45 per cent. of cerium, 20 per cent. of lanthanum, 15 per cent. of “didymium,” and about 20 per cent. of other rare-earth metals. The reaction is carried out in a magnesia-lined crucible, and is started with a firing mixture of barium peroxide, potassium chlorate, and aluminium powder. Considerable evolution of heat takes place and the reduction is extremely rapid; a button of niobium is obtained<sup>4</sup> which, however, is not pure.

Carbon and aluminium were successfully employed as the reducing agents in the following special manner.<sup>5</sup> Pure niobium pentoxide was moulded into filaments about half a millimetre in diameter with the aid of a little paraffin, and these were reduced to the tetroxide by heating to whiteness for four or five hours in carbon powder. The filaments so obtained were then heated to whiteness in a vacuum by means of an alternating current, whereupon rapid reduction to the pure metal took place. In order to prepare larger quantities of niobium the pentoxide is first reduced with aluminium powder, and the product, which contains about 3 per cent. of aluminium and some unchanged oxide, is heated in the electric arc in a vacuum until all the impurities are vaporised (a current of 185 amperes at 40 volts for fifteen hours is required for 20 grams of metal). Perfectly pure niobium obtained in this manner has been used for the investigation of the properties of the metal.

<sup>1</sup> Rose, *Pogg. Annalen*, 1858, 104, 310.

<sup>2</sup> Deville, *Compt. rend.*, 1868, 66, 183; Moissan, *ibid.*, 1901, 133, 20; Larsson, *Zeitsch. anorg. Chem.*, 1896, 12, 189.

<sup>3</sup> Marignac, *Compt. rend.*, 1868, 66, 180; Moissan, *loc. cit.*; compare Goldschmidt and Vautin, *J. Soc. Chem. Ind.*, 1898, 17, 543.

<sup>4</sup> Weiss and Aichel, *Annalen*, 1904, 337, 385; Muthmann, Weiss, and Riedelbauch, *ibid.*, 1907, 355, 64.

<sup>5</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45; 1907, 13, 145.

Niobium pentoxide has been reduced to the metal by means of hydrogen at 7 atmospheres pressure and at 1910° C.,<sup>1</sup> and a fairly pure sample has been obtained by the action of hydrogen on niobium pentachloride at a red heat.<sup>2</sup>

*Colloidal Niobium.*—Sols of niobium have been prepared by sparking electrodes of the metal immersed in *isobutyl* alcohol by means of an induction coil,<sup>3</sup> or by reducing solutions of niobium salts with hydrazine, formic acid or formaldehyde in the presence of gelatose.<sup>4</sup>

**Physical Properties of Niobium.**—Niobium is variously described as a dull grey,<sup>5</sup> steel grey,<sup>6</sup> or white metal with a yellowish tinge,<sup>7</sup> giving a silver-white fracture.<sup>8</sup> The metallic lustre is remarkably permanent, and is not removed even by prolonged boiling with aqua-regia. After being fused *in vacuo*, rhombic crystals several millimetres long are formed.<sup>9</sup> The crystal structure of the metal has been studied.<sup>10</sup> The density of the fused metal is 12·7 or 12·75 after being rolled into thin foil.<sup>11</sup> Other figures which have been obtained for less pure samples are much lower, e.g. 8·4,<sup>12</sup> 7·8,<sup>13</sup> 7·06,<sup>14</sup> 7·37.<sup>15</sup> The hardness of the pure metal is about the same as that of wrought iron, and it will not scratch glass or quartz,<sup>16</sup> but the presence of small quantities of carbon, aluminium, or oxygen increases the hardness considerably; a specimen containing about 3 per cent. of carbon scratched quartz easily.<sup>17</sup> It is not very brittle. It can be hammered into foil 0·05 mm. thick, and it is possible, although difficult, to draw it into wire. It can be welded by hammering at a red heat.<sup>18</sup>

The specific heat between 21° and 100° C. is 0·071, giving 6·61 for the atomic heat, which figure is in conformity with the law of Dulong and Petit.<sup>19</sup> von Bolton's sample melted at 1950° C. *in vacuo*, but a more recent determination gave the melting-point as 1700° C.<sup>20</sup> Niobium displays weak paramagnetism.<sup>21</sup> The electrical resistance of pure niobium wire, 1 metre long and 1 sq. mm. cross-section, is 0·187 ohm; this figure increases with rising temperature. The metal volatilises and scatters comparatively easily when made to glow in a vacuum, and is therefore unsuitable for use as the filament in electric lamps.<sup>22</sup>

**Optical Properties.**—The refractive index of niobium is 1·80, the

<sup>1</sup> Wartenburg, Broy, and Reinicke, *Zeitsch. Elektrochem.*, 1923, 29, 214; compare Newbery and Pring, *Proc. Roy. Soc.*, 1910, A, 92, 276.

<sup>2</sup> Roscoe, *Chem. News*, 1878, 37, 25.

<sup>3</sup> Svedberg, *Ber.*, 1906, 39, 1705.

<sup>4</sup> *German Pat.* 281305 (1913); see also *Eng. Pat.* 25864 (1906); *French Pat.* 371799 (1906).

<sup>5</sup> von Bolton, *loc. cit.*

<sup>6</sup> Roscoe, *loc. cit.*

<sup>7</sup> Muthmann, Weiss, and Riedelbauch, *loc. cit.*

<sup>8</sup> Weiss and Aichel, *loc. cit.*

<sup>9</sup> von Bolton, *loc. cit.*

<sup>10</sup> von Olshausen, *Zeitsch. Kryst. Min.*, 1925, 61, 463; Sonder, *ibid.*, 1922-23, 57, 617.

<sup>11</sup> von Bolton, *loc. cit.*

<sup>12</sup> Muthmann, Weiss, and Riedelbauch, *loc. cit.*

<sup>13</sup> Baur, *Zeitsch. physikal. Chem.*, 1911, 76, 569.

<sup>14</sup> Roscoe, *loc. cit.*

<sup>15</sup> Marignac, *loc. cit.*

<sup>16</sup> von Bolton, *loc. cit.*

<sup>17</sup> Moissan, *loc. cit.*

<sup>18</sup> von Bolton, *loc. cit.*

<sup>19</sup> von Bolton, *loc. cit.* An earlier determination with an impure specimen gave 0·0617 (Muthmann, Weiss, and Riedelbauch, *loc. cit.*).

<sup>20</sup> Guertler and Pirani, *Zeitsch. für Metallkunde*, 1919, 11, 1; 1920, 12, 67.

<sup>21</sup> Loring, *Chem. News*, 1914, 109, 122; Owen, *Ann. Physik*, 1912, [iv], 37, 664; Honda, *ibid.*, 1910, [iv], 32, 1027; Meyer, *Wied. Annalen*, 1899, 68, 324.

<sup>22</sup> von Bolton, *loc. cit.*

coefficient of absorption 2.11, and the reflexion capacity 41.3 per cent. when measured with yellow light of wave-length  $\lambda=5790$ .<sup>1</sup>

The arc spectrum of niobium has been measured in the region  $\lambda=2600$  to  $\lambda=6000$ , using specimens of the pentoxide obtained from several niobium ores and a concave grating of 6 feet focus.<sup>2</sup> The more intense lines are tabulated in the following table:—

### ARC SPECTRUM OF NIOBIUM.

Wave-length.	Relative Intensity of Line.	Wave-length.	Relative Intensity of Line.	Wave-length.	Relative Intensity of Line.
2618.5	8	3759.7	10	4275.3	10
2766.5	10	3781.2	8	4299.8	10
2824.5	8	3787.3	8	4301.3	10
2868.6	8	3791.4	8	4311.5	8
2883.2	8	3798.2	8	4321.6	8
2961.3	10	3810.6	8	4336.6	8
2990.4	10	3825.0	8	4349.2	8
3010.9	10	3894.2	9	4351.8	10
3036.2	10	3914.9	8	4378.2	8
3039.8	10	3937.7	8	4437.5	9
3063.5	10	3966.4	8	4447.5	8
3094.3	10	4022.9	10	4523.6	10
3108.7	8	4032.7	10	4547.0	8
3130.9	8	4059.1	10	4564.7	10
3163.5	8	4079.9	10	4573.3	8
3225.6	8	4101.1	10	4579.6	8
3247.7	10	4124.0	10	4581.8	8
3274.1	10	4130.1	8	4587.2	8
3358.5	8	4137.3	10	4664.0	8
3498.7	8	4139.9	10	4667.5	10
3554.8	9	4152.8	10	5079.1	8
3563.7	10	4163.8	8	5195.4	8
3576.0	8	4164.9	8	5664.9	8
3580.4	10	4168.3	10	5665.8	8
3664.8	8	4191.1	10	5671.2	10
3698.0	8	4192.2	8	5838.8	8
3713.2	8	4218.1	8	5900.7	10
3726.4	8	4229.3	8	6661.1	10
3740.0	8	4262.2	8	6677.5	8

The arc and spark spectra in the ultra-violet region have also been photographed and measured.<sup>3</sup> The spectral structure of niobium resembles that of vanadium, and various regularities have been discovered in it.<sup>4</sup> In order to be able to establish spectrographically the

<sup>1</sup> Wartenberg, *Verh. Deut. physikal. Ges.*, 1910, 12, 105.

<sup>2</sup> Hildebrand, *J. Amer. Chem. Soc.*, 1908, 30, 1672.

<sup>3</sup> McLennan and Liggett, *Trans. Roy. Soc. Canada*, 1926, 20, 377.

<sup>4</sup> Jack, *Proc. Roy. Irish Acad.*, 1912, A, 30, 42; Paulson, *Physikal. Zeitsch.*, 1915, 16, 352; Meggers, *J. Washington Acad. Sci.*, 1924, 14, 442; Meggers and Kiess, *J. Optical Soc. Amer.*, 1926, 12, 417; Laporte, *ibid.*, 1926, 13, 1.

presence of traces of a foreign element in a substance, de Gramont determined which of the lines in the spectrum produced by a condensed spark discharge are the last to appear as the quantity of foreign element is gradually reduced. These are not necessarily the most intense lines in the arc or spark spectrum. The wave-lengths of the ultimate lines given by niobium in this manner with a crown Uvial glass spectrograph are : <sup>1</sup> 4101.0, 4079.7, 4059.0, 3358.4, in Ångström units.

Eder and Valenta <sup>2</sup> have measured a large number of lines in the flame spectrum given by niobium pentoxide between carbon electrodes. The flame spectrum of niobium between carbon electrodes consists of a blue cone with a yellowish-green shell. <sup>3</sup> The band spectrum of niobium is composed of a very large number of lines which are comparatively sharp but not strong.

The X-ray spectra of niobium have been investigated. <sup>4</sup> Aston was unable to obtain a definite mass spectrum of the metal. <sup>5</sup> The arrangement of the electron groups in the atom has been considered by Lessheim and Samuel. <sup>6</sup> Niobium is not radioactive. <sup>7</sup>

**Chemical Properties.** <sup>8</sup>—When heated in hydrogen, pure, finely divided niobium is converted into a dark grey powder containing a maximum of 1.12 per cent. of hydrogen, which corresponds to a hydride NbH. An impure sample of niobium absorbed 7.5 per cent. of its weight of hydrogen at a red heat. Niobium does not tarnish in the air at ordinary temperatures. When a compact piece of the metal is gradually heated in air it first becomes yellow, then blue, and finally becomes coated with a brownish-blue film of oxide which hinders further oxidation ; the finely divided metal yields the pentoxide only slowly when strongly heated in air or oxygen. The glowing, finely divided metal decomposes water vigorously, with evolution of hydrogen. Heated in nitrogen at 1000° C. it becomes coated with a nitride. Filings of the metal decompose ammonia at a red heat with formation of a nitride which yields ammonia and niobic acid with caustic potash. The metal is attacked by chlorine at about 200° C. with formation of the pentachloride ; bromine gives the pentabromide at higher temperatures ; iodine is without action. <sup>9</sup> Sulphur and selenium are absorbed with considerable evolution of heat and the formation of a black sulphide or selenide. The pure metal is insoluble in sulphuric acid, hydrochloric

<sup>1</sup> de Gramont, *Compt. rend.* 1920, 171, 1106 ; *Revue de Métallurgie*, 1922, 19, 20 ; Twyman, *Wave-length Tables for Spectrum Analysis* (Adam Hilger, Ltd., London), 1923, 81.

<sup>2</sup> Eder and Valenta, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, [11a], 119, 559.

<sup>3</sup> Mott, *Trans. Amer. Electrochem. Soc.*, 1917, 31, 272.

<sup>4</sup> The examination of the X-ray spectra and the bearing of the results on the structure of the niobium atom and atoms of many other metals has been reviewed by Coster (*Phil. Mag.*, 1922, 43, 1070). More recent measurements of the K, L, and M series of the X-ray spectra are given in the papers cited. K series : Leide, *Compt. rend.*, 1925, 180, 1203 ; *Zeitsch. Physik*, 1926, 39, 686 ; Schrör, *Ann. Physik*, 1926, 80, 297 ; see also Moseley, *Phil. Mag.*, 1914, [vi], 27, 708. L series : Coster and Mulder, *Zeitsch. Physik*, 1926, 38, 264 ; see also Friman, *Phil. Mag.*, 1916, [vi], 32, 498. M series : Dauvillier, *Compt. rend.*, 1926, 183, 193.

<sup>5</sup> Aston, *Phil. Mag.*, 1924, [vi], 47, 385.

<sup>6</sup> Lessheim and Samuel, *Zeitsch. Physik*, 1926, 40, 220.

<sup>7</sup> Strong, *Amer. Chem. J.*, 1909, 42, 147 ; compare Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576.

<sup>8</sup> Weiss and Aichel, *loc. cit.* ; Muthmann, Weiss, and Riedelbauch, *loc. cit.* ; von Bolton, *loc. cit.* ; Moissan, *Compt. rend.*, 1901, 133, 20.

<sup>9</sup> Barr, *J. Amer. Chem. Soc.*, 1908, 30, 1671.

acid, nitric acid, and aqua-regia, but it is attacked by these acids when it is alloyed with other metals. It is slowly dissolved by hot hydrofluoric acid, more rapidly in the presence of platinum. Alkali solutions are without action on niobium, but the metal is converted into a niobate when fused with solid caustic potash, potassium carbonate, etc. Carbon dioxide, sulphur dioxide, phosphorus pentoxide, arsenic pentoxide, chromium sesquioxide, iodic acid, lead oxide, and mercuric chloride are all reduced by niobium when heated with it at high temperatures.

**Electromotive Behaviour.**<sup>1</sup>—The electromotive behaviour of niobium is of interest in that it is considerably influenced by cathodic and anodic polarisation. On being immersed in concentrated caustic potash solution or in 10 per cent. ammonium hydroxide, or on being made the cathode in the electrolysis of water, caustic potash, or ammonium chloride for a few minutes, the metal is activated and its potential towards normal potassium chloride increases. On the other hand, on being immersed in concentrated nitric acid, chromic acid, perchloric acid, potassium permanganate, or thiocyanic acid, or on being made the anode in the electrolysis of water, potassium cyanide, chromic acid, or hydrochloric acid, the metal becomes passive and the potential drops to a remarkable extent. Anodically polarised niobium displays *valve action* (see p. 178) to a pronounced degree. A specimen of niobium which was not very compact (the valve action varies with the degree of compactness), when used as the anode in from 1 to 5 per cent. sulphuric acid, gave only a momentary current with an applied E.M.F. of 112 volts. There was a slight evolution of gas, and the electrode became covered with a greenish-yellow or iridescent blue film which was insoluble in the common acids, but was dissolved by hydrofluoric acid or on making the metal the anode in nitric acid. In an electrolyte consisting of a 0.1 per cent. solution of ammonium phosphate, the E.M.F. necessary to overcome the insulating effect of the oxide-gas layer on the metal is no less than 530 volts. Valve action has also been observed with a large number of other electrolytes. In the cases of hydrochloric acid, sodium chloride, nitric acid, sodium nitrate, acetic acid, potassium bromide and potassium iodide, the anode is disintegrated and dissolves with formation of the pentavalent niobium compound, followed by precipitation of niobic acid; hydrofluoric acid acts similarly, but niobic acid is not precipitated.

The valve action displayed by niobium renders it useful in the construction of electrolytic cell "rectifiers." An alternating current does not pass through 10 per cent. sulphuric acid when both electrodes are made of niobium even at a pressure of 120 volts; if one of the electrodes is substituted for platinum a unidirectional current is produced.<sup>2</sup>

**Atomic Weight of Niobium.**—The first determinations were carried out by Hermann<sup>3</sup> and Rose,<sup>4</sup> but these are now only of historical interest. In 1864 Blomstrand<sup>5</sup> analysed niobium pentachloride but obtained

<sup>1</sup> Muthmann and Frauenberger, *Sitzungsber. K. Bayr. Akad. Wiss. Munich*, 1904, [ii], 221; Schulze, *Ann. Phys.*, 1908, 25, 775; Sborgi, *Gazzetta*, 1912, [ii], 42, 331; Kiehl and Hart, *J. Amer. Chem. Soc.*, 1928, 50, 2337.

<sup>2</sup> von Bolton, *Zeitsch. Elektrochem.*, 1907, 13, 145.

<sup>3</sup> Hermann, *J. prakt. Chem.*, 1856, 68, 73.

<sup>4</sup> Rose, *Pogg. Annalen*, 1858, 104, 439.

<sup>5</sup> Blomstrand, *Acta Univ. Lund*, 1864; see *A Recalculation of the Atomic Weights*, Clarke, Smithsonian Institution, 3rd ed., 1910, p. 335.

discordant figures. They were all higher than the atomic weight of molybdenum, the next higher element in the periodic system, and it seems certain that Blomstrand's material was not free from tantalum.

In the following year Marignac<sup>1</sup> published the results of about twenty very carefully conducted analyses of potassium niobium oxyfluoride,  $2\text{KF}\cdot\text{NbOF}_3\cdot\text{H}_2\text{O}$ ; from his data the following figures for the atomic weight of niobium can be calculated:<sup>2</sup>

$$(a) \frac{2[2\text{KF}\cdot\text{NbOF}_3\cdot\text{H}_2\text{O}]}{\text{Nb}_2\text{O}_5} = \frac{100}{44\cdot36}; \text{ hence Nb} = 93\cdot37.$$

$$(b) \frac{2\text{KF}\cdot\text{NbOF}_3\cdot\text{H}_2\text{O}}{\text{K}_2\text{SO}_4} = \frac{100}{57\cdot82}; \quad \text{,,} \quad \text{Nb} = 94\cdot10.$$

$$(c) \frac{\text{Nb}_2\text{O}_5}{\text{K}_2\text{SO}_4} = \frac{44\cdot36}{57\cdot82}; \quad \text{,,} \quad \text{Nb} = 93\cdot70.$$

Marignac's material contained traces of titanium, and he therefore assumed that the higher limit would most probably be the more correct, and accordingly suggested an atomic weight of 94. This figure was confirmed by Marignac's analyses of niobium pentachloride and was accepted until 1908, when Balke and Smith<sup>3</sup> redetermined the ratio

$$\frac{2\text{NbCl}_5}{\text{Nb}_2\text{O}_5},$$

using material of more reliable purity. The pentachloride was decomposed by water with the aid of a small quantity of nitric acid, and the oxide so produced was ignited and weighed. The mean of nine experiments gave the ratio

$$\frac{2\text{NbCl}_5}{\text{Nb}_2\text{O}_5} = \frac{1}{49\cdot305}.$$

This gives an atomic weight of 93·52, which is in harmony with the vapour-density determinations of niobium pentachloride and niobium oxychloride carried out previously by Deville and Troost.<sup>4</sup> In 1915 Smith and Van Haagen<sup>5</sup> criticised the foregoing method on the following grounds: (a) The pentachloride used may have contained traces of oxychloride; (b) the residual oxide may have retained traces of chlorine; (c) slight loss of niobium may have occurred, because niobium pentoxide is volatile in hydrogen chloride. These investigators obtained an appreciably lower figure, using a totally different method. Pure sodium metaniobate was decomposed by sulphur monochloride vapour and the residue of sodium chloride was weighed, the niobium being expelled either as chloride or oxychloride. Seven experiments gave the mean ratio

$$\frac{\text{NaNbO}_3}{\text{NaCl}} = \frac{2\cdot80759}{1}; \text{ whence Nb} = 93\cdot12.$$

<sup>1</sup> Marignac, *Arch. Sci. phys. nat.*, 1865, [ii], 23; *Ann. Chim. Phys.*, 1866, [iv], 8, 16, 28.

<sup>2</sup> The fundamental values set out on p. viii of the General Introduction have been used. The same fundamental values have been employed in the recalculation of the subsequent values for the atomic weight of niobium mentioned in this section.

<sup>3</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1645.

<sup>4</sup> Deville and Troost, *Compt. rend.*, 1865, 60, 1221; 1863, 56, 891.

<sup>5</sup> Smith and Van Haagen, *J. Amer. Chem. Soc.*, 1915, 37, 1783.

The values for the atomic weight of niobium as determined by the various investigators since 1864 are summarised in the following table:—

### ATOMIC WEIGHT OF NIOBIUM.

Authority.	Date.	Ratio Determined.	Number of Experiments.	Atomic Weight.
Blomstrand	1864	$2\text{NbCl}_5/\text{Nb}_2\text{O}_5$	11	96·23
		$\text{NbCl}_5/5\text{AgCl}$	6	99·10
		$\text{Nb}_2\text{O}_5/10\text{AgCl}$	6	97·46
Marignac	1865	$2[2\text{KF.NbOF}_3.\text{H}_2\text{O}]/\text{Nb}_2\text{O}_5$	20	93·37
		$2\text{KF.NbOF}_3.\text{H}_2\text{O}/\text{K}_2\text{SO}_4$	20	94·10
		$\text{Nb}_2\text{O}_5/\text{K}_2\text{SO}_4$	20	93·70
Balke and Smith	1908	$2\text{NbCl}_5/\text{Nb}_2\text{O}_5$	9	93·52
Smith and Van Haagen.	1915	$\text{Na.NbO}_3/\text{NaCl}$	7	93·12

The value 93·1 was adopted in 1916 by the International Committee on Atomic Weights; this was altered to 93·3 in 1929.

**Alloys.**—Investigation into the formation of alloys of niobium with other elements has hitherto been scanty, and even where alloying is known to take place the conditions for the alloy formation and the properties of the products have received little attention. Niobium appears to alloy with iron in all proportions; the alloy containing 90 per cent. of iron and 10 per cent. of niobium is extremely hard.<sup>1</sup> Niobium, usually in conjunction with tantalum because of the difficulty of their separation, can be used for incorporation into special steels.<sup>2</sup>

Aluminium-niobium alloys are best produced by the Goldschmidt process. A product which contains about 3 per cent. of aluminium is harder than glass or quartz; its density is 7·5.<sup>3</sup> A brittle alloy of chromium and niobium is obtained by fusing green chromium oxide and niobium together in the electric furnace.<sup>4</sup>

Alloys of niobium and tantalum with nickel and zirconium have also been prepared.<sup>5</sup> It is claimed that the latter can be heated to whiteness in air without oxidation or vaporisation.

Potassium, sodium, magnesium, and mercury can be distilled over niobium without formation of alloys; arsenic, antimony, and tellurium do not form alloys below 500° to 600° C.

<sup>1</sup> von Bolton, *loc. cit.*

<sup>2</sup> *British Pat.* 152371 (1918).

<sup>3</sup> Goldschmidt and Vautin, *J. Soc. Chem. Ind.*, 1893, 17, 543; von Bolton, *loc. cit.*

<sup>4</sup> Moissan, *Compt. rend.*, 1901, 133, 20; *Bull. Soc. chim.*, 1902, [iii], 27, 431.

<sup>5</sup> *Canada Pats.* 209342, 214118 (1921); *U.S. Pat.* 1334089 (1920).



## CHAPTER VII.

### COMPOUNDS OF NIOBIUM.

**General.**—The compounds of niobium are not so numerous as those of vanadium. The following oxides,<sup>1</sup>  $Nb_2O_3$ ,  $NbO_2$ ,  $Nb_2O_5$ , are known, but only the pentoxide gives rise to salts, viz. the niobates.<sup>2</sup> The acid character of niobium pentoxide or “niobic acid” is very weak; the niobates are decomposed, for instance, by carbon dioxide, and are readily hydrolysed to the pentoxide. Niobic acid is, in fact, very comparable in its method of preparation and behaviour to silicic acid and stannic acid.

Reduction of pentavalent niobium compounds in acid solution with zinc yields solutions which appear to contain the niobium in the tetravalent state and probably also the trivalent state. The solution first becomes blue, then olive-green, and finally dark brown. Reduction of a boiling, dilute solution of niobic acid in concentrated hydrochloric or sulphuric acid may yield the brown solution immediately. The course of the reaction is considerably affected by such conditions as the acidity of the solution, the reducing agent employed, the physical condition of the reducing agent, and the presence of foreign substances. The final stage of the reduction can usually be depended on as being only approximately trivalent (see p. 181). Electrolytic methods of reduction, using platinum and amalgamated lead electrodes, have also been employed.<sup>3</sup>

The blue solutions gradually precipitate brown flakes, which are thereafter slowly converted into white niobic acid. Similar brown precipitates are obtained by the addition of ammonium hydroxide to the brown solutions. Marignac<sup>4</sup> concluded from the amount of potassium permanganate required to oxidise the brown precipitate that its composition was  $Nb_3O_5$ , which can be alternatively written  $NbO.2NbO_2$ . This formula cannot, however, be definitely accepted, as the experimental data do not exclude the approximate empirical formula  $Nb_3O_{4\frac{1}{2}}$ , from which it would follow that the brown precipitate is composed of niobium sesquioxide together with small proportions of unreduced pentoxide. The blue solution functions as a powerful reducing agent, and will, for instance, precipitate copper from copper sulphate solution, and generally is a stronger reducing agent than trivalent titanium solution. On being evaporated *in vacuo* it leaves a damp blue mass, which on being dissolved in concentrated hydrochloric acid and treated with ammonium chloride

<sup>1</sup> The existence of the oxide  $NbO$  is doubtful.

<sup>2</sup> The natural ores called niobites consist of niobates.

<sup>3</sup> Stähler, *Ber.*, 1914, 47, 841; Ott, *Zetsch. Elektrochem.*, 1912, 18, 349; Kiehl and Hart, *J. Amer. Chem. Soc.*, 1928, 50, 1614.

<sup>4</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 15.

gives a precipitate of "niobium blue," very similar in appearance to "molybdenum blue."<sup>1</sup> No definite salts have hitherto been isolated, however, from reduced niobium solutions, but an *ammonium niobium sulphate*, which has the probable formula  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Nb}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ , and an *acid ammonium niobium sulphate*,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Nb}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , have been prepared. The halides of niobium are devoid of saline character.

Niobic acid displays a much less pronounced tendency than vanadic acid to form heteropoly-compounds with other acids, but *oxaloniobates* are known. It reacts with hydrogen peroxide to form *perniobic acid*,  $\text{HNbO}_4 \cdot x\text{H}_2\text{O}$ , salts of which are known. The double niobium oxy-fluorides also take up active oxygen.

### NIOBIUM AND HYDROGEN.

The absorption of hydrogen by pure metallic niobium under different conditions of temperature and pressure has not been investigated. An impure sample absorbed 8 per cent. of hydrogen after fifteen hours' exposure to the gas at a high temperature.<sup>2</sup> In another experiment<sup>3</sup> a substance of empirical formula  $\text{NbH}$  was obtained. This substance has also been prepared by fusing potassium niobium fluoride,  $\text{K}_2\text{NbF}_7$ , with potassium fluoride (which has the effect of rendering the subsequent reaction less violent) and then reducing the product with sodium by heating strongly in a wrought-iron crucible. The excess of sodium is distilled off and the residue extracted repeatedly with water, and finally with water containing a small quantity of hydrofluoric acid. The hydride is left behind as a black or dark grey powder.<sup>4</sup> Its density varies from 6.0 to 6.6.<sup>5</sup> The specific heat of the hydride appears to decrease with increase of temperature; an impure sample gave the value 0.0834 between 0° and 440° C.<sup>6</sup> It resembles the metal in that it is insoluble in hydrochloric acid, nitric acid, dilute sulphuric acid, and aqua-regia, but it is attacked by concentrated sulphuric acid, hydrofluoric acid, and molten potassium hydrogen sulphate. On being heated in air it burns readily with incandescence to niobium pentoxide and water. It is scarcely affected by being heated in hydrogen, but it reacts with sulphur to form a black sulphide, and with chlorine and hydrochloric acid to form various niobium chlorides.

Other niobium-hydrogen compounds or alloys of doubtful composition have been obtained by reduction of niobium oxytrichloride,  $\text{NbOCl}_3$ , with hydrogen,<sup>7</sup> and by using metallic niobium as the cathode in the electrolysis of dilute sulphuric acid.<sup>8</sup>

### Niobium and the Halogens.

The halides and oxyhalides of niobium are set out in the following table:

<sup>1</sup> See this series, Vol. VII., Part III. (1926), p. 131.

<sup>2</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 90.

<sup>3</sup> von Bolton, *Zeitsch. Elektrochem.*, 1907, 13, 145.

<sup>4</sup> Marignac, *Compt. rend.*, 1868, 66, 180.

<sup>5</sup> Kruss and Nilson, *Öfvers. K. Vet.-Akad. Förh.*, 1887, No. 5; *Ber.*, 1887, 20, 1691; compare Roscoe, *Chem. News*, 1878, 37, 25.

<sup>6</sup> Krüss and Nilson, *loc. cit.*

<sup>7</sup> Blomstrand, *Acta Univ. Lund*, 1864; Roscoe, *loc. cit.*

<sup>8</sup> von Bolton, *loc. cit.*

## HALIDES AND OXYHALIDES OF NIOBIUM.

Valency.	Fluorine.	Chlorine.	Bromine.	Iodine.
"Di"-valent	..	Nb <sub>6</sub> Cl <sub>14</sub> .7H <sub>2</sub> O Nb <sub>6</sub> Cl <sub>12</sub> (OH) <sub>2</sub> .8H <sub>2</sub> O Nb <sub>6</sub> Cl <sub>12</sub> Br <sub>2</sub> .7H <sub>2</sub> O	..	..
Trivalent	..	NbCl <sub>3</sub> Nb <sub>2</sub> Cl <sub>4</sub> (OH) <sub>2</sub> .5H <sub>2</sub> O Nb <sub>2</sub> Cl <sub>3</sub> (OH) <sub>3</sub> .3H <sub>2</sub> O	..	..
Pentavalent	NbF <sub>5</sub> NbOF <sub>3</sub> * NbO <sub>2</sub> F*	NbCl <sub>5</sub> NbOCl <sub>3</sub>	NbBr <sub>5</sub> NbOBr <sub>3</sub>	..

The pentavalent halides and oxyhalides, as in the case of other niobium compounds, are the most stable. It is remarkable that the pentavalency is maintained with increase in the atomic weight of the halogen. All the halogen compounds are characterised by their ready tendency to undergo hydrolysis on the addition of water or even in damp air with precipitation of niobic acid and formation of the hydrogen halide. Their preparation can, therefore, be effected only in the dry way: (a) synthetically, or (b) by the action of chlorine, carbon tetrachloride, or sulphur monochloride on the oxide or sulphide. They do not possess saline properties, and cannot be prepared by the action of the halogen acids on the oxide.

Definite compounds of niobium and iodine are unknown, although tantalum pentiodide and vanadium tri-iodide have been prepared.

The divalent chloro-compounds are probably more correctly represented as chloroniobium acid,  $\text{HNb}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$ , and its derivatives, in analogous manner to chlorotantalum acid,  $\text{HTa}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$ , the composition of which has recently been reinvestigated.

## NIOBIUM AND FLUORINE.

**Niobium Pentafluoride**,  $\text{NbF}_5$ , is the only known compound of niobium and fluorine, and even this cannot be obtained in the free state by a wet method because of the extreme readiness with which it hydrolyses. Niobium pentoxide dissolves readily in hydrofluoric acid, but evaporation of the solution leaves a residue of the unchanged oxide. Niobium pentafluoride has been prepared synthetically<sup>1</sup> by passing dry fluorine over the gently heated metal contained in a boat in a platinum tube. The product is freed from platinum tetrafluoride, a little of which is formed at the same time, by distillation *in vacuo* at 100° to 110° C. An alternative method consists in treating niobium pentachloride with anhydrous hydrogen fluoride in a freezing mixture and purifying by redistillation.<sup>2</sup>

\* Does not exist in the free state.

<sup>1</sup> Ruff and Zedner, *Ber.*, 1909, 42, 493.

<sup>2</sup> Ruff and Schiller, *Zeitsch. anorg. Chem.*, 1911, 72, 329.

Niobium pentafluoride forms colourless, highly refractive prisms; density 3.2932 at 18° C. It melts at 75.5° C., and boils at 217° to 220° C. under a pressure of 760 mm. of mercury. It is extremely hygroscopic and deliquesces rapidly in air. It is reduced by hydrogen at 236° C. in contact with platinum to an unstable lower blue fluoride. Excess of concentrated alkali hydroxide or alkali carbonate solutions attack it with formation of the alkali niobate. It dissolves in toluene, paraffin, carbon bisulphide, and other organic solvents.

*Double Fluorides of Niobium Pentafluoride.*—Niobium pentafluoride shows a strong tendency to form stable double fluorides with the fluorides of other metals. These are conveniently prepared by the action of carbonates of the metals on solutions of niobium pentoxide in a large excess of hydrofluoric acid, or by the addition of a large excess of hydrofluoric acid to solutions of the oxyfluorides of the metals. In the absence of excess of hydrofluoric acid hydrolysis takes place as usual with the formation of niobium oxytrifluoride,  $\text{NbOF}_3$ . The precipitation of these double fluorides indicates the probable existence in solution of niobium pentafluoride; stability is imparted by the formation of complex anions containing several fluorine atoms.

When viewed from the point of view of the Werner co-ordination theory, it is observed that the co-ordination number seven is frequent in the double fluorides as well as in the niobium oxyhalides. Many members of the series  $2\text{R}\cdot\text{F}\cdot\text{NbF}_5$  or  $[\text{NbF}_7]\text{R}_2$ , and of the series  $2\text{R}\cdot\text{X}\cdot\text{NbOX}_3$  or  $[\text{NbO}_5^{\text{X}}]\text{R}_2$ , are known, where R represents a metal and X is fluorine, chlorine, or bromine. The co-ordination numbers six and eight also occur, but less frequently, thus:  $\text{CsF}\cdot\text{NbF}_5$  or  $[\text{NbF}_6]\text{Cs}$ , and  $3\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $[\text{NbF}_6^{\text{F}}](\text{NH}_4)_3$ . The change in the co-ordination number can be seen in the double ammonium oxyfluorides:  $\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $[\text{NbO}_4^{\text{F}}](\text{NH}_4)$ ;  $2\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $[\text{NbO}_5^{\text{F}}](\text{NH}_4)_2$ ;  $3\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $[\text{NbO}_6^{\text{F}}](\text{NH}_4)_3$ , all of which are known.

The following double fluorides of niobium have been prepared: <sup>1</sup>

*Ammonium Niobium Fluoride.*—(See below under Potassium Niobium Fluoride.)

*Cadmium Niobium Fluoride*,  $3\text{NbF}_5\cdot 5\text{CdF}_2\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$  or  $\text{Nb}_3\text{Cd}_5\text{F}_{25}\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$ , is obtained in long, transparent prisms by the action of cadmium carbonate on a solution of niobic acid in concentrated hydrofluoric acid. It is insoluble in water.

*Cæsium Niobium Fluoride*,  $\text{CsF}\cdot\text{NbF}_5$  or  $\text{CsNbF}_6$ , is obtained in fine needles by repeated crystallisation of cæsium niobium oxyfluoride,  $\text{Cs}_2\text{NbOF}_5$ , from hydrofluoric acid.<sup>2</sup> Another cæsium niobium fluoride having the probable composition  $7\text{CsF}\cdot\text{NbF}_5$  or  $\text{Cs}_7\text{NbF}_5$  has been prepared by the action of a solution of cæsium hydroxide in hydrofluoric acid on niobic acid in the same solvent.<sup>3</sup>

*Cobalt Niobium Fluoride*,  $3\text{NbF}_5\cdot 5\text{CoF}_2\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$  or  $\text{Nb}_3\text{Co}_5\text{F}_{25}$ .

<sup>1</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 3, 19, 68; Santesson, *Bull. Soc. chim.*, 1875, [ii], 24, 38, 67.

<sup>2</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1903, 30, 1637.

<sup>3</sup> Pennington, *ibid.*, 1896, 18, 59.

$5\text{HF}\cdot 28\text{H}_2\text{O}$ , forms dark red, prismatic crystals, which are prepared similarly to the corresponding cadmium salt.

*Copper Niobium Fluoride*,  $\text{NbF}_5\cdot 2\text{CuF}_2\cdot \text{HF}\cdot 9\text{H}_2\text{O}$  or  $\text{NbCuF}_9\cdot \text{HF}\cdot 9\text{H}_2\text{O}$ , forms large, dark blue crystals, which are obtained similarly to the cadmium salt.

*Ferrous Niobium Fluoride*,  $2\text{NbF}_5\cdot 3\text{FeF}_2\cdot 4\text{HF}\cdot 19\text{H}_2\text{O}$  or  $\text{Nb}_2\text{Fe}_3\text{F}_{16}\cdot 4\text{HF}\cdot 19\text{H}_2\text{O}$ , is obtained in greenish-yellow, thin prisms by dissolving iron and niobic acid in equivalent proportions in hydrofluoric acid.

*Manganese Niobium Fluoride*,  $3\text{NbF}_5\cdot 5\text{MnF}_2\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$  or  $\text{Nb}_3\text{Mn}_5\text{F}_{25}\cdot 28\text{H}_2\text{O}$ , forms rose-coloured, long prisms, which are obtained similarly to the cadmium salt.

*Mercury Niobium Fluoride*,  $\text{NbF}_5\cdot 3\text{HgF}_2\cdot 8\text{H}_2\text{O}$  or  $\text{NbHg}_3\text{F}_{11}\cdot 8\text{H}_2\text{O}$ , is obtained by dissolving mercuric oxide and niobic acid in hydrofluoric acid. Concentration of the solution after removal of mercuric fluoride yields a white mass which consists of aggregates of short prismatic needles.

*Nickel Niobium Fluoride*,  $2\text{NbF}_5\cdot 3\text{NiF}_2\cdot 4\text{HF}\cdot 19\text{H}_2\text{O}$  or  $\text{Nb}_2\text{Ni}_3\text{F}_{16}\cdot 4\text{HF}\cdot 19\text{H}_2\text{O}$ , forms thin, green needles which are prepared by dissolving equivalent quantities of niobic acid and nickel carbonate in hydrofluoric acid. Concentration of the mother-liquor gives dark green, flat prisms of the composition  $3\text{NbF}_5\cdot 5\text{NiF}_2\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$  or  $\text{Nb}_3\text{Ni}_5\text{F}_{25}\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$ .

*Potassium Niobium Fluoride*,  $\text{NbF}_5\cdot 2\text{KF}$  or  $\text{K}_2\text{NbF}_7$ , is obtained by cooling a concentrated solution of potassium niobium oxyfluoride,  $\text{NbOF}_3\cdot 2\text{KF}\cdot \text{H}_2\text{O}$  or  $\text{K}_2\text{NbOF}_5\cdot \text{H}_2\text{O}$ , in hydrofluoric acid. It forms small, glistening, rhombic needles,  $a : b : c = 0.6682 : 1 : 0.4699$ . It is isomorphous with the corresponding tantalum salt but not with potassium titanium fluoride,<sup>1</sup>  $\text{K}_2\text{TiF}_6$ , and hence is used in one method for the separation of titanium from niobium and tantalum (see p. 128). It is stable at  $100^\circ \text{C}$ ., but loses hydrogen fluoride at considerably higher temperatures. In damp air it is slowly converted into the oxyfluoride,  $\text{K}_2\text{NbOF}_5$ . Its solution in hot water precipitates the hydrated oxyfluoride,  $\text{K}_2\text{NbOF}_5\cdot \text{H}_2\text{O}$ , and leaves an acid solution.<sup>2</sup>

The corresponding sodium niobium fluoride is unknown. *Ammonium niobium fluoride* cannot be prepared in the pure state because hydrolysis takes place even in the presence of excess of hydrofluoric acid. A solution of ammonium niobium oxyfluoride,  $3\text{NH}_4\text{F}\cdot \text{NbOF}_3$ , in hydrofluoric acid precipitates the double salt  $2\text{NH}_4\text{F}\cdot \text{NbF}_5\cdot \text{NH}_4\text{F}\cdot \text{NbOF}_3$  or  $(\text{NH}_4)_3\text{NbF}_8\cdot \text{NbOF}_3$  in masses of small prisms.

*Rubidium Niobium Fluoride*,  $\text{RbNbF}_6$  or  $\text{RbF}\cdot \frac{1}{2}\text{NbF}_5$ , is obtained by repeated crystallisation of rubidium niobium oxyfluoride,  $\text{Rb}_2\text{NbOF}_5$ , from hydrofluoric acid.<sup>3</sup> The double salt  $\text{Rb}_2\text{NbF}_7$ , or  $2\text{RbF}\cdot \text{NbF}_5$ , has also been reported.<sup>4</sup>

*Zinc Niobium Fluoride*,  $3\text{NbF}_5\cdot 5\text{ZnF}_2\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$  or  $\text{Nb}_3\text{Zn}_5\text{F}_{25}\cdot 5\text{HF}\cdot 28\text{H}_2\text{O}$ , is prepared in long prisms by dissolving zinc and an equivalent quantity of niobic acid in hydrofluoric acid.

**Oxyfluorides.**—Two oxyfluorides of niobium having the compositions  $\text{NbOF}_3$  and  $\text{NbO}_2\text{F}$  are known. The former has been obtained in small crystals by the action of hydrogen chloride on a fused mixture

<sup>1</sup> Hall, *J. Amer. Chem. Soc.*, 1904, 26, 1240.

<sup>2</sup> Ruff and Schiller, *loc. cit.*; Metzener, *Ber.*, 1913, 46, 983.

<sup>3</sup> Balke and Smith, *loc. cit.*

<sup>4</sup> Pennington, *loc. cit.*

of niobium pentoxide and calcium fluoride at a red heat.<sup>1</sup> The existence of the latter has been recognised only in double salts with potassium fluoride; it has not been isolated in the free state.

Double salts of niobium oxytrifluoride,  $\text{NbOF}_3$ , are obtained by the action of fluorides of the metals on solutions of niobium pentoxide in hydrofluoric acid, excess of the latter being avoided, otherwise the double fluorides are produced. These salts are much more stable than the double fluorides of niobium and other metals, and are, in fact, among the most stable of the pentavalent niobium compounds. The double oxyfluorides which are most readily prepared possess the general formula  $2\text{R}\cdot\text{F}\cdot\text{NbOF}_3\cdot x\text{H}_2\text{O}$ , where R stands for a monovalent metal. Recrystallisation of double oxyfluorides having other compositions frequently yields salts of this type. These facts indicate the existence of a stable, divalent, complex anion of constitution  $[\text{NbOF}_5]'$ , the stability of which is confirmed by the great difficulty that is experienced in the electrolytic reduction of solutions of potassium niobium oxyfluoride,  $\text{K}_2\text{NbOF}_5\cdot\text{H}_2\text{O}$ .<sup>2</sup> It is of interest to note that double oxyfluorides of vanadium, tantalum, and molybdenum having similar compositions are also known. Double oxyfluorides of the alkali metals react with hydrogen peroxide to yield *alkali niobium peroxyfluorides*, which are described on p. 168.

The following *double oxyfluorides* of niobium, or *fluoroxyniobates*, have been prepared:<sup>3</sup>

*Ammonium Niobium Oxyfluorides*.—The following are known:  $\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $\text{NH}_4\text{NbOF}_4$ ;  $5\text{NH}_4\text{F}\cdot 3\text{NbOF}_3\cdot\text{H}_2\text{O}$  or  $(\text{NH}_4)_5\text{Nb}_3\text{O}_3\text{F}_{14}\cdot\text{H}_2\text{O}$ ;  $2\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $(\text{NH}_4)_2\text{NbOF}_5$ ;  $3\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $(\text{NH}_4)_3\text{NbOF}_6$ . Of these, the compound  $2\text{NH}_4\text{F}\cdot\text{NbOF}_3$  is the commonest, and is readily prepared by the action of ammonium fluoride on a solution of niobium pentoxide in hydrofluoric acid. It behaves similarly to the corresponding potassium salt (see next page), but is not isomorphous with it. It is isomorphous with ammonium tungsten oxyfluoride,  $2\text{NH}_4\text{F}\cdot\text{WO}_2\text{F}_2$ , and forms rhombic bipyramids in which  $a : b : c = 0.4184 : 1 : 1.0058$ . It can be heated to  $170^\circ\text{C}$ . without loss in weight. Its co-ordinated formula is  $[\text{NbO}^{\text{F}_5}](\text{NH}_4)_2$ .

By using excess of niobium pentoxide in the last preparation the compound  $5\text{NH}_4\text{F}\cdot 3\text{NbOF}_3\cdot\text{H}_2\text{O}$  is obtained. This is also very comparable in its behaviour to the corresponding potassium salt. The mother-liquor yields green crystals of composition  $\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $[\text{NbO}^{\text{F}_4}]\text{NH}_4$  on being evaporated. If excess of ammonium fluoride is employed, crystals of the compound  $3\text{NH}_4\text{F}\cdot\text{NbOF}_3$  or  $[\text{NbO}^{\text{F}_6}](\text{NH}_4)_3$  are produced.<sup>4</sup> All these double ammonium oxyfluorides can be heated to  $100^\circ\text{C}$ . without undergoing decomposition.

*Cæsium Niobium Oxyfluoride*,  $2\text{Cs}\cdot\text{F}\cdot\text{NbOF}_3$  or  $\text{Cs}_2\text{NbOF}_5$  or  $[\text{NbO}^{\text{F}_5}]\text{Cs}_2$ , is prepared similarly to the corresponding potassium salt (see below). It forms trigonal crystals.

<sup>1</sup> Joly, *Compt. rend.*, 1875, 8r, 1266.

<sup>2</sup> Ott, *Dissertation* (Munich), 1911, 51.

<sup>3</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 19, 68; *Compt. rend.*, 1868, 66, 180; Pennington, *J. Amer. Chem. Soc.*, 1896, 18, 38, 67; Balke and Smith, *ibid.*, 1908, 30, 1637.

<sup>4</sup> Baker, *J. Chem. Soc.*, 1879, 35, 760.

*Copper Niobium Oxyfluoride*,  $\text{CuF}_2 \cdot \text{NbOF}_3 \cdot 4\text{H}_2\text{O}$  or  $\text{CuNbOF}_5 \cdot 4\text{H}_2\text{O}$  or  $[\text{Nb}_2\text{O}_5] \text{Cu} \cdot 4\text{H}_2\text{O}$ , is prepared by the action of copper fluoride on a solution of niobium pentoxide in hydrofluoric acid. It yields blue, monoclinic prisms which are very readily soluble in water and which are stable at  $100^\circ \text{C}$ . They are isomorphous with copper titanium fluoride,  $\text{CuTiF}_6 \cdot 4\text{H}_2\text{O}$ , and with copper tungsten oxyfluoride,  $\text{CuWO}_2\text{F}_4 \cdot 4\text{H}_2\text{O}$ .

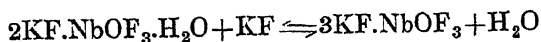
*Potassium Niobium Oxyfluorides*.—The following are known:  $4\text{KF} \cdot 3\text{NbOF}_3 \cdot 2\text{H}_2\text{O}$  or  $\text{K}_4\text{Nb}_3\text{O}_3\text{F}_{13} \cdot 2\text{H}_2\text{O}$ ;  $5\text{KF} \cdot 3\text{NbOF}_3 \cdot \text{H}_2\text{O}$  or  $\text{K}_5\text{Nb}_3\text{O}_3\text{F}_{14} \cdot \text{H}_2\text{O}$ ;  $2\text{KF} \cdot \text{NbOF}_3 \cdot \text{H}_2\text{O}$  or  $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$ ;  $3\text{KF} \cdot \text{NbOF}_3$  or  $\text{K}_3\text{NbOF}_6$ . Of these potassium compounds the salt  $2\text{KF} \cdot \text{NbOF}_3 \cdot \text{H}_2\text{O}$  or  $[\text{Nb}_2\text{O}_5] \text{K}_2 \cdot \text{H}_2\text{O}$  is the most important, and is, in fact, one of the commonest of niobium compounds, as it is the usual end product in the working of niobium minerals, and is the form in which niobium is separated from tantalum by the classical method due to Marignac (see p. 128). It is prepared by the addition of potassium fluoride to a hydrofluoric acid solution of niobium pentoxide, or by recrystallisation of other potassium niobium oxyfluorides or of potassium niobium fluoride,  $\text{K}_2\text{NbF}_7$ , from water. It undergoes recrystallisation unchanged in very thin leaflets from pure water. In the presence of a slight excess of hydrofluoric acid it forms thin, monoclinic scales which are isomorphous with potassium fluoroxytungstate,  $2\text{KF} \cdot \text{WO}_2\text{F}_2 \cdot \text{H}_2\text{O}$ , and with potassium titanium fluoride,  $2\text{KF} \cdot \text{TiF}_4 \cdot \text{H}_2\text{O}$ . Its crystal elements are:  $a : b : c = 0.992 : 1 : 0.980$ ;  $\beta = 103^\circ 46'$ . It loses almost all its water at  $100^\circ \text{C}$ ., but undergoes no further change and remains completely soluble in water when heated to  $200^\circ \text{C}$ . One part of the salt by weight dissolves in from 12.5 to 13 parts of water between  $17^\circ$  and  $21^\circ \text{C}$ . It is much more soluble in hot water and in water containing hydrogen fluoride or hydrogen peroxide, and is also much more soluble than the potassium tantalum oxyfluorides. The solution is precipitated by the addition of caustic soda or caustic potash; the precipitate is soluble in a slight excess of the alkali, but separates out again in crystalline form when large excess is added. In this respect the compound behaves differently from potassium titanium fluoride, but the reaction is not, however, available for the separation of niobium and titanium, as, when both metals are present, the precipitate also contains both. Hall and Smith<sup>1</sup> have made a study of the differential action of seventy-four bases, both inorganic and organic, on solutions of potassium niobium oxyfluoride and potassium titanium fluoride.

The compound  $5\text{KF} \cdot 3\text{NbOF}_3 \cdot \text{H}_2\text{O}$  or  $\text{K}_5\text{Nb}_3\text{O}_3\text{F}_{14} \cdot \text{H}_2\text{O}$  is obtained from the mother-liquor in the preparation of the above salt when the potassium fluoride has been added only sparingly to the solution of niobic acid in hydrofluoric acid. The new mother-liquor thus obtained yields crystals of the composition  $4\text{KF} \cdot 3\text{NbOF}_3 \cdot 2\text{H}_2\text{O}$  or  $\text{K}_4\text{Nb}_3\text{O}_3\text{F}_{13} \cdot 2\text{H}_2\text{O}$ . The former of these gives, apparently, hexagonal prisms. They lose only part of their water at  $100^\circ \text{C}$ .; above this temperature hydrogen fluoride is evolved.

When the quantity of potassium fluoride added to the solution of niobic acid in hydrofluoric acid is somewhat greater than that required for the formation of the salt  $2\text{KF} \cdot \text{NbOF}_3 \cdot \text{H}_2\text{O}$ , crystals of a salt having

<sup>1</sup> Hall and Smith, *Chem. News*, 1905, 92, 253.

the composition  $3\text{KF.NbOF}_3$  or  $\text{K}_3\text{NbOF}_6$  are obtained. This compound has also been prepared by fusing niobic acid with excess of potassium hydrogen fluoride.<sup>1</sup> It is stable at  $100^\circ\text{C}$ . Its solution in hot water yields crystals of  $2\text{KF.NbOF}_3\cdot\text{H}_2\text{O}$ , so that the change



appears to be reversible. A hydrofluoride of composition  $3\text{KF.NbOF}_3$ . HF has been obtained from solutions containing large excess of hydrofluoric acid or of potassium fluoride. Slow crystallisation from concentrated solutions gives rise to very beautiful prismatic crystals, isomorphous with the double potassium tin fluoride,  $3\text{KF.SnF}_4\cdot\text{HF}$ ;  $a : b : c = 0.6279 : 1 : 0.4900$ ;  $\beta = 93^\circ 14'$ . This substance is also quite stable at  $100^\circ\text{C}$ ., and loses hydrogen fluoride only on being very strongly heated.

If a solution of the compound  $2\text{KF.NbOF}_3\cdot\text{H}_2\text{O}$  is boiled for twelve hours while steam is introduced, a white, soft, micro-crystalline powder is obtained, the composition of which is  $2\text{KF.3NbO}_2\text{F}$  or  $\text{K}_2\text{Nb}_3\text{O}_6\text{F}_5$ .<sup>2</sup> A compound of the formula  $\text{NbO}_2\text{F}$  has not hitherto been isolated.

The compounds  $\text{KF.Nb}_2\text{O}_5\cdot 3\text{H}_2\text{O}$  and  $3\text{KF.2Nb}_2\text{O}_5\cdot 5\text{H}_2\text{O}$  are of doubtful constitution. They are obtained as crystalline powders by fusing niobium pentoxide with potassium fluoride and extracting the melt with boiling water.<sup>3</sup>

*Rubidium Niobium Oxyfluoride*,  $2\text{RbF.NbOF}_3$  or  $\text{Rb}_2\text{NbOF}_5$  or  $[\text{NbO}^{\text{F}_5}]^-\text{Rb}_2$ , is prepared similarly to the corresponding potassium compound.

*Sodium Niobium Oxyfluorides*.—These are not so well defined as the potassium salts. Similar methods of preparation give rise to a precipitate of  $2\text{NaF.NbOF}_3\cdot 2\text{H}_2\text{O}$ , which is, however, always associated with some of the salt  $\text{NaF.NbOF}_3\cdot\text{H}_2\text{O}$ , and the two are difficult to separate. The compound  $3\text{NaF.NbOF}_3$  has, however, been obtained pure. A sodium-calcium-niobium oxyfluoride,  $\text{NaCaNb}_2\text{O}_6\text{F}$ , is also known.<sup>4</sup> It is obtained by fusing lime, niobium pentoxide and sodium fluoride together. It forms colourless octahedra of density 4.196 to 4.341, and its refractive index for sodium light is 2.148 to 2.150; these figures agree with those given by natural *pyrochlore* (see p. 121).

*Thallium Niobium Oxyfluoride*,  $2\text{TlF.NbOF}_3$  or  $\text{Tl}_2\text{NbOF}_5$  or  $[\text{NbO}^{\text{F}_5}]^-\text{Tl}_2$ , is obtained in colourless, transparent, rhombic crystals by the action in solution of thallium fluoride on niobium pentafluoride.

*Zinc Niobium Oxyfluoride*,  $\text{ZnF}_2\cdot\text{NbOF}_3\cdot 6\text{H}_2\text{O}$  or  $\text{ZnNbOF}_5\cdot 6\text{H}_2\text{O}$  or  $[\text{NbO}^{\text{F}_5}]^-\text{Zn}\cdot 6\text{H}_2\text{O}$ , results from the action of zinc fluoride on a solution of niobic acid in hydrofluoric acid. It gives rise to rhombic, hexagonal crystals, which are isomorphous with those given by zinc titanium fluoride,  $\text{ZnF}_2\cdot\text{TiF}_4\cdot 6\text{H}_2\text{O}$ .

<sup>1</sup> Baker, *J. Chem. Soc.*, 1879, 35, 761.

<sup>2</sup> Krüss and Nilson, *Offvers. K. Vet.-Akad. Förh.*, 1887, No. 5; *Ber.*, 1887, 20, 1689.

<sup>3</sup> Petersen, *J. prakt. Chem.*, 1889, [ii], 40, 287.

<sup>4</sup> Holmquist, *Zeitsch. Kryst. Min.*, 1899, 31, 306.



## NIOBIUM AND CHLORINE.

**Chloroniobium Chloride** or *niobium "dichloride,"*  $Nb_6Cl_{14} \cdot 7H_2O$  or  $[Nb_6Cl_{12}]Cl_2 \cdot 7H_2O$ .<sup>1</sup>—This compound is prepared by heating 1 part of niobium pentachloride with 7 parts of 3 per cent. sodium amalgam in a hard-glass combustion tube from which the air has previously been exhausted. The product is allowed to cool in a vacuum, is extracted with hot water, filtered from a brown oxide formed at the same time, and then evaporated with the addition of hydrochloric acid. It forms black, shining crystals, which give an olive-green powder, soluble in hot water. It is only slowly decomposed by ammonium hydroxide; concentrated boiling nitric acid precipitates niobic acid. Only two of the chlorine atoms are ionised in solution. On being treated with the equivalent quantity of caustic soda it yields *chloroniobium hydroxide*,  $[Nb_6Cl_{12}](OH)_2 \cdot 8H_2O$ , as a black, micro-crystalline precipitate, which in turn forms *chloroniobium bromide*,  $Nb_6Cl_{12}Br_2 \cdot 7H_2O$ , when evaporated with hydrobromic acid. Chloroniobium chloride and chloroniobium hydroxide are both soluble in excess of caustic soda, from which solution the addition of excess of concentrated hydrochloric acid precipitates a brown powder having the composition  $Nb_6Cl_{14} \cdot 9H_2O$ . This substance is less soluble than the olive-green compound into which it is converted by boiling water. The available evidence suggests that the brown compound differs constitutionally from the green compound; <sup>2</sup> their behaviour recalls the different forms in which chromium trichloride is known to exist.<sup>3</sup>

**Niobium Trichloride**,  $NbCl_3$ , is prepared by leading the vapour of niobium pentachloride through a heated tube.<sup>4</sup> It is also formed in small quantity by the action of carbon tetrachloride vapour on niobium pentoxide contained in a hard-glass tube,<sup>5</sup> and has probably been prepared in solution by the electrolytic reduction of the pentachloride.<sup>6</sup> It forms a black, crystalline crust with an almost metallic lustre, which closely resembles the appearance of a film of sublimed iodine. It is not decomposed by water or ammonia, but is readily oxidised by dilute nitric acid to niobium pentoxide. On being heated to a red heat in an atmosphere of carbon dioxide, a sublimate of niobium oxytrichloride,  $NbOCl_3$ , is produced, the carbon dioxide undergoing reduction to the monoxide.

**Niobium Tetrachloride** is reported to have been obtained in solution by the electrolytic reduction of a solution of sodium niobate in hydrochloric acid.<sup>7</sup>

**Niobium Pentachloride**,  $NbCl_5$ , is the most important of the chlorides of niobium, and is the material from which the other chlorides are prepared. It can be obtained by several methods :

<sup>1</sup> It should be noted that the formula  $HTa_2Cl_7 \cdot 4H_2O$  has been recently ascribed to the corresponding tantalum chloride, as well as similar formulæ to analogous compounds of molybdenum and tungsten. The formulæ here given for niobium dichloride and its derivatives are, therefore, perhaps incorrect.

<sup>2</sup> Harned, *J. Amer. Chem. Soc.*, 1913, 35, 1078.

<sup>3</sup> See this series, Vol. VII., Part III. (1926), p. 26.

<sup>4</sup> Roscoe, *Chem. News*, 1878, 37, 26.

<sup>5</sup> Delafontaine and Linebarger, *J. Amer. Chem. Soc.*, 1896, 18, 532.

<sup>6</sup> Ott, *Dissertation* (Munich, 1911); compare Stähler, *Ber.*, 1914, 47, 842.

<sup>7</sup> Ott, *loc. cit.*

(a) By heating metallic niobium in chlorine at a red heat.<sup>1</sup>

(b) A mixture of niobium pentoxide and carbon is gently heated in a stream of chlorine, air being excluded. The pentachloride is sublimed away from any oxychloride simultaneously produced by raising the temperature at the conclusion of the reaction.<sup>2</sup>

(c) By the action of the vapour of carbon tetrachloride on niobium pentoxide heated to 230° to 250° C.<sup>3</sup> Some of the oxychloride is formed at the same time, but the change to the pentachloride is complete if the heating is carried out in a sealed tube at 200° to 225° C.<sup>4</sup> The same change takes place if the niobium pentoxide is subjected to the action of a mixture of chlorine and carbon tetrachloride vapour,<sup>5</sup> or chlorine and sulphur dichloride,<sup>6</sup> or phosphorus pentachloride,<sup>7</sup> or sulphur monochloride.<sup>8</sup> In the last case the pentachloride is removed from excess of sulphur monochloride by distillation.

(d) By carefully heating niobium sulphide in chlorine free from oxygen.<sup>9</sup>

Niobium pentachloride crystallises in long, yellow, transparent needles. Density 2.73 to 2.77.<sup>10</sup> The specific electrical conductivity of the fused substance between 220° and 235° C. is  $0.22 \times 10^{-6}$  reciprocal ohms (the corresponding figure for copper at ordinary temperatures is  $64 \times 10^4$ ), so that fused niobium pentachloride is an insulator of the order of the best conductivity water.<sup>11</sup> It melts at 212° C. to a red liquid, which volatilises readily and boils at 240.5° C.<sup>12</sup> Its vapour is yellow. Its density between 280° and 300° C. = 9.45 (air = 1. NbCl<sub>5</sub> requires 9.35). The chloride sublimes unchanged in the vapour of carbon bisulphide, and dissolves readily in sulphur monochloride to a red solution and in carbon tetrachloride to a yellow solution; both these solvents yield crystals on being concentrated. It is also soluble in chloroform, alcohol, and ether; a nitride of niobium is precipitated when ammonia is passed into the ether solution. Niobium pentachloride undergoes ready hydrolysis; on being exposed to damp air it evolves hydrochloric acid fumes and becomes coated with a skin of niobic acid. It is completely decomposed by water to hydrochloric acid and niobic acid, which latter can be obtained pure by repeated washing with water. It dissolves in concentrated hydrochloric acid to produce a clear solution, and in concentrated sulphuric acid with evolution of hydrochloric acid gas.

Double chlorides of niobium pentachloride with chlorides of other metals to correspond with the double fluorides given by niobium pentafluoride are not known. A double compound with piperidine, NbCl<sub>5</sub>.

<sup>1</sup> von Bolton, *Zeitsch. Elektrochem.*, 1907, 13, 147; compare Moissan, *Compt. rend.*, 1901, 133, 20; *Bull. Soc. chim.*, 1902, [iii], 27, 431.

<sup>2</sup> Rose, *Pogg. Annalen*, 1858, 104, 433; Rose and Weber, *ibid.*, 1853, 90, 462; compare Biltz and Voigt, *Zeitsch. anorg. Chem.*, 1921, 120, 71.

<sup>3</sup> Funk and Niederländer, *Ber.*, 1928, 61 B, 249, 1385; Demarçay, *Compt. rend.*, 1887, 104, 111; compare Camboulives, *ibid.*, 1910, 150, 175.

<sup>4</sup> Hall and Smith, *Chem. News*, 1905, 92, 277; Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1926, 156, 213.

<sup>5</sup> Ruff and Schiller, *ibid.*, 1911, 72, 329.

<sup>6</sup> Bourion, *Ann. Chim. Phys.*, 1910, [viii], 20, 565.

<sup>7</sup> Pennington, *J. Amer. Chem. Soc.*, 1896, 18, 61.

<sup>8</sup> Smith, *ibid.*, 1898, 20, 292; Hall and Smith, *loc. cit.*

<sup>9</sup> Biltz and Gonder, *Ber.*, 1907, 40, 4969; Biltz and Voigt, *loc. cit.*

<sup>10</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1637.

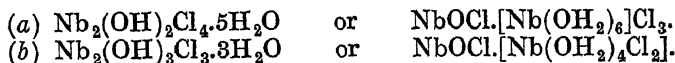
<sup>11</sup> Biltz and Voigt, *loc. cit.*

<sup>12</sup> Deville and Troost, *Compt. rend.*, 1865, 60, 1221; 1867, 64, 294.

$6C_5H_{11}N$ , has been prepared, however, by addition of the organic base to a concentrated alcoholic solution of the pentachloride.<sup>1</sup> It forms white needles which undergo decomposition on attempts to recrystallise. Similar compounds are formed with *aniline*, *pyridine*, etc.<sup>2</sup>

**Niobium Oxychlorides.**—The most important niobium oxychlorine compound is niobium oxytrichloride,  $NbOCl_3$ , which is described below.

By the electrolytic reduction of a solution of niobium pentoxide in (a) concentrated hydrochloric acid and (b) dilute hydrochloric acid, and subsequent evaporation *in vacuo* or in an atmosphere of carbon dioxide, two compounds having the following compositions have been reported :<sup>3</sup>



*Chloroniobium hydroxide*,  $[\text{Nb}_6\text{Cl}_{12}](\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , has been mentioned in describing chloroniobium chloride (see p. 149).

**Niobium Oxytrichloride**,  $NbOCl_3$ .—This compound is of historical interest in that it was one of the oxy-halogen compounds prepared originally by Rose in which the oxygen atom was overlooked. Rose called this substance "hyponiobium chloride"; its correct formula, and hence the true valency of niobium, were first established by Blomstrand.<sup>4</sup>

Niobium oxytrichloride is prepared by the action of chlorine on a mixture of niobium pentoxide and carbon, or on the lower oxide,  $NbO_2$ ,<sup>5</sup> or by the action of the vapours of carbon tetrachloride on the pentoxide.<sup>6</sup> Some niobium pentachloride is produced in the same reaction, and this is removed either by distilling it away at the lowest temperature possible in an atmosphere of carbon dioxide, or by subliming the product in a current of chlorine over the ignited oxide.<sup>7</sup> The oxychloride has also been prepared by passing the vapours of niobium pentachloride over niobium pentoxide at a red heat.<sup>8</sup>

Niobium oxytrichloride forms white, silky crystals, which sublime to silky needles on being heated in a sealed tube. It is very stable. It can be volatilised at  $400^\circ \text{C}$ . without melting; its vapour density at  $440^\circ \text{C}$ . is 7.89, and at  $860^\circ \text{C}$ . 7.87<sup>9</sup> (air=1.  $NbOCl_3$  requires 7.47). Its vapour is colourless. On being gently heated in hydrogen, carbon dioxide, or chlorine, it sublimes unchanged; with very strong heating in hydrogen or carbon dioxide, however, it decomposes and forms niobium pentoxide and niobium pentachloride (hydrogen also produces some of the lower oxides). It is soluble in alcohol and ether. Like the pentachloride it undergoes ready hydrolysis with water, producing niobic acid and hydrochloric acid; it is attacked by damp air. It dissolves in alkalis, also in concentrated sulphuric

<sup>1</sup> Renz, *Zeitsch. anorg. Chem.*, 1903, 36, 103.

<sup>2</sup> Hall, *loc. cit.*; Funk and Niederländer, *loc. cit.*

<sup>3</sup> Ott, *Dissertation* (Munich; 1911).

<sup>4</sup> Blomstrand, *Annalen*, 1865, 135, 168.

<sup>5</sup> Deville and Troost, *Compt. rend.*, 1865, 60, 1221.

<sup>6</sup> Delafontaine and Linebarger, *J. Amer. Chem. Soc.*, 1896, 18, 532; *Chem. News*, 1896, 74, 33; compare preparation of niobium pentachloride.

<sup>7</sup> Hall and Smith, *loc. cit.*

<sup>8</sup> Deville and Troost, *Compt. rend.*, 1867, 64, 294.

<sup>9</sup> Deville and Troost, *loc. cit.*

acid, to form a clear liquid with evolution of hydrochloric acid gas, but it is only very sparingly soluble in concentrated hydrochloric acid.

*Double Salts of Niobium Oxytrichloride.*—Niobium oxytrichloride gives rise to two series of double salts with *alkali chlorides* and with the organic bases *pyridine* and *quinoline*. These have the general formulæ  $\text{NbOCl}_3 \cdot \text{RCl}$  and  $\text{NbOCl}_3 \cdot 2\text{RCl}$ . They are prepared either by addition of the alkali hydrochloric or organic base to a solution of niobic acid in concentrated hydrochloric acid, or by the action of the alkali chloride or organic base on niobium oxytrichloride in alcohol solution. They crystallise well, are stable in dry air but are decomposed by water.<sup>1</sup> The following are known :

$\text{NbOCl}_3 \cdot 2\text{NH}_4\text{Cl}$	. . .	Very unstable.
$\text{NbOCl}_3 \cdot 2\text{RbCl}$	. . .	Yellow, regular octahedra.
$\text{NbOCl}_3 \cdot 2\text{CsCl}$	. . .	Do. do. do.
$\text{NbOCl}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$	. . .	Pale greenish-yellow crystals.
$\text{NbOCl}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{H}_2\text{O}$	. . .	Colourless crystals.
$\text{NbOCl}_3 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{H}_2\text{O}$	. . .	Large, colourless, transparent prisms.
$\text{NbOCl}_3 \cdot \text{C}_9\text{H}_7\text{N} \cdot \text{HCl}$	. . .	Almost colourless needles or greenish-yellow truncated prisms.
$\text{NbOCl}_3 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot \text{HCl}$	. . .	Almost colourless needles.

The corresponding bromine compounds are very comparable, but attempts to prepare corresponding iodo-derivatives were unsuccessful owing to the insolubility of niobic acid in hydriodic acid. Double compounds of vanadium oxytrichloride with pyridine, and tantalum oxytrichloride with pyridine and quinoline, have also been prepared.

#### NIOBIUM AND BROMINE.

**Niobium Pentabromide,  $\text{NbBr}_5$ .**—This is the only bromine compound of niobium hitherto prepared. It is obtained by the action of bromine vapour on the coarsely powdered metal,<sup>2</sup> or on a mixture of niobium pentoxide and carbon in the absence of air.<sup>3</sup> In the latter case some of the oxybromide is also formed. Niobium pentabromide is a fine, purple-red powder, very similar to red phosphorus in appearance. The fused substance forms garnet-red prisms. On being strongly heated it becomes yellow, and volatilises. It melts at about  $150^\circ \text{C}$ ., and distils undecomposed in an inert atmosphere at about  $270^\circ \text{C}$ . It can be distilled unchanged in an atmosphere of nitrogen or carbon dioxide. It is very hygroscopic, hydrolyses rapidly in damp air, and is decomposed by water with a hissing noise and considerable evolution of heat into niobic acid and hydrobromic acid. It is soluble in absolute alcohol and in dry ethyl bromide.

**Niobium Oxytribromide,  $\text{NbOBr}_3$ ,** is prepared by the action of bromine on a mixture of niobium pentoxide and carbon. The method is that by which the pentabromide is produced, but in this case the proportion of carbon present is much smaller. The product is distilled in an atmosphere of bromine or nitrogen.<sup>4</sup> It is a bright yellow, voluminous substance, which sublimes without melting in an atmosphere of bromine, but is converted completely into niobium pentoxide on being sublimed in an atmosphere of carbon dioxide. It fumes in damp

<sup>1</sup> Weinland and Storz, *Ber.*, 1906, 39, 3056; *Zeitsch. anorg. Chem.*, 1907, 54, 223.

<sup>2</sup> Barr, *J. Amer. Chem. Soc.*, 1908, 30, 1668.

<sup>3</sup> Rose, *Pogg. Annalen*, 1858, 104, 442.

<sup>4</sup> Barr, *loc. cit.*

air and is decomposed by water with formation of niobic acid and hydrobromic acid. It is soluble in hot concentrated sulphuric and hydrochloric acids, in absolute alcohol and dry ethyl bromide.

*Double Salts of Niobium Oxytribromide.*—These correspond exactly to the double salts of niobium oxytrichloride described above, and are prepared by analogous methods. The following are known :<sup>1</sup>

NbOBr <sub>3</sub> .2RbBr	. . .	Small, dark red octahedra.
NbOBr <sub>3</sub> .2CsBr	. . .	Pale yellow octahedra.
NbOBr <sub>3</sub> .C <sub>5</sub> H <sub>5</sub> N.HBr	. . .	Orange-red crystals.
NbOBr <sub>3</sub> .C <sub>6</sub> H <sub>7</sub> N.HBr	. . .	Do. prisms.

These double salts are even more unstable in damp air than the corresponding chlorine compounds.

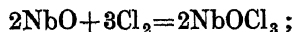
*Chloroniobium bromide*, [Nb<sub>5</sub>Cl<sub>12</sub>]Br<sub>2</sub>.7H<sub>2</sub>O, has been mentioned in describing the properties of chloroniobium chloride (see p. 149).

#### NIOBIUM AND IODINE.

Definite compounds of niobium and iodine are unknown. The preparation of an iodide from the pentabromide has been reported<sup>2</sup> but no details are supplied. A pyridine addition compound of the pentiodide, NbI<sub>5</sub>.(C<sub>5</sub>H<sub>5</sub>N.HI)<sub>6</sub>, has been described,<sup>3</sup> but its existence lacks confirmation.<sup>4</sup>

#### NIOBIUM AND OXYGEN.

**Niobium Monoxide**, NbO, is of considerable interest as a compound of divalent niobium, but its existence is doubtful. Attempts to prepare it by reduction of the pentoxide with hydrogen at high temperatures and in the carbon electric vacuum furnace<sup>5</sup> have not been successful. It is stated to be formed together with the dioxide, NbO<sub>2</sub>, by treating the pentoxide with hydrogen at about 150 atmospheres pressure and 2500° C.<sup>6</sup> Rose<sup>7</sup> obtained it by reducing potassium niobium oxyfluoride, K<sub>2</sub>NbOF<sub>5</sub>, with sodium in an iron crucible and then removing the fluorides of sodium and potassium in the product with water. Both Rose and Hermann<sup>8</sup> overlooked the presence of the oxygen atom, and looked upon this substance as being metallic niobium. A study of the amount of oxygen absorbed in its conversion into the pentoxide showed, however, that it was more probably the oxide NbO.<sup>9</sup> This conclusion is supported by the following facts: (1) Niobium monoxide is stated to be prepared also by reducing niobium oxytrichloride, NbOCl<sub>3</sub>, or niobium oxytrifluoride, NbOF<sub>3</sub>, with magnesium;<sup>10</sup> (2) it is converted into niobium oxytrichloride, NbOCl<sub>3</sub>, on being heated in a stream of chlorine,



<sup>1</sup> Weinland and Storz, *loc. cit.*

<sup>2</sup> Barr, *loc. cit.*

<sup>3</sup> Renz, *Zeitsch. anorg. Chem.*, 1903, 36, 106.

<sup>4</sup> Weinland and Storz, *loc. cit.*

<sup>5</sup> Ruff, Seiferheld, and Suda, *Zeitsch. anorg. Chem.*, 1913, 82, 373; compare Maignac, *Compt. rend.*, 1868, 66, 180.

<sup>6</sup> Newbery and Pring, *Proc. Roy. Soc.*, 1916, [A], 92, 276.

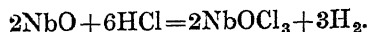
<sup>7</sup> Rose, *Pogg. Annalen*, 1858, 104, 310.

<sup>8</sup> Hermann, *J. prakt. Chem.*, 1871, 3, 386.

<sup>9</sup> Delafontaine, *Arch. Sci. phys. nat.*, 1866, [ii], 27, 167.

<sup>10</sup> Deville and Troost, *Compt. rend.*, 1865, 60, 1221.

(3) it is converted into niobium oxytrichloride on being dissolved in hydrochloric acid,



The monoxide has been variously described, according to the method of preparation, as a black powder, or glistening crystals, or beautiful black cubes. Its density varies from 6.3 to 6.7, and it is a good conductor of electricity. On being heated in air it oxidises readily to the pentoxide with considerable evolution of heat. It dissolves in hydrofluoric acid and hydrochloric acid with evolution of hydrogen, and a pentavalent niobium salt is formed in solution. It is also dissolved by boiling potassium hydroxide to form potassium niobate. This behaviour of niobium monoxide towards acids and alkali indicates that divalent salts of niobium are too unstable to exist. A divalent chloride of tantalum has, however, recently been isolated (see p. 192).

**Niobium Sesquioxide**,  $\text{Nb}_2\text{O}_3$ , has been prepared (a) as a bluish-black powder by reducing niobium pentoxide with magnesium powder; the magnesium oxide so formed and excess of magnesium are removed with dilute hydrochloric acid; <sup>1</sup> (b) as a bright grey powder with a bluish tinge by heating the pentoxide in a stream of hydrogen at 1250° C. The latter method yields a product which is free from both metal and higher oxides.<sup>2</sup> The pure product melts at 1780° C. Its electrical conductivity has been measured.<sup>3</sup> On being mixed with carbon and heated in hydrogen at 1200° C. it yields niobium carbide, NbC.

**Niobium Dioxide**,  $\text{NbO}_2$ .—Like the sesquioxide, this oxide is obtained by reducing the pentoxide with hydrogen at a high temperature.<sup>4</sup> It has also been prepared by the electrolysis of fused potassium niobium oxyfluoride,  $\text{K}_2\text{NbOF}_6$ , in a platinum vessel, which acts as the cathode, and using an anode of the same material.<sup>5</sup> Niobium dioxide is a black powder which is stable in air at ordinary temperatures; on being heated in air it forms the white pentoxide. It is not attacked by hot or cold acids, including hydrofluoric acid and aqua-regia; boiling potassium hydroxide solutions dissolve it slowly. Its crystal structure has been studied by Goldschmidt.<sup>6</sup>

**Niobium Pentoxide**, *Niobic Anhydride*,  $\text{Nb}_2\text{O}_5$ , is probably the commonest compound of niobium. It is obtained in the treatment of niobium-bearing minerals (see p. 124), and is the starting material in the preparation of other niobium compounds. It is precipitated in the hydrated state by the hydrolysis of nearly all pentavalent niobium salts, and is formed in the gravimetric estimation of niobium (see p. 130).

It can be prepared by heating metallic niobium or any of the lower oxides, or the sulphide, carbide, or nitride of niobium, in air or oxygen. Ammonium niobium oxyfluoride,  $(\text{NH}_4)_2\text{NbOF}_6$ , also yields the pentoxide on being heated in air. Solutions of the alkali niobates yield a white gel of the hydrated pentoxide when treated with mineral acids, sulphuric acid being usually preferred. Insoluble niobates on fusion

<sup>1</sup> Smith and Maas, *Zeitsch. anorg. Chem.*, 1894, 7, 98.

<sup>2</sup> Friederich and Sittig, *ibid.*, 1925, 143, 293; 1925, 144, 169; 1925, 145, 127.

<sup>3</sup> Friederich, *Zeitsch. Physik*, 1925, 31, 813.

<sup>4</sup> Delafontaine, *loc. cit.*; Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1926, 156, 213; compare Newbery and Fring, *loc. cit.*

<sup>5</sup> Ott, *Dissertation* (Munich, 1911).

<sup>6</sup> Goldschmidt and others, *Amer. Chem., Abs.*, 1926, 20, 3414.

with potassium hydrogen sulphate, and extraction with water, yield a residue of niobic acid, which is repeatedly washed with water containing a little ammonia to remove the adhering sulphuric acid. The gel is then ignited, preferably with the addition of a small quantity of ammonium carbonate, and a residue of pure, dry niobium pentoxide is obtained. The pentafluoride, oxyfluorides, and double alkali fluorides similarly yield the pentoxide if they are evaporated with concentrated sulphuric acid until all the hydrogen fluoride has been evolved; the residue is carefully washed and ignited. It is a difficult matter to wash precipitated niobic acid free from adsorbed mineral acids because of its colloidal character. Traces of alkali, which may also be present in the product, are best avoided by starting with the ammonium salt.

*Properties.*—Anhydrous niobium pentoxide is a white, amorphous, tasteless, odourless powder which remains white on being heated,<sup>1</sup> although some samples assume a temporary yellow colour while hot.<sup>2</sup> It is a remarkably stable substance and can be heated to 1750° C. without undergoing decomposition.<sup>3</sup> When precipitated niobium pentoxide is heated to dull redness it glows brightly for a short time, the extent of the glow and the temperature at which it occurs depending on the method of preparation. Various explanations of this have been put forward: (a) Allotropic transformation; (b) increase in size of particles; (c) transition from amorphous to crystalline state. Recently, Debye-Scherrer X-ray spectrograms, made on samples of the oxide before and after glowings, have shown that transition from the amorphous to a crystalline state takes place. The same explanation is found to hold good for the glowing of tantalum pentoxide, ferric oxide, chromium sesquioxide, titanium dioxide, and other oxides,<sup>4</sup> and is consistent with the fact that niobium pentoxide assumes a crystalline form on being very strongly heated.<sup>5</sup> Fusion with borax also yields green, rhombic prisms.<sup>6</sup> Microscopic, biaxial, rhombic plates<sup>7</sup> and cubes<sup>8</sup> have also been reported. The melting-point is about 1520° C.<sup>9</sup> The density varies with the method of preparation; it usually lies between 4·37 and 4·53,<sup>10</sup> but decomposition of the pentachloride in air and subsequent ignition gave a product the density of which varied between 4·88 and 5·05,<sup>11</sup> and hydrolysis of the oxychloride followed by ignition gave samples the densities of which were as high as 5·26.<sup>12</sup> The crystalline modifications have densities varying between 4·57 and 4·76.<sup>13</sup> The specific heat of niobium pentoxide between 0° and 100° C. is 0·1184, and increases at higher temperatures.<sup>14</sup> The magnetic susceptibility<sup>15</sup> and electrical conductivity<sup>16</sup> have been measured. When

<sup>1</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 63.

<sup>2</sup> Wöhler, *Pogg. Annalen*, 1839, 48, 92; Rose, *ibid.*, 1861, 112, 549; Ott, *loc. cit.*; Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 66.

<sup>3</sup> Read, *J. Chem. Soc.*, 1894, 65, 313.

<sup>4</sup> Böhm, *Zeitsch. anorg. Chem.*, 1925, 149, 217.

<sup>5</sup> Rose, *loc. cit.*

<sup>6</sup> Ebelmen, *Compt. rend.*, 1851, 33, 525; *Ann. Chim. Phys.*, 1851, [iii], 33, 34; Mallard, *Ann. Mines*, 1887, [viii], 12, 427.

<sup>7</sup> Nordenskiöld, *Pogg. Annalen*, 1861, 114, 612.

<sup>8</sup> Knop, *Annalen*, 1871, 159, 56; *Zeitsch. Kryst. Min.*, 1887, 12, 610.

<sup>9</sup> Ruff, Seiferheld, and Suda, *Zeitsch. anorg. Chem.*, 1913, 82, 397.

<sup>10</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 19; Ott, *loc. cit.*

<sup>11</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1643.

<sup>12</sup> Rose, *loc. cit.*

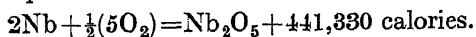
<sup>13</sup> Rose, *loc. cit.*; Holmquist, *Bull. Geol. Inst. Ups.*, 1896–97, 3, 207.

<sup>14</sup> Krüss and Nilson, *Zeitsch. physikal. Chem.*, 1887, 1, 391.

<sup>15</sup> Berkman and Zocher, *ibid.*, 1926, 124, 318.

<sup>16</sup> Friederich, *Zeitsch. Physik*, 1925, 31, 813.

1 gram of metallic niobium burns to the pentoxide, 2350 calories of heat are evolved.<sup>1</sup> The calculated heat of formation of the pentoxide is given by the equation



Niobium pentoxide is reduced to the dioxide,  $\text{NbO}_2$ , and the sesquioxide,  $\text{Nb}_2\text{O}_3$ , on being strongly heated in a stream of hydrogen at ordinary pressures.<sup>2</sup> Reduction in the carbon electric vacuum furnace at high temperatures and pressures yields a mixture of the lower oxides.<sup>3</sup> Ammonia at a white heat brings about partial conversion into the nitride.<sup>4</sup> Heated in a current of hydrogen chloride, the oxide is completely volatilised without undergoing reduction, and yields a white hydrochloride,  $\text{Nb}_2\text{O}_5 \cdot x\text{HCl}$ .<sup>5</sup> Vanadium pentoxide,  $\text{V}_2\text{O}_5$ , molybdenum trioxide,  $\text{MoO}_3$ , and tungsten trioxide,  $\text{WO}_3$ , are also completely volatilised when heated in hydrogen chloride. The oxide is readily attacked by carbon tetrachloride vapour at  $220^\circ \text{C}$ . with formation of niobium pentachloride; tantalum pentoxide is unaffected under the same conditions.<sup>6</sup> Sulphur monochloride and phosphorus pentachloride produce the pentachloride or oxychloride, according to the conditions, and chlorine reacts similarly if the pentoxide is previously mixed with charcoal. Hydrogen sulphide and carbon bisulphide vapour yield an oxysulphide at high temperatures. Niobium pentoxide is stable towards light, but becomes markedly photo-sensitive and undergoes reduction in the presence of certain organic liquids and reducing solutions, particularly glycerol. The process depends to some extent on the presence of impurities, notably stannic and tungstic acids, zirconium compounds, and titanitic acid.<sup>7</sup>

After being strongly ignited, niobium pentoxide becomes insoluble in all acids other than hydrofluoric acid, but is dissolved by molten potassium hydrogen sulphate, ammonium hydrogen sulphate, and borax. It is also insoluble in solutions of alkalis, but is converted into the alkali niobates by fusion with alkali hydroxides and carbonates.

*Hydrates of Niobium Pentoxide. Colloidal Niobium Pentoxide.*—Niobium pentoxide does not combine directly with water to form acids of definite composition. Two hydrates of the oxide, namely,  $3\text{Nb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  and  $3\text{Nb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ , have been reported,<sup>8</sup> but their existence is very improbable. The term *niobic acid* is applied to the more or less hydrated pentoxide. When niobium pentachloride or niobium oxytrichloride,  $\text{NbOCl}_3$ , is hydrolysed with excess of water there is produced a white, amorphous, hydrated gel,<sup>9</sup> which can also be obtained by the action of sulphuric acid or hydrochloric acid on alkali niobates; <sup>10</sup> the precipitate is redissolved by excess of acid. Similar solutions are

<sup>1</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 84.

<sup>2</sup> Compare Nichols, *Phys. Review*, 1925, [ii], 25, 376; Newbery and Pring, *Proc. Roy. Soc.*, 1916, [A], 92, 276.

<sup>3</sup> Ruff, Seiferheld, and Suda, *Zeitsch. anorg. Chem.*, 1913, 82, 397.

<sup>4</sup> Rose, *Pogg. Annalen*, 1860, **111**, 426.

<sup>5</sup> Hall and Smith, *J. Amer. Chem. Soc.*, 1905, 27, 1389; *Proc. Amer. Phil. Soc.*, 1905, 44, 197. According to Smith and Maas (*Zeitsch. anorg. Chem.*, 1894, 7, 96), the white product is a hydrochloride of niobium dioxide, and has the formula  $2\text{NbO}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ .

<sup>6</sup> Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1926, 156, 213.

<sup>7</sup> Renz, *Helv. Chim. Acta*, 1921, 4, 961.

<sup>8</sup> Santesson, *Bull. Soc. chim.*, 1875, [ii], 24, 38, 67.

<sup>9</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 46; Rose, *Pogg. Annalen*, 1861, **112**, 557.

<sup>10</sup> Rose, *loc. cit.*; Weinland and Storz, *Zeitsch. anorg. Chem.*, 1907, 54, 232.



obtained by fusing a niobate with potassium hydrogen sulphate and extracting the melt with water; <sup>1</sup> the extract, however, readily clouds, with precipitation of the acid.

The gel can be dried at room temperature to a horny mass; at 100° C. it becomes a white powder which still contains varying proportions of water, according to the history of the sample; it is completely dehydrated at about 300° C. The gel is insoluble in water, but on being washed undergoes peptisation and passes through the filter-paper. This can be prevented by the addition of a small quantity of an electrolyte (for example, ammonium nitrate or ammonium carbonate) to the water. The gel is only slightly soluble in concentrated hydrochloric acid, with probable formation of niobium oxytrichloride, but the residue, after decantation, undergoes peptisation very readily to yield a clear hydrosol from which all the hydrochloric acid can be removed by dialysis.<sup>2</sup> The hydrosol prepared in this manner clouds if allowed to stand overnight or if boiled. The gel is more readily soluble in concentrated sulphuric acid; <sup>3</sup> the solution remains clear on being diluted, but it is precipitated by sulphur dioxide.<sup>4</sup> The gel dissolves also in hydrobromic acid and perchloric acid, and is readily taken up by hydrofluoric acid.

Hydrosols of both niobium pentoxide and tantalum pentoxide have been prepared by fusing each of these oxides with alkali in a silver crucible, dissolving the melt in water and dialysing the product for about ten days. Concentration over sulphuric acid yields a hydrosol containing 2.571 grams of niobium pentoxide per litre; the dispersed phase is negatively charged. The sols so obtained are quite stable, and are not coagulated even when heated, but they are precipitated by all strong electrolytes except bases, which impart stability through preferential adsorption of hydroxyl ions. They are very sensitive to chloride, sulphate, sulphite and nitrate ions.<sup>5</sup> Hydrosols of niobium pentoxide and tantalum pentoxide differ in their behaviour towards carbon dioxide; whereas the tantalum pentoxide coagulates and is precipitated fairly rapidly, the niobium pentoxide is not precipitated after a day under the same conditions. This difference in respective rates of coagulation has been used to separate niobium from tantalum, but the separation is not quantitative (see p. 129).

The remarkable optical properties displayed by hydrosols of vanadium pentoxide (see p. 58) have not hitherto been observed with niobium pentoxide or tantalum pentoxide.

In addition to dissolving in acids, freshly precipitated niobium pentoxide dissolves in caustic soda and in caustic potash, and hence it appears to possess weakly amphoteric character. Its colloidal state in solution has hitherto prevented any direct determination of its basicity or acidity. According to Weinland and Storz <sup>6</sup> it is comparable to silicic acid, and is more strongly acid than titanitic acid. That niobic acid is a very weak acid is shown by the readiness with which the niobates are (a) hydrolysed and (b) decomposed by mineral acids,

<sup>1</sup> Rose, *Pogg. Annalen*, 1861, 112, 551; 1861, 113, 109; Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 66.

<sup>2</sup> Wöhler, *Pogg. Annalen*, 1839, 48, 92; Marignac, *Ann. Chim. Phys.*, 1866, [iv], 3, 16.

<sup>3</sup> Compare Kiehl and Hart, *J. Amer. Chem. Soc.*, 1928, 50, 1613.

<sup>4</sup> Weiss and Landecker, *loc. cit.*

<sup>5</sup> Hauser and Lewite, *Zeitsch. angew. Chem.*, 1912, 25, 100.

<sup>6</sup> Weinland and Storz, *loc. cit.*

sulphur dioxide, and even so weak an acid as carbon dioxide, with precipitation of niobic acid. Solutions of vanadates, on the other hand, on being treated with dilute acids yield the complex acid vanadates. Niobic acid combines in varying proportions with basic oxides of metals, which suggests that niobium pentoxide forms condensed complex anions containing several niobium atoms. It is most probable, however, that many of these niobates are not distinct chemical identities, but consist of isomorphous mixtures of simple salts. Their general insolubility in water and the readiness with which they undergo hydrolysis in contact with water have prevented any close investigation into their constitution, and hence into the constitution of niobic acid.

Niobic acid possesses the ability to form complex poly-acids with other acids (for example, with tungstic and oxalic acids). There are by no means as many of these known as in the case of vanadic acid, as they have not hitherto received much attention.

#### NIOBATES.

The alkali niobates are most conveniently prepared by the action of caustic alkalis on niobic acid or on solutions of niobium oxytrifluoride. Other compounds of niobic acid and bases are generally prepared by fusing niobic acid with the oxide, hydroxide, carbonate, or other salt of the metal. Occasionally double decomposition of a soluble alkali niobate and a soluble salt of the metal has been employed. Larsson's method<sup>1</sup> consists in precipitating a solution of potassium niobate with a salt of a metal; the dried precipitate is fused for thirty-six hours at a high temperature with boric acid, and the melt is boiled with water to which hydrochloric acid has been added. The residue consists of crystals of the insoluble niobate of the metal, usually the metaniobate.

Niobates obtained by any of these methods contain the basic oxide and acid oxide in proportions which vary from 1:4 to 5:1. The molecular complexities of most of them, as well as the complexity of the ions present in their solutions, are at present not understood; in many cases they are probably isomorphous mixtures of simpler salts. A revision of their composition is necessary. Many crystalline niobates are known, however, the composition of which appears to correspond to that of *metaniobates*,  $RNbO_3$  or  $R_2O.Nb_2O_5$ , and *hexaniobates*,  $R_3Nb_6O_{19}$  or  $4R_2O.3Nb_2O_5$ . A few *pyroniobates*,  $R_4Nb_2O_7$  or  $2R_2O.Nb_2O_5$ , have also been prepared. The *orthoniobates*,  $R_3NbO_4$  or  $3R_2O.Nb_2O_5$ , like the orthovanadates, are very unstable and but little known, although their existence has been recognised in minerals.

Niobates are usually insoluble in water; even many of the alkali niobates are insoluble. Insoluble alkali niobates are formed when niobium pentoxide is fused with only small proportions of alkali carbonate. 7:6 Sodium niobate,  $7Na_2O.6Nb_2O_5.xH_2O$ , is insoluble in solutions of high sodium-ion concentration, and is therefore precipitated by the addition of sodium salts to solutions of potassium niobate. Ammonium niobates are unknown; when excess of an ammonium salt is added to a solution of an alkali niobate, a voluminous precipitate is thrown down which is rapidly decomposed by water to yield niobic

<sup>1</sup> Larsson, *Zeitsch. anorg. Chem.*, 1896, 12, 197.

acid.<sup>1</sup> This instability of ammonium salts is consistent with the weakness of niobic acid, which is also shown in the ease with which niobates are decomposed by water and acids to precipitate niobic acid. Arsenious, arsenic, oxalic, tartaric, citric and malonic acids do not produce precipitates with solutions of alkali niobates, probably because of the formation of soluble complex salts. Phosphoric, hydrocyanic and acetic acids yield precipitates with concentrated solutions of alkali niobates.

The following niobates are known, but the constitution of some of them is not beyond doubt:—

*Aluminium Niobate*,  $\text{Al}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5 \cdot 12\text{H}_2\text{O}$ , is obtained as a white precipitate by the action of a solution of alum on sodium metaniobate,  $\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ .<sup>2</sup>

*Barium Niobate*.—A salt having the composition  $7\text{BaO} \cdot 6\text{Nb}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$  is prepared by treating a hot solution of the corresponding sodium salt with dilute barium chloride solution.<sup>3</sup>

*Cadmium Metaniobate*.—The anhydrous salt,  $\text{CdO} \cdot \text{Nb}_2\text{O}_5$ , is obtained by fusing potassium niobate with cadmium chloride. It forms yellowish-brown, glistening crystals, the density of which is 5.93.<sup>4</sup> The hydrated salt  $\text{CdO} \cdot \text{Nb}_2\text{O}_5 \cdot 8\frac{1}{2}\text{H}_2\text{O}$  is thrown down as a pale yellow precipitate on adding a solution of a cadmium salt to sodium metaniobate.<sup>5</sup>

*Cæsium Niobates*.—Fusion of niobium pentoxide and cæsium carbonate and extraction of the melt with water yields monoclinic crystals which have the composition  $4\text{Cs}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ , and which are isomorphous with the rubidium salt. Addition of alcohol to the aqueous solution furnishes crystals of  $7\text{Cs}_2\text{O} \cdot 6\text{Nb}_2\text{O}_5 \cdot 30\text{H}_2\text{O}$ .<sup>6</sup>

*Calcium Metaniobate*,  $\text{CaO} \cdot \text{Nb}_2\text{O}_5$ , is prepared by fusing niobium pentoxide with calcium fluoride in an excess of potassium fluoride;<sup>7</sup> or the pyro-salt  $2\text{CaO} \cdot \text{Nb}_2\text{O}_5$  is fused with boric acid and the melt extracted with water containing hydrochloric acid.<sup>8</sup> It forms bright red, long, thin, apparently rhombic needles, which are doubly refracting.<sup>9</sup> Density 4.12 to 4.48.

*Calcium Pyroniobate*,  $2\text{CaO} \cdot \text{Nb}_2\text{O}_5$ , is prepared by fusing with calcium chloride either niobium pentoxide or the precipitate obtained by the action of calcium chloride on potassium niobate solution; the melt is extracted with water containing hydrochloric acid,<sup>10</sup> when the salt remains in small, colourless, glistening, prismatic crystals.<sup>11</sup> Density at 17° C. 4.484.

Isomorphous mixtures of calcium niobates and sodium niobates have also been prepared.<sup>12</sup> A calcium niobate occurs in the mineral *pyrochlore*.

*Cobalt Metaniobate*,  $\text{CoO} \cdot \text{Nb}_2\text{O}_5$ , is prepared by heating together the two oxides at about 1100° C., or by fusing the precipitate thrown down

<sup>1</sup> Weiss and Landecker, *loc. cit.*; Bullheimer, *Chem. Zeit.*, 1900, 24, 870; Schoeller and Jahn, *Analyst*, 1927, 52, 504.

<sup>2</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1637.

<sup>3</sup> Bedford, *ibid.*, 1905, 27, 1218; see also Larsson, *loc. cit.*

<sup>4</sup> Larsson, *loc. cit.*

<sup>5</sup> Balke and Smith, *loc. cit.*

<sup>6</sup> Balke and Smith, *loc. cit.*

<sup>7</sup> Joly, *Compt. rend.*, 1875, 81, 268; *Chem. News*, 1875, 32, 114; *Annales Scientifiques de l'École Normale Supérieure, Paris*, 1877, [ii], 6, 172.

<sup>8</sup> Larsson, *loc. cit.*

<sup>9</sup> Holmquist, *Zeitsch. Kryst. Min.*, 1899, 31, 306.

<sup>10</sup> Joly, *loc. cit.*; Larsson, *loc. cit.*

<sup>11</sup> Compare Holmquist, *loc. cit.*

<sup>12</sup> Holmquist, *loc. cit.*

by the action of cobalt nitrate on potassium niobate solution with boric acid. It is a dark blue, crystalline powder. Density 5.56.<sup>1</sup>

*Copper Metaniobate*.—The anhydrous meta-salt  $\text{CuO.Nb}_2\text{O}_5$  consists of black, glistening crystals which are prepared similarly to the corresponding cobalt salt. Density 5.60.<sup>2</sup> Addition of copper sulphate to an aqueous solution of sodium metaniobate,  $\text{Na}_2\text{O.Nb}_2\text{O}_5.7\text{H}_2\text{O}$ , yields a green precipitate of the hydrated compound  $\text{CuO.Nb}_2\text{O}_5.3\frac{1}{2}\text{H}_2\text{O}$ . A *dihydrate* has been obtained by drying at  $100^\circ\text{C}$ .<sup>3</sup>

*Iron Niobates*.—*Ferrous metaniobate*,  $\text{FeO.Nb}_2\text{O}_5$ , is obtained more or less impure by fusing niobium pentoxide, ferrous fluoride, and excess of potassium chloride in a platinum crucible to a bright red heat. It forms long, steel-grey prisms.<sup>4</sup> A *ferric niobate*,  $2\text{Fe}_2\text{O}_3.3\text{Nb}_2\text{O}_5.8\text{H}_2\text{O}$ , has been obtained by the action of ferric chloride on sodium metaniobate.<sup>5</sup> Iron niobates enter into the composition of the natural niobites and tantalites.

*Lithium Niobate*,  $7\text{Li}_2\text{O}.6\text{Nb}_2\text{O}_5.26\text{H}_2\text{O}$ , is a crystalline substance which results from the action of lithium nitrate on a concentrated solution of potassium niobate,  $\text{K}_2\text{O}.3\text{Nb}_2\text{O}_5.5\text{H}_2\text{O}$ .<sup>6</sup>

*Magnesium Metaniobate (Anhydrous)*,  $\text{MgO.Nb}_2\text{O}_5$ , is prepared by fusing with boric acid the precipitate thrown down on the addition of magnesium chloride to a solution of potassium niobate. It yields short, prismatic, doubly refracting crystals.<sup>7</sup> The *heptahydrate*,  $\text{MgO.Nb}_2\text{O}_5.7\text{H}_2\text{O}$ , is obtained in white flakes by the addition of magnesium chloride to a solution of sodium metaniobate and drying on the water-bath.<sup>8</sup> Drying at  $100^\circ\text{C}$ . yields a *tetrahydrate*.<sup>9</sup>

If the precipitate thrown down by the addition of magnesium chloride to a solution of potassium niobate is fused with excess of magnesium chloride,<sup>10</sup> or if niobium pentoxide is fused with excess of magnesium chloride under definite conditions,<sup>11</sup> the salt  $4\text{MgO.Nb}_2\text{O}_5$  is obtained. This compound is remarkable for the high proportion of basic oxide present. It is alternatively described according to the method of preparation as consisting of (a) very small, white, hexagonal plates or prisms, of density 4.43; (b) of colourless or pale yellow, broad, transparent, hexagonal leaves belonging to the rhombic system, density 4.37. It is only slowly attacked by acids. This salt is sometimes accompanied by crystals of the *orthoniobate*,  $3\text{MgO.Nb}_2\text{O}_5$ , and in one preparation *magnesium pyrovanadate*,  $2\text{MgO.Nb}_2\text{O}_5$ , was produced.<sup>12</sup> The latter consisted of small, steel grey, glistening prisms, which became white when brought to a red heat.

*Manganese Metaniobate*,  $\text{MnO.Nb}_2\text{O}_5$ , is prepared by fusing together niobium pentoxide, manganese fluoride and potassium chloride. It forms red, transparent, rhombic prisms, density<sup>13</sup> 4.94. This salt is probably a constituent of the natural *niobites* (see p. 117). By fusing together niobium pentoxide, ferrous fluoride and manganese fluoride, Joly succeeded in preparing a substance which very closely resembled the natural niobites from Greenland. Analysis showed this substance to be an isomorphous mixture of ferrous metaniobate and manganese

<sup>1</sup> Larsson, *loc. cit.*; Hedvall, *Zeitsch. anorg. Chem.*, 1915, 93, 391.

<sup>2</sup> Larsson, *loc. cit.*

<sup>3</sup> Balke and Smith, *loc. cit.*

<sup>4</sup> Joly, *loc. cit.*

<sup>5</sup> Rose, *Pogg. Annalen*, 1861, 112, 480; 1861, 113, 292.

<sup>6</sup> Balke and Smith, *loc. cit.*

<sup>7</sup> Larsson, *loc. cit.*

<sup>8</sup> Balke and Smith, *loc. cit.*

<sup>9</sup> Rose, *loc. cit.*

<sup>10</sup> Larsson, *loc. cit.*

<sup>11</sup> Joly, *loc. cit.*

<sup>12</sup> Joly, *loc. cit.*

<sup>13</sup> Joly, *loc. cit.*

metaniobate, of the composition  $(\frac{2}{3}\text{FeO}.\frac{1}{3}\text{MnO})\text{Nb}_2\text{O}_5$ , which is approximately the composition of the niobites from Limoges.

Another manganese niobate,  $3\text{MnO}.5\text{Nb}_2\text{O}_5$ , has been obtained by adding manganese sulphate to potassium niobate and fusing the precipitate with boric acid. It consists of small, greyish-yellow, prismatic rods, density 4.97.<sup>1</sup>

*Mercury Niobate.*—A salt having the probable composition  $\text{Hg}_2\text{O}.\text{Nb}_2\text{O}_5.3\text{H}_2\text{O}$  has been obtained by the action of mercurous nitrate on sodium niobate solution.<sup>2</sup>

*Potassium Niobates* are generally produced by fusion of the metal or the pentoxide with potassium hydroxide, potassium carbonate, or potassium nitrate,<sup>3</sup> or by the action of solutions of caustic potash or of potassium carbonate on niobic acid.<sup>4</sup> They are among the most stable of the niobates; their solutions can be boiled without precipitation of the acid. On being treated with sodium salts, for example sodium chloride, sodium niobates are precipitated.

When a solution of potassium niobium oxyfluoride,  $\text{K}_2\text{NbOF}_5$ , is boiled with potassium bicarbonate, a light, powdery, practically insoluble precipitate of the 1 : 3 salt,  $\text{K}_2\text{O}.3\text{Nb}_2\text{O}_5.5\text{H}_2\text{O}$ , is thrown down.<sup>5</sup>

1 : 2 Potassium niobate,  $\text{K}_2\text{O}.2\text{Nb}_2\text{O}_5.5\frac{1}{2}\text{H}_2\text{O}$ , remains undissolved in the crystalline residue left after fusing equimolecular proportions of niobic acid and potassium carbonate and extracting the melt with water.<sup>6</sup>

Thin, transparent plates of the anhydrous 3 : 4 salt,  $3\text{K}_2\text{O}.4\text{Nb}_2\text{O}_5$ , remain undissolved when niobic acid is fused with about twice its weight of potassium sulphate for several hours at a red heat and the melt is extracted with water.<sup>7</sup>

Potassium metaniobate,  $\text{KNbO}_3$  or  $\text{K}_2\text{O}.\text{Nb}_2\text{O}_5$ , is obtained as beautiful, straw-yellow, rectangular plates by fusing a mixture of equimolecular proportions of potassium carbonate and niobic acid; in this case the niobic acid is previously fused with calcium fluoride. The crystals are extracted from the product with boiling, dilute sulphuric acid.<sup>8</sup>

8 : 7 Potassium niobate,  $8\text{K}_2\text{O}.7\text{Nb}_2\text{O}_5.32\text{H}_2\text{O}$ , precipitates out on slow evaporation of solutions of either the 4 : 3 salt or the 7 : 6 salt. It forms rhombic bipyramids which can be recrystallised unchanged;  $a : b : c = 0.9584 : 1 : 0.7083$ . Twenty-three molecules of water are lost at 100° C. It readily yields supersaturated solutions. When its aqueous solutions are treated with a current of carbon dioxide they precipitate salts which contain a larger proportion of niobic acid.<sup>9</sup>

7 : 6 Potassium niobate,  $7\text{K}_2\text{O}.6\text{Nb}_2\text{O}_5.27\text{H}_2\text{O}$ , is precipitated by the addition of alcohol to an aqueous solution of the 4 : 3 salt. The product is redissolved in water and reprecipitated several times.<sup>10</sup>

<sup>1</sup> Larsson, *loc. cit.*

<sup>2</sup> Rose, *loc. cit.*

<sup>3</sup> Moissan, *Compt. rend.*, 1901, 133, 20; *Bull. Soc. chim.*, 1902, [iii], 27, 431; Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 67; von Bolton, *Zeitsch. Elektrochem.*, 1907, 13, 147.

<sup>4</sup> Rose, *Pogg. Annalen*, 1861, 113, 109; Russ, *Zeitsch. anorg. Chem.*, 1902, 31, 53.

<sup>5</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 20.

<sup>6</sup> Santesson, *Bull. Soc. chim.*, 1875, [ii], 24, 53.

<sup>7</sup> Joly, *loc. cit.*

<sup>8</sup> Joly, *loc. cit.*

<sup>9</sup> Marignac, *loc. cit.*; Balke and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1637.

<sup>10</sup> Balke and Smith, *loc. cit.*

4 : 3 Potassium niobate,  $4\text{K}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$ , is the commonest of the potassium niobates. It forms large monoclinic prisms which are isomorphous with 4 : 3 potassium tantalate,  $4\text{K}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$ . Niobic acid is fused with from two to three times its weight of potassium carbonate in the blowpipe until carbon dioxide is no longer evolved; the melt is extracted with water and the extract is either evaporated *in vacuo* or allowed to evaporate spontaneously. The crystals effloresce in the air and lose twelve molecules of water of crystallisation at  $100^\circ\text{C}$ . At a red heat the salt becomes yellow but does not melt; after being so heated it is only partially soluble in water.<sup>1</sup>

3 : 2 Potassium niobate,  $3\text{K}_2\text{O} \cdot 2\text{Nb}_2\text{O}_5 \cdot 13\text{H}_2\text{O}$ , is obtained in rhombic crystals by adding excess of potassium hydroxide to a solution of the 4 : 3 salt and evaporating slowly. It effloresces rapidly in the air and loses seven molecules of water of crystallisation at  $100^\circ\text{C}$ .<sup>2</sup>

2 : 1 Potassium niobate or potassium pyroniobate,  $2\text{K}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 11\text{H}_2\text{O}$ , is an insoluble powder which is obtained by fusing the 1 : 2 salt with excess of potassium carbonate and extracting the product with water.<sup>3</sup>

5 : 2 Potassium niobate and 3 : 1 potassium niobate (the ortho-salt) have also been reported.<sup>4</sup>

*Rubidium Niobates*.—When niobium pentoxide is fused with rubidium carbonate and the melt is extracted with water, fine, silky needles of composition  $3\text{Rb}_2\text{O} \cdot 4\text{Nb}_2\text{O}_5 \cdot 9\frac{1}{2}\text{H}_2\text{O}$  are left behind. Concentration of the filtrate yields monoclinic crystals of  $4\text{Rb}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ , which are isomorphous with the corresponding tantalum salt and with the corresponding caesium niobate and tantalate.  $a : b : c = 0.8815 : 1 : 1.0491$ ;  $\beta = 95^\circ 53'$ . It slowly loses some of its water on exposure to air.<sup>5</sup>

*Silver Metaniobate*,  $\text{Ag}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , is obtained as a white precipitate by the addition of silver nitrate to an aqueous solution of sodium metaniobate. It becomes pale yellow on being dried and gradually darkens in sunlight.<sup>6</sup> Addition of dilute silver nitrate solution to a solution of  $7\text{Na}_2\text{O} \cdot 6\text{Nb}_2\text{O}_5$  precipitates the corresponding silver salt,  $7\text{Ag}_2\text{O} \cdot 6\text{Nb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , which is a white, insoluble substance.<sup>7</sup>

*Sodium Niobates* are comparable to the potassium niobates. They differ in that they can be precipitated from solutions of potassium niobates by the action of neutral sodium salts. The usual method of preparation consists in fusing niobium pentoxide with caustic soda in varying proportions and, after washing away excess of caustic soda, crystallising the product from water. It is to be noted, however, that this method, in the hands of different investigators, has yielded several sodium niobates which differ in the relative amounts of base and acid present. It appears that the only sodium niobates hitherto prepared which can be definitely regarded as chemical individuals are the meta-salt,  $\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$ , and the 7 : 6 salt,  $7\text{Na}_2\text{O} \cdot 6\text{Nb}_2\text{O}_5 \cdot 31\text{H}_2\text{O}$  or  $32\text{H}_2\text{O}$ .<sup>8</sup> The commonest potassium niobate is the 4 : 3 salt; 4 : 3 sodium niobate has not been prepared.<sup>9</sup>

<sup>1</sup> Marignac, *loc. cit.*; Balke and Smith, *loc. cit.*; von John, *Chem. News*, 1909, 100, 154.

<sup>2</sup> Marignac, *loc. cit.*; Hermann, *J. prakt. Chem.*, 1871, 3, 419; compare Bedford, *Amer. Chem. Soc.*, 1905, 27, 1218.

<sup>3</sup> Santesson, *loc. cit.*

<sup>4</sup> Russ, *loc. cit.*

<sup>5</sup> Balke and Smith, *loc. cit.*

<sup>6</sup> Balke and Smith, *loc. cit.*

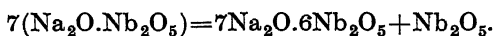
<sup>7</sup> Bedford, *loc. cit.*

<sup>8</sup> Bedford, *loc. cit.*; Smith and Van Haagen, *J. Amer. Chem. Soc.*, 1915, 37, 1783.

<sup>9</sup> Schoeller and Jahn, *Analyst*, 1926, 51, 613.

2 : 3 Sodium niobate,  $2\text{Na}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ , is said to have been prepared in small crystals by fusing niobium pentoxide with caustic soda and extracting the melt with boiling water,<sup>1</sup> but Bedford<sup>2</sup> was unable to obtain the compound by this process.

*Sodium Metaniobate*,  $\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5$  or  $\text{NaNbO}_3$ .—Anhydrous sodium metaniobate is obtained in white, strongly refractive, cubic crystals by ignition of the 7 : 6 salt, or by fusing equimolecular proportions of niobic acid and sodium carbonate in a flux of sodium fluoride. Excess of sodium fluoride is removed from the melt with water, in which the niobate crystals are insoluble. Density, 4.512 to 4.559.<sup>3</sup> Hydrated sodium metaniobate,  $\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$  or  $7\text{H}_2\text{O}$ , is contained in the residue obtained after a fused mixture of niobium pentoxide and caustic soda has been extracted with a small volume of cold water, or in the residue obtained after boiling niobium pentoxide with caustic soda solution. Extraction of these residues with hot water yields small, glistening, triclinic crystals, which have also been obtained by the slow, spontaneous evaporation of the mother-liquors from the 7 : 6 salt.  $a : b : c = 0.9559 : 1 : 0.8894$ ;  $\alpha = 71^\circ 20'$ ,  $\beta = 105^\circ 30'$ ,  $\gamma = 54^\circ 7'$ . One gram of the hydrated salt dissolves in 75 cc. of water at  $100^\circ \text{C}$ . and in 200 cc. of water at  $14^\circ \text{C}$ . Aqueous solutions slowly become cloudy on standing in the air, probably through the action of carbon dioxide, which precipitates the 1 : 4 salt,  $\text{Na}_2\text{O} \cdot 4\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ . Addition of alcohol to the aqueous solution yields the 7 : 6 salt,



Niobic acid, or more probably acid niobates, remain in solution. On the other hand, by passing a stream of carbon dioxide through an aqueous solution of the 7 : 6 salt, the 1 : 1 salt or metaniobate is precipitated; these two sodium niobates hence are mutually convertible.<sup>4</sup>

7 : 6 Sodium niobate,  $7\text{Na}_2\text{O} \cdot 6\text{Nb}_2\text{O}_5 \cdot 31\text{H}_2\text{O}$  or  $32\text{H}_2\text{O}$  or  $36\text{H}_2\text{O}$ , is prepared (a) by adding a large excess of caustic soda to a solution of potassium niobium oxyfluoride,  $\text{K}_2\text{NbOF}_6$ , washing the heavy precipitate of sodium niobate with cold water and crystallising the product from boiling water; (b) by fusing niobium pentoxide with about four times its weight of caustic soda or sodium carbonate, washing the melt with cold water to remove excess of caustic soda, and crystallising the product from boiling water; (c) by fusing niobium pentoxide with potassium carbonate in a gold or platinum crucible and precipitating the aqueous extract with sodium chloride solution. A micro-crystalline powder is usually obtained, but the salt crystallises in prisms which can be dried in the air without undergoing decomposition. It is readily and completely soluble in water, the aqueous solutions appearing to contain the undecomposed salt, because on the addition of salts of barium, silver or zinc, the corresponding 7 : 6 niobates of these metals are precipitated. Treatment of the aqueous solution with carbon dioxide, however, precipitates the meta-salt, which is also obtained by spontaneous evaporation of the mother-liquors from which the 7 : 6 salt has been crystallised.<sup>5</sup>

<sup>1</sup> Santesson, *loc. cit.*

<sup>2</sup> Bedford, *loc. cit.*

<sup>3</sup> Holmquist, *Zeitsch. Kryst. Min.*, 1899, 31, 306.

<sup>4</sup> Rose, *loc. cit.*; Joly, *loc. cit.*; Santesson, *loc. cit.*; Balke and Smith, *loc. cit.*; Smith and Van Haagen, *loc. cit.*

<sup>5</sup> Hermann, *loc. cit.*; Bedford, *loc. cit.*; Balke and Smith, *loc. cit.*; von John, *loc. cit.*; Smith and Van Haagen, *loc. cit.*; Schoeller and Jahn, *loc. cit.*

3 : 4,<sup>1</sup> 8 : 7, 6 : 5,<sup>2</sup> 3 : 2,<sup>3</sup> and 3 : 1<sup>4</sup> sodium niobates have also been reported, but their identities are doubtful.

A double sodium ammonium niobate of probable formula  $5(\text{NH}_4)_2\text{O} \cdot \text{Na}_2\text{O} \cdot 24\text{Nb}_2\text{O}_5 \cdot 30\text{H}_2\text{O}$  or  $[\frac{5}{6}(\text{NH}_4)_2, \frac{1}{3}\text{Na}_2]\text{O} \cdot 4\text{Nb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  has been prepared by the addition of ammonium sulphate or ammonium chloride to a solution of sodium niobate.<sup>5</sup> Similarly, addition of caustic potash which contains some caustic soda to a solution of potassium niobate has yielded a sodium potassium niobate,  $\text{Na}_2\text{O} \cdot 3\text{K}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ .<sup>6</sup>

*Thorium Niobate*,  $5\text{ThO}_2 \cdot 16\text{Nb}_2\text{O}_5$ , is prepared by adding thorium sulphate to a solution of potassium niobate, fusing the precipitate with borax and boiling the melt with water containing hydrochloric acid. It forms doubly refracting, prismatic needles; density 5.21.<sup>7</sup>

*Yttrium Niobates*.—Larsson's method yields very small needles of the composition  $\text{Y}_2\text{O}_3 \cdot 3\text{Nb}_2\text{O}_5$ ; density 4.83. The metaniobate,  $\text{Y}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$ , is obtained by fusing a mixture of niobium pentoxide and yttrium chloride in excess of potassium chloride at a white heat; alternatively, the precipitate obtained by the addition of yttrium chloride to a solution of potassium niobate is fused with anhydrous yttrium chloride.<sup>8</sup> It forms doubly refracting, white octahedra; density 5.52. This compound is of interest in that it is probably a constituent of the natural *ytrotantalites* and *fergusonites* (see p. 120).

*Zinc Metaniobate*,  $\text{ZnO} \cdot \text{Nb}_2\text{O}_5$ , is prepared by Larsson's method.<sup>9</sup> It forms brown, apparently rhombic aggregates; density 5.69. Addition of zinc sulphate to a solution of the 7 : 6 sodium salt yields a white, insoluble precipitate of  $7\text{ZnO} \cdot 6\text{Nb}_2\text{O}_5 \cdot 25\text{H}_2\text{O}$ .<sup>10</sup>

*Zirconium Niobate*.—The salt  $\text{ZrO}_2 \cdot 5\text{Nb}_2\text{O}_5$  has been obtained in cloudy, rod-like needles, similarly to the thorium salt; density 5.14.<sup>11</sup> This salt is remarkable for its large content of acid oxide.

In addition to the foregoing, more or less impure niobates of *beryllium*, *cerium*, *lanthanum* and *nickel* have been prepared.<sup>12</sup>

Niobic acid also reacts with *hydroxylamine*. When the 4 : 3 potassium niobate is digested for several days with concentrated ammonium hydroxide and hydroxylamine hydrochloride, a precipitate is obtained which, after being washed and dried, has the composition  $3\text{NH}_2\text{OH} \cdot \text{HNbO}_3$ . The same process frequently yields the compound  $5\text{NH}_2\text{OH} \cdot 2\text{HNbO}_3 \cdot \text{H}_2\text{O}$ . These are both sparingly soluble, white substances, which decompose explosively on being heated. In contact with water at ordinary temperatures some hydroxylamine and a little niobic acid pass into solution. Analogous compounds with hydroxylamine are also given by vanadic acid (see p. 75), phosphoric acid, tungstic acid, etc.<sup>13</sup>

The double salts (see pp. 146-148 and 152) that are formed from niobium oxytrifluoride,  $\text{NbOF}_3$ , and niobium oxytrichloride,  $\text{NbOCl}_3$ , with the halides of the metals can in some cases also be looked upon as salts of niobium pentoxide. *Sodium niobium oxyfluoride*,  $2\text{NaF} \cdot \text{NbOF}_3 \cdot 2\text{H}_2\text{O}$ , can be written  $\text{Nb}_2\text{O}_5 \cdot 4\text{NaF} \cdot 6\text{HF} \cdot \text{H}_2\text{O}$ . These double fluorides are hence alternatively styled *fluoroxyjniobates*. This name is not to be

<sup>1</sup> Hermann, *loc. cit.*<sup>2</sup> Rose, *loc. cit.*<sup>3</sup> Bedford, *loc. cit.*<sup>4</sup> Joly, *loc. cit.*<sup>5</sup> Rose, *loc. cit.*<sup>6</sup> Marignac, *loc. cit.*<sup>7</sup> Larsson, *Zeitsch. anorg. Chem.*, 1896, 12, 197; Holmquist, *loc. cit.*<sup>8</sup> Joly, *loc. cit.*; Larsson, *loc. cit.*<sup>9</sup> Larsson, *loc. cit.*<sup>10</sup> Bedford, *loc. cit.*<sup>11</sup> Larsson, *loc. cit.*; Holmquist, *loc. cit.*<sup>12</sup> Larsson, *loc. cit.*<sup>13</sup> Hofmann and Kohlschütter, *Zeitsch. anorg. Chem.*, 1898, 16, 473.



preferred, because the ions which are formed in the solutions appear to be of the type  $[\text{NbOF}_3.n\text{F}]^{n-}$ . The above-mentioned sodium salt, for instance, most probably yields the complex ion  $[\text{NbOF}_3]^{-}$ .

#### HETEROPOLY-NIOBATES.

The *oxalo-niobates* constitute the only well-defined series of heteropoly-niobates. Indications of the formation of salts of other heteropoly-acids containing complex anions depend on the following observations:

(a) Niobium pentoxide yields complex compounds with tungsten trioxide,  $\text{WO}_3$ .<sup>1</sup>

(b) Addition of potassium chromate to a solution of niobium oxytrichloride yields a yellow precipitate of complex constitution.<sup>2</sup>

(c) The precipitation of niobic acid is hindered in the presence of titanous acid.<sup>3</sup>

(d) Whereas niobic acid is readily precipitated from solutions of niobates by the action of very weak acids, arsenic acid, citric acid, tartaric acid and malonic acid behave like oxalic acid and do not yield precipitates.<sup>4</sup>

(e) Addition of sodium phosphate to a solution of niobium oxytrichloride or phosphoric acid to a concentrated solution of an alkali niobate yields a precipitate which contains both phosphoric acid and niobic acid.<sup>5</sup>

(f) Many complex *titano-niobates*, *silico-niobates*, *titano-silico-niobates*, *uranyl-titanoniobates*, *silico-zircononiobates*, and *tantalo-niobates* occur naturally.

**Oxalo-niobates** or *niobo-oxalates* correspond to the vanado-oxalates, and contain both oxalic acid and niobic acid radicals in the complex anion. The only known series possesses the general formula  $3\text{R}\cdot_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 6\text{C}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , where R stands for an alkali metal. The sodium, potassium and rubidium salts are prepared by fusing one molecular proportion of niobium pentoxide with three molecular proportions of the alkali carbonate in a platinum crucible. The aqueous extract of the melt is poured into hot oxalic acid solution; concentration and cooling, or addition of alcohol or acetone, then brings about precipitation of the complex salt. Comparison of the electrical conductivity measurements of solutions of the alkali oxalo-niobates with those of the alkali hydrogen oxalates determined under the same conditions indicates that the oxalo-niobates are hydrolysed in aqueous solution, and that their anions contain a complex oxalo-niobic acid radical.<sup>6</sup>

*Ammonium Oxalo-niobate*,  $3(\text{NH}_4)_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 6\text{C}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , is prepared by fusing niobium pentoxide with potassium carbonate, dissolving the melt in water and precipitating the solution with hydrochloric acid. The hydrated niobic acid so obtained is then dissolved in a solution of ammonium hydrogen oxalate. Cooling, or addition of alcohol, yields beautiful, glistening crystals which, however, readily undergo hydrolysis in water with precipitation of niobic acid.

*Potassium Oxalo-niobate*,  $3\text{K}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 6\text{C}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , can be recrystal-

<sup>1</sup> Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 158; Gibbs, *Amer. J. Sci.*, 1877, [iii], 14, 63.

<sup>2</sup> Blomstrand, *Acta Univ. Lund*, 1864.

<sup>3</sup> Hall and Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 195.

<sup>4</sup> Hall, *loc. cit.*; Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 100.

<sup>5</sup> Russ, *Pogg. Annalen*, 1861, 112, 480; 1861, 113, 292.

<sup>6</sup> Russ, *Zeitsch. anorg. Chem.*, 1902, 31, 42.

lised unchanged from water, and also separates on the addition of acetone to its aqueous solution. It loses two molecules of water of crystallisation between 60° and 65° C. and the remainder at 150° C., at which temperature decomposition begins. When heated in a stream of chlorine, carbon tetrachloride, or hydrogen chloride, it leaves a residue of potassium chloride and niobium pentoxide. Its solution reacts acid towards phenolphthalein, and yields precipitates with salts of a large number of metals, but not with zinc, manganese or mercuric salts. Attempts to prepare other potassium niobium oxalates have been unsuccessful.

*Rubidium Oxalo-niobate*,  $3\text{Rb}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 6\text{C}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , is obtained in small needles by precipitation from its aqueous solutions with alcohol. It forms supersaturated solutions very readily.

*Sodium Oxalo-niobate*,  $3\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 6\text{C}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ , is similar to the potassium salt, but displays a greater tendency to form supersaturated solutions.

*Barium Oxalo-niobate*,  $5\text{BaO} \cdot \text{Nb}_2\text{O}_5 \cdot 10\text{C}_2\text{O}_3 \cdot 20\text{H}_2\text{O}$ , does not belong to the alkali series described above. It is prepared either by the addition of barium chloride to a solution of potassium oxalo-niobate, or by digestion of a mixture of barium oxalate and hydrated niobium pentoxide in a solution of oxalic acid. The crystals are soluble in oxalic acid solution but insoluble in water and in cold hydrochloric and nitric acids.

*Oxalo-niobic Acid*.—Attempts to prepare the normal oxalo-niobic acid,  $\text{Nb}_2(\text{C}_2\text{O}_4)_5$ , by the action of niobic acid on oxalic acid solutions, were not successful. When a large excess of oxalic acid was employed, crystals of a compound having the composition  $\text{Nb}(\text{C}_2\text{O}_4\text{H})_5$  were only once obtained; when an excess of niobic acid was employed, the compound  $\text{Nb}_2\text{O}_5 \cdot \text{C}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  or  $4\text{H}_2\text{O}$  was formed. Both of these compounds are unstable in the dry state,<sup>1</sup> but in faintly acid solution oxalo-niobic acid is much more stable than oxalo-tantalalic acid, which is preferentially hydrolysed by the addition of tannin. This reaction has recently been recommended for the separation and estimation of niobium and tantalum.<sup>2</sup>

#### PERNIOBIC ACID AND THE PERNIOBATES.

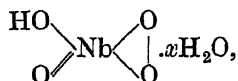
*Perniobic Acid*.—When niobic acid is treated with hydrogen peroxide it becomes yellow owing to the formation of a perniobic acid,  $\text{HNbO}_4 \cdot x\text{H}_2\text{O}$ . This compound has been isolated by carefully treating one of the potassium perniobates,  $\text{K}_4\text{Nb}_2\text{O}_{11} \cdot 3\text{H}_2\text{O}$ , with sulphuric acid and dialysing the mixture until it was free from both potassium sulphate and excess of sulphuric acid; the gelatinous product was then dried over concentrated sulphuric acid.<sup>3</sup> Perniobic acid, thus prepared, is an amorphous, yellow powder, insoluble in water. At 100° C. it is decomposed with liberation of oxygen. Dilute sulphuric acid is without action on it at ordinary temperatures, but on warming the mixture decomposition ensues with formation of hydrogen peroxide. Concentrated sulphuric acid liberates ozonised oxygen. The acid is much more stable than pervanadic acid, which is consistent with the general rule that in the same group the stability of the per-acid increases with

<sup>1</sup> Russ, *loc. cit.*; Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 76.

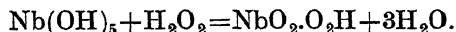
<sup>2</sup> Powell and Schoeller, *Analyst*, 1925, 50, 485.

<sup>3</sup> Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1899, 20, 341.

increase in atomic weight of the element. The active oxygen content agrees with the formula



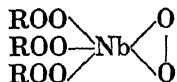
so that perniobic acid can be looked upon as being derived from hydrogen peroxide by replacement of a hydrogen atom by the  $\text{NbO}\cdot_2$  group :



A hydrosol of perniobic acid is obtained by adding 30 per cent. hydrogen peroxide to niobic acid and gently warming the mixture on the water-bath; the cooled product is treated in the cold with more hydrogen peroxide, excess of which is removed by dialysis. The hydrosol has the consistency of glycerine. It is converted into a yellow gel either by standing for a long time or by the action of electrolytes.<sup>1</sup>

Another compound of niobic acid and hydrogen peroxide, of doubtful constitution, has been prepared by treating a solution of niobic acid in concentrated hydrochloric acid with 3 per cent. hydrogen peroxide. The mixture is allowed to stand overnight, and the yellow precipitate, after being washed with water and dried, has the composition  $\text{Nb}(\text{OH})_6$  or  $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$ . On being heated it loses water and oxygen.<sup>2</sup>

**Perniobates.**—Perniobates having the general formula  $\text{R}'_2\text{NbO}_8$ , where R stands for an alkali metal, can be prepared by the action of excess of hydrogen peroxide on solutions of niobates which also contain alkali hydroxide or alkali carbonate; addition of alcohol precipitates the perniobates as white powders, which are washed with alcohol and ether. The rubidium and caesium salts become dark on being exposed to the air, but otherwise the perniobates are stable in air, and they are not decomposed in cold aqueous solution. Addition of sulphuric acid does not yield a precipitate in the cold, but on boiling, a yellow precipitate, which is probably niobium perhydroxide, is thrown down and oxygen is evolved.<sup>3</sup> The following constitutional formula has been ascribed to the perniobates :



but the evidence for this formula is weak. In addition to this series the only well-defined perniobate is the potassium salt,  $\text{K}_4\text{Nb}_2\text{O}_{11} \cdot 3\text{H}_2\text{O}$ .

The following perniobates are known :

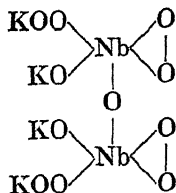
*Potassium Perniobate*,  $\text{K}_4\text{Nb}_2\text{O}_{11} \cdot 3\text{H}_2\text{O}$ , is prepared by treating the saturated aqueous extract from the fusion of niobium pentoxide and excess of caustic potash with hydrogen peroxide in small quantity, warming gently on the water-bath, and filtering; more hydrogen peroxide is added to the filtrate, which is precipitated with alcohol; the precipitate is treated in aqueous solution with more hydrogen peroxide, caustic potash, and alcohol. It forms a soluble, white powder, which evolves oxygen on being warmed; dilute sulphuric acid produces

<sup>1</sup> Melikoff and Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 457.

<sup>2</sup> Hall and Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 209; *J. Amer. Chem. Soc.*, 1905, 27, 1400.

<sup>3</sup> Balke and Smith, *ibid.*, 1908, 30, 1657.

hydrogen peroxide, and concentrated sulphuric acid produces ozonised oxygen. Analysis shows that the ratio  $K_2O : Nb_2O_5 : \text{active oxygen}$  is 2 : 1 : 4, from which result the salt can be looked upon as the potassium salt of *pyro-perniobic acid*,



When the salt is allowed to remain in solution for some time it slowly precipitates another potassium perniobate, the composition of which closely approximates to the formula  $KNbO_4 \cdot xH_2O$ .

*Potassium Perniobate*,  $K_3NbO_8$ , is prepared by the action of caustic potash and 3 per cent. hydrogen peroxide on 4 : 3 potassium niobate. It yields tetragonal crystals.

*Sodium Perniobate*,  $Na_3NbO_8$ , is obtained as a white powder by the action of caustic soda and 3 per cent. hydrogen peroxide on 7 : 6 sodium niobate.

*Rubidium Perniobate*,  $Rb_3NbO_8$ , is obtained as a white, crystalline powder by the action of rubidium carbonate and excess of hydrogen peroxide on 4 : 3 rubidium niobate.

*Cæsium Perniobate*,  $Cs_3NbO_8$ , is prepared similarly to the rubidium salt.

The following *double perniobates* have also been isolated :  $KCaNbO_8 \cdot 4H_2O$  ;  $NaCaNbO_8 \cdot 4H_2O$  ;  $KMgNbO_8 \cdot 7H_2O$  ;  $RbMgNbO_8 \cdot 7\frac{1}{2}H_2O$  ;  $NaMgNbO_8 \cdot 8H_2O$  ;  $CsMgNbO_8 \cdot 8H_2O$ .

**Niobium Peroxyfluorides or Fluoroxypeniobates.**—Like niobic acid, the alkali niobium oxyfluorides have the property of taking up active oxygen by reaction with hydrogen peroxide.

*Potassium Niobium Peroxyfluoride.*—When potassium niobium oxyfluoride,  $K_2NbOF_5 \cdot H_2O$ , is dissolved in 3 per cent. hydrogen peroxide, fine, white, greasy leaflets of potassium niobium peroxyfluoride or *potassium fluoroxypeniobate*,  $K_2NbO_2F_5 \cdot H_2O$  or  $2KF \cdot NbO_2F_3 \cdot H_2O$ , are obtained. This compound is stable in dry air. At  $100^\circ C$ . it loses water and at  $150^\circ C$ . it loses oxygen. Its aqueous solutions decompose only very slowly ; the solubility is decreased by the addition of hydrogen peroxide and increased by the addition of hydrofluoric acid.<sup>1</sup>

*Sodium Niobium Peroxyfluoride* or *sodium fluoroxypeniobate*,  $Na_3NbO_2F_6 \cdot H_2O$  or  $3NaF \cdot NbO_2F_3 \cdot H_2O$ , is prepared by the action of hydrogen peroxide on sodium niobium oxyfluoride,  $3NaF \cdot NbOF_3$ . It forms yellow, almost transparent crystals, which become cloudy on exposure to the air.<sup>2</sup>

*Rubidium Niobium Peroxyfluoride* or *rubidium fluoroxypeniobate*,  $Rb_3NbO_2F_6 \cdot H_2O$  or  $2RbF \cdot NbO_2F_3 \cdot H_2O$ , is obtained similarly, as thin, yellow plates, from rubidium niobium oxyfluoride,  $2RbF \cdot NbOF_3$ .<sup>3</sup>

#### NIOBIUM AND SULPHUR.

**Sulphides.**—Definite sulphides of niobium have not been prepared. Solutions of alkali niobates do not yield precipitates with hydrogen

<sup>1</sup> Piccini, *Zeitsch. anorg. Chem.*, 1892, 2, 22 ; Hall and Smith, *loc. cit.*

<sup>2</sup> Balke and Smith, *loc. cit.*

<sup>3</sup> Balke and Smith, *loc. cit.*

sulphide or alkali sulphides,<sup>1</sup> but some evidence of the formation of sulphides in the dry way has been obtained. When metallic niobium is heated with sulphur, direct combination takes place with the formation of a black powder, which is probably the disulphide,  $\text{NbS}_2$ .<sup>2</sup> This compound is perhaps also formed by burning the hydride in sulphur vapour,<sup>3</sup> or by the action at high temperatures of the mixed vapours of carbon bisulphide and hydrogen sulphide on niobium pentoxide.<sup>4</sup> The analytical data for these preparations are not, however, conclusive.

**Oxysulphides.**—The action of carbon bisulphide vapour or hydrogen sulphide on niobium pentoxide, sodium niobate or niobium oxytrichloride gives rise to a black powder which assumes a metallic appearance on being rubbed, and which conducts electricity well. This is probably an oxysulphide of niobium,  $\text{Nb}_x\text{O}_y\text{S}_z$ , but its exact composition varies with the experimental conditions, and its individuality is a matter of doubt.<sup>5</sup> Oxysulphides of niobium of doubtful composition, mixed with potassium sulphide, are also produced by the action of carbon bisulphide vapour on potassium oxalo-niobate.<sup>6</sup>

**Sulphates.**—Electrolytic reduction of solutions of niobic acid in sulphuric acid furnishes solutions which contain the niobium either as  $\text{Nb}_2\text{O}_3$  or  $\text{Nb}_3\text{O}_7$ , according to the experimental conditions, but no sulphates of niobium have been isolated from these solutions. Reddish-brown crystals of an *ammonium niobium sulphate*, which have the probable composition  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Nb}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ , have, however, been prepared by electrolytic reduction, as well as an *acid ammonium niobium sulphate*,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Nb}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ . The latter is a brown powder which is somewhat stable in a dry atmosphere. It dissolves in water to give a brown solution which oxidises rapidly, becoming successively blue, green, and finally colourless; addition of ammonium hydroxide or hydrochloric acid produces a blue coloration immediately.<sup>7</sup>

Evaporation of a solution of niobium oxysulphide in sulphuric acid and heating to  $340^\circ \text{C}$ . yields a compound of the composition  $\text{Nb}_2\text{O}_5 \cdot \text{SO}_3$ , which can be alternatively written  $\text{NbO}_2 \cdot \text{SO}_4 \cdot \text{NbO}_2$ , *i.e.* as *hyponiobic sulphate*. At  $420^\circ \text{C}$ . the product has the composition  $2\text{Nb}_2\text{O}_5 \cdot \text{SO}_3$ .<sup>8</sup>

#### NIOBIUM AND NITROGEN.

The absorption of nitrogen by metallic niobium under different conditions of temperature and pressure has not been investigated. Two substances have, however, been prepared, to which the formulæ  $\text{NbN}$  and  $\text{Nb}_3\text{N}_5$  have been ascribed, from their analytical data.

**Niobium Mononitride**,  $\text{NbN}$ , is obtained by heating a mixture of niobium pentoxide and lampblack in an atmosphere of nitrogen at

<sup>1</sup> Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 72.

<sup>2</sup> von Bolton, *Zeitsch. Elektrochem.*, 1907, 13, 148.

<sup>3</sup> Krüss and Nilson, *Ber.*, 1887, 20, 1691.

<sup>4</sup> Biltz and Voigt, *Zeitsch. anorg. Chem.*, 1922, 120, 75; Biltz and Gonder, *Ber.*, 1907, 40, 4963; compare Russ, *Zeitsch. anorg. Chem.*, 1902, 31, 81.

<sup>5</sup> Rose, *Pogg. Annalen*, 1860, 111, 193; Delafontaine, *Arch. Sci. phys. nat.*, 1866, [ii], 27, 173; Rammelsberg, *J. prakt. Chem.*, 1869, 108, 95; Hermann, *ibid.*, 1871, 3, 393; Biltz and Kircher, *Ber.*, 1910, 43, 1645.

<sup>6</sup> Russ, *loc. cit.*

<sup>7</sup> Stähler, *Ber.*, 1914, 47, 842; Ott, *Dissertation* (Munich, 1911); *Zeitsch. Elektrochem.*, 1912, 18, 349.

<sup>8</sup> Gmelin-Kraut, *Handbuch der anorganischen Chemie* (Heidelberg), 1912, 6, 233.

temperatures between 1200° and 1300° C. It is a bright grey powder with a yellowish lustre, melting at 2300° abs.; density 8.4. The specific electrical resistance is  $2 \times 10^{-4}$  ohms per cc. at room temperature and  $4.5 \times 10^{-4}$  ohms per cc. at the melting-point. It is insoluble in all acids and in aqua-regia. On being heated it loses much of its nitrogen content, even when heated in an atmosphere of nitrogen. When heated either in air or mixed with copper oxide it forms niobium pentoxide. Its crystal structure has been studied by the Debye-Scherrer method.<sup>1</sup>

**Triniobium Pentanitride**,  $Nb_3N_5$ , has been obtained by the action of ammonia gas on an ether solution of niobium pentachloride,<sup>2</sup> but it is most conveniently prepared synthetically. Finely powdered niobium is subjected to prolonged heating at about 1000° C. in an atmosphere of pure, dry nitrogen. It is a black powder which is stable in the air. On being heated in air it glows and forms the pentoxide, but it is not oxidised by lead chromate even at high temperatures. It is not attacked by boiling water, hydrochloric, nitric or sulphuric acids. Boiling caustic potash solutions are also without action on it, but molten caustic potash decomposes it with the evolution of ammonia.<sup>3</sup>

Other nitrides of niobium of doubtful composition have been obtained by the action of ammonia on niobium pentoxide,<sup>4</sup> niobium oxychloride<sup>5</sup> and niobium pentachloride.

**Ferrocyanides.**—As might be anticipated from its very weakly acid nature, niobium pentoxide does not give rise to any cyanides. By the action of hydrochloric acid and potassium ferrocyanide on solutions of niobic acid, three brown powders have been obtained. The following are some of the formulæ that have been allotted to them:  $KNb[Fe(CN)_6]_2$ ;  $K_2Nb_{1.2}[Fe(CN)_6]$ ;  $K_9(NbO)_5.[Fe(CN)_6]_6 \cdot 10H_2O$ ; but the evidence for these is weak.<sup>6</sup>

#### NIOBIUM AND CARBON.

Metallic niobium in the molten state absorbs graphite slowly to yield carbides of unknown composition. These are insoluble in all acids, including hydrofluoric acid, and are brittle and very hard; they scratch quartz and glass.<sup>7</sup> Reduction of niobium pentoxide with carbon in the electric furnace gives rise to similar products.<sup>8</sup> A definite carbide having the composition NbC has recently been prepared by heating niobium sesquioxide,  $Nb_2O_3$ , mixed with carbon, in hydrogen at 1200° C. It is a greyish-violet powder which melts at about 3650° abs. Its hardness after fusion lies between 9 and 10. Its specific electrical resistance at ordinary temperatures is  $1.47 \times 10^{-4}$  ohms per cc. Its density is 7.56.<sup>9</sup> The crystal structure has been studied by the Debye-Scherrer

<sup>1</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 143, 293; Friederich, *Zeitsch. Physik*, 1925, 31, 813; Becker and Ebert, *ibid.*, 1925, 31, 268.

<sup>2</sup> Hall and Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 203; *J. Amer. Chem. Soc.*, 1905, 27, 1395.

<sup>3</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 92; Moissan, *Compt. rend.*, 1901, 133, 20.

<sup>4</sup> Rose, *Pogg. Annalen*, 1860, III, 426, 429.

<sup>5</sup> Joly, *Annales Scientifiques de l'École Normale Supérieure, Paris*, 1877, [ii], 6, 154.

<sup>6</sup> Wyrouboff, *Ann. Chim. Phys.*, 1876, [v], 8, 444; Atterberg, *Bull. Soc. chim.*, 1875, [ii], 24, 355; compare Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 100.

<sup>7</sup> Moissan, *loc. cit.*; *Bull. Soc. chim.*, 1902, [iii], 27, 431.

<sup>8</sup> von Bolton, *Zeitsch. Elektrochem.*, 1907, 13, 145.

<sup>9</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 144, 169; compare Becker and Ebert, *Zeitsch. Physik*, 1925, 31, 268.

method. Long, dark blue needles of a carbide having the same composition were also obtained by heating a mixture of potassium niobate,  $K_2O \cdot 3Nb_2O_5$ , potassium carbonate and sugar charcoal to a high temperature in a graphite crucible. The product was purified by washing with sulphuric acid and water.<sup>1</sup>

The last-mentioned reaction at lower temperatures has also furnished greyish-violet crystalline niobium compounds containing both carbon and nitrogen,<sup>2</sup> and which appear to contain varying proportions of nitride and carbide of niobium.

A substance which had the probable composition  $Nb_2O_5 \cdot N_5C$  was obtained as a black powder by the action of cyanogen on niobium pentoxide at a red heat.<sup>3</sup>

*Niobo-oxalates* are described on p. 165.

<sup>1</sup> Joly, *Annales Scientifiques de l'École Normale Supérieure, Paris*, 1877, [ii], 6, 142.

<sup>2</sup> Joly, *loc. cit.*; *Bull. Soc. chim.*, 1876, [ii], 25, 506.

<sup>3</sup> Rose, *Pogg. Annalen*, 1860, **111**, 427.

## CHAPTER VIII.

### TANTALUM AND ITS ALLOYS.

Symbol, Ta. Atomic Weight, 181·3 (O=16).

**Preparation of Metallic Tantalum.**—For the industrial preparation of tantalum a tantalite is used which contains at least 60 per cent. of tantalum pentoxide and the minimum quantity of titanium.<sup>1</sup> The finely pulverised mineral is fused with either caustic potash or potassium hydrogen sulphate. In the former case the aqueous extract contains potassium tantalate and potassium niobate, which undergo hydrolysis and precipitate mixed tantalic and niobic acids when boiled with sulphuric or nitric acid; in the latter case the mixed tantalic and niobic acids are left in the insoluble residue after extraction with water. The niobium is removed<sup>2</sup> by dissolving the mixed acids in hydrofluoric acid; sufficient potassium fluoride is then added to produce the double fluorides,  $K_2TaF_7$  and  $K_2NbOF_5 \cdot H_2O$ , which are then separated by repeated fractional crystallisation. Considerable secrecy has been maintained concerning the details of the large-scale processes employed to convert potassium tantalum fluoride, or the tantalum pentoxide obtained from it by hydrolysis, into metallic tantalum which possesses good mechanical properties. It is understood, however, that reduction is effected by one of the following methods: (1) The double fluoride is heated with potassium or sodium at a high temperature; the product is washed with water and mineral acid, pressed into rods and fused in an electrically heated vacuum furnace, whereby all traces of impurities are removed and a ductile material is obtained.<sup>3</sup> (2) The molten double fluoride is electrolysed between an anode of impure tantalum and a cathode of pure tantalum, or of other conductive and inert material, in a vessel made of tantalum pentoxide, magnesia, or other refractory substance.<sup>4</sup> The product is fused in a vacuum furnace as in the previous process.

Tantalum can also be prepared in small quantities by passing an alternating electric current through rods of tantalum dioxide (see p. 196)

<sup>1</sup> Analytical data of samples of ore utilised on the commercial scale are set out on p. 119. By-products produced during the working-up of the rare earths for cerium and thorium compounds for use in the manufacture of incandescent mantles, as well as by-products from certain tin and tungsten ores, are also available as sources of tantalum.

<sup>2</sup> The various methods available for the removal of metals other than niobium are discussed on pp. 124 *et seq.*

<sup>3</sup> Berzelius, *Pogg. Annalen*, 1825, 4, 10; von Bolton, *Zeitsch. Elektrochem.*; 1905, 11, 45; *German Pat.* 155548 (1905); *J. Chem. Soc., Abs.*, 1905, 88, [ii], 96; Balke, *Chem. Met. Eng.*, 1922, 26, 1272; *J. Ind. Eng. Chem.*, 1923, 15, 560.

<sup>4</sup> *U.S. Pat.* 947983 (1910); *Eng. Pat.* 24234 (1906).



sealed into a glass bulb in which a good vacuum is maintained during the heating.<sup>1</sup> This is not, however, an industrial process.

The malleability and ductility of tantalum are destroyed by the presence of even traces of foreign bodies; 0.1 per cent. of carbon, for instance, renders the material brittle. Older laboratory reactions which gave rise to more or less pure tantalum deficient in mechanical properties consisted in reducing tantalum pentoxide with "mixed metal"<sup>2</sup> (see p. 134) or with carbon in the electric furnace;<sup>3</sup> the equilibrium conditions of the reduction of tantalum pentoxide by carbon at high temperatures have been investigated by Slade and Higson.<sup>4</sup> The thermite process yields an alloy of tantalum and aluminium.<sup>5</sup>

*Colloidal Tantalum.*—A sol of tantalum has been prepared by sparking tantalum electrodes immersed in isobutyl alcohol using an induction coil. The sol appears brownish-black by transmitted light and black by reflected light; it keeps only for one to two weeks.<sup>6</sup>

**Physical Properties.**<sup>7</sup>—Tantalum is a white metal with a greyish tinge and is very similar to platinum in colour and general appearance. When it is heated to 1600° C. *in vacuo* it assumes a crystalline form.<sup>8</sup> Examination of the powdered metal by X-ray analysis has shown that the arrangement of the atoms is on the plan of a body-centred cube of side 3.272 Å, obtained by dividing the space of a crystal into equal closely packed cubes and placing an atom at each cube corner and each cube centre; the distance between the nearest atoms is 2.833 Å.<sup>9</sup> The specific gravity of the fused metal is 16.6; a sample drawn into wire 0.05 mm. diameter had a density of 16.5;<sup>10</sup> the density calculated from X-ray data is 17.09.<sup>11</sup>

Pure tantalum possesses valuable mechanical properties, in which it closely resembles molybdenum and tungsten. It can be worked in the cold state to a remarkable extent without being previously annealed, although it is subject to strain-hardening, much like copper and silver. Photomicrographs of cold-worked and annealed tantalum are given in the reference cited.<sup>12</sup> The metal can be rolled into sheet 0.1 mm. thick or even less,<sup>13</sup> and can be drawn into filament wire 0.08 mm. diameter. The ultimate tensile strength of the hard-drawn wire (0.08 mm. diameter) is 93 kilograms per square millimetre or 57 tons per square inch; this figure increases as the diameter of the wire diminishes, reaching 150 to 160 kilograms per square millimetre for wire 0.05 mm. thick, which is considerably higher than the value for hard-drawn copper, nickel, or platinum; the tensile strength of a carbon steel containing 0.89 per cent. of carbon is about 52 tons per square inch. Young's modulus of elasticity for tantalum wire (0.08 mm. diameter) in kilograms per square

<sup>1</sup> von Bolton, *loc. cit.*

<sup>2</sup> Weiss and Aichel, *Annalen*, 1904, 337, 370; Muthmann, Weiss, and Riedelbauch, *ibid.*, 1907, 355, 58.

<sup>3</sup> Moissan, *Compt. rend.*, 1902, 134, 211; *Bull. Soc. chim.*, 1902, [ii], 27, 434.

<sup>4</sup> Slade and Higson, *J. Chem. Soc.*, 1919, 115, 211.

<sup>5</sup> Goldschmidt and Vautin, *J. Soc. Chem. Ind.*, 1898, 17, 543; von Bolton, *loc. cit.*

<sup>6</sup> Svedberg, *Ber.*, 1906, 39, 1705; see also *Eng. Pat.* 25864 (1906); *French Pat.* 371799 (1906); *German Pat.* 281305 (1913).

<sup>7</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45, 503, 722; Siemens, *Chem. News*, 1909, 100, 223; Balke, *Chem. Met. Eng.*, 1922, 27, 1271.

<sup>8</sup> A photomicrograph is given by Jeffries, *Engineering*, 1918, 106, 240.

<sup>9</sup> Hull, *Proc. Amer. Inst. Elec. Engineers*, 1919, 38, 1445; *Phys. Review*, 1921, 17, 571.

<sup>10</sup> See also Hinrichsen and Sahlbom, *Ber.*, 1906, 39, 2605.

<sup>11</sup> Hull, *loc. cit.*      <sup>12</sup> Jeffries, *loc. cit.*      <sup>13</sup> *Eng. Pat.* 247507 (1925).

millimetre is 19,000. The Brinell hardness number is 46, compared with 290 for tungsten, 147 for molybdenum, and from 100 to 300 for steels; <sup>1</sup> the hardness is increased by the addition of small quantities of silicon, carbon, boron, aluminium, tin or titanium, and by traces of oxygen. When heated to redness and hammered, the metal becomes so hard through the formation of an oxide film that a diamond will not scratch it, <sup>2</sup> and at the same time it retains its toughness. <sup>3</sup> When heated in a poor vacuum, tantalum becomes very brittle and is easily powdered; its ductility and toughness are restored by heating in a good vacuum to a white heat. <sup>4</sup> The compressibility under pressure has been determined; <sup>5</sup> the average fractional change in volume caused by 1 megabar pressure <sup>6</sup> between applications of 100 and 500 megabars at 20° C. is  $0.54 \times 10^{-6}$ . The linear coefficient of expansion per °C. from 0° to 400° C. is approximately  $6.46 \times 10^{-6}$ , as determined with a Fizeau dilatometer; <sup>7</sup> this figure is less than that given by platinum and enables tantalum to be fused into glass. An earlier determination <sup>8</sup> over the range 0° to 50° C. gave a linear expansion of  $7.9 \times 10^{-6}$ . The cubical coefficient of expansion is  $24 \times 10^{-6}$ ; the atomic volume is 10.9, and the calculated internal pressure of the atom, using the last two figures, is 455,000 megabars. <sup>10</sup>

The melting-point of tantalum lies between 2850° and 3000° C.; the most recent determinations are: 2798° C., <sup>11</sup> 2850° C., <sup>12</sup> 2910° C., <sup>13</sup> 3000° C., <sup>14</sup> 3030° C. <sup>15</sup> The specific heat in calories per gram per degree between 16° and 100° C. is 0.0365, and increases at higher temperatures; the coefficient of thermal conductivity is 0.130 calories per cc. at 17° C. and 0.129 calories at 100° C. <sup>16</sup> Tantalum displays weak paramagnetism; the magnetic susceptibility decreases with the temperature. <sup>17</sup> The electrical behaviour of tantalum has received considerable attention because of its application in the manufacture of electric lamps. The electrical resistance of 1 cc. of a sample which had been well annealed by heating for a period of between 100 and 200 hours *in vacuo* at 1900° C. was 14.6 microhms at 20° C.; <sup>18</sup> the corresponding figure for copper is 1.87. The electrical resistance increases with increase in temperature; the variation over the range from

<sup>1</sup> Engle, *Trans. Amer. Inst. Min. Met. Eng.*, 1925, 71, 691.

<sup>2</sup> Grove-Palmer, *Metallurgist* (Supplement to *The Engineer*), 1927, 3, 185.

<sup>3</sup> *The Engineer*, 1908, 106, 297.

<sup>4</sup> Tiede and Birnbräuer, *Zeitsch. anorg. Chem.*, 1914, 87, 148.

<sup>5</sup> Richards and Bartlett, *J. Amer. Chem. Soc.*, 1915, 37, 480.

<sup>6</sup> One megabar equals 0.987 of "an atmosphere."

<sup>7</sup> Disch, *Zeitsch. Physik*, 1921, 5, 173; compare Worthing, *Phys. Review*, 1926, 28, 200.

<sup>8</sup> von Bolton, *loc. cit.*

<sup>9</sup> Richards, *J. Amer. Chem. Soc.*, 1924, 46, 1419.

<sup>10</sup> Richards, *ibid.*, 1926, 48, 3076.

<sup>11</sup> Forsythe, *Astrophys. J.*, 1911, 34, 353; *Engineering*, 1912, 93, 189.

<sup>12</sup> Pirani and Meyer, *Verh. Deut. physikal. Ges.*, 1911, 13, 540; *Engineering*, 1912, 94, 364.

<sup>13</sup> Waidner and Burgess, *J. Physique*, 1907, 6, 380.

<sup>14</sup> Pirani, *Verh. Deut. physikal. Ges.*, 1910, 12, 301.

<sup>15</sup> Worthing, *Phys. Review*, 1926, 28, 181.

<sup>16</sup> Barratt and Winter, *Ann. Physik*, 1925, [iv], 77, 5; see also Worthing, *loc. cit.*

<sup>17</sup> Loring, *Chem. News*, 1914, 109, 122; Owen, *Ann. Physik*, 1912, [iv], 37, 657, 666, 698.

<sup>18</sup> Pirani, *Zeitsch. Elektrochem.*, 1907, 13, 344; compare Pecheux, *Compt. rend.*, 1911, 153, 1140; Schulze, *Zeitsch. für. Metallkunde*, 1923, 15, 33.

—180° to 2000° C. has been measured by Pirani.<sup>1</sup> At 2000° C. the resistance is more than six times that at room temperatures; at —180° C. it is reduced to approximately one-third. The influence on the electrical conductivity of pressures varying from 700 to 2000 atmospheres has also been measured.<sup>2</sup> For an investigation of the Hall effect and allied phenomena, see the reference cited.<sup>3</sup> Tantalum has been employed as one of the elements in thermocouples, with copper or tungsten as the other element; <sup>4</sup> a tantalum/tungsten thermocouple is stated to be four times as sensitive as platinum/platinum-rhodium.

**Optical Properties.**—The refractive index of tantalum is 2.05, the coefficient of absorption 2.31, and the reflexion capacity 43.8 per cent. when measured with yellow light of wave-length  $\lambda=5790$ .<sup>5</sup> The spectral emissivity and the radiation intensity and their variation with temperature have been measured by Worthing.<sup>6</sup> For a comparison of the radiation constants of tantalum, platinum, osmium and carbon, see the references cited.<sup>7</sup> The flame spectrum of tantalum between carbon electrodes consists of a blue cone with a reddish-yellow edge.<sup>8</sup>

The strongest lines in the arc spectrum of tantalum from wave-length 7000 Å to wave-length 3000 Å, and their relative intensities, are set out in the table on p. 176.<sup>9</sup>

The spark spectrum of tantalum has been examined from wave-length 4700 Å to wave length 2180 Å.<sup>10</sup> The strongest lines and their relative intensities are set out in the table on p. 176.

The visible portion of the spark spectrum between tantalum electrodes is very weak, and the individual lines are measureable only with difficulty.<sup>11</sup> The lines between  $\lambda=2000$  and  $\lambda=4700$  in the spectrum of the spark discharge under water are the same as in air, unlike most other metals.<sup>12</sup>

In order to be able to establish spectrographically the presence of traces of a foreign element in a substance, de Gramont determined which of the lines in the spectrum produced by a condensed spark discharge are the last to disappear as the quantity of foreign element is gradually reduced. The ultimate lines given by tantalum in this manner have the following wave-lengths, expressed in Ångström units:<sup>13</sup> (a) In

<sup>1</sup> Pirani, *Verh. Deut. physikal. Ges.*, 1910, 12, 335; see also Pechoux, *loc. cit.*; Worthing, *Phys. Review*, 1926, 28, 197; Beckman, *Physikal. Zeitsch.*, 1917, 18, 507; Holborn, *Ann. Physik*, 1919, 59, 145; Bridgman, *Proc. Nat. Acad. Sci.*, 1917, 3, 10.

<sup>2</sup> Beckmann, *loc. cit.*

<sup>3</sup> Smith, *Phys. Review*, 1916, 8, 79.

<sup>4</sup> Worthing, *ibid.*, 1912, 34, 153; Morugina, *Zeitsch. tech. Phys.*, 1926, 7, 488.

<sup>5</sup> Wartenberg, *Verh. Deut. physikal. Ges.*, 1910, 12, 105.

<sup>6</sup> Worthing, *Phys. Review*, 1926, 28, 174.

<sup>7</sup> Coblenz, *Bulletin Bureau of Standards, Washington*, 1909, 5, No. 3, 339; Jolley, *The Electrician*, 1909, 63, 700, 755; Lavender, *ibid.*, 1909, 64, 306; Paterson, *ibid.*, 1916, 77, 822.

<sup>8</sup> Mott, *Trans. Amer. Electrochem. Soc.*, 1917, 31, 272.

<sup>9</sup> Eder and Valenta, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, 119, 582; Exner and Haschek, *ibid.*, 1898, 107, 813; Josewski, *Zeitsch. wiss. Photochem.*, 1918, 17, 85; Rütten and Morsch, *ibid.*, 1905, 3, 181; see also Stanley, *Lines in the Arc Spectra of Elements* (Adam Hilger, Ltd., London, 1911).

<sup>10</sup> Exner and Haschek, *loc. cit.*; *B.A. Reports*, 1908, 119.

<sup>11</sup> Eder and Valenta, *Sitzungsber. K. Akad. Wiss. Wien*, 1909, 118, 1902.

<sup>12</sup> Konen and Finger, *Zeitsch. Elektrochem.*, 1909, 15, 165; Konen, *Zeitsch. wiss. Photochem.*, 1909, 7, 329; compare Allin and Ireton, *Trans. Soc. Canada*, 1927, [iii], 21, 127.

<sup>13</sup> de Gramont, *Compt. rend.*, 1920, 171, 1106; Twyman, *Wave-length Tables for Spectrum Analysis* (Adam Hilger, Ltd., London), 1923, 84.

## ARC SPECTRUM OF TANTALUM.

Wave-length.	Relative Intensity of Line.	Wave-length.	Relative Intensity of Line.	Wave-length.	Relative Intensity of Line.
6675.7	9	5989.9	5	4064.7	5
6621.4	9	5877.6	5	4061.5	5
6612.1	9	5811.2	6	4027.0	5
6575.1	9	5780.8	5	3999.4	4
6516.3	10	5776.9	5	3996.3	4
6514.5	9	5665.0	8	3821.9	10
6505.7	9	4574.5	5	3642.2	10
6485.6	10	4566.0	4	3626.8	9
6450.5	10	4552.1	4	3607.5	7
6430.9	10	4531.0	5	3511.2	8
6428.8	6	4511.1	10	3497.9	5
6389.6	10	4486.2	4	3480.7	5
6361.0	9	4415.9	4	3468.9	4
6356.3	9	4386.2	4	3407.1	4
6325.2	9	4279.2	4	3371.6	5
6309.7	10	4206.0	10	3358.6	4
6268.8	10	4181.3	4	3318.9	5
6256.8	10	4178.0	4	3311.3	9
6154.7	5	4148.0	5	3223.9	4
6047.4	5	4136.3	5	3181.0	4
6045.6	5	4129.5	5	3103.4	4
5997.4	6	4105.2	4	3069.3	4
5944.2	5	4068.0	6		

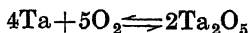
## SPARK SPECTRUM OF TANTALUM.

Wave-length.	Relative Intensity of Line.	Wave-length.	Relative Intensity of Line.	Wave-length.	Relative Intensity of Line.
4607.0	5	4032.7	5	3717.3	8
4205.5	5	3966.4	5	3713.2	6
4191.1	6	3905.8	10	3688.2	5
4168.3	8	3832.0	6	3633.7	8
4164.8	8	3819.0	5	3659.7	6
4163.8	8	3808.1	5	3651.3	6
4137.3	7	3798.3	6	3580.5	6
4124.0	10	3791.4	6	3576.0	5
4101.1	10	3787.2	5	3535.5	6
4079.9	12	3742.6	5	3432.9	5
4059.1	15	3726.4	5	3225.6	5

the visible region, 6045.5 and 5997.4; (b) using a crown Uviol spectrograph, 3631.9, 3406.9, 3318.8, 3311.2; (c) using a quartz spectrograph, 2963.8.

The X-ray spectra of tantalum have been investigated.<sup>1</sup> The emission of electrons from tantalum when heated to high temperatures has received considerable investigation.<sup>2</sup> Electron emission from the cold metal has been studied by Rother,<sup>3</sup> and the arrangement of electron groups in the atom by Lessheim and Samuel.<sup>4</sup> Tantalum is not radioactive.<sup>5</sup>

**Chemical Properties.**<sup>6</sup>—Tantalum is not affected by air or moisture at ordinary temperatures and does not "rust." When the metal is heated in the form of sheet or thick wire in air it becomes yellow at about 400° C.,<sup>7</sup> and with increasing temperature blue, and finally black. Above a dull red heat a film of the white pentoxide is produced, which to a large extent prevents further oxidation. Very thin tantalum wire can, however, be ignited in air by a match. In oxygen tantalum wire glows without flame at a white heat, and yields the pentoxide if the pressure of oxygen is greater than 20 mm. The reaction,



appears to be reversible, and proceeds completely from right to left *in vacuo* at high temperatures; this enables pure tantalum metal to be produced directly from the pentoxide (see p. 172). Tantalum absorbs large volumes of hydrogen when heated in the gas, and yields a brittle product even when the amount of hydrogen present is less than 0.1 per cent.;<sup>8</sup> the absorbed gas is completely removed by fusion in a good vacuum. Tantalum also absorbs nitrogen and, in minute quantities, helium and argon.<sup>9</sup> It reacts slowly with sulphur and selenium, with probable formation of the sulphide and selenide; hydrogen sulphide is without action at 600° C.<sup>10</sup> Tantalum is attacked readily by fluorine,<sup>11</sup> and burns when gently heated in chlorine, the penta-

<sup>1</sup> For the results of the examination of K, L, and M series of the high-frequency spectra of tantalum, see the following references. K series: Cabrera, *Compt. rend.*, 1923, 176, 740; Réchou, *ibid.*, 1925, 180, 1107; Stephenson and Cork, *Phys. Review*, 1926, 27, 138, 530. L series: Moseley, *Phil. Mag.*, 1914, [vi], 27, 710; Siegbahn and Friman, *ibid.*, 1916, [vi], 32, 47; *Ann. Physik*, 1916, [iv], 49, 616; Schrör, *ibid.*, 1926, [iv], 80, 297; Coster, *Compt. rend.*, 1921, 173, 77; Auger and Dauvillier, *ibid.*, 1923, 176, 1297; Coster, *Phys. Review*, 1922, [ii], 19, 20; Cork, *ibid.*, 1923, [ii], 21, 326; Wennerlöf, *Zeitsch. Physik*, 1927, 41, 524; Nishina, *Phil. Mag.*, 1925, [vi], 49, 521. M series: Stenström, *Ann. Physik*, 1918, [iv], 57, 347; Dauvillier, *Compt. rend.*, 1926, 183, 193; Hjalmar, *Zeitsch. Physik*, 1923, 15, 65.

<sup>2</sup> Harker and Kaye, *Proc. Roy. Soc.*, 1913, A, 88, 522; Horton and Davies, *ibid.*, 1919, A, 95, 333; Roy, *ibid.*, 1926, A, 112, 599; Rodebush, *J. Amer. Chem. Soc.*, 1923, 45, 997; Dushman, Rowe, Ewald, and Kidner, *Phys. Review*, 1925, 25, 338; Dushman, *ibid.*, 1923, 21, 623; Suhrmann, *Zeitsch. Physik*, 1923, 13, 17, 342; Hüttemann, *Ann. Physik*, 1914, [iv], 52, 816; Spanner, *ibid.*, 1924, 75, 609; Hyde, *Electrical World*, 1910, 55, 1654.

<sup>3</sup> Rother, *Ann. Physik*, 1926, 81, 317.

<sup>4</sup> Lessheim and Samuel, *Zeitsch. Physik*, 1926, 40, 220.

<sup>5</sup> Strong, *Amer. Chem. J.*, 1909, 42, 147; Harkins and Guy, *Proc. Acad. Washington*, 1925, 11, 628.

<sup>6</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45, 722.

<sup>7</sup> Compare Balke, *Chem. Met. Eng.*, 1922, 27, 1272.

<sup>8</sup> Osterheld, *Zeitsch. Elektrochem.*, 1913, 19, 585.

<sup>9</sup> Sieverts and Bergner, *Ber.*, 1912, 45, 2576.

<sup>10</sup> Moissan, *Compt. rend.*, 1902, 134, 212.

<sup>11</sup> Ruff and Schiller, *Ber.*, 1909, 42, 494.

halide being formed in each case; it can be made to combine with bromine, but does not react with iodine. Solutions of chlorine are also without action, but carbonyl chloride attacks the metal. The red-hot powder decomposes water with liberation of hydrogen.

Tantalum is remarkably resistant to corrosion by acids, and is, in fact, referred to as a "noble" metal. It is not attacked by hydrochloric acid, nitric acid or aqua-regia, whether hot or cold, dilute or concentrated; it is not attacked by hot dilute sulphuric acid, but boiling concentrated sulphuric acid dissolves it slowly. It dissolves in hydrofluoric acid, however, although when both metal and acid are very pure, solution takes place only very slowly. A mixture of hydrofluoric acid and nitric acid attacks the metal rapidly, and in contact with platinum or carbon it is readily dissolved by hydrofluoric acid with evolution of hydrogen. Tantalum excellently withstands exposure to sea air, sea-water, sulphur dioxide, and mine effluents.<sup>1</sup>

The vapours of the alkali metals are without action even at 2000° C.<sup>2</sup> Boiling solutions of the alkalis attack tantalum slowly; fusion with caustic potash in air yields a tantalate.

**Electromotive Behaviour.**—The behaviour of tantalum in electrolytic cells is remarkable, and accounts for the rapid extension of its application in electrolytic cell "rectifiers." If a rod of tantalum is made the cathode in an electrolytic cell and a strip of platinum the anode, and connection is made to the usual battery, the current passes through the cell as in the case of the commoner metals. If the connections to the battery are now reversed and the tantalum rod is made the anode, there is an instantaneous flow of current, but within a few seconds the current drops to a negligibly small value or ceases altogether. With an applied *direct* current E.M.F. of 75 volts, the current passing is less than 1 milliampère when sulphuric acid of the concentration ordinarily used in storage batteries is the electrolyte.<sup>3</sup> Tantalum therefore displays the phenomenon known as "*valve action*," in that it allows the passage of an electric current in one direction but not in the other. The effect is not restricted to sulphuric acid, but takes place in most electrolytes, excepting, however, fluorides.<sup>4</sup> The valve action is most probably due to the formation of an extremely thin layer of oxygen gas on the surface of the tantalum. This gas film penetrates the blue, iridescent oxide layer<sup>5</sup> produced by anodic oxidation of the tantalum when connection is made, and provides excellent electrical insulation for the whole anode.<sup>6</sup> If the applied E.M.F. is sufficiently increased, however, fine sparks become visible, and with further increase of the applied E.M.F. the insulation breaks down and an appreciable current passes. The voltage at which this occurs is termed the "maximum voltage" of the cell, and with an electrolyte which consists of a 0.02 per cent. solution of potassium carbonate it is 900 volts,<sup>7</sup> which is a much higher figure than is given by other metals

<sup>1</sup> Grove-Palmer, *loc. cit.*; Guertler and Liepus, *Zeitschrift für Metallkunde*, 1925, 17, 310.

<sup>2</sup> Fredenhagen, *Physikal. Zeitsch.*, 1913, 14, 1047.

<sup>3</sup> Balke, *J. Ind. Eng. Chem.*, 1923, 15, 561.

<sup>4</sup> Compare Kuessner, *Zeitsch. Elektrochem.*, 1910, 16, 754.

<sup>5</sup> See Dunham, *Science*, 1927, 65, 525.

<sup>6</sup> Schulze, *Ann. Physik*, 1907, 22, 543; 1909, 28, 787; *Trans. Faraday Soc.*, 1913, 9, 266; *Zeitsch. Elektrochem.*, 1914, 20, 592; *Zeitsch. Physik*, 1921, 6, 237.

<sup>7</sup> Schulze, *Ann. Physik*, 1907, 23, 226.

showing valve action, namely, aluminium, niobium, magnesium, antimony, bismuth, zirconium, zinc and cadmium.<sup>1</sup> The "maximum voltage" of a metal depends on its physical condition, on the thickness of the oxide and gas films, and on the composition and ionic concentration of the electrolyte; <sup>2</sup> it usually increases with increasing dilution of the electrolyte. Valve action occurs with fused salts in much the same way as in aqueous solutions; the maximum voltage is, however, usually lower than the lowest maximum given by aqueous solutions.<sup>3</sup>

According to Schulze, valve action differs from the related phenomenon of passivity in that in the former case the oxide skin, although very thin, is of definite thickness <sup>4</sup> and prevents the passage of the current, whereas in the latter case the oxide film is an electrical conductor of molecular thickness.<sup>5</sup>

If an electrolytic cell containing electrodes made of tantalum and lead is connected to a source of *alternating* current, the current passes freely during that portion of the cycle when the tantalum is the cathode, but little or no current passes when the tantalum is functioning as the anode. The result is that the alternating current is converted into a pulsating direct current, and the cell is referred to as a "rectifier." The electrolyte used industrially in rectifiers is accumulator acid, with the addition of 1 per cent. ferrous sulphate.<sup>6</sup> The current obtained can be used for charging storage batteries, for the electro-deposition of metals, and for other electrochemical operations which require direct current.<sup>7</sup> It has been found possible by using two tantalum electrodes in a single cell to rectify the current so that both half-periods pass in the same direction, giving rise to a non-pulsating and almost constant direct current. Tantalum has the great advantage over aluminium (which is the only other metal used to any extent as a rectifier) that it is much more resistant to the action of acids and alkalis, and hence enjoys a longer life and offers a much larger choice of electrolytes.

*Electrode Potential.*—This can be determined only in solutions of fluorides, since tantalum shows valve action in all other electrolytes, and even in the case of fluorides there is some reason to believe that oxide formation takes place, vitiating the results. The potential at the electrode

Tantalum (passive)/tantalum pentafluoride (0.006 mole.),

is +1.537 volt; <sup>8</sup> H=zero. Passive tantalum is obtained by anodic polarisation; the corresponding figure for the active material is +0.165 volt. The potential obviously depends on the state of the metal; after being rubbed with emery, tantalum gives a low energy potential which

<sup>1</sup> Schulze, *Ann. Physik*, 1907, 24, 43; 1908, 25, 775; 1908, 26, 372; 1909, 28, 787; 1911, 34, 657; *Zeitsch. Elektrochem.*, 1908, 14, 333.

<sup>2</sup> Schulze, *Ann. Physik*, 1913, 41, 593; 1921, 65, 223; Taylor and Inglis, *Phil. Mag.*, 1903, 5, 301; Baird and Mercer, *Trans. Faraday Soc.*, 1911, 7, 1; de Bruyne and Sanderson, *ibid.*, 1927, 23, 42; *U.S. Pats.* 1602951 (1919), 1330581 (1920).

<sup>3</sup> Schulze, *Zeitsch. Elektrochem.*, 1911, 17, 509.

<sup>4</sup> Schulze, *ibid.*, 1912, 18, 22; compare Newbery, *Proc. Roy. Soc.*, 1914, [A], 114, 103.

<sup>5</sup> Schulze, *Trans. Faraday Soc.*, 1913, 9, 286.

<sup>6</sup> Engle, *Trans. Amer. Inst. Min. Met. Eng.*, 1925, 71, 691; Anon., *The Engineer*, 1925, 140, 235.

<sup>7</sup> Balke, *loc. cit.*; compare Schulze, *Ann. Physik*, 1914, 44, 1106.

<sup>8</sup> Hevesy and Slade, *Zeitsch. Elektrochem.*, 1912, 18, 1001; see also Hevesy, *Phil. Mag.*, 1912, [vi], 23, 643.

slowly returns to the normal figure.<sup>1</sup> The cathodic overvoltage in normal sulphuric acid is 0.39 to 0.50 volt.<sup>2</sup>

**Atomic Weight of Tantalum.**—The earliest investigations into the atomic weight of tantalum were carried out by Berzelius,<sup>3</sup> Rose,<sup>4</sup> Hermann,<sup>5</sup> and Blomstrand,<sup>6</sup> but the various values they obtained are now only of historical interest, as the materials used were not pure. In 1866, Marignac<sup>7</sup> made four analyses of pure potassium tantalum fluoride,  $K_2TaF_7$ , by heating the salt with concentrated sulphuric acid to remove hydrofluoric acid; the potassium sulphate thus formed was extracted with water and the residue ignited and weighed as tantalum pentoxide, with the following mean results: <sup>8</sup>

$$\frac{2K_2TaF_7}{Ta_2O_5} = \frac{100}{56.59}; \text{ hence Ta} = 183.8.$$

$$\frac{K_2TaF_7}{K_2SO_4} = \frac{100}{44.295}; \text{ ,, Ta} = 182.1.$$

$$\frac{2K_2SO_4}{Ta_2O_5} = \frac{44.295}{56.59}; \text{ ,, Ta} = 183.7.$$

Four analyses of the corresponding ammonium salt,  $(NH_4)_2TaF_7$ , were also made, with the result:

$$\frac{2(NH_4)_2TaF_7}{Ta_2O_5} = \frac{100}{63.25}; \text{ hence Ta} = 182.3.$$

Despite the facts (a) that the figures for individual determinations differed by several whole units and (b) that the results as a whole were obviously discordant, Marignac's work formed the basis for the accepted atomic weight of tantalum (namely, 183) for forty years. The suitability of the double fluorides for use in the determination of the atomic weight has been questioned.<sup>9</sup>

In 1906, Hinrichsen and Sahlbom<sup>10</sup> used a very simple method. Metallic tantalum was converted directly into the oxide by heating in oxygen. The mean of five experiments gave the following ratio:

$$\frac{2Ta}{Ta_2O_5} = \frac{81.902}{100}; \text{ hence Ta} = 181.02.$$

The extreme values of the individual determinations still differed by more than a unit, and it is doubtful whether metallic tantalum can be obtained sufficiently pure for atomic weight determination.

Balke in 1910<sup>11</sup> hydrolysed tantalum pentachloride,  $TaCl_5$ , to the pentoxide,  $Ta_2O_5$ , with water and a small quantity of nitric acid. The mean of eight experiments gave:

<sup>1</sup> Schmidt, *Zeitsch. physikal. Chem.*, 1923, 106, 105.

<sup>2</sup> Newbery, *J. Chem. Soc.*, 1916, 109, 1108; compare Thiel and Hammerschmidt, *Zeitsch. anorg. Chem.*, 1924, 132, 20; Osterheld, *Zeitsch. Elektrochem.*, 1913, 19, 585.

<sup>3</sup> Berzelius, *Pogg. Annalen*, 1825, 4, 6.

<sup>4</sup> Rose, *ibid.*, 1856, 99, 78.

<sup>5</sup> Hermann, *J. prakt. Chem.*, 1857, 70, 193.

<sup>6</sup> Blomstrand, *Acta Univ. Lund*, 1864.

<sup>7</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 9, 251; *Arch. Sci. phys. nat.*, 1866, [ii], 26, 89.

<sup>8</sup> The fundamental values set out on p. viii of the General Introduction have been used in the calculations. The same fundamental values have been employed in the recalculation of the subsequent values for the atomic weight of tantalum mentioned in this section.

<sup>9</sup> Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 151; *Chem. News*, 1905, 92, 210.

<sup>10</sup> Hinrichsen and Sahlbom, *Ber.*, 1906, 39, 2600.

<sup>11</sup> Balke, *J. Amer. Chem. Soc.*, 1910, 32, 1127.



$$\frac{2\text{TaCl}_5}{\text{Ta}_2\text{O}_5} = \frac{100}{61.7355}; \text{ hence Ta} = 181.49.$$

The difference between the extreme values was 0.14. In the following year hydrolysis of the pentabromide with water and nitric acid was used by Chapin and Smith,<sup>1</sup> who from eight experiments obtained the ratio :

$$\frac{2\text{TaBr}_5}{\text{Ta}_2\text{O}_5} = \frac{2.6212}{1}; \text{ hence Ta} = 181.80.$$

The difference between the extreme values was 0.23. It will be observed that the value given by the pentabromide is appreciably higher than that given by the pentachloride, although the figures for individual determinations by each method were reasonably concordant. Sears and Balke<sup>2</sup> subsequently found that tantalum pentoxide is slightly volatile at ignition temperatures, and since it occludes nitric and other acids it is useless for work requiring great accuracy.<sup>3</sup> In a fresh attempt to establish the atomic weight, Sears and Balke treated the pentachloride with silver in the presence of hydrofluoric acid. Five experiments gave the mean ratio :

$$\frac{\text{TaCl}_5}{5\text{Ag}} = \frac{66.4338}{100}; \text{ hence Ta} = 181.05.$$

But the extreme values showed a difference of 0.46, from which it was concluded that the tantalum pentachloride used varied slightly in its composition, and that this salt is also unsuitable for use in the determination of the atomic weight. This conclusion has been confirmed.<sup>4</sup>

The values for the atomic weight of tantalum as determined by the various investigators since 1866 are set out in the following table:

#### ATOMIC WEIGHT OF TANTALUM.

Authority.	Date.	Ratio Determined.	Number of Experiments.	Mean Atomic Weight.
Marignac . . .	1866	$2\text{K}_2\text{TaF}_7/\text{Ta}_2\text{O}_5$	4	183.3
		$\text{K}_2\text{TaF}_7/\text{K}_2\text{SO}_4$	4	182.1
		$2\text{K}_2\text{SO}_4/\text{Ta}_2\text{O}_5$	4	183.7
		$2[(\text{NH}_4)_2\text{TaF}_7]/\text{Ta}_2\text{O}_5$	4	182.3
Hinrichsen and Sahlbom.	1906	$2\text{Ta}/\text{Ta}_2\text{O}_5$	5	181.02
Balke . . . . .	1910	$2\text{TaCl}_5/\text{Ta}_2\text{O}_5$	8	181.49
Chapin and Smith .	1911	$2\text{TaBr}_5/\text{Ta}_2\text{O}_5$	8	181.80
Sears and Balke . .	1915	$\text{TaCl}_5/5\text{Ag}$	5	181.05

The International Committee on Atomic Weights adopted the value 181.5 in 1912, and this figure was altered to 181.3 in 1929. The decimal place is, however, obviously uncertain.

<sup>1</sup> Chapin and Smith, *J. Amer. Chem. Soc.*, 1911, 33, 1497.

<sup>2</sup> Sears and Balke, *ibid.*, 1915, 37, 833.

<sup>3</sup> This observation affects the accuracy of all the foregoing investigations.

<sup>4</sup> Sears, *J. Amer. Chem. Soc.*, 1917, 39, 1582.

**Uses.**—Tantalum is used in the arts only in the metallic form, no applications having been found for its compounds; the uses of the metal are restricted by its costliness, which arises from the necessity for preparing it in specially constructed vacuum electric furnaces. In 1924 the world's annual production was probably not greater than ten tons of ore, containing about 56 per cent. of tantalum,<sup>1</sup> but new applications are being developed. The largest factor in the consumption of tantalum is its recent application as an electrode in alternating current electrolytic rectifiers, now familiar in radio practice.<sup>2</sup> It can also be used for the filaments of thermionic valves,<sup>3</sup> for the electrodes in Röntgen tubes<sup>4</sup> (for both of which its property of absorbing gases renders it particularly suitable), and for the cathodes in electro-chemical apparatus. For the last purpose it is stated to have the advantage over platinum that it is mechanically stronger, can be used in nitric acid solution, and does not alloy with zinc or cadmium; gold and platinum can also be deposited on a tantalum cathode and subsequently removed with aqua-regia.<sup>5</sup> On the other hand, it has the serious disadvantage that it tends to become brittle on absorption of hydrogen, and then gives unsatisfactory results.<sup>6</sup> Tantalum electrodes coated with platinum have been used with success.<sup>7</sup> Other uses of tantalum depend on its inertness under ordinary conditions and its resistance to attack by most acids. It is suitable for the manufacture of certain surgical and dental instruments, as it is not attacked by the ordinary antiseptics and chemicals used. A surface film which is almost as hard as agate can be produced on the metal by heat treatment. Analytical weights made with tantalum have received the approval of the International Atomic Weight Committee.<sup>8</sup> Its use is also suggested in place of the more expensive platinum for the manufacture of laboratory dishes, crucibles, stirrers, etc., but this application is restricted by the comparatively low temperature at which it begins to oxidise and by its solubility in hydrofluoric acid. To overcome these drawbacks it is recommended that the metal be either alloyed, plated or sheathed with platinum,<sup>9</sup> or that nickel-tantalum alloys be substituted.

Tantalum was used for several years for the filaments of incandescent electric lamps, as it was found to be electrically more efficient for the same candle-power than the carbon filaments which had previously been employed, and it also enjoyed a longer life. In 1912, however, it was in turn displaced by tungsten, which gave a still greater efficiency, and had the advantages of a higher melting-point in conjunction with a higher ratio of hot to cold electrical resistance<sup>10</sup> and lower cost. Tantalum electric lamps are no longer made, but it has been suggested

<sup>1</sup> Taylor, *Eng. and Min. J.*, 1924, 114, 842.

<sup>2</sup> Robinson, *Experimental Wireless*, 1925, 2, 889; Anon., *The Engineer*, 1925, 140, 235.

<sup>3</sup> Fleming, *Engineering*, 1909, 87, 883; Anon., *Eng. and Min. J.*, 1923, 116, 817; Balke, *Industrial and Engineering Chemistry*, 1923, 15, 561.

<sup>4</sup> Siemens, *Engineering*, 1909, 87, 601.

<sup>5</sup> Balke, *loc. cit.*; Brunck, *Chem. Zeit.*, 1912, 36, 1233; 1914, 38, 565.

<sup>6</sup> Osterheld, *Zeitsch. Elektrochem.*, 1913, 19, 585; Wegelin, *Chem. Zeit.*, 1913, 37, 989.

<sup>7</sup> Arndt, *Elektrotech. Zeitsch.*, 1921, 42, 345.

<sup>8</sup> *Nature*, 1911, 87, 251.

<sup>9</sup> *Eng. Pats.* 23050 (1912), 198246 (1922).

<sup>10</sup> For data relating to the comparative behaviour of carbon, tantalum, tungsten, and osmium lamps, see Balke, *loc. cit.*; Paterson, *The Electrician*, 1916, 77, 822; Crouch, *ibid.*, 1910, 64, 806; Jolley, *ibid.*, 1909, 63, 700, 755; Lavender, *ibid.*, 1909, 64, 306; Hirst, *J. Inst. Elec. Eng.*, 1908, 41, 636; Swinburne, *ibid.*, 1907, 38, 211.

that they would be preferable when it is difficult to place a sufficient length of very fine tungsten wire to produce the resistance required on the ordinary circuit; the higher electrical resistance of tantalum would enable a shorter wire or one of larger diameter to be employed. Tantalum lamps are also well able to resist vibration and shock.<sup>1</sup> It is highly improbable that the use of tantalum for electric lamps would have been followed by a steady demand for tantalum ores, because one pound (avoirdupois) of tantalum suffices for no less than 20,000 lamps.

Tantalum pentoxide is stated to be effective as a catalyst in the oxidation of hydrocarbons.<sup>2</sup>

**Alloys.**—Tantalum yields alloys with a large number of other metals, but their mechanical properties and the systems produced have hitherto received little investigation. They are prepared by compressing the two metals and heating them to a high temperature in a good vacuum.

*Aluminium* alloys well with up to about 3.5 per cent. of tantalum, which has no effect, however, on the mechanical strength, ductility, and working properties of aluminium.<sup>3</sup> Reduction of tantalum pentoxide by the thermite process yields hard, brittle alloys.<sup>4</sup> A substance the composition of which corresponds with the formula  $TaAl_3$  has been obtained by reducing potassium tantalum fluoride,  $K_2TaF_7$ , with aluminium filings at a high temperature. It is described as an iron-grey crystalline powder, of density 7.02, which is scarcely attacked by acids.<sup>5</sup>

*Copper* alloys are mechanically strong and acid resisting.<sup>6</sup>

*Gold* alloys resemble copper alloys. Gold-copper-tantalum alloys have also been made.<sup>7</sup>

*Iron* alloys with tantalum in all proportions. Those alloys containing from 5 to 10 per cent. of iron are hard and ductile.<sup>8</sup> Guillet<sup>9</sup> has examined the effect of tantalum up to 1.05 per cent. on the structure and mechanical properties of steels prepared with tantalum-iron in the electric furnace. In the case of normal steels the usual pearlitic structure was present, the effect of the tantalum being to produce more regular distribution of the pearlite. Quenched steels displayed their usual structure. Mechanical tests showed only slight increases in the breaking load, the limit of elasticity, and the resistance to shock. The same effects can be readily obtained by the addition of small proportions of nickel and other metals to the steel. The influence of tantalum on the characteristics in the shearing test is also small.<sup>10</sup> It appears, therefore, that the effect of tantalum on steel is too small to enable tantalum steels to attain any special importance. It has also been shown that no advantage is gained by substituting tantalum for nickel, cobalt or molybdenum in high-speed steels.<sup>11</sup> According to Guertler,<sup>12</sup> tantalum

<sup>1</sup> Anon., *The Electrician*, 1910, 65; *Marine Supplement*, 107.

<sup>2</sup> *U.S. Pat.* 1636855 (1927), 1562480 (1925).

<sup>3</sup> Schirmeister, *Stahl und Eisen*, 1915, 35, 999.

<sup>4</sup> Goldschmidt and Vautin, *J. Soc. Chem. Ind.*, 1898, 17, 543.

<sup>5</sup> Marignac, *Arch. Sci. phys. nat.*, 1868, [ii], 31, 101.

<sup>6</sup> *German Pat.* 284241 (1913).

<sup>7</sup> *Ibid.*

<sup>8</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45, 722.

<sup>9</sup> Guillet, *Compt. rend.*, 1907, 145, 327.

<sup>10</sup> Portevin, *Carnegie Scholarship Memoirs, Iron and Steel Institute*, 1909, 1, 277.

<sup>11</sup> French and Digges, *Trans. Amer. Soc. for Steel Treating*, 1925, 8, 681.

<sup>12</sup> Guertler, *Giesserei*, 1921, 8, 134; *J. Iron Steel Inst., Abstr.*, 1922, 105, 605.

in cast iron forms mixed crystals with the iron and precipitates the carbon as graphite.

Iron undergoes "cementation" when heated in finely divided iron-tantalum alloy containing about 30 per cent. of tantalum; the interior consists of a solid solution, which is bounded by a brilliant external layer the thickness of which increases with rise of temperature and with increase in the duration of heating. Copper and brass have been similarly treated.<sup>1</sup>

*Magnesium*.—A magnesium-tantalum alloy which contains about 3.5 per cent. of magnesium has been obtained by reducing tantalum pentoxide with magnesium powder in a stream of hydrogen.<sup>2</sup>

*Molybdenum* alloys with tantalum in all proportions. Alloys containing from 10 to 40 per cent. tantalum have been suggested for the construction of chemical and electrical apparatus.<sup>3</sup> When the molybdenum content is less than 5 per cent., the product can be drawn into wire 0.1 mm. diameter.

*Nickel*.—Addition of from 5 to 10 per cent. of tantalum to nickel considerably increases the resistance of the nickel to acids,<sup>4</sup> and also its ductility. An alloy containing 30 per cent. of tantalum is not attacked by prolonged boiling with aqua-regia or other acids, and unlike tantalum it can be heated in air without undergoing oxidation; it is also very tough and can be easily rolled, hammered, and drawn, but may become brittle when strongly heated.<sup>5</sup> Nickel-tantalum alloys which contain from 5 to 20 per cent. of chromium are also resistant to heat and corrosion.<sup>6</sup> An alloy which contains 75 per cent. of nickel, 11 per cent. of iron, and 14 per cent. of tantalum and niobium is claimed to be suitable for electrical resistances and electrical heating apparatus.<sup>7</sup>

*Platinum* alloys containing from 0.5 to 20 per cent. of tantalum are hard, withstand heat, as well as the action of acids and fused potassium hydrogen sulphate, and are more resistant to the action of aqua-regia than platinum.<sup>8</sup> They possess the mechanical properties of platinum-iridium alloys and are less expensive; the relative quantities of tantalum and iridium required to produce the same hardness and mechanical resistance are stated to be 1 : 5. Platinum-tantalum alloys hence have been recommended for various purposes in place of platinum or platinum-iridium. Tantalum can also be coated with platinum, and can then be utilised in high-temperature work.<sup>9</sup>

*Silicon*.—Small amounts of silicon do not affect the ductility of tantalum and increase its hardness.<sup>10</sup> A substance the composition of which agrees with the formula  $TaSi_2$  has been obtained by heating a mixture of tantalum pentoxide and silica in the presence of aluminium. It is described as a greyish-blue substance which forms four-sided prisms of density 8.8. It is stable in air, oxidises when heated in oxygen, and is insoluble in most acids; it is attacked by fused caustic soda.<sup>11</sup>

<sup>1</sup> Laissus, *Compt. rend.*, 1926, 182, 1152.

<sup>2</sup> Smith and Maas, *Zeitsch. anorg. Chem.*, 1894, 7, 96.

<sup>3</sup> U.S. Pat. 1385072 (1921).

<sup>4</sup> Rowe, *Metal Industry*, 1922, 20, 263.

<sup>5</sup> Anon., *Eng. and Min. J.*, 1915, 99, 815.

<sup>6</sup> U.S. Pat. 1541301 (1925), 1588518 (1926).

<sup>7</sup> Canada Pat. 209342 (1921); U.S. Pat. 1445253 (1923).

<sup>8</sup> French Pat. 477270 (1914); German Pat. 360006 (1919); Eng. Pat. 200074 (1923).

<sup>9</sup> Eng. Pat. 23050 (1912); U.S. Pat. 1180164 (1916).

<sup>10</sup> von Bolton, *loc. cit.*

<sup>11</sup> Honigschmidt, *Monatsh.*, 1907, 28, 1017.

*Tungsten* alloys with tantalum in all proportions.<sup>1</sup> Alloys of tungsten and tantalum which also contain cobalt, chromium or molybdenum have also been prepared.<sup>2</sup>

*Zirconium* alloys<sup>3</sup> can be heated to whiteness without undergoing oxidation.<sup>4</sup>

Sodium, potassium, mercury and silver do not alloy with tantalum even at high temperatures; <sup>5</sup> attempts to prepare alloys with arsenic, antimony, lead, zinc and tellurium have also failed, but the formation of an alloy with silver, copper and tin for making a dental amalgam with mercury has recently been claimed.<sup>6</sup>

<sup>1</sup> *U.S. Pat.* 1520794 (1925); von Bolton, *loc. cit.*

<sup>2</sup> *Eng. Pat.* 152371 (1918); *U.S. Pats.* 1389679 and 1449338 (1923).

<sup>3</sup> *Canada Pat.* 214118 (1921); *U.S. Pats.* 1248648 (1917), 1334089 (1920).

<sup>4</sup> See also *German Pat.* 293952 (1913).

<sup>5</sup> von Bolton, *loc. cit.*; Moissan, *Compt. rend.*, 1902, 134, 411; Fredenhagen, *Physikal. Zeitsch.*, 1913, 14, 1047.

<sup>6</sup> *U.S. Pat.* 1574714 (1926).

## CHAPTER IX.

### COMPOUNDS OF TANTALUM.

**General.**—As in the case of niobium, the only well-defined tantalum compounds are those derived from the pentoxide, namely, the tantalates. Tantalum compounds display a much feebler tendency to undergo reduction than niobium compounds, and this is shown in the fact that only two oxides,  $Ta_2O_5$  and  $TaO_2$ , are known, and even the existence of the latter has recently been questioned.<sup>1</sup> When niobium pentoxide is heated to redness in hydrogen at  $1250^\circ C.$  reduction to the sesquioxide,  $Nb_2O_3$ , ensues,<sup>2</sup> but under similar conditions tantalum pentoxide remains unchanged.<sup>3</sup> Acid solutions of pentavalent niobium salts also undergo reduction with nascent hydrogen, whereas pentavalent tantalum salts are unaffected. It is of some interest to note, however, that evidence for the existence of a dichloride has recently been obtained.

Tantalum pentoxide possesses only very weakly acidic properties. Its salts even with the strong alkalis are readily hydrolysed by boiling in aqueous solution. Its complex heteropoly-acids with other acids are ill-defined, but it takes up active oxygen to form a stable *pertantallic acid*,  $HTaO_4 \cdot xH_2O$ .

#### TANTALUM AND HYDROGEN.

Tantalum adsorbs hydrogen directly, or when it is used as the cathode in the electrolysis of dilute sulphuric acid,<sup>4</sup> but no definite hydrides have been isolated. One volume of tantalum in the form of wire, 0.3 mm. diameter, takes up 775 volumes of hydrogen at room temperatures<sup>5</sup> and 46 volumes at about  $800^\circ C.$ <sup>6</sup> The appended table gives the number of milligrams of hydrogen at 760 mm. pressure adsorbed by 100 grams of tantalum at different temperatures.<sup>7</sup>

The amount of gas taken up decreases with increasing temperature, and at a given temperature (above  $450^\circ C.$ ) is proportional to the square root of the gas pressure. The curve produced is similar to that given by palladium. Most of the hydrogen is expelled by heating to redness in

<sup>1</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 145, 127.

<sup>2</sup> Compare Ruff, Seiferheld, and Suda, *ibid.*, 1913, 82, 373.

<sup>3</sup> A hydrated tantalum sesquioxide,  $Ta_2O_3 \cdot xH_2O$ , is stated to be formed by the addition of caustic soda to solid tantalum trichloride (Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1925, 148, 3; *Ber.*, 1922, 55, 1473).

<sup>4</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 50; Osterheld, *ibid.*, 1913, 19, 585; Harding and Smith, *J. Amer. Chem. Soc.*, 1918, 40, 1529; Coehn and Baumgarten, *Zeitsch. physikal. Chem.*, 1927, 130, 545.

<sup>5</sup> Sieverts and Bergner, *Ber.*, 1911, 44, 2394.

<sup>6</sup> Thiel and Hammerschmidt, *Zeitsch. anorg. Chem.*, 1923, 132, 15.

<sup>7</sup> Sieverts and Bergner, *loc. cit.*

## ADSORPTION OF HYDROGEN BY TANTALUM.

Temperature, ° C.	17	100	188	263	314	417	474	530
Hydrogen, mgm.	419	400	377	327	297	212	157	107

a vacuum, but the small remaining quantity is removed only by fusing the material in a vacuum in the electric furnace. All the metallic tantalum now made is subjected to the latter treatment so as to drive off occluded gases and other volatile impurities.

When heated in hydrogen, tantalum wire undergoes a structural alteration, becoming brittle and crystalline; it retains these properties after the hydrogen has been removed by heating to a high temperature *in vacuo*. According to earlier investigators,<sup>1</sup> the hydrogen absorbed at high temperatures is chemically combined with the tantalum, and it is stated that a hydride can also be obtained by the action of hydrogen on tantalum pentachloride.

## Tantalum and the Halogens.

The halides and oxyhalides of tantalum are set out in the following table:

## HALIDES AND OXYHALIDES OF TANTALUM.

Valency.	Fluorine.	Chlorine.	Bromine.	Iodine.
"Di"-valent	..	HTa <sub>3</sub> Cl <sub>7</sub> .4H <sub>2</sub> O HTa <sub>3</sub> Cl <sub>6</sub> Br.4H <sub>2</sub> O.	HTa <sub>3</sub> Br <sub>7</sub> .4H <sub>2</sub> O HTa <sub>3</sub> Br <sub>6</sub> Cl.4H <sub>2</sub> O HTa <sub>3</sub> Br <sub>6</sub> I.4H <sub>2</sub> O HTa <sub>3</sub> Br <sub>6</sub> OH.xH <sub>2</sub> O	..
Trivalent .	..	TaCl <sub>3</sub>	TaBr <sub>3</sub> *	..
Pentavalent	TaF <sub>5</sub> TaOF <sub>3</sub> *	TaCl <sub>5</sub> TaOCl <sub>3</sub> * TaO <sub>2</sub> Cl	TaBr <sub>5</sub> TaOBr <sub>3</sub>	TaI <sub>5</sub>

\* These compounds have not been isolated in the free state.

The pentavalent halides are the most stable, but even these can be prepared only in the dry way because of the readiness with which they undergo hydrolysis. The trichloride is obtained by reduction of the pentachloride with a powdered metal (lead, aluminium, zinc); the same process has also given a dichloride and perhaps a tetrachloride,<sup>2</sup> but their formation awaits independent confirmation. The preparation of the *chloroacid*, HTa<sub>3</sub>Cl<sub>7</sub>.4H<sub>2</sub>O, is of interest in that corresponding

<sup>1</sup> Pirani, *Zeitsch. Elektrochem.*, 1905, 11, 555; compare Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 91.

<sup>2</sup> Ruff and Thomas, *Ber.*, 1922, 55, [B], 1466; *Zeitsch. anorg. Chem.*, 1925, 148, 1.

chloroacids of molybdenum,  $\text{HMo}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$ , and of tungsten,  $\text{HWo}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$ , have been obtained. The formation of the pentiodide is somewhat remarkable; niobium has not as yet yielded any iodine compounds, and vanadium has given only the tri-iodide. It is unusual for a metal falling in Groups IV. to VIII. to form an iodine derivative in which the maximum valency of the group is displaced.

#### TANTALUM AND FLUORINE.

Metallic tantalum and tantalum pentoxide are both dissolved by hydrofluoric acid, but evaporation of the solutions yields a residue which consists either of a tantalum oxyfluoride of variable composition or of the hydrated pentoxide.

**Tantalum Pentafluoride**,  $\text{TaF}_5$ , is the only known fluoride of tantalum, and has been successfully isolated by methods that avoid hydrolysis: (1) Tantalum and fluorine are brought into reaction exactly as in the preparation of niobium pentafluoride.<sup>1</sup> (2) Tantalum pentachloride is treated in the cold with dry hydrofluoric acid; the hydrochloric acid liberated and excess of hydrofluoric acid are evaporated off, and the resulting tantalum pentafluoride is purified by redistillation in a platinum crucible between  $300^\circ$  and  $400^\circ$  C.<sup>2</sup> (3) The double barium tantalum fluoride,  $3\text{BaF}_2 \cdot 2\text{TaF}_5$ , is very strongly heated in a platinum tube, one end of which is kept cold.<sup>3</sup>

Tantalum pentafluoride forms hygroscopic, colourless, doubly refracting, tetragonal prisms which melt at  $96.8^\circ$  C. and boil between  $229.2^\circ$  and  $229.5^\circ$  C. at 760 mm. pressure. Its density varies between 4.981 at  $15^\circ$  C. and 4.744 at  $19.5^\circ$  C. It is soluble in water; solution is followed by hydrolysis which, however, does not proceed so readily as with tantalum pentachloride, niobium pentafluoride, and vanadium pentafluoride.<sup>4</sup> The aqueous solution evolves hydrogen fluoride on being evaporated, and leaves an insoluble tantalum oxyfluoride which is converted into tantalum pentoxide on being ignited. Caustic alkalis and alkali carbonates in concentrated solution attack the pentafluoride vigorously, and yield an alkali tantalum oxyfluoride of composition  $4\text{R} \cdot \text{F} \cdot \text{Ta}_2\text{O}_5 \cdot 2\text{TaF}_5$ . Dilute alkalis yield tantallic acid, while fusion with potassium fluoride yields the double fluoride  $2\text{KF} \cdot \text{TaF}_5$ . Tantalum pentafluoride is also soluble in cold sulphur monochloride, sulphuryl chloride, stannic chloride, arsenious chloride, antimony pentachloride, alcohol, chloroform, glacial acetic acid, and acetic anhydride.

*Double Fluorides of Tantalum Pentafluoride.*—When solutions of tantalum pentoxide in hydrofluoric acid are treated with solutions of the fluorides of the alkali (and other) metals, double fluorides are obtained which possess the general formula  $n\text{R} \cdot \text{F} \cdot \text{TaF}_5$ , where  $n$  usually varies between 1 and 3; in the most important series  $n=2$ . These double fluorides are much more stable than tantalum pentafluoride. They were among the first tantalum compounds to receive examination,<sup>5</sup> and still form an important class of tantalum compounds. A study of their isomorphism with the corresponding compounds of niobium

<sup>1</sup> Ruff and Schiller, *Ber.*, 1909, 42, 494; Schiller, *Dissertation* (Danzig, 1911).

<sup>2</sup> Ruff and Schiller, *Zeitsch. anorg. Chem.*, 1911, 72, 331.

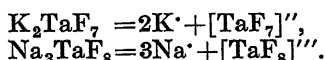
<sup>3</sup> Hahn and Puetter, *ibid.*, 1923, 127, 153.

<sup>4</sup> Hevesy and Slade, *Zeitsch. Elektrochem.*, 1912, 18, 1001.

<sup>5</sup> Berzelius, *Pogg. Annalen*, 1825 and 1826, 4 and 6; Rose, *ibid.*, 1856, 99, 481; Marignac, *Ann. Chim. Phys.*, 1866, [iv], 9, 249.



enabled the formula of "tantalic acid" (and hence of other tantalum compounds) to be correctly established (see p. 123); precipitation of potassium tantalum fluoride,  $2\text{KF}\cdot\text{TaF}_5$ , still constitutes the classical method for the separation of tantalum from niobium (see p. 128), and analyses of this salt provided the first reliable data for the atomic weight of tantalum. Balke<sup>1</sup> repeated and confirmed the previous investigations of Marignac, and showed that tantalum pentafluoride forms several double salts with almost every one of the alkali fluorides, from which it appears that the preparation of any particular double fluoride in the pure state is not an easy matter; the purest to be prepared hitherto are the potassium salt,  $2\text{KF}\cdot\text{TaF}_5$ , and the sodium salt,  $3\text{NaF}\cdot\text{TaF}_5$ . The greater stability of these double fluorides as compared with tantalum pentafluoride has led to the assumption that their solutions contain complex anions into which the tantalum enters. The two salts just mentioned ionise, for instance, thus:



When viewed from the point of view of the Werner co-ordination theory, it is observed that in these complexes the common co-ordination number is 7, thus  $[\text{TaF}_7]\text{K}_2$  and  $[\text{TaF}_7]\text{Cu}\cdot 4\text{H}_2\text{O}$ ; the co-ordination number 8 also occurs, thus  $[\text{TaF}_8]\text{Na}_3$  and  $\text{Ta}\left[\begin{smallmatrix} \text{F}_6 \\ \text{O} \end{smallmatrix}\right](\text{NH}_4)_3$ , and less frequently the co-ordination number 6, thus  $[\text{TaF}_6](\text{NH}_4)$ .

The following double fluorides with tantalum pentafluoride are known:

*Acid Tantalum Fluoride* or *tantalum hydrogen fluoride*,  $\text{HF}\cdot\text{TaF}_5$ ,  $6\text{H}_2\text{O}$  or  $\text{HTaF}_6\cdot 6\text{H}_2\text{O}$ , has recently been prepared in clusters of feathery crystals which melt at about  $15^\circ\text{C}$ . by dissolving tantalum pentoxide in hydrofluoric acid and crystallising at about  $-10^\circ\text{C}$ . It can be looked upon as the acid which gives rise to the series  $\text{R}\cdot\text{F}\cdot\text{TaF}_5$ .<sup>2</sup>

*Ammonium Tantalum Fluorides*.—The compound  $\text{NH}_4\text{F}\cdot\text{TaF}_5$  or  $\text{NH}_4\text{TaF}_6$  results from the action of ammonium fluoride on acid tantalum fluoride.<sup>3</sup> When a solution of tantalum pentoxide in hydrofluoric acid is treated with gaseous ammonia and evaporated, the compound  $2\text{NH}_4\text{F}\cdot\text{TaF}_5$  or  $(\text{NH}_4)_2\text{TaF}_7$  is obtained in thin, right-angled plates, or in flattened needles belonging to the tetragonal system. It can be dried at  $100^\circ\text{C}$ . without undergoing decomposition, is readily soluble in water, from which it can be recrystallised unchanged, but the aqueous solution on being boiled throws down a white precipitate. Its preparation in the perfectly pure state is difficult.<sup>4</sup> A compound which has the approximate composition  $3\text{NH}_4\text{F}\cdot\text{TaF}_5$  or  $(\text{NH}_4)_3\text{TaF}_8$  has also been obtained.<sup>5</sup>

*Barium Tantalum Fluoride*,  $3\text{BaF}_2\cdot 2\text{TaF}_5$  or  $\text{Ba}_3\text{Ta}_2\text{F}_{16}$ , separates as a white, micro-crystalline precipitate from the action of barium chloride on a solution of tantalum pentoxide in slight excess of hydrofluoric acid.<sup>6</sup>

<sup>1</sup> Balke, *J. Amer. Chem. Soc.*, 1905, 27, 1140.

<sup>2</sup> Hahn and Puetter, *loc. cit.*

<sup>3</sup> Hahn and Puetter, *loc. cit.*

<sup>4</sup> Berzelius, *loc. cit.*; Marignac, *Ann. Chim. Phys.*, 1866, [iv], 9, 272.

<sup>5</sup> Balke, *loc. cit.*

<sup>6</sup> Hahn and Puetter, *loc. cit.*

*Cæsium Tantalum Fluorides.*—Substances having the compositions  $\text{CsF} \cdot \text{TaF}_5$  and  $2\text{CsF} \cdot \text{TaF}_5$  are prepared by crystallising a mixture of cæsium fluoride and tantalum fluoride from dilute hydrofluoric acid, using excess of tantalum fluoride or of cæsium fluoride respectively. The former yields glistening, rhombohedral crystals, and the latter thin needles.<sup>1</sup> A stable, crystalline salt of the composition  $15\text{CsF} \cdot \text{TaF}_5$  has also been reported.<sup>2</sup>

*Copper Tantalum Fluoride*,  $\text{CuF}_2 \cdot \text{TaF}_5 \cdot 4\text{H}_2\text{O}$  or  $\text{CuTaF}_7 \cdot 4\text{H}_2\text{O}$ , can be obtained in blue, transparent, rhombic crystals by the action of copper oxide on a solution of tantalum pentoxide in excess of hydrofluoric acid. It is very readily soluble in water.<sup>3</sup>

*Lithium Tantalum Fluoride*,  $\text{LiF} \cdot \text{TaF}_5 \cdot 2\text{H}_2\text{O}$  or  $\text{LiTaF}_6 \cdot 2\text{H}_2\text{O}$ , is obtained in colourless, prismatic crystals when a solution of tantalum pentoxide in excess of hydrofluoric acid is treated with lithium carbonate.<sup>4</sup>

*Potassium Tantalum Fluoride*,  $2\text{KF} \cdot \text{TaF}_5$  or  $\text{K}_2\text{TaF}_7$  or  $[\text{TaF}_7]\text{K}_2$ , is the commonest of the double fluorides, and is in fact one of the commonest of tantalum compounds. It is prepared by adding potassium fluoride to a warm solution of tantalum pentoxide in hydrofluoric acid, or by boiling tantic acid with potassium hydrogen fluoride,  $\text{KHF}_2$ , and cooling the product. The preparation of potassium tantalum fluoride by this method has already been referred to in describing the separation and estimation of niobium and tantalum (see pp. 128–9). It can also be obtained by the action of caustic potash or potassium carbonate on a solution of tantalum pentoxide in hydrofluoric acid.<sup>5</sup>

Potassium tantalum fluoride crystallises in small, thin, rhombic needles, which are isomorphous with the corresponding niobium compound  $\text{K}_2\text{NbF}_7$ . The density is variously reported as being 4.56 and 5.24.<sup>6</sup> The salt is stable in dry air at ordinary temperatures. On being heated the pure substance decrepitates, melts to a clear liquid, and leaves a blue, infusible mass.<sup>7</sup> It dissolves in water, but hydrolysis takes place, the extent of which depends on the conditions. In water containing very little hydrofluoric acid, 1 part of the salt dissolves in 200 parts of water at 15° C.; in the presence of rather more hydrofluoric acid 1 part dissolves in 150 to 160 parts of water, at 15° C.<sup>8</sup> Ruff and Schiller<sup>9</sup> have shown that the solubility increases (1) with rise in temperature, (2) with increase in the concentration of hydrofluoric acid, (3) with decrease in the concentration of potassium fluoride. The aqueous solution reacts acid to litmus, and on being boiled precipitates a white,<sup>10</sup> insoluble, potassium tantalum oxyfluoride,  $\text{Ta}_2\text{O}_5 \cdot 4\text{KF} \cdot 2\text{TaF}_5$  or  $\text{Ta}_2\text{O}_5 \cdot 2(2\text{KF} \cdot \text{TaF}_5)$ ; this reaction is used to detect the presence of tantalum in a niobium compound, since a solution of

<sup>1</sup> Balke, *J. Amer. Chem. Soc.*, 1905, 27, 1151.

<sup>2</sup> Pennington, *ibid.*, 1896, 18, 38. Balke (*loc. cit.*) was unable to obtain this very complex salt.

<sup>3</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 9, 247.

<sup>4</sup> Balke, *loc. cit.*

<sup>5</sup> Berzelius, *loc. cit.*; Marignac, *loc. cit.*

<sup>6</sup> Gmelin-Kraut, *Handbuch der anorganischen Chemie* (Heidelberg), 1913, 6, 313.

<sup>7</sup> Rose, *loc. cit.*; Balke, *loc. cit.*; Hahn and Puetter, *loc. cit.*

<sup>8</sup> Marignac, *loc. cit.*

<sup>9</sup> Ruff and Schiller, *Zeitsch. anorg. Chem.*, 1911, 72, 342.

<sup>10</sup> Compare Noyes and Bray, *Qualitative Analysis for the Rare Elements* (Macmillan, London), 1927, 106.

potassium niobium fluoride,  $K_2NbF_7$ , does not throw down a precipitate on being boiled.<sup>1</sup> Addition of caustic soda precipitates tantalic acid.

*Rubidium Tantalum Fluoride*,  $2RbF.TaF_5$  or  $Rb_2TaF_7$ , is obtained in white needles similarly to the analogous potassium compound. It dissolves in 40 parts of water.<sup>2</sup>

*Sodium Tantalum Fluorides*.—Slow evaporation of a solution of sodium tantalate in hydrofluoric acid precipitates the two compounds,  $3NaF.TaF_5$  or  $Na_3TaF_8$ , and  $2NaF.TaF_5.H_2O$  or  $Na_2TaF_7.H_2O$ , the former first.<sup>3</sup>  $Na_3TaF_8$  yields rhombic prisms,  $a : b : c = 0.6017 : 1 : 0.2799$ , and dissolves in from 20.5 to 20.9 parts of water at 25° C.  $Na_2TaF_7.H_2O$  gives rise to six-sided plates belonging to the rhombic system,  $a : b : c = 0.838 : 1 : 1.274$ ; it loses its water of crystallisation at 100° C., and can be heated to 150° C. without undergoing decomposition. Evaporation of its mother-liquors yields the salt  $NaF.TaF_5$  or  $NaTaF_6$  in regular, cubic crystals.

Analogous sodium niobium fluorides have not been isolated.

*Thallium Tantalum Fluoride*,  $2TlF.TaF_5$  or  $Tl_2TaF_7$ , is obtained in glistening crystals by the action of thallium fluoride on tantalum pentoxide in hydrofluoric acid.<sup>4</sup>

*Zinc Tantalum Fluoride*,  $ZnF_2.TaF_5$ , is prepared by the action of zinc oxide on a solution of tantalum pentoxide in excess of hydrofluoric acid; concentration yields a hygroscopic, crystalline mass.<sup>5</sup>

Tantalum pentafluoride also forms crystalline *double salts* with *pyridine*, *methylamine*, and other *organic bases*. The following compounds with *pyridine* have been prepared: <sup>6</sup>  $3(C_5H_5N.HF).2TaF_5.2H_2O$ ;  $C_5H_5N.HF.TaF_5$ .

#### *Oxyfluorides.*

Vanadium yields more or less stable oxyfluorides, and an oxyfluoride of pentavalent niobium,  $NbOF_3$ , has been prepared in the dry way, but in the case of tantalum, free oxyfluorides are unknown. Tantalum oxytrifluoride,  $TaOF_3$ , does occur, however, in combination with ammonium and potassium fluorides in some double salts. The latter are not so numerous as the analogous niobium compounds, and differ from them also in method of preparation, since they are not formed in the presence of hydrofluoric acid, which gives rise to the double fluorides described above. On being boiled, the double oxyfluorides of tantalum undergo ready hydrolysis, and precipitate either tantalic acid or an oxyfluoride in which the proportion of tantalic acid is greater than in the original salt.

*Ammonium Tantalum Oxyfluorides* or *ammonium fluoroxytantalates*.—A substance which has the composition  $3NH_4F.TaOF_3$  or  $[TaO^{F_6}](NH_4)_3$  has been obtained by dissolving tantalic acid in a hot, concentrated solution of ammonium fluoride and cooling, whereupon large transparent octahedra are thrown down.<sup>7</sup> This fluoride is isomorphous

<sup>1</sup> Compare Powell and Schoeller, *Analyst*, 1925, 50, 495.

<sup>2</sup> Pennington, *loc. cit.*; Balke, *loc. cit.*; E. F. Smith, *Chem. News*, 1905, 92, 209; *Proc. Amer. Phil. Soc.*, 1904, 44, 151.

<sup>3</sup> Marignac, *loc. cit.*; Balke, *loc. cit.*

<sup>4</sup> Ephraim and Heymann, *Ber.*, 1909, 42, 4461.

<sup>5</sup> Marignac, *loc. cit.*

<sup>6</sup> Balke, *loc. cit.*

<sup>7</sup> Joly, *Compt. rend.*, 1875, 81, 1266; *Annales Scientifiques de l'École Normale Supérieure*, Paris, 1877, [ii], 6, 160; compare Balke, *J. Amer. Chem. Soc.*, 1905, 27, 1140.

both with the corresponding niobium salt,  $3\text{NH}_4\text{F} \cdot \text{NbOF}_3$ , and with the double fluorides of some metals in which the oxygen atom is substituted by another fluoride atom, for example ammonium titanium fluoride,  $3\text{NH}_4\text{F} \cdot \text{TiF}_4$ . Evaporation of ammonia from the mother-liquors and cooling yields crystals of the compound  $3\text{NH}_4\text{F} \cdot \text{HF} \cdot \text{TaOF}_3$ .<sup>1</sup>

*Potassium Tantalum Oxyfluoride*,  $4\text{KF} \cdot 2\text{TaF}_5 \cdot \text{Ta}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5 \cdot 2(2\text{KF} \cdot \text{TaF}_5)$ .—(See under Potassium Tantalum Fluoride,  $2\text{KF} \cdot \text{TaF}_5$ , on p. 190.) Two other potassium tantalum oxyfluorides have been reported,  $2\text{KF} \cdot \text{TaOF}_3$ <sup>2</sup> and  $3\text{KF} \cdot \text{TaOF}_3$ .<sup>3</sup>

#### TANTALUM AND CHLORINE.

**Tantalum Dichloride,  $\text{TaCl}_2$ , and Tantalum Trichloride,  $\text{TaCl}_3$ ,** are both stated to be obtained by reducing the pentachloride with aluminium in the presence of aluminium chloride; the product is heated to  $600^\circ \text{C}$ . so as to volatilise the aluminium salt, and the residue is extracted with cold water. The trichloride dissolves readily and leaves the dichloride as a dark olive-green powder,<sup>4</sup> which oxidises on exposure to air and is converted into the pentoxide on being heated. The dichloride dissolves in warm water with evolution of hydrogen to form an oxychloride of trivalent tantalum. Cold dilute caustic soda solution dissolves it without evolution of hydrogen or alteration in valency, but on being warmed, the solution oxidises readily, evolves hydrogen, and precipitates an unstable brown lower oxide which is also thrown down by the addition of ammonia to the aqueous solution of the dichloride, or by the action of nitric acid or other strong oxidising agent on the acid solution. The composition of the green powder and the existence of tantalum dichloride have been rendered doubtful by the investigations of Lindner and Feit,<sup>5</sup> who reduced tantalum pentachloride with lead powder at  $600^\circ \text{C}$ . in an atmosphere of nitrogen, and extracted the product with dilute hydrochloric acid, from which, after removal of lead with hydrogen sulphide, six-sided, dark green crystals of a *chloro-acid* having the composition  $\text{HTa}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$  were obtained. This compound loses only three of its water molecules at  $205^\circ \text{C}$ ., and at slightly higher temperatures undergoes decomposition with evolution of hydrochloric acid. It contains a complex ion the chlorine atoms of which scarcely dissociate in alcohol solution; in water, dissociation is followed by hydrolysis, with the splitting off of two molecules of hydrochloric acid. The co-ordinated formula is  $\text{H}[\text{Ta}_3\text{Cl}_7 \cdot \text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$ , analogous to the formulæ for the corresponding molybdenum and tungsten chloro-acids.<sup>6</sup> The formula was previously written both as  $\text{TaCl}_2 \cdot 2\text{H}_2\text{O}$ <sup>7</sup> and as  $(\text{Ta}_3\text{Cl}_{12})\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ .<sup>8</sup>

A study of the reactions of this chloro-acid of tantalum shows that in acid solution only one of the seven chlorine atoms is dissociated, and

<sup>1</sup> Joly, *loc. cit.*

<sup>2</sup> Hall and Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 179.

<sup>3</sup> Joly, *loc. cit.*

<sup>4</sup> Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1925, 148, 1; *Ber.*, 1922, 55 B, 1466.

<sup>5</sup> Lindner and Feit, *Zeitsch. anorg. Chem.*, 1924, 137, 66; Lindner and others, *Ber.*, 1922, 55 B, 1458.

<sup>6</sup> Lindner and Feit, *loc. cit.*; Lindner, *Zeitsch. anorg. Chem.*, 1927, 162, 203; compare Ruff and Thomas, *ibid.*, 1925, 148, 19.

<sup>7</sup> Chabrié, *Compt. rend.*, 1907, 144, 804.

<sup>8</sup> Chapin, *J. Amer. Chem. Soc.*, 1910, 32, 329.

a number of compounds have been prepared which are derived from the chloro-acid by substitution either of this differently held chlorine atom or of the co-ordinated water :<sup>1</sup>

(i) A *monobromochloro-acid*,  $H[Ta_3Cl_5.Br.H_2O].3H_2O$ , is obtained as green crystals by the action of hydrobromic acid on tantalum pentachloride.

(ii) A *sulphatochloro-acid*,  $H_2[Ta_3Cl_5.SO_4].H_2O$ , is obtained by treating tantalum pentachloride with dilute sulphuric acid.

(iii) Evaporation of the *alcohol* solution of the chloro-acid yields a brown resinous mass of composition  $H[Ta_3Cl_5.Cl.C_2H_5OH].C_2H_5OH$ .

(iv) With *pyridine* and hydrochloric acid in aqueous or alcoholic solutions, deep green, crystalline compounds are produced:  $C_5H_5N.H[Ta_3Cl_5.Cl.C_5H_5N]$ ;  $C_5H_5N.H[Ta_3Cl_5.Br.C_5H_5N]$ . All these compounds have the co-ordination number 8, and all of them contain the group  $(Ta_3Cl_5)$  as part of the complex anion, which is probably a derivative of the complex anion  $[Ta_3Cl_5]^-$ . The acid of composition  $H_2Ta_3Cl_5$  is unknown, but a green, crystalline *pyridinium salt*,  $(C_5H_5N_2)H_2[Ta_3Cl_5].3H_2O$ , has been prepared. Other pyridinium derivatives in which the co-ordination number is 7 or 9 are known.<sup>2</sup> On being treated with aqueous caustic potash, the chloro-acid loses two of its chlorine atoms and yields a dark brown, amorphous precipitate of composition  $[Ta_3Cl_5(H_2O)_5].OH$  aq. in which the co-ordination number is 10.

**Tantalum Trichloride**,  $TaCl_3$ , is prepared by reducing the pentachloride with aluminium in the presence of aluminium chloride and heating the product to between 350° and 400° C.<sup>3</sup> It is a dark green substance which yields intensely green aqueous solutions without evolution of hydrogen. These solutions are fairly stable, and oxidise only slowly on being exposed to air; the rate of oxidation is accelerated by the presence of alkali and checked by the addition of acids.

**Tantalum Tetrachloride**,  $TaCl_4$ .—The formation of a green substance the composition of which agreed with that of a tetrachloride was observed during the preparation of the trichloride, but from the data available it was impossible to decide if it was a simple compound or a mixture of the pentachloride and the trichloride.<sup>4</sup>

**Tantalum Pentachloride**,  $TaCl_5$ , is the best known of the chlorides of tantalum. It has been prepared by several methods:

(i) By the action of chlorine<sup>5</sup> or carbonyl chloride<sup>6</sup> on heated metallic tantalum. The pentachloride can be sublimed away.

(ii) By the action of carbon tetrachloride,<sup>7</sup> carbon tetrachloride and chlorine,<sup>8</sup> sulphur monochloride and chlorine,<sup>9</sup> or phosphorus pentachloride<sup>10</sup> on tantalum pentoxide.

<sup>1</sup> Compare Ruff and Thomas, *loc. cit.*

<sup>2</sup> Lindner, *loc. cit.*

<sup>3</sup> Ruff and Thomas, *Ber.*, 1922, 55 B, 1466.

<sup>4</sup> Ruff and Thomas, *loc. cit.*

<sup>5</sup> Berzelius, *Pogg. Annalen*, 1825 and 1826, 4 and 6; Moissan, *Compt. rend.*, 1902, 134, 211; *Bull. Soc. chim.*, 1902, [iii], 27, 434; Lindner and Feit, *Zeitsch. anorg. Chem.*, 1924, 132, 10.

<sup>6</sup> Lindner and others, *loc. cit.*

<sup>7</sup> Demarcay, *Compt. rend.*, 1887, 104, 111; Hall and Smith, *Proc. Amer. Phil. Soc.*, 1905, 44, 202; *J. Amer. Chem. Soc.*, 1905, 27, 1393; *Chem. News*, 1905, 92, 277; Funk and Niederländer, *Ber.*, 1928, 61 B, 249, 1385.

<sup>8</sup> Ruff and Schiller, *Zeitsch. anorg. Chem.*, 1911, 72, 330.

<sup>9</sup> Hall, *J. Amer. Chem. Soc.*, 1904, 26, 1243; Bourion, *Ann. Chim. Phys.*, 1910, [viii], 20, 566; Sears and Balke, *J. Amer. Chem. Soc.*, 1915, 37, 835.

<sup>10</sup> Pennington, *ibid.*, 1896, 18, 64.

(iii) By the action of chlorine on a heated mixture of tantalum pentoxide and sugar charcoal.<sup>1</sup>

Tantalum pentachloride is usually obtained as a yellow powder which forms a mass of white crystals on being melted or sublimed. Its melting-point is variously reported as 211.3° C.,<sup>2</sup> 221° C.,<sup>3</sup> and between 230° and 240° C.,<sup>4</sup> and its boiling-point as 241.6°<sup>5</sup> and 233° C.<sup>6</sup> Its density at 17° C. is 3.68,<sup>7</sup> and its vapour density at 360° C. is 12.8 (air = 1); TaCl<sub>5</sub> requires 12.5, so that decomposition does not take place at this temperature. The electrical conductivity in the fused state is  $0.30 \times 10^{-6}$  reciprocal ohms (the corresponding figure for copper at ordinary temperatures is  $64 \times 10^4$ ), so that molten tantalum pentachloride is an insulator of the order of the best conductivity water.<sup>8</sup> It is quite stable in dry air, and sublimes unchanged in chlorine or in carbon dioxide. When brought into contact with water it emits a hissing noise, and decomposes into tantalic acid and hydrochloric acid, with evolution of heat. It is only sparingly soluble in hot concentrated hydrochloric acid, but with addition of water it dissolves completely to an opalescent solution which does not throw down a precipitate even on being boiled. Concentrated hydrochloric acid attacks it, hydrogen chloride fumes being evolved, but the tantalic acid formed at the same time is dissolved; the solution becomes cloudy on being boiled, and throws down a gelatinous precipitate of tantalic acid on being cooled.<sup>9</sup> Tantalum pentachloride is soluble in cold alcohol, chloroform, carbon tetrachloride and carbon bisulphide; solutions in these solvents yield crystalline addition compounds when treated with organic compounds. The following *addition compounds* with *pyridine* and *piperidine* have been isolated:<sup>10</sup> TaCl<sub>5</sub>.2C<sub>5</sub>H<sub>5</sub>N; TaCl<sub>5</sub>.6C<sub>5</sub>H<sub>11</sub>N.2C<sub>2</sub>H<sub>5</sub>OH. Rose<sup>11</sup> was unable to obtain double chlorides of tantalum pentachloride and the alkali chlorides which would correspond to the double fluorides.

**Oxychlorides.**—A tantalum oxychloride of composition TaO<sub>2</sub>Cl has been obtained by subliming tantalum pentachloride in a vacuum at 500° C.<sup>12</sup> Various oxychlorides of unknown composition are stated to be obtained by the action of tantalum pentachloride on alcohol solutions of hydrochloric acid.<sup>13</sup> The following *pyridine* and *quinoline addition compounds* have been prepared:<sup>14</sup> 4TaO<sub>2</sub>Cl.7C<sub>5</sub>H<sub>5</sub>N; Ta<sub>2</sub>O<sub>3</sub>Cl<sub>4</sub>.4(C<sub>5</sub>H<sub>5</sub>N.HCl); 2TaOCl<sub>3</sub>.3(C<sub>5</sub>H<sub>5</sub>N.HCl).2C<sub>2</sub>H<sub>5</sub>OH; TaOCl<sub>3</sub>.2(C<sub>5</sub>H<sub>5</sub>N.HCl).2C<sub>2</sub>H<sub>5</sub>OH; 2TaOCl<sub>3</sub>.3(C<sub>5</sub>H<sub>5</sub>N.HCl).2C<sub>2</sub>H<sub>5</sub>OH; TaOCl<sub>3</sub>.2(C<sub>9</sub>H<sub>7</sub>N.HCl).2C<sub>2</sub>H<sub>5</sub>OH.

#### TANTALUM AND BROMINE.

**Bromotantalum Bromide** or *tantalum dibromide*.—The anhydrous substance is unknown. A compound which has the composition (Ta<sub>3</sub>Br<sub>7</sub>)Br.3½H<sub>2</sub>O or Ta<sub>3</sub>Br<sub>14</sub>.7H<sub>2</sub>O is obtained by reducing

<sup>1</sup> Biltz and Voigt, *Zeitsch. anorg. Chem.*, 1921, 120, 71; Rose and Weber, *Pogg. Annalen*, 1846, 69, 115; 1853, 90, 458.

<sup>2</sup> Deville and Troost, *Compt. rend.*, 1865, 60, 1221; 1867, 64, 294.

<sup>3</sup> Rose, *Pogg. Annalen*, 1846, 69, 115.

<sup>4</sup> Biltz and Voigt, *loc. cit.*

<sup>5</sup> Deville and Troost, *loc. cit.*

<sup>6</sup> Lindner and Feit, *loc. cit.*

<sup>7</sup> Balke, *J. Amer. Chem. Soc.*, 1910, 32, 1131.

<sup>8</sup> Biltz and Voigt, *loc. cit.*

<sup>9</sup> Rose, *Pogg. Annalen*, 1856, 99, 66, 575; Weinland and Storz, *Zeitsch. anorg. Chem.*, 1907, 54, 223.

<sup>10</sup> Lindner and Feit, *loc. cit.*; see also Funk and Niederländer, *loc. cit.*

<sup>11</sup> Rose, *loc. cit.*

<sup>12</sup> Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1925, 148, 1.

<sup>13</sup> Weinland and Storz, *loc. cit.*

<sup>14</sup> Lindner and Feit, *loc. cit.*

tantalum pentabromide with sodium amalgam at a red heat in the absence of air; the product is extracted with water which has been acidified with hydrobromic acid, and the extract concentrated. Minute, black, hexagonal crystals result, which give a dark green powder. They yield an intensely green aqueous solution which is apparently stable in air. Addition of ammonium hydroxide precipitates brown flakes of an unstable lower hydroxide of tantalum. When the compound containing seven atoms of bromine is treated with silver nitrate solution, only one atom of bromine is removed as silver bromide, which indicates that six atoms of bromine form part of a complex anion and do not undergo ionisation as Br<sup>-</sup> ions. Similarly, when the aqueous solution of bromotantalum bromide is treated with equimolecular proportions of caustic soda in the cold, dark green, thin, hexagonal plates of *bromotantalum hydroxide*,  $(\text{Ta}_3\text{Br}_6)\text{OH}\cdot 5\text{H}_2\text{O}$ , are obtained. Evaporation of the hydroxide with hydrochloric acid yields *bromotantalum chloride*,  $(\text{Ta}_3\text{Br}_6)\text{Cl}\cdot 3\frac{1}{2}\text{H}_2\text{O}$ , which is very similar in appearance and general properties to bromotantalum bromide. Evaporation of the hydroxide with hydriodic acid gives rise to *bromotantalum iodide*,  $(\text{Ta}_3\text{Br}_6)\text{I}\cdot 3\frac{1}{2}\text{H}_2\text{O}$ , in long, hexagonal prisms. All these substances contain the group  $(\text{Ta}_3\text{Br}_6)$ , which, however, has not been separately isolated.<sup>1</sup>

It is important to note that recent investigation into the composition of the analogous chlorine compound of tantalum, viz. *chlorotantalum chloride* (see p. 192), has shown that the formula  $\text{H}\cdot\text{Ta}_3\text{Cl}_6\cdot\text{Cl}\cdot 4\text{H}_2\text{O}$  is to be preferred to the older formula  $\text{Ta}_3\text{Cl}_6\cdot\text{Cl}\cdot 4\text{H}_2\text{O}$ . By analogy, the composition of the bromine compound is  $\text{H}\cdot\text{Ta}_3\text{Br}_6\cdot\text{Br}\cdot 4\text{H}_2\text{O}$ , and this assumption receives confirmation from the fact that the acid  $\text{H}[\text{Ta}_3\text{Br}_6\cdot\text{Br}\cdot\text{H}_2\text{O}]$  has recently been prepared.<sup>2</sup> The foregoing formulæ for the hydroxy-, chloro- and iodo-derivatives also presumably require correction.

**Tantalum Tribromide,  $\text{TaBr}_3$ .**—A substance having this composition has not been definitely isolated and analysed, but it is stated to be formed during the reduction of tantalum pentabromide with hydrogen. It is a green powder which yields an intensely green aqueous solution in which the compound is only weakly ionised. The green colour is discharged by the action of oxidising agents; addition of ammonia precipitates characteristic brown flakes.<sup>3</sup>

**Tantalum Pentabromide,  $\text{TaBr}_5$ ,** can be prepared either by distilling bromine on to powdered tantalum heated to between  $260^\circ$  and  $300^\circ\text{C}$ .,<sup>4</sup> or by passing bromine vapour over a heated mixture of freshly ignited tantalum pentoxide and sugar charcoal, all air being previously removed by means of carbon dioxide. The product is sublimed in an atmosphere of carbon dioxide to render it free from excess of bromine. The salt crystallises in long, yellow plates. The density of the sublimed material is 4.67. It melts at about  $240^\circ\text{C}$ . to a transparent, red liquid, and boils at about  $320^\circ\text{C}$ ., giving a yellow vapour. When heated in hydrogen above its sublimation temperature, reduction to the metal and the lower bromides takes place. It fumes strongly in air, and is rapidly attacked by water, with precipitation of tantalic acid. Methyl and

<sup>1</sup> Chapin, *J. Amer. Chem. Soc.*, 1910, 32, 324.

<sup>2</sup> Lindner, *Zeitsch. anorg. Chem.*, 1927, 162, 209.

<sup>3</sup> Van Haagen, *Thesis, Univ. of Pennsylvania* (1909).

<sup>4</sup> Krishnaswami, *Nature*, 1928, 122, 845.

ethyl alcohols react with it readily, and with such considerable evolution of heat that they take fire.<sup>1</sup>

**Oxybromide.**—The formation of a yellow tantalum oxybromide,  $TaOBr_3$ , has been observed during the distillation of tantalum pentabromide.<sup>2</sup> No double salts with it are known.

#### TANTALUM AND IODINE.

Tantalum and iodine do not combine directly even when heated together for eight hours at  $280^\circ C.$  in a sealed tube.<sup>3</sup> Attempts to prepare an iodide by the action of iodine on a mixture of tantalum pentoxide and carbon were also unsuccessful.<sup>4</sup>

**Tantalum Pentiodide**,  $TaI_5$ , has been obtained by distilling tantalum pentabromide in a stream of dry hydrogen iodide and purifying the product by redistilling it in an atmosphere of carbon dioxide. It is an almost black substance which melts to a brown liquid, and is decomposed by water similarly to the pentabromide, but not so vigorously.

*Bromotantalum iodide* has been referred to on p. 195.

No oxyiodides of tantalum have been prepared.

#### TANTALUM AND OXYGEN.

**Tantalum Dioxide**,  $TaO_2$ , has been prepared as a dark brown powder by heating rods made of a mixture of tantalum pentoxide and paraffin in powdered charcoal at about  $1700^\circ C.$ <sup>5</sup> or by reducing the pentoxide at a high temperature with magnesium.<sup>6</sup> It is stated to be formed also during the electrolysis of solutions of salts of the metals using a tantalum anode.<sup>7</sup> On being heated in air it takes up oxygen and forms the pentoxide. It is insoluble in acids, but dissolves in molten potassium hydroxide to form potassium tantalate.

**Tantalum Pentoxide**,  $Ta_2O_5$ , is one of the commonest compounds of tantalum. The anhydrous substance is produced by direct oxidation of the metal or by ignition of hydrated tantalum pentoxide, which is obtained by the methods described below. The removal of niobium and other metals has been described when dealing with the extraction of tantalum and niobium from their natural ores.

Anhydrous tantalum pentoxide, as usually prepared, is a white, non-volatile,<sup>8</sup> tasteless, odourless, amorphous powder, which remains white at high temperatures.<sup>9</sup> When heated to dull redness it glows and assumes a crystalline form (rhombic prisms), isomorphous with niobium pentoxide;<sup>10</sup> the same change takes place when the amorphous substance is fused with boric acid or microcosmic salt.<sup>11</sup> Its melting-point

<sup>1</sup> Rose, *Pogg. Annalen*, 1856, 99, 87; Van Haagen, *J. Amer. Chem. Soc.*, 1910, 32, 729; Chapin and Smith, *ibid.*, 1911, 33, 1499.

<sup>2</sup> Chapin and Smith, *loc. cit.*

<sup>3</sup> Van Haagen, *loc. cit.*

<sup>4</sup> Rose, *loc. cit.*; Moissan, *Compt. rend.*, 1902, 134, 211.

<sup>5</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45; compare Friederich and Sittig, *loc. cit.*; Ruff, Seiferheld, and Suda, *Zeitsch. anorg. Chem.*, 1913, 82, 397.

<sup>6</sup> Smith and Maas, *ibid.*, 1894, 7, 98.

<sup>7</sup> Brunck, *Chem. Zeit.*, 1912, 36, 1233.

<sup>8</sup> Compare Sears and Balke, *J. Amer. Chem. Soc.*, 1915, 37, 835.

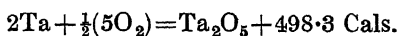
<sup>9</sup> Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 81.

<sup>10</sup> Tammann, *Ann. Physik*, 1902, [iv], 9, 249; Böhm, *Zeitsch. anorg. Chem.*, 1925, 149, 217.

<sup>11</sup> Ebelmen, *Ann. Chim. Phys.*, 1851, 33, 54; Mallard, *Ann. Mines*, 1887, [viii], 12, 427; Nordenskiöld and Chydenius, *Öfvers. K. Vet.-Akad. Förh.*, 1860, 3; *Pogg. Annalen*, 1860, 110, 645; Holmquist, *Bull. Geol. Inst. Ups.*, 1896-97, 3, 205.



has been determined under different conditions with discordant results : 1875° C.,<sup>1</sup> 1620° C.<sup>2</sup> Its density is approximately 7.5, but the figure obtained varies with the method of preparation, increasing with rise in temperature of ignition and prolongation of duration of heating.<sup>3</sup> The electrical resistivity has been measured.<sup>4</sup> One gram of metallic tantalum evolves 1373 calories of heat when burnt directly to the pentoxide in a bomb calorimeter ; 1 gram of aluminium under the same conditions evolves 6970 calories.<sup>5</sup> The calculated heat of formation of tantalum pentoxide is as follows :



Tantalum pentoxide is a remarkably stable substance. It is not attacked by chlorine, hydrogen chloride, carbon tetrachloride, bromine or hydrogen bromide even at high temperatures,<sup>6</sup> but if it is previously mixed with carbon these reagents do attack it. When heated with phosphorus pentachloride or phosphorus trichloride in an air-free sealed tube at 200° C. it is converted into the pentachloride.<sup>7</sup> Sulphur is without action on it ; hydrogen sulphide produces traces of tantalum disulphide at high temperatures ; carbon disulphide produces tantalum disulphide at a white heat.<sup>8</sup> Carbon, at high temperatures and in the absence of air, reduces the pentoxide to a carbide, TaC,<sup>9</sup> or to a mixture of the lower oxides ;<sup>10</sup> in the presence of air a mixture of the carbide and nitride is produced.<sup>11</sup> Reduction with aluminium yields an aluminium-tantalum alloy. The oxide is insoluble in all acids except hydrofluoric acid. According to some investigators the solution of tantalum pentoxide in hydrofluoric acid loses some of its tantalum content on being evaporated ;<sup>12</sup> according to others, however, no such loss takes place.<sup>13</sup> It has recently been shown that pure tantalum pentoxide, prepared by oxidation of the metal, does not show any volatility when evaporated in hydrofluoric acid, and any loss that takes place has been attributed to the presence of traces of alkali in the pentoxide.<sup>14</sup> The amount of the loss varies with the alkali content, and the pentoxide can be completely volatilised by heating with ammonium fluoride. No loss of tantalum takes place in the presence

<sup>1</sup> Ruff, Seiferheld, and Suda, *Zeitsch. anorg. Chem.*, 1913, 82, 398.

<sup>2</sup> Wartenberg, Broy, and Reinicke, *Zeitsch. Elektrochem.*, 1923, 29, 251.

<sup>3</sup> Rose, *Pogg. Annalen*, 1848, 74, 285 ; 1857, 100, 428 ; Marignac, *Ann. Chim. Phys.*, 1866, [iv], 9, 254 ; Deville and Troost, *Compt. rend.*, 1867, 64, 294 ; Holmquist, *loc. cit.* ; Hinrichsen and Sahlbom, *Ber.*, 1906, 39, 2600 ; Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 84 ; Balke, *J. Amer. Chem. Soc.*, 1910, 32, 1131.

<sup>4</sup> Friederich, *Zeitsch. Physik*, 1925, 31, 813.

<sup>5</sup> Moose and Parr, *J. Amer. Chem. Soc.*, 1924, 46, 2660 ; compare Muthmann, Weiss, and Riedelbauch, *loc. cit.*

<sup>6</sup> Smith and Maas, *Zeitsch. anorg. Chem.*, 1894, 7, 96 ; Delafontaine and Linebarger, *J. Amer. Chem. Soc.*, 1896, 18, 535 ; Ruff and Thomas, *Zeitsch. anorg. Chem.*, 1926, 156, 213 ; Travers, *Compt. rend.*, 1918, 166, 494.

<sup>7</sup> Pennington, *J. Amer. Chem. Soc.*, 1896, 18, 64.

<sup>8</sup> Smith and Maas, *loc. cit.* ; Biltz and Kircher, *Ber.*, 1910, 43, 1644.

<sup>9</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 144, 169.

<sup>10</sup> Ruff, Seiferheld, and Suda, *loc. cit.* ; compare Slade and Higson, *J. Chem. Soc.*, 1919, 115, 211.

<sup>11</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 143, 293.

<sup>12</sup> Rose, *Pogg. Annalen*, 1856, 99, 481 ; Levy, *Analyst*, 1901, 26, 64 ; 1915, 40, 204 ; Travers, *loc. cit.* ; Van Haagen and Smith, *J. Amer. Chem. Soc.*, 1911, 33, 1505.

<sup>13</sup> Ruff and Schiller, *Zeitsch. anorg. Chem.*, 1911, 72, 329 ; compare also Schoeller and Powell, *Analyst*, 1928, 53, 258.

<sup>14</sup> Hahn and Puetter, *Zeitsch. anorg. Chem.*, 1923, 127, 153.

of concentrated sulphuric acid. The oxide is volatile in hydrogen chloride at 900° C.<sup>1</sup> When prepared by precipitation in the presence of nitric acid or sulphuric acid the ignited material retains traces of these acids.<sup>2</sup> Ignited tantalum pentoxide is also dissolved by fusion with potassium hydrogen sulphate, ammonium hydrogen sulphate, caustic potash, or a mixture of sodium carbonate and borax.<sup>3</sup>

*Hydrates of Tantalum Pentoxide, Colloidal Tantalum Pentoxide, Tantallic Acid.*—When tantalum pentachloride or pentabromide is treated with water, or when a solution of a tantalate is boiled with dilute acids, a gelatinous precipitate of more or less hydrated tantalum pentoxide is thrown down. Insoluble tantalates on fusion with potassium hydrogen sulphate and extraction of the melt with water give the gel. In dealing with double fluorides of tantalum it is necessary to remove all the hydrofluoric acid by evaporation with concentrated sulphuric acid, otherwise double fluorides are obtained.

As in the case of hydrated niobium and vanadium pentoxides, it is a difficult matter to remove traces of mineral acids from the precipitate. Treatment with water gives rise to a cloudy hydrosol which passes through an ordinary filter. This can be prevented by addition to the wash-water of a small quantity of ammonia or acetic acid.<sup>4</sup> In the preparation of anhydrous tantalum pentoxide, traces of acids can be removed by igniting the gel in admixture with a small quantity of ammonium carbonate.

Hydrated tantalum pentoxide is a white, amorphous substance. A crystalline form is stated to be obtained when tantalum pentachloride is treated rapidly with water; the precipitate thrown down is dried slowly and again treated with water.<sup>5</sup> A granular variety is produced when sodium tantalate solution is treated with sulphur dioxide and the flaky precipitate is dried.<sup>6</sup> Tantalum pentoxide gel becomes incandescent and loses its water content when it is rapidly heated to 500° C., unless it has been previously aged by washing with water. This "glow" phenomenon is also displayed by hydrated chromium sesquioxide, by aluminium oxide, and by titanium dioxide. The composition of the gel, when dried at 100° C., varies with the method of preparation. Various hydrates have been reported,<sup>7</sup> but their composition must be regarded as accidental, because recent investigation<sup>8</sup> has shown that continuous variation in the water content takes place with variation in the vapour-pressure. The curves obtained were very similar to those given by gels of stannic oxide and silica. A true tantallic acid is, therefore, unknown, but the name is used for the more or less hydrated pentoxide. The properties of a hydrosol of tantalum pentoxide prepared by dialysis of the aqueous extract of an alkali niobate are referred to on p. 180.

Hydrated tantalum pentoxide or tantallic acid is very comparable in its properties to niobic acid (see p. 157). It is soluble in excess

<sup>1</sup> Travers, *loc. cit.*

<sup>2</sup> Sears and Balke, *loc. cit.*

<sup>3</sup> Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 98.

<sup>4</sup> Weiss and Landecker, *ibid.*, 1909, 64, 87; *Chem. News*, 1909, 99, 3.

<sup>5</sup> Rose, *Pogg. Annalen*, 1848, 74, 245.

<sup>6</sup> Abegg, *Handbuch der anorganischen Chemie* (Leipzig), 1907, 3, iii, 859.

<sup>7</sup> Rose, *Pogg. Annalen*, 1857, 100, 417; Rammelsberg, *ibid.*, 1869, 136, 177, 325; Hermann, *J. prakt. Chem.*, 1857, [i], 70, 195; 1872, [ii], 5, 66.

<sup>8</sup> Jander and Schulz, *Zeitsch. anorg. Chem.*, 1925, 144, 225.

of strong acids to form a colloidal solution.<sup>1</sup> The hydrate, which is prepared by precipitation from cold dilute solutions of alkali tantalates by means of dilute sulphuric acid, dissolves in hot concentrated sulphuric acid, and is reprecipitated by diluting the cooled solution with water; hydrated niobium pentoxide is not reprecipitated, however, under similar circumstances, and its solution remains clear.<sup>2</sup> Hydrated tantalum pentoxide differs from titanium dioxide in that it yields a flesh-coloured insoluble addition compound with ammonium salicylate, whilst titanium dioxide passes into solution.<sup>3</sup> Whereas niobic acid and titanitic acid are practically completely soluble in hydrogen peroxide, tantalalic acid, when precipitated hot, is almost insoluble, and when precipitated cold is only partly soluble.<sup>4</sup> Certain weak acids, for example oxalic acid and tartaric acid, dissolve tantalum pentoxide, probably because of the formation of soluble heteropoly-acids.

#### TANTALATES.

Tantalum pentoxide is insoluble in solutions of caustic alkalis and alkali carbonates, but on being fused with these substances reacts to produce the alkali tantalates. Tantalates of the metals are obtained by double decomposition, using a soluble alkali tantalate and a soluble salt of the metal. Tantalates of the alkaline earths have also been obtained by fusing tantalum pentoxide with the chloride of the alkaline earth.

The tantalates display wide variations in composition, the proportions of basic oxide to acid oxide ranging from 1 : 3 to 5 : 1, but, as in the cases of the vanadates and niobates, it is probable that many of those which have been prepared and described are really isomorphous mixtures of simpler compounds. According to Marignac,<sup>5</sup> the only true chemical compounds are the 1 : 1 or *meta*-salts, of the general formula  $R \cdot 2O \cdot Ta_2O_5$ , and the 4 : 3 or *hexabasic* salts, of the general formula  $4R \cdot 2O \cdot 3Ta_2O_5$ . According to a recent investigation,<sup>6</sup> the members of the latter series are more correctly represented as 7 : 5 salts, for example  $7K_2O \cdot 5Ta_2O_5 \cdot 24H_2O$ , and not as 4 : 3 salts; they can be alternatively written as derivatives of the hypothetical ortho-acid,  $H_3TaO_4$ , in which each of the four oxygen atoms has been replaced by a co-ordinated ( $TaO_4$ ) group, thus  $H_7[Ta(TaO_4)_4]$ ; for example,  $K_7[Ta(TaO_4)_4] \cdot 12H_2O$ . This class of alkali tantalates is of importance because it includes the only soluble tantalates known, other alkali tantalates and the tantalates of all other metals being insoluble in water.

The soluble alkali tantalates undergo ready hydrolysis; when their aqueous solutions are boiled, precipitation of a more acid salt takes place and some alkali base passes into solution. Separation of the base in this manner is naturally favoured by the presence of acids, and even so weak an acid as carbon dioxide or hydrogen sulphide precipitates tantalalic acid or an acid salt; with the stronger acids (sulphurous acid, sulphuric acid, hydrochloric acid, nitric acid, etc., but not with hydrofluoric acid) precipitation of tantalalic acid takes place readily, but excess of the strong mineral acid redissolves the precipitate. Potassium chloride

<sup>1</sup> Jander and Schulz, *loc. cit.*

<sup>2</sup> Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 86.

<sup>3</sup> Lange, *Zeitsch. Naturwiss., Halle*, 1910, 82, 29.

<sup>4</sup> Hahn and Gille, *Zeitsch. anorg. Chem.*, 1920, 112, 283.

<sup>5</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 9, 249.

<sup>6</sup> Jander and Schulz, *Zeitsch. anorg. Chem.*, 1925, 144, 231.

and ammonium salts also precipitate tantallic acid from solutions of tantalates. Arsenious acid, arsenic acid, hydrocyanic acid, tartaric acid and citric acid do not, however, hydrolyse solutions of alkali tantalates; this difference in behaviour is attributed to the formation of soluble salts of heteropoly-acids. Addition of caustic soda or concentrated solutions of sodium salts to a solution of potassium tantalate yields a precipitate of sodium tantalate which is insoluble in the presence of a high concentration of sodium ions.

Measurements of the electrical conductivity of solutions of alkali tantalates have been made,<sup>1</sup> but no definite conclusions are deducible as to the complexity of the ions present.

Some reactions of tantalates have been described when dealing with the detection of tantalum (see p. 132).

The following tantalates are known :

*Ammonium Tantalate*,  $(\text{NH}_4)_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , is obtained as a flocculent precipitate by the addition of ammonium chloride to a solution of 4 : 3 sodium tantalate.<sup>2</sup> An *ammonium potassium tantalate*,  $(\text{NH}_4)_2\text{O} \cdot \text{K}_2\text{O} \cdot 4\text{Ta}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , has also been obtained by the same reaction, using potassium tantalate.

*Barium Tantalate*,  $4\text{BaO} \cdot 3\text{Ta}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ , results from the action of a barium salt in solution on a solution of 4 : 3 sodium or potassium tantalate.<sup>3</sup>

*Cæsium Tantalates*.—Fusion of tantalum pentoxide with cæsium carbonate and extraction with water yields monoclinic crystals of the 4 : 3 salt,  $4\text{Cs}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ ; addition of alcohol to its aqueous solution precipitates the 7 : 6 salt,  $7\text{Cs}_2\text{O} \cdot 6\text{Ta}_2\text{O}_5 \cdot 38\text{H}_2\text{O}$ .<sup>4</sup>

*Calcium Metatantalate*,  $\text{CaO} \cdot \text{Ta}_2\text{O}_5$ , is obtained as a crystalline mass by fusing calcium chloride with tantalum pentoxide. Fusion of this salt with more calcium chloride gives crystals of the 2 : 1 or *pyro-salt*,  $2\text{CaO} \cdot \text{Ta}_2\text{O}_5$ .<sup>5</sup> *Calcium pyrotantalate* is present in some of the natural tantalum ores, for example in *fergusonite* and *mikrolite*.<sup>6</sup>

*Cobalt Tantalate*,  $\text{CoO} \cdot \text{Ta}_2\text{O}_5$ .—A compound having this probable composition has recently been prepared by heating the two oxides together at high temperatures.<sup>7</sup>

*Iron Tantalates*.—The meta-salt,  $\text{FeO} \cdot \text{Ta}_2\text{O}_5$ , has been obtained more or less pure by fusing tantalum pentoxide and ferrous fluoride with excess of potassium chloride.<sup>8</sup> Iron tantalates occur naturally in *niobites* and *tantalites*. The ore *tapiolite* has the approximate composition  $\text{FeO} \cdot \text{Ta}_2\text{O}_5$ ; the tantalum may be partially substituted by niobium.<sup>9</sup>

*Lithium Tantalate*,  $7\text{Li}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 40\text{H}_2\text{O}$ , is precipitated in six-sided plates when lithium hydroxide solution is added to a solution of 7 : 5 potassium tantalate.<sup>10</sup>

<sup>1</sup> Jander and Schulz, *loc. cit.*

<sup>2</sup> Rose, *Pogg. Annalen*, 1857, 102, 55.

<sup>3</sup> Rose, *loc. cit.*; see also Hedvall and Zweigbergk, *Zeitsch. anorg. Chem.*, 1919, 108, 119.

<sup>4</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1666.

<sup>5</sup> Joly, *Compt. rend.*, 1875, 81, 267; *Annales Scientifiques de l'École Normale Supérieure, Paris*, 1876, 125.

<sup>6</sup> Nordenskiöld, *Zeitsch. Kryst. Min.*, 1901, 34, 692; Flink, *ibid.*, 1901, 34, 681; Simpson, *Chem. News*, 1909, 99, 77.

<sup>7</sup> Hedvall, *Zeitsch. anorg. Chem.*, 1915, 93, 313.

<sup>8</sup> Joly, *loc. cit.*

<sup>9</sup> Dana, *A System of Mineralogy* (Wiley, New York), 1896, 6th ed., p. 738; Simpson, *Min. Mag.*, 1917, 18, 107; *J. Chem. Soc., Abs.*, 1917, [ii], 112, 377.

<sup>10</sup> Jander and Schulz, *loc. cit.*

*Magnesium Tantalates.*—The 4 : 3 salt,  $4\text{MgO} \cdot 3\text{Ta}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ , separates out on the addition of a soluble magnesium salt to a solution of a tantalate. Fusion of magnesium chloride and tantalum pentoxide has given large hexagonal plates of the 4 : 1 salt,  $4\text{MgO} \cdot \text{Ta}_2\text{O}_5$ .<sup>1</sup>

*Mercurous Tantalate*,  $4\text{Hg}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , is a greenish-yellow compound which is precipitated by mixing a mercurous salt and a tantalate in solution.<sup>2</sup>

*Potassium Tantalates.*—The 4 : 3 salt,  $4\text{K}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$ , is prepared by fusing tantalum pentoxide with excess of caustic potash in a silver crucible; the aqueous extract is evaporated in a vacuum. It forms monoclinic prisms,  $a : b : c = 0.7164 : 1 : 0.5475$ ;  $\beta = 95^\circ 19'$ . It is stable in air and can be crystallised from its aqueous solutions unchanged, but boiling the solution precipitates a more acid salt.<sup>3</sup> According to the more recent investigations of Jander and Schulz,<sup>4</sup> the crystals obtained by the foregoing reaction are six-sided prisms of the 7 : 5 salt,  $7\text{K}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$ ; varying proportions of tantalum pentoxide and caustic potash were employed with the same result, but evaporation was effected either over phosphorus pentoxide or on the water-bath, and the crystals were washed with alcohol.

*Potassium Metatantalate*,  $\text{K}_2\text{O} \cdot \text{Ta}_2\text{O}_5$ , is produced when the 4 : 3 salt is heated and the product washed with water. It is insoluble in water. The 2 : 3 salt,  $2\text{K}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ , is precipitated out by the action of carbon dioxide on the aqueous extract of a fused mixture of tantalum pentoxide and potassium carbonate.<sup>5</sup> Continued boiling of this salt with water yields the 1 : 2 salt,  $\text{K}_2\text{O} \cdot 2\text{Ta}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ . The anhydrous 3 : 7 salt has also been reported.

*Rubidium Tantalate*,  $4\text{Rb}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ , is obtained in transparent, colourless, monoclinic prisms by fusing tantalum pentoxide with rubidium carbonate and extracting the melt with water. It is isomorphous with the corresponding niobium salt and with 4 : 3 caesium tantalate.<sup>6</sup>

*Silver Tantalate*,  $4\text{Ag}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , is a yellowish-white substance formed by the action of a silver salt on a tantalate in solution.<sup>7</sup>

*Sodium Tantalates.*—4 : 3 Sodium tantalate,  $4\text{Na}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 25\text{H}_2\text{O}$ , is prepared by fusing tantalum pentoxide with caustic soda in a silver crucible; excess of caustic soda is removed by washing with water, and the residue is crystallised from hot water.<sup>8</sup> Another method consists in adding a concentrated solution of sodium chloride to the aqueous extract from a fused mixture of tantalum pentoxide and potassium carbonate, when the salt separates as a dense, micro-crystalline powder.<sup>9</sup> It forms six-sided plates,  $a : c = 1 : 1.0167$ . It loses most of its water of crystallisation between  $105^\circ$  and  $110^\circ$  C., but the remainder (apparently five molecules) appears to be water of constitution, as its removal takes place only at much higher temperatures, with decom-

<sup>1</sup> Joly, *loc. cit.*

<sup>2</sup> Rose, *loc. cit.*

<sup>3</sup> Rose, *Pogg. Annalen*, 1857, 100, 559; Marignac, *Ann. Chim. Phys.*, 1866, [iv], 9, 259.

<sup>4</sup> Jander and Schulz, *loc. cit.*

<sup>5</sup> Rose, *loc. cit.*; Rammelsberg, *Pogg. Annalen*, 1869, 136, 177, 325.

<sup>6</sup> Balke and Smith, *loc. cit.*

<sup>7</sup> Rose, *Pogg. Annalen*, 1857, 101, 11; see also Sears and Balke, *J. Amer. Chem. Soc.*, 1915, 37, 841.

<sup>8</sup> Rose, *loc. cit.*

<sup>9</sup> Schoeller and Jahn, *Analyst*, 1926, 51, 613.

position. It is soluble in 493 parts of water at 13.5° C. and in 162 parts of boiling water, but at the latter temperature hydrolysis takes place, with precipitation of a salt which is richer in acid. The solution is alkaline to litmus.<sup>1</sup> According to Jander and Schulz,<sup>2</sup> the composition of the foregoing salt when crystallised at ordinary temperatures is  $7\text{Na}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 40\text{H}_2\text{O}$  or  $\text{Na}_7[\text{Ta}(\text{TaO}_4)_4] \cdot 20\text{H}_2\text{O}$ ; when crystallised at 100° C. it forms needles, the composition of which is  $7\text{Na}_2\text{O} \cdot 5\text{Ta}_2\text{O}_5 \cdot 22\text{H}_2\text{O}$  or  $\text{Na}_7[\text{Ta}(\text{TaO}_4)_4] \cdot 11\text{H}_2\text{O}$ .

*Sodium Metatantalate*,  $\text{Na}_2\text{O} \cdot \text{Ta}_2\text{O}_5$ , is obtained from the 4 : 3 salt either by heating the latter strongly and washing the residue with water, or by the addition of alcohol to its aqueous solution. In the latter case the metatantalate contains two molecules of water when dried at 100° C. When an aqueous solution of the 4 : 3 salt is treated with carbon dioxide or hydrogen sulphide, the 1 : 3 salt,  $\text{Na}_2\text{O} \cdot 3\text{Ta}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ , or the 2 : 7 salt,  $2\text{Na}_2\text{O} \cdot 7\text{Ta}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ , is obtained.

#### HETERO-TANTALATES.

The evidence for the formation of complex heteropoly-acids with tantic acid is very comparable to that set forth in the case of niobic acid (see p. 165). Solutions of tantalates are readily hydrolysed in aqueous solution by boiling, and even more readily by the addition of mineral acids, acetic acid or succinic acid; in the presence, however, of arsenious acid, arsenic acid, tartaric acid or citric acid no precipitation of tantic acid takes place. Again, tincture of galls yields a yellow precipitate with solutions of tantalates which have been rendered feebly acid with sulphuric acid; this reaction does not, however, take place in the presence of ordinary tartaric acid, racemic acid or citric acid. Tartaric acid also prevents the formation of the precipitates which are thrown down on the addition of potassium ferrocyanide or potassium ferricyanide to faintly acid solutions of tantalates, and hinders the precipitation of tantic acid from solutions in inorganic acids by the action of ammonia. In all these cases it is assumed that complex acids or their salts are produced, in consequence of which the usual reaction does not take place.

None of these complex acids has, however, been isolated, and only one well-defined salt, namely, *potassium oxalo-tantalate*,  $5\text{K}_2\text{O} \cdot \text{Ta}_2\text{O}_5 \cdot 10\text{C}_2\text{O}_3$ , is known. This compound has been prepared by fusing tantic acid with potassium carbonate, dissolving the product in water, and adding oxalic acid.<sup>3</sup> It undergoes hydrolysis more readily than potassium oxalo-niobate.

Tantic acid dissolves in oxalic acid, but not so freely as niobic acid; the solution, which presumably contains *oxalo-tantic acid*, is also more readily hydrolysed than solutions of oxalo-niobic acid.<sup>4</sup>

Among naturally occurring complex tantalates the following have been observed, but exact analyses are not always available: *titanotantalates*, *silicotantalates*, *stannotantalates*, *antimonyl-tantalates*, *uranotantalates*, *urano-titanotantalates*.

<sup>1</sup> Rose, *loc. cit.*; Wedekind and Maas, *Zeitsch. angew. Chem.*, 1910, 23, 2315.

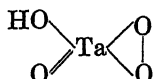
<sup>2</sup> Jander and Schulz, *loc. cit.*

<sup>3</sup> Russ, *Zeitsch. anorg. Chem.*, 1902, 31, 90.

<sup>4</sup> Weiss and Landecker, *ibid.*, 1909, 64, 70; *Chem. News*, 1910, 101, 26; Powell and Schoeller, *Analyst*, 1925, 50, 485.

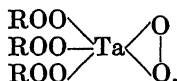
PERTANTALIC ACID AND THE PERTANTALATES.

**Pertantalic Acid**,  $\text{HTaO}_4 \cdot x\text{H}_2\text{O}$ , is the analogue of perniobic acid and pervanadic acid. It differs from them in its greater stability. Pervanadic acid is a yellow substance which is rapidly decomposed on being warmed; pertantalic acid is a white solid which can be heated for some time at  $100^\circ \text{C}$ . without undergoing decomposition. (This behaviour is remarkable in a per-acid.) Pertantalic acid is prepared similarly to perniobic acid, using dilute sulphuric acid and the potassium perniobate,  $\text{K}_3\text{TaO}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$ . Analysis shows that it contains one atom of active oxygen for each tantalum atom, and the following constitutional formula has been assigned to it:



It is not attacked by dilute sulphuric acid in the cold, but on warming the mixture hydrogen peroxide is formed. Pervanadic acid, on the other hand, is decomposed by cold dilute sulphuric acid. Perniobic acid occupies an intermediate position in the order of stability.<sup>1</sup>

Pertantalates are prepared by the action of excess of hydrogen peroxide on solutions of the 4 : 3 alkali tantalates; addition of alcohol precipitates them as white, crystalline compounds which yield hydrogen peroxide with warm dilute sulphuric acid and ozonised oxygen with concentrated sulphuric acid. On being boiled with water they evolve oxygen. Their composition usually corresponds to the formula  $\text{R}_3\text{TaO}_8 \cdot x\text{H}_2\text{O}$ ; they contain four atoms of active oxygen for each tantalum atom, and the following constitutional formula has been assigned to them:



The following are known in this series:<sup>2</sup>

$\text{Na}_3\text{TaO}_8 \cdot \text{H}_2\text{O}$	.	.	.	A white, amorphous powder.
$\text{Na}_3\text{TaO}_8 \cdot 14\text{H}_2\text{O}$	.	.	.	Pale yellow crystals.
$\text{K}_3\text{TaO}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$	.	.	.	A white, crystalline mass.
$\text{Rb}_3\text{TaO}_8$	.	.	.	Do. do. do.
$\text{Cs}_3\text{TaO}_8$	.	.	.	Do. do. do.

also the following double salts:<sup>3</sup>  $\text{KCaTaO}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ ;  $\text{KMgTaO}_8 \cdot 7\text{H}_2\text{O}$ ;  $\text{NaCaTaO}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ ;  $\text{NaMgTaO}_8 \cdot 8\text{H}_2\text{O}$ ;  $\text{RbMgTaO}_8 \cdot 9\text{H}_2\text{O}$ .

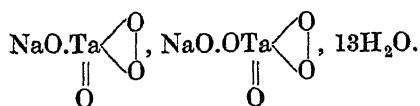
In addition to the above, a sodium pertantalate of the composition  $\text{Na}_2\text{Ta}_2\text{O}_9 \cdot 13\text{H}_2\text{O}$  has been prepared by treating an aqueous extract of the residue which is obtained when a solution of 4 : 3 sodium tantalate is evaporated to dryness with a few drops of hydrogen peroxide and then adding a little alcohol. A white, amorphous powder of the composition indicated is thrown down. It yields hydrogen peroxide with dilute sulphuric acid. The ratio  $\text{Na}_2\text{O} : \text{Ta}_2\text{O}_5 : \text{active oxygen}$  is 1 : 1 : 3,

<sup>1</sup> Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.*, 1899, 20, 344; Sieverts and Müller, *ibid.*, 1928, 173, 297.

<sup>2</sup> Melikoff and Pissarjewsky, *loc. cit.*; Balke, *J. Amer. Chem. Soc.*, 1905, 27, 1140.

<sup>3</sup> Balke and Smith, *ibid.*, 1908, 30, 1668.

and when the salt is treated with freshly precipitated aluminium hydroxide, two-thirds of the active oxygen is retained by the precipitate, the other third passing into the filtrate. These figures agree with the constitutional formula



This sodium pertantalate, therefore, appears to be a double salt,  $\text{NaTaO}_4 \cdot \text{NaO} \cdot \text{TaO}_4 \cdot 13\text{H}_2\text{O}$ .

**Tantalum Peroxyfluorides** or *Fluoroxypertantalates*.—The alkali tantalum oxyfluorides also have the property of taking up oxygen by reaction with hydrogen peroxide.

When potassium tantalum fluoride is dissolved in 4 per cent. hydrogen peroxide solution which contains a small amount of hydrofluoric acid, crystals of potassium tantalum peroxyfluoride,  $2\text{KF} \cdot \text{TaO}_2\text{F}_3 \cdot \text{H}_2\text{O}$ , are obtained. This is a remarkably stable substance; it loses water at  $100^\circ \text{C}$ . and oxygen only at higher temperatures. With concentrated hydrofluoric acid it yields hydrogen peroxide.<sup>1</sup> The corresponding rubidium salt,  $2\text{RbF} \cdot \text{TaO}_2\text{F}_3 \cdot \text{H}_2\text{O}$ , is prepared similarly.<sup>2</sup>

#### TANTALUM AND SULPHUR.

Only one sulphide of tantalum, namely, the disulphide,  $\text{TaS}_2$ , is known, and this is prepared by a dry method. Hydrogen sulphide does not precipitate any sulphides when passed into a solution of a tantalate, nor does reduction take place; it is without appreciable action on tantalum pentoxide even at  $1200^\circ \text{C}$ .<sup>3</sup>

**Tantalum Disulphide** is most conveniently prepared by passing a dry mixture of hydrogen sulphide and carbon disulphide vapour over tantalum pentoxide between  $900^\circ$  and  $1300^\circ \text{C}$ .<sup>4</sup> It has also been obtained by the action of carbon disulphide on tantalum pentoxide at a white heat,<sup>5</sup> by the action of hydrogen sulphide on tantalum pentachloride, or by gently heating tantalum in sulphur vapour,<sup>6</sup> but the true composition of the products in these cases is somewhat uncertain. Tantalum disulphide is a black powder with a metallic lustre; when heated above  $1200^\circ \text{C}$ . it forms yellowish crystals. It burns in air or oxygen with evolution of sulphur dioxide; the tantalum pentoxide simultaneously produced contains sulphuric anhydride. Hydrogen attacks it only feebly; chlorine does so more readily. It takes up traces of water, which it retains very firmly; at high temperatures the absorbed water reacts to form hydrogen sulphide and tantalum oxides. Concentrated solutions of potassium polysulphides and boiling hydrochloric acid are without action; it is slowly attacked by cold nitric acid, hydrofluoric acid, sulphuric acid, or a mixture of nitric acid and hydrofluoric acid; boiling nitric acid and aqua-regia oxidise it completely to tantalum pentoxide and sulphuric acid.

<sup>1</sup> Piccini, *Zeitsch. anorg. Chem.*, 1892, 2, 24; Balke, *J. Amer. Chem. Soc.*, 1905, 27, 1140.

<sup>2</sup> Balke and Smith, *ibid.*, 1908, 30, 1666.

<sup>3</sup> Biltz and Kircher, *Ber.*, 1910, 43, 1636.

<sup>4</sup> Biltz and Kircher, *loc. cit.*

<sup>5</sup> Rose, *Pogg. Annalen*, 1856, 99, 575.

<sup>6</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 45.



*Sulphates.*—No sulphates of tantalum have been definitely prepared. A fused mass of tantalum pentoxide and potassium hydrogen sulphate after extraction with boiling water is crystalline and contains the sulphate radical, and it has been assumed that a sulphate of tantalum is present. After drying at 100° C. the product in one case<sup>1</sup> had the composition  $3\text{Ta}_2\text{O}_5 \cdot \text{SO}_3 \cdot 9\text{H}_2\text{O}$ , but this was most probably the hydrolytic decomposition product of an unstable sulphate present in the melt or in solution.<sup>2</sup>

A chlorosulphatotantalum acid,  $\text{H}_2[\text{Ta}_3\text{Cl}_6 \cdot \text{SO}_4] \cdot \text{H}_2\text{O}$ , is referred to on p. 198.

#### TANTALUM AND NITROGEN.

Tantalum reacts slowly with nitrogen when heated in the gas; combination commences at about 900° C. One gram of tantalum wire absorbed 2.2 cc. of nitrogen in one hour between 920° and 1030° C.,<sup>3</sup> and this was not expelled by heating *in vacuo*. In an earlier investigation<sup>4</sup> thirty-one hours' exposure at 1000° C. gave an absorption equal to 17.3 per cent. of the weight of tantalum.

**Tantalum Mononitride**,  $\text{TaN}$ , has been prepared by heating the metal first in hydrogen and then in nitrogen,<sup>5</sup> or by the action of hydrogen and nitrogen on tantalum pentachloride vapour.<sup>6</sup> It is a dark blue or black substance which melts at 3070° abs. with some loss of nitrogen. Its dissociation pressures have been studied.<sup>7</sup> Density = 14.1. Direct heating of tantalum in nitrogen has also given rise to a black *dinitride*,  $\text{Ta}_2\text{N}_3$ , which is not attacked by concentrated hydrochloric, nitric or sulphuric acids. It evolves ammonia when fused with caustic alkalis, and burns with incandescence to the pentoxide when heated in air.<sup>8</sup>

**Tritantalum Pentanitride**,  $\text{Ta}_3\text{N}_5$ , has been obtained as a bright red, amorphous powder by passing ammonia over heated tantalum pentachloride. On being heated in air it forms the pentoxide, and when fused with caustic potash it evolves ammonia.<sup>9</sup>

Nitrides of doubtful composition are also formed by the action of ammonia<sup>10</sup> or cyanogen<sup>11</sup> on the heated pentoxide. Fusion of a mixture of tantalum pentoxide and carbon in excess of sodium carbonate under ordinary conditions also gives rise to a tantalum-nitrogen product.<sup>12</sup>

#### TANTALUM AND CARBON.

Reduction of tantalum pentoxide with carbon in the electric furnace yields carbides or alloys of variable composition.<sup>13</sup> Traces of carbon

<sup>1</sup> Hermann, *J. prakt. Chem.*, 1857, 70, 201.

<sup>2</sup> Compare Sears, *J. Amer. Chem. Soc.*, 1926, 48, 346.

<sup>3</sup> Sieverts and Bergner, *Ber.*, 1911, 44, 2395.

<sup>4</sup> Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 92.

<sup>5</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 143, 293; Becker and Ebert, *Zeitsch. Physik*, 1925, 31, 271.

<sup>6</sup> Van Arkel and de Boer, *Zeitsch. anorg. Chem.*, 1925, 148, 348; see also Joly, *Bull. Soc. chim.*, 1876, [ii], 25, 506; *Chem. News*, 1876, 33, 251; *Annales Scientifiques de l'École Normale Supérieure*, Paris, 1877, 149.

<sup>7</sup> Slade and Higson, *J. Chem. Soc.*, 1919, 115, 216.

<sup>8</sup> Muthmann, Weiss, and Riedelbauch, *loc. cit.*

<sup>9</sup> Joly, *loc. cit.*; see also Rose, *Pogg. Annalen*, 1857, 100, 146; 1859, 106, 141.

<sup>10</sup> Rose, *ibid.*, 1856, 99, 66; 1844, 63, 317; 1846, 69, 115.

<sup>11</sup> Rose, *ibid.*, 1857, 100, 146.

<sup>12</sup> Friederich and Sittig, *loc. cit.*

<sup>13</sup> Compare Ruff, Seiferheld, and Suda, *Zeitsch. anorg. Chem.*, 1913, 82, 397.

render tantalum hard without affecting its ductility ; when the carbon content exceeds 1 per cent. the product is extremely hard but brittle ; tantalum containing 0.5 per cent. of carbon can, however, be drawn into wire 0.1 mm. diameter.<sup>1</sup>

**Tantalum Carbide, TaC**, has been prepared by heating a mixture of tantalum pentoxide and carbon in a molybdenum boat at 1250° C. in a stream of hydrogen,<sup>2</sup> or by the action of hydrogen and carbon monoxide on tantalum pentachloride.<sup>3</sup> It is a dark grey or black substance which is insoluble in all acids, and burns to the pentoxide when powdered and heated in air. Density=13.96. It melts with decomposition at 4100° abs., which is probably the highest melting-point yet recorded for a chemical compound. Its hardness coefficient lies between 9 and 10. It is a good conductor of electricity.<sup>4</sup> For its crystal structure see reference cited.<sup>5</sup>

<sup>1</sup> von Bolton, *Zeitsch. Elektrochem.*, 1905, 11, 47.

<sup>2</sup> Friederich and Sittig, *Zeitsch. anorg. Chem.*, 1925, 144, 174.

<sup>3</sup> Van Arkel and de Boer, *ibid.*, 1925, 148, 348.

<sup>4</sup> Friederich, *Zeitsch. Physik*, 1925, 31, 813.

<sup>5</sup> Becker and Ebert, *ibid.*, 1925, 31, 269.

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