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

A TEXT-BOOK OF
INORGANIC CHEMISTRY.

Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.

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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.
			1 H 1·0081							
rst short period .		2 He 4·003	3 Li 6·940	4 Be 9·02	5 B 10·82	6 C 12·010	7 N 14·008	8 O 16·000	9 F 19·00	
cond short period .		10 Ne 20·183	11 Na 22·997	12 Mg 24·32	13 Al 26·97	14 Si 28·06	15 P 31·02	16 S 32·06	17 Cl 35·457	
rst long period	Even series .	18 A 39·944	19 K 39·096	20 Ca 40·08	21 Sc 45·10	22 Ti 47·90	23 V 50·95	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84 27 Co 58·94 28 Ni 58·69
	Odd ,,		29 Cu 63·57	30 Zn 65·38	31 Ga 69·72	32 Ge 72·60	33 As 74·91	34 Se 78·96	35 Br 79·916	
cond long period	Even series .	36 Kr 83·7	37 Rb 85·48	38 Sr 87·63	39 Y 88·92	40 Zr 91·22	41 Nb 92·91	42 Mo 95·95	43 Ma ...	44 Ru 101·7 45 Rh 102·91 46 Pd 106·7
	Odd ,, .		47 Ag 107·880	48 Cd 112·41	49 In 114·76	50 Sn 118·70	51 Sb 121·76	52 Te 127·61	53 I 126·92	
ird long period .		54 Xe 131·3	55 Cs 132·91	56 Ba 137·36	57 La 138·92	58 Ce 140·13 59 Pr 140·92	60 Nd 144·27 61 Il ...	62 Sm 150·43 63 Eu 152·0	64 Gd 156·9 65 Tb 159·2	
urth long period .			66 Dy 162·46 67 Ho 163·5	68 Er 167·2 69 Tm 169·4	70 Yb 173·04 71 Lu 175·0	72 Hf 178·6	73 Ta 180·88	74 W 183·92	75 Re 186·31	76 Os 190·2 77 Ir 193·1 78 Pt 195·23
fth long period	Even series .		79 Au 197·2	80 Hg 200·61	81 Tl 204·39	82 Pb 207·21	83 Bi 209·00	84 Po [210]	85 ..	
	Odd ,, .	86 Rn 222	87 ...	88 Ra 226·05	89 Ac ...	90 Th 232·12	91 Pa 231	92 U 238·07		

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* The Revised Atomic Weights for 1938 are adopted in this Table as given by the International Union of Chemistry in their Eighth Report.

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J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
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ARSENIC.

BY
REECE H. VALLANCE, M.Sc., F.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 original scheme, in addition to a detailed account of the elements of Group O, the general principles of Inorganic and Physical Chemistry were discussed in Volume I. It was later felt, however, that this arrangement was hardly satisfactory, and an Introduction to these principles is now afforded by my Text-book of Physical Chemistry, Volumes I. and II. (1932–35), whilst in future editions the first volume of this Series will deal with the Inert Gases alone.

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 under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferrocyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals 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 fundamental values given in the text.

Since the original scheme was drawn up in 1912, enormous progress has been made in all branches of chemistry, and the original intention of devoting one book only to each Vertical Group in the Periodic Table has had to be abandoned. In several cases it has been necessary to devote a whole book to a single element, as, for example, in the cases of nitrogen, phosphorus, arsenic, oxygen and iron. Further, a separate volume has been devoted to the Metal-Ammines and a comprehensive account of the Organometallic Derivatives is given in Volume XI., which is issued in four parts.

The Editor would draw attention to the unsatisfactory state of the nomenclature of organometallic compounds in general. The designations of compounds in Volume XI. are those used in the original memoirs, since any attempt to alter these in a work of that description would only complicate matters.

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. xvii–xx.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi–xxxi) 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.

Addendum.

With the publication of this volume the original scheme for this series of text-books is now complete. This does not, however, mean stagnation. Far from it! As our knowledge of each section of the work grows, the appropriate volumes will be revised and, if necessary, re-written, in order that the reader may be kept up to date. Where the amount of new work justifies it, a separate book will be devoted to each element, as has already been the case with Nitrogen, Phosphorus, Arsenic, Oxygen and Iron, respectively. Indeed, this revision has already begun.

J. NEWTON FRIEND.

July 1938.

PREFACE.

In this volume the chemistry of arsenic and its inorganic compounds is presented in a manner which, it is hoped, will make clear the present state of our knowledge of the element.

Some of the arsenic compounds have attracted the attention of chemists from the earliest times. The sulphides were known and used in ancient Egypt. White arsenic was recognised early in the Middle Ages and put to uses both good and evil. The element itself was isolated as early as the thirteenth century. In the eighteenth century some scientific understanding of the nature of these materials was gained, and the enormous volume of relevant literature which has appeared during the succeeding two hundred years bears witness to the attractiveness of arsenicals as a subject for research.

The ubiquity of arsenic compounds, disseminated in small quantities both in minerals and in the organic world, has long been recognised. In recent years, so much white arsenic has been isolated as a by-product during the extraction of gold, silver, copper and other metals, that a curious situation has arisen, in that the supplies available considerably exceed the present world requirements. Thus it behoves the chemist to find new directions in which arsenicals may usefully be employed. That some success has already been attained is indicated in these pages. At present the most important application is the widespread use of arsenates in insecticidal dusts and sprays, which are employed to combat the pests which attack fruit and crops of all kinds. The many organic arsenicals which are of therapeutic value are described in another volume of this series.

Arsenious sulphide has been the subject of extensive researches owing to the fact that it may readily be obtained as a hydrosol of considerable stability. Investigation of the factors which influence this stability has greatly added to our knowledge of colloid chemistry.

The Author wishes to acknowledge gratefully the help he has received from the Editor of the series, Dr. J. Newton Friend, and to thank Mr. W. E. Thorneycroft, B.Sc., for useful criticism of the proofs.

REECE H. VALLANCE.

July 1938.

CONTENTS.

PLATE.

F CHIEF JOURNALS CONSULTED AND REVIATIONS EMPLOYED IN THE REFERES.

TED TITLE.	JOURNAL.
Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
	American Chemical Journal.
	American Journal of Science.
	American Mineralogist.
n.	Anales de la Sociedad Española Fisica y Quimica.
	The Analyst.
	Angewandte Chemie. Before 1932 issued as *Zeitsch. angew. Chem.* (*q.v.*).
	Justus Liebig's Annalen der Chemie.
	Annales de Chimie (1719–1815, and 1914 +).
al.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
ys.	Annales de Chimie et de Physique (Paris) (1816–1913).
	Annales des Falsifications.
	Annales des Mines.
	Annalen der Pharmacie (1832–1839).
em.	Annalen der Physik und Chemie (1819–1899).
	Annalen der Physik (1799–1818, and 1900 +).
Beibl.	Annalen der Physik, Beiblattes.
. Jassy	Annales scientifiques de l'Université de Jassy.
ppl.	Annali di Chimica applicata.
l. Gesundheits-	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
ol. Pharmak.	Archiv fur experimentelle Pathologie und Pharmakologie.
ath. Gewerbe-	Archiv fur Gewerbepathologie und Gewerbehygiene.
	Archiv der Pharmazie.
. nat.	Archives des Sciences physique et naturelles, Genève.
	Astrophysical Journal.
o	Atti della Reale Accademia delle Scienze di Torino.
Lincei	Atti della Reale Accademia Lincei.
	British Association Reports.
	Berichte der Deutschen chemischen Gesellschaft.
	See *Sitzungsber. K. Akad. Wiss. Berlin.*
m. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
ikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
h.	Biochemische Zeitschrift.
rm.	Bollettino Chimico-Farmaceutico.
	Botanische Zeitung.
e Cluj.	Buletinul Societâtei de Stiinte din Cluj.
. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
. Japan	Bulletin of the Chemical Society of Japan.
	Bulletin de la Société chimique Belgique.
tchèq.	Bulletin international de l'Académie tchèque des Sciences.
macol.	Bulletin des Sciences pharmacologiques.
	Bulletin de la Société chimique de France.

Abbreviated Title.	Journal.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. chim. roy. Yougoslavie	Bulletin de la Société chimique royale de Yougoslavie.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt fur Mineralogie.
Chem. and Ind.	Chemistry and Industry.
Chem. Ind.	Chemische Industrie.
Chem. Listy	Chemické Listy (Prague).
Chem. News	Chemical News. Publication ceased in 1932.
Chem. Obzor	Chemické Obzor (Prague).
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Chem. Zentr.	Chemisches Zentralblatt.
Chim. et Ind.	Chimie et Industrie.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Con. Met. Chem. Eng.	Continental Metallurgical and Chemical Engineering (Berlin).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dansk. Tids. Farm.	Dansk Tidsskrift for Farmaci.
Dingl. poly. J.	Dingler's polytechnisches Journal. Publication ceased in 1931.
Drude's Annalen	Annalen der Physik (1900–1906).
Electroch. Met. Ind.	Electrochemical and Metallurgical Industry.
Eng. and Min. J.	Engineering and Mining Journal.
Ergeb. exakt. Naturw.	Ergebnisse der exackten Wissenschaften.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Geol. Mag.	Geological Magazine.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Helv. Chim. Acta	Helvetica Chimica Acta.
Ind. Chem.	The Industrial Chemist.
Ind. Eng. Chem.	Industrial and Engineering Chemistry. Before 192 issued as *J. Ind. Eng. Chem.* (*q.v.*).
Ind. Eng. Chem. (*Anal.*)	*Ibid.*, Analytical Section. First issued in 1929. On volume annually.
Int. Zeitsch. Metallographie	Internationale Zeitschrift fur Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-koniglichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch fur Mineralogie.
Jahresber.	Jahresbericht uber die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift fur Naturwissenschaft.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Appl. Chem. (*U.S.S.R.*)	Journal of Applied Chemistry, U.S.S.R.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Education	Journal of Chemical Education, U.S.A.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Econ. Entomol.	Journal of Economic Entomology.
J. Franklin Inst.	Journal of the Franklin Institute, U.S.A.
J. Gasbeleuchtung	Journal fur Gasbeleuchtung.
J. Gen. Chem. (*U.S.S.R.*)	Journal of General Chemistry, U.S.S.R. Before 193 issued as *J. Russ. Phys. Chem. Soc.* (*q.v.*).
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry. In an after 1923 issued as Industrial and Engineerin Chemistry.
J. Indian Chem. Soc.	Journal of the Indian Chemical Society.

Abbreviated Title.	Journal.
J. Inst. Metals.	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Radium	Journal de Physique et de Radium.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physical Chem. (U.S.S.R.)	Journal of Physical Chemistry, U.S.S.R. Before 1931 issued as *J. Russ. Phys. Chem. Soc. (q.v.)*.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal fur praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*). In 1931 continued as two separate journals, namely, J. General Chemistry, U.S.S.R., and J. Physical Chemistry, U.S.S.R.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Tech. Phys. (U.S.S.R.)	Journal of Technical Physics, U.S.S.R.
Kolloid-Zeitsch.	Kolloid-Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Mem. Coll. Sci. Kyōtō.	Memoirs of the College of Science, Kyōtō Imperial University.
Mém. Paris Acad.	Mémoirs présentés par divers savants à l'Académie des Sciences de l'Institut de France.
Mikrochem.	Mikrochemie.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. scient.	Moniteur scientifique. Combined in 1927 with La Revue de Chimie industrielle.
Münch. Med. Wochenschr.	Munchener Medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Gottingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Nuovo Cim.	Il nuovo Cimento.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Öfvers. K. Vet.-Akad. Förh.	Öfversigt af Kongliga Vetenskaps-Akademiens Forhandlingar.
Pflüger's Archiv	Archiv fur die gesammte Physiologie des Menschen und der Thiere.
Pharm. Post	Pharmazeutische Post.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824–1877).
Proc. Amer. Acad. Arts. Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Sciences.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil. Soc. Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Soc. Expt. Biol.	Proceedings of the Society for Experimental Biology and Medicine.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Revue Chim. ind.	La Revue de Chimie industrielle. See *Mon. scient.*
Rocz. Chem.	Roczniki Chemji (Warsaw).
Roy. Inst. Reports	Reports of the Royal Institution.

ABBREVIATED TITLE.	JOURNAL.
Schweigger's J.	Journal für Chemie und Physik.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
Svensk Kem. Tidsk.	Svensk Kemisk Tidskrift.
Techn. Jahresber.	Jahresbericht über die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Farad. Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mém. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau international des Poids et Mesures.
Ukrain. Chem. J.	Ukranian Chemical Journal.
U.S. Bur. Stand. Res. J.	United States Bureau of Standards Research Journal.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie (1877–1899). In 1900 continued as Annalen der Physik.
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie. Since 1932 issued as Angewandte Chemie (*q.v.*).
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift für Chemie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie des Kolloide (continued in Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie. After 1920 issued as Zeitschrift für Kristallographie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. Physik.	Zeitschrift für Physik.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. techn. Phys.	Zeitschrift für technische Physik.
Zeitsch. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Zeitsch. Ver. deut. Ing.	Zeitschrift des Vereins deutscher Ingenieure.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik, 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	13, 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.
1830	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	(3) 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	...	14, 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	4–6	(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	...	24, 25	134	61–63	...	...	...
1845	48–50	53–56	13–15	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	...	1	
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, 2	1
49	7, 8	69–72	25–27	15, 16	57–60	...	28, 29	111–114	15, 16	46–48	...	34, 35	139	76–78	...	2, 3	2, 3
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	4	6, 7
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	...	5	8, 9
53	15, 16	85–88	37–39	3, 4	73–76	...	36, 37	127–130	23, 24	58–60	...	5, 6	143	88–90	...	6	10, 11
54	17, 18	89–92	40–42	5, 6	77–80	...	38, 39	131–134	25, 26	61–63	...	7, 8	144	91–93	6, 7	7	12–14
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	15–18
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	19–22
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	23–27
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	28–33
59	27, 28	109–112	55–57	15, 16	97–100	1	48, 49	151–154	35, 36	76–78	3	17, 18	149	106–108	9, 10	12	34–38

* 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	...	3, 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	1	9, 10	17, 18	...	...
69	...	47, 48	...	149–152		16–18	15, 16	137–140	2	11, 12	19, 20	...	...
1870	...	49, 50	...	153–156	7	19–21	17, 18	141–144	3	13, 14	21, 22	...	...
71	...	(3) 1, 2	...	157–160	...	22–24	19, 20	145–148	4	15, 16	23, 24	...	...
72	...	3, 4	...	161–164	8	25–27	(7) 1, 2	149–150, 201*	5	17, 18	25, 26	...	...
73	...	5, 6	...	165–170	...	28–30	3, 4	201–203	6	19, 20	27, 28	...	...
74	...	7, 8	...	171–174	...	(5) 1–3	5, 6	204, 205	7	21, 22	29, 30	...	...
1875	...	9, 10	...	175–179	...	4–6	7, 8	206, 207	8	23, 24	31, 32	...	...
76	...	11, 12	1	180–183	...	7–9	9, 10	208, 209	9	25, 26	33, 34	...	...
77	...	13, 14	2	184–189	...	10–12	11, 12	210, 211	10	27, 28	35, 36	...	1
78	...	15, 16	3	190–194	...	13–15	13, 14	212, 213	11	29, 30	37, 38	...	2
79	1	17, 18	4	195–199	...	16–18	15, 16	214, 215	12	31, 32	39, 40	...	3
1880	1, 2	19, 20	5	200–205	...	19–21	17, 18	216, 217	13	33, 34	41, 42	...	4
81	2, 3	21, 22	6	206–210	...	22–24	19, 20	218, 219	14	35, 36	43, 44	...	5
82	3, 4	23, 24	7	211–215	...	25–27	(8) 1, 2	220	15	37, 38	45, 46	...	6
83	4, 5	25, 26	8	216–221	...	28–30	3, 4	221	16	39, 40	47, 48	...	7
84	5, 6	27, 28	9	222–226	...	(6) 1–3	5, 6	222	17	41, 42	49, 50	...	8
1885	6, 7	29, 30	10	227–231	...	4–6	7, 8	223	18	43, 44	51, 52	...	9
86	7, 8	31, 32	11	232–236	...	7–9	9, 10	224	19	45, 46	53, 54	...	10
87	9	33, 34	12	237–242	...	10–12	11, 12	225	20	47, 48	55, 56	1	11
88	10	35, 36	13	243–249	...	13–15	13, 14	226	21	49, 50	57, 58	2, 3	12
89	11	37, 38	14	250–255	...	16–18	15, 16	227	22	(3) 1, 2	59, 60	4, 5	13

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

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

* See footnote, p. xxii.

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	13	..	39–42	...	...	...	...	...	...
61	151	112–114	...	11	14	...	43, 44	...	...	...	...	...	...
62	152	115–117	...	11, 12	Continued as J. Chem. Soc.	...	45, 46	...	...	1	...	...	...
63	153	118–120	...	12, 13		...	47, 48	...	...	2	...	...	...
64	154	121–123	...	13		...	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	...	1, 2	16	...	1, 2	...
78	168, 169	Continued as Wied. Annalen.	...	27, 28	...	...	77, 78	...	3–5	17	...	2, 3	...
79	170		...	28, 29, 30	.	...	79, 80	...	6–8	18	...	3, 4	...
1880	171	...	...	30, 31	...	...	81, 82	...	9–11	19	...	4, 5	...
81	172	...	...	31, 32, 33	...	...	83, 84	1	12–14	20	...	5, 6	...
82	173	..	...	33, 34		1	85, 86	2	15–17	21	...	6, 7	...
83	174	...	...	34, 35, 36	...	2	87, 88	3	18–20	22	...	7, 8	...
84	175		...	36, 37, 38	...	3	89, 90	4	21–23	23	...	8, 9, 10	..
1885	176	...	1	38, 39	...	4	91, 92	5	24–26	24	...	10, 11	...
86	177	...	2	40, 41	...	5	93, 94	6	27–29	25	...	11, 12	...
87	A. 178	...	3	42, 43	..	6	95, 96	7	30–32	26	...	12, 13	1
88	179	...	4	43, 44, 45	...	7	97	8	33–35	27	1	13, 14, 15	2
89	180	..	5	45, 46, 47	...	8	98	9	36–38	28	2	15	3, 4

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. Week-blad.	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	3, 4	22	294–298	10–12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299–303	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	310–313	19–21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
1	25, 26	11, 12	26	314–319	22–24	19, 20	239	34	25, 26	83, 84	28, 29	...	25	132, 133
2	27, 28	13, 14	27	320–325	25–27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	...	26	134, 135
3	29, 30	15, 16	28	326–329	28–30	3, 4	241	36	29, 30	87, 88	32, 33	...	27	136, 137
4	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
6	35, 36	21. 22	31	344–350	7–9	9, 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
7	37, 38	23, 24	32	351–357	10–12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	4	31	144, 145
8	39, 40	25, 26	33	358–363	13–15	13, 14	246	41	3, 4	97, 98	42, 43	5	32	146, 147
9	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	25–27	(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
14	Publication ceased	37, 38	39	402–406	(9) 1, 2*	5, 6	252	47	15, 16	109, 110	54, 55	11	38	158, 159
1915		39, 40	40	407–410	3, 4		253	48	17, 18	111, 112	56, 57	12	39	160, 161
16	...	41, 42	41	411–413	5, 6	No Issue	254	49	19, 20	113, 114	58, 59	13	40	162, 163
17	...	43, 44	42	413	7, 8		255	50	21, 22	115, 116	60, 61	14	41	164, 165
18	...	45, 46	43	414–417	9, 10		256	51	23, 24	117	62, 63	15	42	166, 167
19	..	47, 48	44	418–419	11, 12	7, 8	257	52	25, 26	118, 119	64, 65	16	43	168, 169

* Issued in 1914 as Annales de Chimie and Annales de Physique in separate volumes but with identical numbering.

Year.	Dingl. poly J.	Gazzetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc	J. Soc. Chem. Ind.	Monatsh.	Mon. scient.*	Nature.	Phil. Mag.
1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41–43	29, 30
91	279–282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43–45	31, 32
92	283–286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45–47	33, 34
93	287–290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47–49	35, 36
94	291–294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49–51	37, 38
1895	295–298	25	17	67, 68		(6) 1, 2	...	51, 52	27	14	16	45, 46	51–53	39, 40
96	299–302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53–55	41, 42
97	303–306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55–57	43, 44
98	307–310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57–59	45, 46
99	311–314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59–61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61–63	49, 50
1	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63–65	(6) 1, 2
2	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65–67	3, 4
3	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67–69	5, 6
4	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69–71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71–73	9, 10
6	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73–75	11, 12
7	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75–77	13, 14
8	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77–79	15, 16
9	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	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88–90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90–92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89 90	46	33	35	80, 81	92–94	27, 28
1915	330	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94–96	29, 30
16	331	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96–98	31, 32
17	332	47	39	111, 112	9	15, 16	21	95, 96	49	36	38	84	98–100	33, 34
18	333	48	40	113, 114	10	17, 18	22	97, 98	50	37	39	85	100–102	35, 36
19	334	49	41	115, 116	11	19, 20	23	99	51	38	40	86	102–104	37, 38

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* See footnote, p. xxii.

Year.	Phil. Trans.	Physical Review.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	...	6	47–49	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	183	...	..	8	50–52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	...	...	9	52–54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	..	..	10	55–57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	...	..	11	57–59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	...	...	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	...	...	13	60–62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	...	14	62–64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	...	15	64–66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	..	1	16	66, 67	19	109	20	Con- tinued as Annalen der Physik.	39	13	22–25	6, 7	32–34	32–35
1	196, 197	...	2	17	68, 69	20	110	21		40	14	26–29	7	34–36	36–38
2	198, 199	...	3	18	69, 70	21	111	22		41	15	29–33	8	36, 37	39–42
3	200–202	.	4	19	71, 72	22	112	23		42	16	33–37	9	37–39	43–46
4	203	...	5	20	72–74	23	113	24		43	17	38–42	10	39, 40	47–49
1905	204, 205	...	6	21	74, 75, A 76	24	114	25		44	18	43–48	11	40–42	50–53
6	206	...	7	22	77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
7	207	...	8	23	78–80	26	116	27		46	20	52–56	13	43, 44	58–60
8	207–209	..	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
9	209, 210	...	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
910	210	...	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	...	12	27	84–86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	...	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
13	212, 213	1, 2	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	3, 4	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
915	215, 216	5, 6	16	Publication of matter of scientific interest now abandoned.	91	34	124	35		54	28	90–93	21	55	89, 90
16	216, 217	7, 8	17		92	35	125	36		55	29	94–98	22	55	91, 92
17	217	9, 10	18		93, 94	36, 37	126	37		56	30	99–101	23	55	92
18	217	11, 12	19		94, 95	37	127	38		57	31	102–104	24	55	92
19	218, 219	13, 14	20		95, 96	38	128	39		58	32	105–109	25	55*	93

* Remainder of vol. 55 appeared in 1920. The Journal was afterwards continued as Zeitschrift fur Kristallographie.

Year.	Amer. J. Sci.	Analyst.	Angew. Chem.	Annalen.	Annales de Chimie.	Annales de Physique.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Weekblad.	Chem. Zeit.
1920	49, 50	45	...	420–421	(9) 13, 14	(9) 13, 14	9, 10	258	53	27, 28	120, 121	66, 67	17	44
21	(5) 1, 2	46	...	422–425	15, 16	15, 16	11, 12	259	54	29, 30	122, 123	68, 69	18	45
22	3, 4	47	...	426–429	17, 18	17, 18	(12) 1, 2	260	55	31, 32	124, 125	70, 71	19	46
23	5, 6	48	...	430–435	19, 20	19, 20	3, 4	261	56	33, 34	126, 127	72, 73	20	47
24	7, 8	49	...	436–440	(10) 1, 2	(10) 1, 2	5, 6	262	57	35, 36	128, 129	74, 75	21	48
1925	9, 10	50	Previously Zeitsch. angew. Chem. (*q.v.*)	441–445	3, 4	3, 4	7, 8	263	58	37, 38	130, 131	76, 77	22	49
26	11, 12	51		446–451	5, 6	5, 6	9, 10	264	59	39, 40	132, 133	78, 79	23	50
27	13, 14	52		452–459	7, 8	7, 8	11, 12	265	60	41, 42	134, 135	80, 81	24	51
28	15, 16	53		460–467	9, 10	9, 10	13, 14	266	61	43, 44	136, 137	82, 83	25	52
29	17, 18	54		468–477	11, 12	11, 12	15, 16	267	62	45, 46	138, 139	84, 85	26	53
1930	19, 20	55	...	478–484	13, 14	13, 14	17, 18	268	63	47, 48	140, 141	86, 87	27	54
31	21, 22	56	...	485–491	15, 16	15, 16	19, 20	269	64	49, 50	142, 143	88, 89	28	55
32	23, 24	57	45	492–499	17, 18	17, 18	(13) 1, 2	270	65	51, 52	144, 145	90, 91	29	56
33	25, 26	58	46	500–507	19, 20	19, 20	3, 4	271	66	53, 54	Publication ceased.	92, 93	30	57
34	27, 28	59	47	508–515	(11) 1, 2	(11) 1, 2	5, 6	272	67	(5) 1 *		94, 95	31	58
1935	29, 30	60	48	516–521	3, 4	3, 4	7, 8	273	68	2	...	96, 97	32	59
36	31, 32	61	49	522–525	5, 6	5, 6	9, 10	274	69	3	...	98, 99	33	60
37	33, 34	62	50	526–533	7, 8	7, 8	11, 12	275	70	4	...	100, 101	34	61
38	35, 36	63	51	534	9, 10	9, 10	...	276	71	5	...	102, 103	35	62

* Abstracts now issued separately and entitled "Documentation" with no volume numbers.

Year.	Compt. rend.	Dingl. poly. J.	Gazzetta.	Ind. Eng. Chem.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon. Scient.
1920	170, 171	335	50	Previously J. Ind. Eng. Chem.	42	117, 118	12	21, 22	24	100, 101	52	39	41	87
21	172, 173	336	51		43	119, 120	13	23, 24	25	101–103	53	40	42	88
22	174, 175	337	52		44	121, 122	14	25, 26	26	103–105	54	41	43	89
23	176, 177	338	53	15	45	123, 124	Continued as Ind. Eng. Chem. (*q.v.*).	27, 28	27	105, 106	54	42	44	90
24	178, 179	339	54	16	46	125, 126		29, 30	28	107, 108	54, 55	43	45	91
1925	180, 181	340	55	17	47	127, 128		(8) 1, 2	29	109–111	55	44	46	92
26	182, 183	341	56	18	48	Numbering of volumes now ceased.		3, 4	30	112–114	55–58	45	47	93
27	184, 185	342	57	19	49			5, 6	31	115–117	59	46	48	...
28	186, 187	343	58	20	50		...	7, 8	32	118–120	60	47	49, 50	Combined in 1927 with La Revue de Chimie industrielle.
29	188, 189	344	59	21 *	51		...	9, 10	33	121–124	61	48	51–54	
1930	190, 191	345	60	22	52	...	...	11, 12	34	124–128	62	49	55, 56	
31	192, 193	346	61	23	53	...	...	13, 14	35	129–132	Continued as two journals, viz. J. General Chem., U.S.S.R. and J. Physical Chem., U.S.S.R.	50	57, 58	
32	194, 195	Publication ceased.	62	24	54	...	...	15, 16	36	132–135		51	59–61	
33	196, 197		63	25	55	...	...	17, 18	37	136–139		52	62, 63	...
34	198, 199		64	26	56	...	...	19, 20	38	139–141		53	64, 65	...
1935	200, 201	...	65	27	57	...	...	21, 22	39	142–144		54	65–67	...
36	202, 203	...	66	28	58	...	...	23, 24	40	144–147		55	67–69	...
37	204, 205	...	67	29	59	...	...	25, 26	41	147–150		56	70, 71	...
38	206, 207	...	68	30	60	...	...	27, 28	42	150		57	71	...

* A separate "Analytical" volume issued annually from this date, beginning as Volume 1.

ear.	Nature.	Phil. Mag.	Phil. Trans. A.	Physical Review.	Physikal. Zeitsch.	Proc. Roy. Soc. A.	Rec. Trav. chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-chem.	Zeitsch. physikal. Chem.	Zeitsch. physikal. Chem. B.
920	104–106	39, 40	220, 221	15, 16	21	96–98	39	129	40	59	33	109–114	26	94–96	...
21	106–108	41, 42	221, 222	17, 18	22	98–100	40	130	41	60	34	115–120	27	97–99	...
22	109, 110	43, 44	222, 223	19, 20	23	100–102	41	131	42	61	35	120–125	28	100–103	...
23	111, 112	45, 46	223, 224	21, 22	24	102–104	42	132	43	62, 63	36	126–132	29	103–107	...
24	113, 114	47, 48	224	23, 24	25	105, 106	43	133	44	64, 65	37	132–141	30	108–114	...
925	115, 116	49, 50	225	25, 26	26	107–109	44	134	45	65–67	38	142–150	31	114–118	...
26	117, 118	(7) 1, 2	225, 226	27, 28	27	110–113	45	135	46	67–69	39	150–159	32	119–124	...
27	119, 120	3, 4	226, 227	29, 30	28	113–117	46	136	47	70–72	40	159–168	33	125–131	...
28	121, 122	5, 6	227, 228	31, 32	29	117–121	47	137	48	73–75	41	168–177	34	A. 131–139	1
29	123, 124	7, 8	228, 229	33, 34	30	122–126	48	138	49	76–79	42	177–185	35	140–145	2–6
930	125, 126	9, 10	229	35, 36	31	126–130	49	139	50	79–82	43	185–194	36	146–151	6–11
31	127, 128	11, 12	230	37, 38	32	130–134	50	140	51	83–87	44	195–203	37	152–158	12–15
32	129, 130	13, 14	230, 231	39–42	33	134–138	51	141	52	87–91	Continued as Angew. Chem. (*q.v.*).	203–209	38	158–163	15–19
33	131, 132	15, 16	231, 232	43, 44	34	139–143	52	142	53	91–95		210–216	39	163–167	20–23
34	133, 134	17, 18	232–234	45, 46	35	143–147	53	143	54	96–99		216–221	40	167–171	24–27
935	135, 136	19, 20	234, 235	47, 48	36	148–153	54	144	55	100–103	...	221–226	41	172–175	28–31
36	137, 138	21, 22	235, 236	49, 50	37	153–157	55	145	56	104–107	...	226–230	42	175–178	31–34
37	139, 140	23, 24	236, 237	51, 52	38	158–163	56	146	57	108–111	...	230–235	43	178–181	35–38
38	141, 142	25, 26	237, 238	53, 54	39	164	57	147	58	111	...	235	44	181	38

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

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. VI. PART IV.

ARSENIC.

CHAPTER I.

INTRODUCTORY.

The Position of Arsenic in the Periodic Table.—Arsenic is the third of the five elements which constitute Group V B, and is the sixteenth element of the first long period.[1] It shows little resemblance in either physical or chemical properties to the elements of Sub-group A, which are distinctly metallic and more closely resemble their neighbours in Sub-groups IV A and VI A.[2] The higher-valent oxides of vanadium, niobium and tantalum, however, exhibit acidic properties and when hydrated give weak acids, the salts of which with alkalis are of the ortho-, pyro- and meta-types; vanadium pentoxide also enters into the formation of complex heteropoly-compounds (see p. 232), and these facts establish a definite though distant relationship between the two sub-groups.

Group V.	
A. Vanadium Group.	B. Nitrogen Group.
	7 N
	15 P
23 V	
	33 As
41 Nb	
	51 Sb
73 Ta	
	83 Bi
91 Pa	

Arsenic does not exhibit any marked similarity to its neighbours of the horizontal period, germanium (At. No. 32) and selenium (At. No. 34), except that the latter element exhibits an allotropy[3] which is somewhat similar to that of arsenic; the compounds of the three elements are in no way analogous.

Of the elements of Group V B, phosphorus, arsenic and antimony constitute a Döbereiner triad. Arsenic, antimony and bismuth do not

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[1] The general properties of the elements of Group V B are compared in this Series, Vol. VI, Part I (1928), p. 3.

[2] See this Series, Vol. VI, Part III (1929), p. 3.

[3] See this Series, Vol. VII, Part II (1931), p. 289.

form such a triad, the difference in atomic weight of the two last-named being greater because of the intervention of the rare earth elements. The five elements, nevertheless, are related as members of a true natural family. Nitrogen and phosphorus are non-metals, whilst bismuth is distinctly a metal. Antimony also has a well-defined metallic character; the free element has the physical properties of a metal, the gaseous hydride is very unstable, the lower oxide is essentially basic, and antimony trichloride is a salt-like compound. The properties of arsenic, however, are neither essentially metallic nor essentially non-metallic.

The compounds of phosphorus containing the quinquevalent element are generally the most stable; but with antimony and bismuth those of the tervalent element are the most stable, in fact few compounds of quinquevalent bismuth are known. The difference in stability of the ter- and quinque-valent compounds of arsenic is not so marked. Evidence of arsenic existing as a quadrivalent element in certain organic compounds has been observed.[1]

Arsenic exhibits allotropy, which is characteristic of non-metals; the usual, more stable, "metallic" form resembles the typical metals in appearance and in being a fairly good conductor of electricity. Under atmospheric pressure it begins to volatilise at about 450° C. and passes into a vapour containing complex molecules, As_4, which at higher temperatures dissociate to As_2; this complexity is not unusual in non-metals. The yellow allotrope, which is stable at low temperatures, resembles white phosphorus in being soluble in carbon disulphide—a property which emphasises the non-metallic character of this variety. The reactivity of the allotropes, as in the case of phosphorus, differs considerably.

The most important compounds of arsenic are the two oxides, As_2O_3 and As_2O_5, and their derivatives. The basic character of these oxides is very feeble and, even so, is almost wholly confined to the lower oxide. On the other hand, both oxides dissolve in aqueous alkalis, forming arsenites and arsenates analogous to the alkali phosphites and phosphates. The corresponding salts of the heavy metals are generally insoluble and are obtained by precipitation. The acidic properties are best developed in the higher oxide. Arsenious oxide is only slightly soluble in water; it yields an acid solution, although the acid has not been isolated. The oxide is more readily soluble in aqueous hydrochloric acid, yielding a solution possessing reducing properties.

The ready dissolubility of arsenious oxide in hydrochloric acid suggests the formation of arsenic trichloride, $AsCl_3$, but evaporation of the solution causes expulsion of hydrogen chloride and leaves arsenious oxide. No arsenious salts with arsenic as a tervalent cation can exist in water in the absence of free acid owing to hydrolysis.

The chloride, however, may be obtained by heating arsenious oxide with sodium chloride and concentrated sulphuric acid; the hydrogen chloride formed reacts to produce arsenic trichloride, which distils over, the water being retained by the sulphuric acid. The trichloride is not a salt-like substance. It is a colourless, volatile oil which, with a little water, yields a basic chloride, but with excess of water yields the trioxide and hydrochloric acid. The formation of the basic chloride is seen in the dense white fumes emitted when the trichloride is exposed to moist air.

Arsenious oxide is insoluble in dilute sulphuric acid but reacts with fuming sulphuric acid to give a series of very unstable crystalline compounds of general formula $As_2O_3.nSO_3$. These are resolved into arsenious oxide and sulphuric acid on contact with water. The formation of a crystalline arsenyl tartrate, $Na(AsO)C_4H_4O_6$, analogous to potassium antimonyl tartrate, has been cited as evidence of the basic nature of arsenious oxide, but the product may contain the arsenic in a complex anion.

When arsenic burns in air the product is arsenic trioxide and not the pentoxide as in the case of phosphorus. The compounds containing the quinquevalent element are less well-defined and somewhat less stable than the corresponding phosphorus compounds which they resemble. Arsenic pentoxide is formed by the action of an oxidising agent, such as nitric acid, on arsenious oxide; when the solution is evaporated, the arsenic acid which separates has the empirical composition $As_2O_5.4H_2O$, and is probably $2H_3AsO_4.H_2O$; this, on being cautiously heated, loses water, yielding the hydrate $3As_2O_5.5H_2O$. At a higher temperature (180° to 200° C.) it is completely dehydrated, the pentoxide remaining. Neither pyroarsenic acid nor metarsenic acid is obtained as an intermediate product by heating the ortho-acid; the former, however, has been obtained from the aqueous solution (see p. 182).

Arsenic pentoxide is a white deliquescent solid. It exhibits no basic properties, but forms arsenates analogous to the ortho-, meta- and pyro-phosphates. The formation of a pentachloride has not been established, but the pentafluoride has been obtained and is well defined.

With sulphur, arsenic forms three stable sulphides of composition As_2S_2, As_2S_3 and As_2S_5. The two latter possess acidic properties and with metallic sulphides form series of thio-salts, analogous to the arsenites and arsenates. Intermediate oxythio-salts are also known.

Arsenic forms three hydrides, As_4H_2, As_2H_2 and AsH_3. The first two are solid at the ordinary temperature, while the third, arsine, which is the stable hydride, is a gas. Arsine is more stable than the hydrides of antimony and bismuth, and yet is readily oxidised, resembling phosphine in this respect; thus in reducing silver nitrate the arsenic passes into solution as arsenious acid. The trihydride differs from ammonia and phosphine in exhibiting no basic properties, quaternary salts of the type AsH_4X not being known. Substitution of hydrogen by organic radicals, however, yields well-defined organic arsonium salts (see this Series, Vol. XI, Part II). The trihydride resembles hydrogen sulphide and hydrogen selenide in that it may be regarded as a weak acid from which arsenides are derived. The latter do not resemble intermetallic compounds such as are formed by the combination of true metals; they are very numerous, however, and in many cases their composition does not appear to show any relation to the valencies of the components.

The more important compounds of arsenic are formulated in the following table. In addition to these, many which are less well defined or more complex are described in the text.

The organic derivatives of arsenic are very numerous, and in these arsenic exhibits a more striking similarity to nitrogen than is the case in its inorganic compounds. This is especially the case in the derivatives of arsine. The organic compounds are dealt with comprehensively in Vol. XI, Part II, of this Series.

Hydrides	As_4H_2, As_2H_2, AsH_3
Arsenides	M_xAs_y; x and y vary considerably, *e.g.* Na_3As; Zn_3As_2, $ZnAs_2$; Cu_3As, Cu_5As_2, Cu_2As; Fe_2As, Fe_3As_2, $FeAs$
Halides	AsF_3, AsF_5 $AsCl_3$ $AsBr_3$ As_2I_4, AsI_3
Oxyhalides	$AsOCl$, $AsOBr$
Oxides	As_2O_3, As_2O_5
Acids	H_3AsO_3,* $HAsO_2$ * H_3AsO_4,* $As_2O_5.4H_2O$
Arsenites	M'_3AsO_3, $M'AsO_2$, $M'_4As_2O_5$
Arsenates	M'_3AsO_4 $M''_3(AsO_4)_2$, $M''(AsO_3)_2$, $M''_2As_2O_7$
Sulphides	As_2S_2, As_2S_3, As_2S_5
Thio-salts	See pp. 251–253, 274–283.

* Not isolated.

Certain optically active compounds appear to owe their activity to the presence of an asymmetrical tervalent arsenic atom in the molecule.[1]

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[1] Allen and Wells, *J. Amer. Chem. Soc.*, 1933, 55, 3894.

CHAPTER II.

THE OCCURRENCE OF ARSENIC.

ARSENIC is very widely distributed in Nature, but seldom in abundance. The element occurs in the free state, but in too small a quantity to be of economic importance. It is found more frequently in combination with sulphur and as metallic arsenides, sulpharsenides, arsenites and arsenates. The presence of arsenic in the sun has not been observed,[1] but it is frequently detected in meteorites,[2] and has been separated from siderites occurring in Mexico and Ontario.[3]

Native arsenic generally occurs in granular or lamellated masses, sometimes reniform, reticulated or stalactitic; more rarely it is found as rhombohedral crystals, usually acicular. It occurs in veins in crystalline rocks and the older schists, and when freshly exposed it is tin-white and possesses a lustre almost metallic, but superficial oxidation gradually changes the colour to dark grey. The arsenic content varies from 90 to 98 per cent. The element is generally associated with ores of antimony, gold and silver, and with metallic arsenides and sulphides. The native element is brittle and gives an uneven granular fracture; it gives a white streak, has density 5·63 to 5·78, and hardness (Mohs' scale) 3·5. It is abundant in many parts of Germany[4] —Bohemia (Joachimsthal), Harz, Saxony (Marienberg), Vosges; also in Alsace, Italy, Hungary and Norway. It occurs in reniform masses associated with calcite in the Caucasus (Vladikavkaz);[5] in large masses near Kolyban Lake, south of Barnaul in Siberia, and in various localities in Japan, large crystals being found in the red vanadium clay of the Akadani district.[6] In New Zealand it is plentiful in the Kapanga gold-mining district. In America it occurs in thin layers in blue mica slate in New Hampshire; as nodules in gold and silver mines near Leadville, Colorado; in Watson Creek, Fraser River, British Columbia, and in Mexico and Chile. The following are typical percentage analyses of native arsenic:

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[1] Rowland, *Amer. J. Sci.*, 1891, [3], 41, 243; *Chem. News*, 1891, 63, 133; Saha, *Phil. Mag.*, 1920, [6], 40, 808.

[2] Rumler, *Pogg. Annalen*, 1840, 49, 591; Silliman and Hunt, *Amer. J. Sci.*, 1846, [2], 2, 374; Fischer and Duflos, *Pogg. Annalen*, 1847, 72, 479; Daubrée, *Ann. Mines*, 1851, [4], 19, 669; *Compt. rend.*, 1872, 74, 1543; Antipoff, *Zeitsch. Kryst. Min.*, 1900, 32, 426; Borgstrom, *Bull. Geol. Finland*, 1902, p. 12.

[3] Papish and Hanford, *Science*, 1930, 71, 269.

[4] The mineral has been described under various synonyms, e.g. *Scherbenkobalt*, *Fliegelstein*, *Näpfchenkobalt*, etc.—see Dana, "*A System of Mineralogy*" (Wiley, 1899), p. 11; Emmerling, "*Lehrbuch der Mineralogie*," Giessen, 1796, 2, 548; Romé de l'Isle, "*Cristallographie*," Paris, 1783, 3, 26.

[5] Chirvinskii, *Chem. Zentr.*, 1927, [1], 2640.

[6] Iimori, *Bull. Inst. Phys. Chem. Research*, Tokyo, 1930, 9, 762.

Source.	As.	Sb.	Ni.	Fe.	S.	SiO_2.
Joachimsthal [1] .	90·91	1·56	4·64	2·07	Trace	0·55
Montreal [2] . .	98·14	1·65	. .	. .	0·16	0·15
Cornwall [3] . .	94·80	5·15	. .	0·15	0·11	0·10

A massive form of native arsenic having a fibrous foliated structure occurs in Saxony and Chile and is known as *arsenolamprite* (Gk. λαμπρός = lustrous). It differs from the ordinary form in possessing a brilliant lustre; it is lead grey in colour, has density 5·3 to 5·5 and hardness 2. The following are analyses of samples from the above two sources:

Source.	As.	Bi.	Fe.	S.	SiO_2.
Marienberg [4] . .	95·86	1·61	1·01	0·99	. .
Copiapo [5] . .	98·43	. .	1·00	. .	0·05

Werner found 3 per cent. Bi in a similar mineral which he called *arsenik-wismuth*.

Antimonial arsenic from California contains, according to Genth,[6] 90·82 per cent. As and 9·18 per cent. Sb. Arsenical antimony, *allemontite*, is found in reniform masses in various parts of Germany. In colour it is white to reddish-grey, sometimes lustrous, of density 6·2 and hardness 3·5. In composition it approximates to $SbAs_3$ (*i.e.* As 64·85, Sb 35·15). Thus a specimen from Allemont [7] gave As 62·15 per cent., Sb 37·85 per cent.

Compounds of arsenic are extremely widespread. The black crust often found on native arsenic is a mixture of arsenic and arsenious oxide, As_2O_3. This oxide frequently accompanies other arsenical minerals and occurs in two crystalline varieties, *arsenolite* (cubic), usually as minute octahedra in capillary crystallisations or in stellar aggregates, and *claudetite* [8] (monoclinic), in thin plates resembling selenite. Both forms are lustrous and may be transparent to translucent, colourless to white.

The most abundant mineral of arsenic is *arsenopyrite, arsenical pyrites* or *mispickel*,[9] $FeS_2.FeAs_2$, which with other metallic arsenides and sulphides is found usually in igneous rocks. It occurs in veins near Freiburg (Germany), and in beds at Joachimsthal (Bohemia), Tunaberg (Sweden) and Skutterud (Norway). It is associated with tin and

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[1] Janowsky, *Sitzungsber. K. Akad. Wiss. Wien*, 1875, 71, (1), 276.

[2] Norton, *Amer. J. Sci.*, 1903, [4], 15, 92.

[3] Russell and Harwood, *Min. Mag.*, 1925, 20, 299.

[4] Frenzel, *Jahrb. Miner.*, 1874, p. 677.

[5] Hintze, "*Handbuch der Mineralogie*," Leipzig, 1904, 1, 110; *Zeitsch. Kryst. Min.*, 1886, 11, 606.

[6] Genth, *Amer. J. Sci.*, 1863, 33, 191.

[7] Rammelsberg, *Pogg. Annalen*, 1844, 62, 137.

[8] Claudet, *J. Chem. Soc.*, 1868, 21, 179; *Chem. News*, 1868, 17, 128.

[9] *Mispickel* is an old German term of doubtful origin.

copper ores in Cornwall and Devon; with serpentine in Silesia; in the Island of Giglio[1] it is associated with galena, sphalerite and traces of gold. For arsenopyrite from Trentino, Andreatta[2] derived the formula $Fe_{22}As_{20}S_{23}$. In many localities in New South Wales it is highly auriferous.[3] It is widely distributed in North and South America, frequently associated with cobalt and nickel ores, especially in Quebec, Ontario, the Keewatin district,[4] Utah, California and Bolivia. An auriferous deposit occurs in the Bella Coola coast district of British Columbia.[5] It is also found in the Akadani district of Japan. The mineral occurs in orthorhombic crystals, sometimes prismatic or in columns, granular or compact. It is lustrous, white to grey in colour, giving a streak almost black, brittle, of hardness 5·5 to 6·0 and density 5·9 to 6·3. The arsenic content varies from 42 to 46 per cent. Cobalt is frequently present in place of iron, and *danaite* is a variety containing 5 to 10 per cent. of this metal; the name was first applied to New Hampshire specimens, but the mineral is also obtained in Norway and in Chile. Nickeliferous arsenopyrite containing about 5 per cent. nickel is found in Bolivia.

In Sweden the Skellefte district, which includes the important Boliden gold mine, contains the most extensive deposit of arsenic ore in the world.[6] This is chiefly in the form of arsenopyrite, and is associated with ores containing iron, copper, silver and gold (see p. 124).

The sulphides *realgar* or *ruby sulphur*, As_2S_2, and *orpiment*, As_2S_3, are fairly abundant and are mined for their commercial importance both in Europe and Asia. Both are of historical interest (see p. 23) and they are frequently found in association. Realgar, red arsenic sulphide, is found in short monoclinic prisms, orange-red in colour and generally translucent. It gradually changes to orpiment and arsenolite on exposure to light. It occurs associated with ores of silver and lead in Hungary, Bohemia, Saxony and the Harz; in dolomite in Switzerland; on quartz in mica slate in Bosnia; in minute crystals in the Vesuvian lavas and the solfataras near Naples;[7] in sandy clay below lava in Utah; in calcite in California; and as a deposition from the hot springs in Yellowstone National Park. It has been mined in small quantities in Washington. The yellow sulphide, orpiment, the *auri pigmentum* or golden pigment of the Romans, occurs in small orthorhombic crystals, usually in foliated or columnar masses, sometimes with reniform surface. Its yellow colour varies in depth, but it is generally lemon-yellow and translucent. It is found with realgar in Hungary, Bosnia, Albania,[8] Switzerland, Italy, Utah and the Yellowstone Park. In Nevada it occurs in monoclinic crystals.[9] It is mined at Acobambillo in Peru. It is found in brown coal in Styria. There is a large Turkish mine near Julamerk in Kurdestan. The chief Indian source of arsenic

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[1] Montibelli, *Rass. min. met. chim.*, 1926, 65, 73.

[2] Andreatta, *Riv. studi Trentini Sci. Nat.*, 1928, 9, 90; *Mineralog. Abs.*, 1929, 4, 136.

[3] Stillwell, *Proc. Australasian Inst. Mng. Met.*, 1927, p. 97.

[4] Thomson, *Univ. Toronto Studies*, Geol. Series, 1932, No. 32, 33. See also Palache, *Amer. J. Sci.*, 1910, [4], 29, 177.

[5] Dolmage, *Can. Dept. Mines Geol. Survey*, Summary Ret., 1925 A (1926), p. 155.

[6] Heckscher, "*Sweden's Industry*," Federation of Swedish Industries, 1935.

[7] Phipson (*Compt. rend.*, 1862, 55, 108) found 11·16 per cent. arsenic sulphide in sulphur from this source.

[8] Pelloux, *Rev. géol.*, 1932, 13, 4.

[9] Palache and Modell, *Amer. Mineral.*, 1930, 15, 365.

is Chitral[1] in the extreme North, where realgar and orpiment occur associated with fluorspar.

Metallic arsenides are very widespread, the more common being those of cobalt, nickel, iron and copper. The arsenides of cobalt and nickel usually occur in intimate association. *Smaltite* is essentially cobalt arsenide, $CoAs_2$, while *chloanthite* is nickel arsenide, $NiAs_2$. Both occur in cubes or pyritohedra, often in distorted forms. *Safflorite* and *rammelsbergite* are orthorhombic forms of cobalt and nickel arsenides, respectively. *Skutterudite,* found in Norway and Alsace, is similar to smaltite but richer in arsenic, corresponding in composition to $CoAs_3$. *Niccolite, copper nickel* or *arsenical nickel* approximates to NiAs. Iron arsenide occurs as *löllingite,* $FeAs_2$, in orthorhombic prisms, but various other forms of this arsenide are found containing 55 to 70 per cent. As. All the above minerals, together with *gersdorffite,* NiAsS, associated with arsenopyrite and breithauptite (NiSb), occur in the Cross Lake ores of Keewatin,[2] and in Ontario. *Arsenoferrite* is similar in composition to löllingite, but differs from it in being apparently isotropic in character (löllingite is anisotropic). It is similar in appearance and physical properties to smaltite. The following analysis is of arsenoferrite from Jachymov, Czechoslovakia :[3] Fe, 24·88 ; Cu, 1·34 ; Pb, 0·05 ; As, 66·84 ; S, 1·08 ; $CaCO_3$, 4·00 ; $MgCO_3$, 1·57. Total, 99·76 per cent. The crystals have been described as cubic,[4] but X-ray examination shows that this is not the case and that the mineral is identical with löllingite.[5] A similar mineral occurs as dark brown crystals on gneiss at the Binnenthal, Switzerland.[6] Other minerals, mainly iron arsenide, are *leucopyrite,*[7] *geyerite*[8] (containing 5 to 8 per cent. of sulphur) and *glaucopyrite,*[9] a cobaltiferous Spanish mineral. An arsenide of copper known as *domeykite*[10] or *arsenical copper,* Cu_3As, frequently accompanies arsenical ores. It occurs in Chile, mixed with niccolite in Michipicoten Island in Lake Superior, and in the deposits near Långban, Sweden.[11] Arseniferous copper is also found as *algodonite,* Cu_6As, *whitneyite* or *darwinite,* Cu_9As.

Arsenic occurs also in a great variety of other minerals, generally as mixed arsenides and sulphides of the heavy metals or as metallic arsenites and arsenates, anhydrous and hydrated. The more common of these are listed below, with their approximate composition. They are to be found in small quantities widely scattered over Europe,[12] Asia, America and Australia. Thus arsenical minerals in great variety[13] are found in the blendes and lead glances of the Eastern Alps, the former

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[1] *Records Geol. Survey India,* 1930.

[2] Thomson, *Univ. Toronto Studies,* Geol. Series, 1932, No. 32, 33.

[3] Foshag and Short, *Amer. Mineral.,* 1930, 15, 428.

[4] Foshag and Short, *loc. cit.*

[5] Buerger, *Amer. Mineral.,* 1936, 21, 70.

[6] Baumhauer, *Zeitsch. Kryst. Min.,* 1912, 51, 143.

[7] Shepard, "*Treatise on Mineralogy,*" New Haven, 1835, 2, 9.

[8] Behncke, *Pogg. Annalen,* 1856, 98, 187; McCay, *Inaug. Dissertation,* 1883, p. 45.

[9] Sandberger, *J. prakt. Chem.,* 1870, [2], 1, 230; "*Untersuchungen über Erzgange,*" Wiesbaden, 1885, p. 385.

[10] Haidinger, "*Handbuch der bestimmenden Mineralogie,*" Vienna, 1845, p. 562; Domeyko, "*Elementos de mineralojia,*" Santiago, 1879, p. 246.

[11] Aminoff, *Kgl. Svenska Vetenskopsakad. Handl.,* 1931, [3], 9, No. 5, 52.

[12] Wernicke, *Rev. géol.,* 1932, 13, 423; Reh, *Neues Jahrb. Mineral. Geol. Beil. Bd.,* 1932, A 65, 1; Czermak and Schadler, *Tsch. Min. Petr. Mitt.,* 1933, 44, 1.

[13] Czermak and Schadler (*loc. cit.*) give details of the occurrence of 27 arsenic-bearing minerals at 20 localities in the Eastern Alps.

containing more than the latter. The apomagmatic deposits contain less than the corresponding perimagmatic zones and, according to Tornquist,[1] the arsenic content of these minerals indicates the possibility of three distinct mineralisation periods. Other arsenic-rich districts in Europe and America have been mentioned; in Asia they are to be found in Siberia, Turkestan, India, China,[2] especially Yunnan Province, and Japan.[3] These arsenical minerals are not, in themselves, of commercial value, but since they occur largely in ore veins and are always associated with other minerals, they frequently become of importance in metallurgical practice.

For the sake of easy reference the foregoing minerals are given in the accompanying tables, together with their approximate chemical composition and more important physical characteristics.

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[1] Tornquist, *Verhandl. geol. Bundesanstalt*, 1930, p .197; *Chem. Zentr.*, 1931, [1], 1087.

[2] Slessor, *Proc. Australasian Inst. Mng. Met.*, 1927, p. 51; Muccioli, *Notiz. chim.-ind.*, 1927, 2, 699.

[3] *Imp. Geol. Surv. of Japan*, Report No. 95, 1926; Kawai, *J. Geol. Soc. Tokyo*, 1925, 32, 106.

MINERALS CONTAINING ARSENIC.

Name.	Approximate Composition.	Hardness (Mohs' Scale).	Density.	Usual Form.	Arsenic Content, per cent. Approx.
Native Arsenic . . .	As	3·5	5·63 to 5·78	(Rhombohedral)	90 to 98
Arsenolamprite . . .	As	2	5·3 to 5·5	Rhombohedral, fibrous	90 to 98
OXIDES:					
Arsenolite . . .	As_2O_3	1·5	3·70 to 3·72	Octahedral	75·8
Claudetite . .	As_2O_3	2·5	3·85 to 4·15	Monoclinic	75·8
SULPHIDES:					
Orpiment	As_2S_3	1·5 to 2·0	3·4 to 3·5	Orthorhombic	61
Realgar	AsS	1·5 to 2·0	3·56	Monoclinic	70
ARSENIDES:					
Algodonite . . .	Cu_6As	4	7·62	Massive, granular	15 to 17
Allemontite . . .	$SbAs_3$	3·5	6·2	Rhombohedral	65
Arite . . .	$Ni(SbAs)$	..	7·1 to 7·5	Massive	11 to 33
Arsenoferrite .	$FeAs_2$	5·5	6·42	Granular, orthorhombic	66 to 67
Chloanthite . .	$NiAs_2$	5·5 to 6·0	6·4 to 6·6	Pyritohedral	64 to 76
Domeykite . .	Cu_3As	3·0 to 3·5	6·7 to 7·7	Reniform and botryoidal	26 to 29
Geyerite . . .	$FeAs_2$	..	6·25 to 6·8	Massive	55 to 62
Huntilite . . .	Ag_3As	..	6·27 to 7·47	Granular	18·8
Leucopyrite . .	Fe_3As_4 to Fe_2As_3	5·0 to 5·5	7·0 to 7·2	Orthorhombic	64
Lollingite	$FeAs_2$	5·0 to 5·5	7·0 to 7·4	Orthorhombic	62 to 72
Niccolite	$NiAs$	5·0 to 5·5	7·33 to 7·67	Massive (crystals rare)	47 to 53·5
Rammelsbergite .	$(Ni, Co, Fe)As_2$	5·5 to 6·0	6·9 to 7·2	Orthorhombic	68 to 71·5
Safflorite . . .	$(Co, Fe)As_2$	4·5 to 5·0	6·9 to 7·3	Orthorhombic	66 to 71
Skutterudite . .	$CoAs_3$	6	6·72 to 7·86	Pyritohedral	77·8 to 79·2
Smaltite	$CoAs_2$	5·5 to 6·0	6·4 to 6·6	Pyritohedral	64 to 76
Sperrylite . . .	$PtAs_2$	6 to 7	10·6	Cubic	41
Whitneyite (Darwinite) .	Cu_9As	3·5	8·4 to 8·6	Massive, granular	11·5 to 12·3

Name.	Approximate Composition.	Hardness (Mohs' Scale).	Density.	Usual Form.	Arsenic Content, per cent. Approx.
ARSENOSULPHIDES:					
Alloclasite	$Co(As, Bi)S$	4·5	6·6	Columnar	28 to 33
Arsenopyrite (Mispickel)	$FeAsS$	5·5 to 6·0	5·9 to 6·3	Orthorhombic	42 to 46
Baumhauerite	$4PbS.3As_2S_3$	3	5·33	Monoclinic	26
Binnite	$3Cu_2S.As_2S_3$	2·5 to 3·0	4·5	Massive	30
Clarite	$3Cu_2S.As_2S_5$	3·5	4·46	Monoclinic	17·5 to 18·0
Cobaltite (Cobalt glance)	$CoS_2.CoAs_2$	5·5	6·0 to 6·3	Cubic, pyritohedral	42·5 to 45·5
Corynite	$Ni(As, Sb)S$	4·5 to 5·0	6	Octahedral	37 to 38
Dufrénoysite	$2PbS.As_2S_3$	3	5·56	Orthorhombic	20 to 22
Enargite	$3Cu_2S.As_2S_5$	3	4·45	Orthorhombic	13·5 to 19·5
Epigenite	$4Cu_2S.3FeS.As_2S_5$	3·5	4·45	Orthorhombic	12 to 13
Gersdorffite	$NiS_2.NiAs_2$	5·5	5·6 to 6·2	Cubic, pyritohedral	34·5 to 46
Glaucodote (Danaite)	$(Fe, Co)AsS$	5	5·9 to 6	Orthorhombic	43 to 44
Guitermanite	$3PbS.As_2S_3$	3	5·94	Massive	14 to 15
Jordanite	$4PbS.As_2S_3$	3	6·4	Orthorhombic	10 to 13
Luzonite	$3Cu_2S.As_2S_5$	3·5	4·42	Massive	16·5
Pacite	$FeS_2.4FeAs_2$	..	6·0 to 6·3	Orthorhombic	..
Pearceite	$9Ag_2S.As_2S_3$	3	6·1 to 6·2	Monoclinic	..
Proustite	$3Ag_2S.As_2S_3$	2 to 2·5	5·57 to 5·64	Rhombohedral	14·8 to 15·6
Rathite	$3PbS.2As_2S_3$	3	5·3 to 5·4	Orthorhombic	..
Regnolite	$5CuS.FeS.ZnS.As_2S_5$	3·5	4·5	Tetrahedral	15
Reniformite	$5PbS.As_2S_5$	..	6·45	Reniform aggregates	10
Rittingerite	$Ag_3As(S, Se)_4$	2 to 2·5	5·63	Monoclinic	..
Sartorite	$PbS.As_2S_3$	3	5·4	Orthorhombic	28 to 29
Seligmannite	$CuPbAsS_3$	3	..	Orthorhombic	..
Tennantite	$4Cu_2S.As_2S_3$	3 to 4·5	4·4 to 4·5	Tetrahedral	25 to 28
Tetrahedrite (Fahlerz)	$(Sb, As)_2S_3$	3 to 4·5	4·7 to 4·9	Tetrahedral	0 to 20
Wolfachite	$Ni(As, Sb)S$	4·5 to 5·0	6·4	Orthorhombic	38·8
Xanthoconite	$3Ag_2S.As_2S_5$	2	5·0 to 5·2	Rhombohedral	13·5 to 14·5

Name.	Approximate Composition.	Hardness (Mohs' Scale).	Density.	Usual Form.
ARSENITES AND ARSENATES:				
Adamite	$Zn_2(OH)AsO_4$	3·5	4·35	Prismatic
Adelite	$Ca(MgOH)AsO_4$	5	3·73	Monoclinic
Allactite	$Mn_3As_2O_8.4Mn(OH)_2$	4·5	3·85	Monoclinic
Annabergite	$Ni_3As_2O_8.8H_2O$	. .	3·3	Monoclinic
Armangite	$Mn_3(AsO_3)_2$	4	. .	Trigonal
Arseniopleite	MnFeCaPbMg basic arsenate	. .	. .	Massive
Arseniosiderite	$Ca_3Fe_4(OH)_9(AsO_4)_3$	1·2	3·52	Tetragonal
Arsenoklasite	$Mn_5(OH)_4As_2O_8$	. .	4·16	Crystalline films
Atelestite	$(BiO)_2.Bi(OH)_2.AsO_4$	3·0 to 4·5	6·4	Monoclinic
Barthite	$3Zn(AsO_2)_2.Cu(OH)_2.H_2O$	3	4·2	Monoclinic (?)
Bayldonite	$(Pb, Cu)_2(OH)AsO_4.0{\cdot}5H_2O$	4·5	5·35	Mammillated
Berzelite	$(Ca, Mg, Mn)_3As_2O_8$	5	4·07 to 4·09	Massive
Beudantite	$(Cu, Pb)_2Fe_2O_5(SO_3)(P, As)_2O_5.H_2O$	3·5 to 4·5	4·0 to 4·3	Rhombohedral
Brandtite	$Ca_2MnAs_2O_8.2H_2O$	5·0 to 5·5	3·67	Triclinic
Cabrerite	$(Ni, Mg)_3As_2O_8.8H_2O$	2	3	Monoclinic
Cahnite	$4CaO.B_2O_3.As_2O_5$	3	3·15	Tetragonal
Carminite	$Pb_3Fe_{10}(AsO_4)_{12}$	2·5	4·1	Orthorhombic
Caryinite	$(Pb, Mn, Ca, Mg)_3As_2O_8$	3·0 to 3·5	4·25	Massive
Chalcophyllite	$Cu_7(OH)_8As_2O_8.10H_2O$	2	2·4 to 2·66	Rhombohedral
Chenevixite	$Cu_2(FeO)_2As_2O_8.3H_2O$	3·5 to 4·5	3·9	Massive
Chondrarsenite	$Mn_3(OH)_3AsO_4$	3	4·2	Granular
Clinoclasite	$Cu_3(OH)_3AsO_4$	2·5 to 3·0	4·2 to 4·4	Monoclinic
Cœrulite	$CuO.2Al_2O_3.As_2O_5.8H_2O$	. .	2·803	Massive clay-like
Conichalcite	$(Cu, Ca)_2(OH)AsO_4.0{\cdot}25H_2O$	4·5	4·123	Reniform
Cornwallite	$Cu_5(OH)_4As_2O_8.H_2O$	4·5	4·165	Massive
Durangite	$Na(AlF)AsO_4$	5	3·94 to 4·07	Monoclinic

Name.	Approximate Composition.	Hardness (Mohs' Scale).	Density.	Usual Form.
Ecdemite	$Pb_6Cl_4As_2O_7$	2·5 to 3·0	6·89 to 7·14	Pyramidal
Erinite	$Cu_5(OH)_4As_2O_8$	4·5 to 5·0	4·04	Mammillated
Erythrite ("Cobalt Bloom")	$Co_3As_2O_8.8H_2O$	1·5 to 2·5	2·9	Monoclinic
Euchroite	$Cu_2(OH)AsO_4.3H_2O$	3·5 to 4	3·39	Orthorhombic
Finnemanite . . .	$3Pb_3(AsO_3)_2.PbCl_2$	2 to 3	7·08 to 7·265	Hexagonal
Flinkite	$Mn_3(OH)_4AsO_4$	4·0 to 4·5	3·87	Orthorhombic
Forbesite	$H_2(Ni, Co)_2As_2O_8.8H_2O$	2·5	3·09	Fibrocrystalline
Georgiadesite . . .	$Pb_3As_2O_8.3PbCl_2$	3·5	7·1	Orthorhombic
Haidingerite . . .	$CaHAsO_4.H_2O$	1·5 to 2·5	2·85	Orthorhombic
Hemafibrite . . .	$Mn_3(OH)_3AsO_4.H_2O$	3	3·5 to 3·65	Orthorhombic
Hœrnesite	$Mg_3As_2O_8.8H_2O$	1	2·47	Monoclinic
Kottigite	$Zn_3As_2O_8.8H_2O$	2·5 to 3·0	3·1	Monoclinic
Legrandite . . .	$Zn_{14}(OH)(AsO_4)_9.12H_2O$	. .	. .	Monoclinic
Leucochalcite . . .	$Cu_2(OH)AsO_4.H_2O$	. .	. .	Needles
Lindackerite . . .	$Cu_6Ni_3(OH)_4(AsO_4)_4SO_4.5H_2O$	2·0 to 2·5	2·0 to 2·5	Orthorhombic
Liroconite . . .	$Cu_9Al_4(OH)_{15}(AsO_4)_5.20H_2O$	2·0 to 2·5	2·9 to 3·0	Monoclinic
Liskeardite . . .	$(Al, Fe)AsO_4.8H_2O$	. .	3·01	Fibrous crusts
Mazapilite . . .	$Ca_3Fe_2(FeO)_2(OH)_2(AsO_4)_4.5H_2O$	4·5	3·56 to 3·57	Orthorhombic
Mimetite	$3Pb_3(AsO_4)_2.PbCl_2$	3·5	6·7 to 7·3	Hexagonal
Mixite	$Cu_{10}Bi(OH)_8(AsO_4)_5.7H_2O$	3 to 4	3·79	Acicular
Olivenite	$Cu_2(OH)AsO_4$	3	4·1 to 4·4	Prismatic
Pharmacolite . . .	$CaHAsO_4.2H_2O$	2·0 to 2·5	2·7	Monoclinic
Pharmacosiderite . .	$Fe_4(OH)_3(AsO_4)_3.6H_2O$	2·5	2·9 to 3·0	Tetrahedral
Picropharmacolite . .	$(Ca, Mg)_3As_2O_8.6H_2O$	. .	2·6	Foliated
Pitticite	$Fe_{20}(OH)_{21}\{(As, P)O_4\}_{10}(SO_4)_3.9H_2O$	2 to 3	2·2 to 2·5	Reniform
Rhagite	$Bi_{10}(OH)_{18}(AsO_4)_4$	5	6·82	Mammillated
Roesslerite . . .	$MgHAsO_4.7H_2O$	. .	3·15	Monoclinic

Name.	Approximate Composition.	Hardness (Mohs' Scale).	Density.	Usual Form.
Roselite	$(Co, Ca, Mg)_3As_2O_8.2H_2O$	3·5	3·5 to 3·6	Triclinic
Sarkinite	$Mn_2(OH)AsO_4$	4 to 5	4·17 to 4·19	Monoclinic
Schultenite . . .	$PbHAsO_4$	. .	5·94	Monoclinic
Scorodite	$FeAsO_4.2H_2O$	3·5 to 4·0	3·1 to 3·3	Orthorhombic
Svavite	$Cu_5(F, Cl, OH)(AsO_4)_3$	. .	. .	. .
Symplesite . . .	$Fe_3As_2O_8.8H_2O$	2·5	2·96	Monoclinic
Trichalcite . . .	$Cu_3As_2O_8.5H_2O$	2·5	3	Columnar
Trigonite	$(MnH)Pb_3(AsO_3)_3$	2 to 3	8·28	Monoclinic
Trippkeite . . .	nCuO.As_2O_3	. .	. .	Tetragonal
Trogerite	$(UO_2)_3As_2O_8.12H_2O$	. .	3·3	Tetragonal
Tyrolite	$Cu_5(OH)_4As_2O_8.3·5H_2O$	1 to 1·5	3·0 to 3·1	Orthorhombic
Uranospinite . .	$Ca(UO_2)_2As_2O_8.8H_2O$	2 to 3	3·45	Orthorhombic
Veszelyite . . .	$(Cu, Zn)_7(OH)_8(As, P)_2O_8.5H_2O$	3·5 to 4·0	3·53	Triclinic (?)
Walpurgite . . .	$Bi_{10}(UO_2)_3(AsO_4)_7.10H_2O$	3·5	5·76	Triclinic
Wapplerite . . .	$(Ca, Mg)HAsO_4.3·5H_2O$	2·0 to 2·5	2·48	Monoclinic
Xanthiosite . . .	$Ni_3(AsO_4)_2$	4	4·98	Amorphous
Yukonite	$(Ca_3, Fe_2)As_2O_8.2Fe(OH)_3.5H_2O$	2 to 3	2·65	. .
Zeunerite	$Cu(UO_2)_2As_2O_8.8H_2O$	2·0 to 2·5	3·2	Tetragonal

The Ubiquity of Arsenic.—Arsenic is even more widespread than s suggested by the foregoing list of minerals. It is to be found in small uantities in many other metallic ores, especially those of copper, lead, ron and antimony. Although the arsenic content may be very small, he flue dusts obtained during the smelting of these ores constitute an nportant source of arsenic compounds (see p. 125). Iron pyrites enerally contains [1] 1 to 2 per cent., although more than 4 per cent. has een found in samples from Freiberg.[2] It is consequently often present ith pyrites in coal [3] and anthracite, and the combustion of these leads o its presence in the atmosphere.[4] That this occurs to an appreciable xtent in large industrial cities has been shown by the examination of tmospheric dusts gathered from office shelves, porticoes, etc., in the entre of Newcastle-on-Tyne,[5] revealing the presence of 65 to 530 parts f As_2O_3 per million. A similar examination of dusts from turret oors in public buildings of Leeds yielded [6] 120 to 350 p.p.m. As_2O_3, hilst samples from churches at Harehills, two miles from the city entre, and Whitkirk, on the extreme outskirts, gave 200 and 40 p.p.m. espectively.

Spectroscopic examination of the carbon arc light usually reveals he presence of arsenic.[7]

Arsenic is present in many primitive rocks, in limestones and marls,[8] lays,[9] sands [10] and gravels. It has been estimated [11] that the percentage mount in the earth's crust is 0·000011, while the atomic proportion nay be 0·00005. Analysis of a composite sample of 329 rocks available n the United States yielded [12] 0·00074 per cent. As_2O_5; while analyses f 46 samples of the common types and grades of phosphate rock from he same country gave a range of 0·0005 to 0·0163 per cent. As_2O_5.[13] ative sulphur frequently contains arsenic.[14] Javan sulphur containing bout 30 per cent. arsenic is known as *sulphurite*.[15]

Owing to the prolonged action of air and moisture on arsenical res, soluble compounds of arsenic find their way into the soil,[16] into

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[1] H. A. Smith, *Chem. News*, 1871, 23, 221; *Proc. Manchester Lit. Phil. Soc.*, 1871, 10, 32; 1872, 11, 172.

[2] Breithaupt and Plattner, *Pogg. Annalen*, 1849, 77, 135.

[3] Campbell, *Chem. News*, 1860, 2, 218; *Phil. Mag.*, 1860, [4], 20, 304; 21, 318; R. A. mith, *ibid.*, 1860, [4], 20, 408; Fischer and Rust, *Zeitsch. Kryst. Min.*, 1882, 7, 209; oherty, *Chem. News*, 1896, 73, 191.

[4] Ramage, *Nature*, 1927, 119, 783.

[5] Dunn and Bloxam, *J. Soc. Chem. Ind.*, 1933, 52, 189 T.

[6] Manley, see Dunn and Bloxam, *loc. cit.*

[7] Kayser and Runge, *Wied. Annalen*, 1893, 52, 93.

[8] Daubrée, *Ann. Mines*, 1851, [4], 19, 669; *Compt. rend.*, 1858, 47, 959; 1872, 74, 541; Sandberger, *Neues Jahrb. Min.*, 1882, p. 158; Kunkel, *Zeitsch. physiol. Chem.*, 905, 44, 511.

[9] Becker, *Arch. Pharm.*, 1849, [2], 57, 129; Sonnenschein, *ibid.*, 1870, [2], 143, 245; udwig and Reguard, *Bull. Soc. franç. Min.*, 1882, 5, 3.

[10] Campbell, *loc. cit.*; Kunkel, *loc. cit.*

[11] Vernadsky, *Centr. Min.*, 1912, p. 758; "*Geochimie*," Paris, 1924, p. 16. See also larke and Washington, *Proc. Nat. Acad. Sci.*, 1922, 8, 108; "*The Composition of the arth's Crust*," Washington, 1924.

[12] Clarke and Steiger, *J. Washington Acad.*, 1914, 4, 60.

[13] Hill, Marshall, and Jacob, *Ind. Eng. Chem.*, 1932, 24, 1306.

[14] Phipson, *Compt. rend.*, 1862, 55, 108; Gibbs and James, *J. Amer. Chem. Soc.*, 1905, 7, 1484.

[15] Rinne, *Centr. Min.*, 1902, p. 499.

[16] Carrigou, *Compt. rend.*, 1902, 135, 1113; Gautier, *ibid.*, p. 1115; Rechert and relles, *Anal. Quim. Argentina*, 1921, 9, 89.

subterranean waters,[1] streams, and eventually the sea.[2] Thus virgin soils in Colorado have been found to contain 2·5 to 5 p.p.m. of arsenic,[3] while the underlying marl contained 4 to 15 p.p.m. Sulphides of arsenic occur in the waters of the Norris Geyser and of other hot springs at Yellowstone National Park.[4] Arsenic is frequently reported present in mineral waters.[5] For the Choussy Well water, La Bourboule, 5·8 to 6·5 mg. As per litre was recorded [6] for the season 1928 to 1929. Water from the brackish shore lakes of East Prussia contains [7] 1 to 4 mg. As per 1000 litres; the muds from these lakes are found to be much richer in arsenic, containing from 2 to 30 g. per ton of dry weight; this is probably due to the extraction of arsenic from the water by minute water organisms. Samples of Baltic Sea water from nearby contained about 1 mg. As per 1000 litres.[8] Chapman examined 16 samples of sea water from points within 4 miles of the Nore lightship and found 0·14 to 1·0 part of arsenic per million.[9] According to Atkins and Wilson,[10] the element is present in sea water principally in the form of arsenite, in amounts equal to, or greater than, the phosphate content; if this be so, previous determinations of phosphates in sea water by methods involving preliminary treatment with nitric acid have included also arsenates. The arsenic content of sea water varies with the depth, owing to absorption by algæ. Gautier [11] examined water of the Atlantic Ocean taken at various depths in the neighbourhood of the Azores, and found the arsenic content at depths of 10, 1335 and 5943 metres respectively to be 25, 10 and 80 parts per million. These high values are attributed to volcanic actions which take place thereabout.

It will readily be understood that traces of arsenic are found in many plants and plant products, and consequently may be assimilated by animals and man. If the quantities of arsenic present are considerable, as they may be when artificial application of insecticidal dust or sprays (see p. 301) has been resorted to, an important problem arises owing to the physiological action of arsenical compounds (see p. 289). The element has been detected in the ashes of many plants,[12] and in wood charcoal.[13] Amounts up to 0·025 part As in 100,000 have been found [14] in many vegetables and nuts; fruits generally contained less, 0·005 to 0·012, while mushrooms contained 0·006 part per 100,000. Almonds, red haricot beans, lettuce and celery were richest in arsenic, with

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[1] Carrigou, *loc. cit.*; Bado, *Bol. Acad. Ciencias Cordoba*, 1918, 23, 85; Bado and Zanetta, *Anal. Quim. Argentina*, 1921, 9, 24.

[2] Daubrée, *Ann. Mines*, 1851, [4], 19, 669; *Compt. rend.*, 1851, 32, 827; Bertrand, *ibid.*, 1902, 134, 1434; *Bull. Soc. chim.*, 1902, [3], 27, 843

[3] Headden, *Proc. Colorado Scientific Soc.*, 1910, 9, 345.

[4] Hague, *Amer. J. Sci.*, 1887, [3], 34, 171. Weed and Pirsson, *ibid.*, 1891, [3], 42, 401.

[5] Carrigou, *loc. cit.*; Gautier, *Compt. rend.*, 1903, 137, 232; Gautier and Clausmann, *Compt. rend.*, 1904, 139, 101; Taboury, *Bull. Soc. chim.*, 1909, [4], 5, 865, Goy and Rudolph, *Zeitsch. angew. Chem.*, 1927, 40, 945.

[6] Clogne, Courtois and Cazala, *Compt. rend.*, 1930, 190, 1133. See also Willm, *Bull. Soc. chim.*, 1880, [2], 33, 292.

[7] Goy and Rudolph, *loc. cit.*

[8] See also Lockemann, *Zeitsch. angew. Chem.*, 1926, 39, 1146.

[9] Chapman, *Analyst*, 1926, 51, 548.

[10] Atkins and Wilson, *J. Marine Biol. Assoc.*, 1927, 14, 609.

[11] Gautier, *Compt. rend.*, 1903, 137, 374.

[12] Legrip, *Dingl. Poly. J.*, 1845, 97, 389; Stein, *J. prakt. Chem.*, 1850, [1], 51, 302; 53, 37; Carrigou, *Compt. rend.*, 1902, 135, 1113; Gautier and Clausmann, *Compt. rend.*, 1904, 139, 101; Jadin and Astruc, *ibid.*, 1912, 154, 893; 1913, 156, 2023; 1914, 159, 268.

0·020 to 0·025 part per 100,000. Arsenic appears to be present always in hops grown under natural conditions. Thus Lindemann [1] found 0·004 to 0·025 part per 100,000 in untreated hops, this arsenic being derived apparently from the soil. In strongly sulphured hops there was 0·07 to 0·13 part per 100,000. Some of this arsenic passes to the wort on boiling and is adsorbed by the yeast during fermentation. Wine yeasts exhibit this adsorptive power to a somewhat greater degree than brewing yeasts. Both beer and wines are liable to contain arsenic. In the former it may be derived largely from glucose (see p. 289) used in production, as was shown to be the case [2] after an outbreak of arsenical poisoning in 1900. Malts may become contaminated with arsenic from the coal or coke used as fuel in the drying operations.[3] Examination of five samples of red wines from Baden showed the presence of 0 to 0·66 mg. As per litre,[4] and traces of the element have been detected in Californian wines,[5] but it is not a normal constituent and the amounts are insignificant.

In tobacco small quantities of arsenic also occur; the following contents of samples from various sources are due to Popp: [6] from the Palatinate 5·1, from Brazil 4·6, from Macedonia 0·70, and from Java 0·33 parts As per million. These quantities are sufficiently small to be harmless, but Remington [7] found 6·0 to 28·9 parts As per million (*i.e.* 0·05 to 0·27 grains As_2O_3 per lb.) in American manufactured plug and smoking tobaccos—this quantity exceeds the accepted legal limit for foods (see p. 290). About half the arsenic in pipe tobacco, however, is evolved in smoke,[8] and about half that in plug tobacco is soluble in water.

The absorption of arsenic by marine algæ has been referred to (p. 18); certain Chinese medicinal algæ have an exceptionally high arsenic content.[9]

The presence of arsenic in animal organisms has been widely demonstrated, but there has been considerable controversy as to whether it may be regarded as a normal constituent. The quantity present undoubtedly depends to a high degree on the amount of the element available in the environment of the organism. Thus, whereas freshwater crustaceans and shellfish from rivers containing only minute traces of arsenic were found by Chapman [10] to contain only about 0·4 to 1·5 parts per million, marine crustaceans and shellfish contained amounts up to 174 parts per million, estimated as As_2O_3 on the wet substance. The following maximum quantities were found: in British oysters, 10 parts; Portuguese oysters, 70 parts; escallops, 85 parts; mussels, 119 parts; cockles, whelks and periwinkles, 40 parts; prawns, 174 parts; shrimps, 50 parts. The boiled edible portion of lobster contained 36 to 40 parts As_2O_3 per million for three specimens, but a fourth specimen gave

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[1] Lindemann, *Wochschr. Brau.*, 1932, 49, 257.

[2] Kelynack and Kirkby, "*Report on Arsenical Poisoning in Beer Drinkers*," London, 1901; Reynolds, *Brit. Med. J.*, 1900, p. 1769.

[3] Luff, "*Report of Royal Commission on Arsenical Poisoning*," London, 1901.

[4] Remy and Richter, *Zeitsch. Unters. Lebensm.*, 1929, 58, 624; Remy, *ibid.*, 1931, 62, 513.

[5] Gibbs and James, *J. Amer. Chem. Soc.*, 1905, 27, 1484.

[6] Popp, *Zeitsch. angew. Chem.*, 1928, 41, 838.

[7] Remington, *J. Amer. Chem. Soc.*, 1927, 49, 1410.

[8] Gross and Nelson (*Amer. J. Pub. Health*, 1934, 24, 36) found 8·3 to 50 p.p.m. As_2O_3 in tobacco, and stated that about one-third of the amount volatilised.

[9] Read and Gow, *Chinese J. Physiol.*, 1927, 1, 99.

[10] Chapman, *Analyst*, 1926, 51, 548.

105 parts. Experiments with American large-mouth black bass[1] showed that whereas no arsenic could be detected in the normal domesticated fish, bass from Rock River contained 0·106 to 1·60 parts per million (estimated as As_2O_3), and from the Mississippi 0·066 to 0·156 parts per million, while those kept in arsenic-treated water contained 0·58 to 0·96 part per million. It was observed that bass retained in arsenic-bearing water appeared to develop the power of eliminating the element from their bodies. An examination of cod and herring gave the following results[2] expressed in parts of As per million: cod, muscular tissue 0·4 to 0·8, liver 0·7 to 3·2, cod-liver oil 3·0 to 4·5; herring, muscular tissue 2·0, oil 9·0. Thus the concentration is higher in the oily liver than in the muscular tissue. The arsenic appears to be present as fat-soluble compounds, probably acidic since they may be extracted with dilute alkaline solutions. Chapman concluded that in lobster the element occurs in a complex organic substance or mixture of substances since it is not readily reducible by hydrogen and can be extracted by alcohol or acetone.

Gautier[3] examined a large number of animals and found no arsenic in the muscles or adipose tissue, but it was always present in small quantity in the thyroid gland, of which he concluded it was a normal constituent. Kunkel,[4] however, denied this, not finding the element as a normal constituent of any animal organ, and many investigators[5] have put forward evidence as to its presence[6] or absence[7] normally in the human body, the problem having been the subject of much discussion. It appears to be established that arsenic is not normally present in the liver of man[8] or of the domestic animals,[9] although in the case of arsenic poisoning (see p. 296) it is in the liver that the element is largely concentrated. But it is frequently found to be present in all parts of the human body,[10] and if the element does play any physiological rôle in the organism, the part is not confined to any one organ. Arsenic is not necessarily present in healthy human blood, but Gautier observed its presence in the blood of women during the menstrual period. Guthmann and Grass,[11] however, found that in

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[1] Wieber, Gross and Slaughter, *Trans. Amer. Fisheries Soc.*, 1931, 61, 150.

[2] Sadolin, *Dansk. Tids. Farm.*, 1928, II, No. 7, 186; *Biochem. Zeitsch.*, 1928, 201, 323.

[3] Gautier, *Compt. rend.*, 1899, 129, 929; 1900, 130, 284; 131, 361; 1902, 134, 1394; 135, 812; *Chem. News*, 1903, 88, 189; *Bull. Soc. chim.*, 1876, [2], 25, 483, 530; 1902, [3], 27, 847; 1903, [3], 29, 31, 913.

[4] Kunkel, *Zeitsch. physiol. Chem.*, 1905, 44, 511.

[5] See Bertrand, *Bull. Soc. chim.*, 1902, [3], 27, 843, 1903, [3], 29, 790; *Ann. Pasteur Inst.*, 1902, 16, 553; *Ann. Chim. Phys.*, 1903, [7], 29, 790; *Compt. rend.*, 1902, 134, 1434; Fordyce, Rosen and Myers, *Arch. Intern. Med.*, 1923, 31, 739.

[6] Danger and Flandin, *Compt. rend.*, 1840, 11, 1038; 1841, 12, 118; 1843, 16, 136, 391; Chevallier, *J. Chim. Méd.*, 1841, [2], 7, 84; Barbot, Fauré and Magonty, *ibid.*, 1841, [2], 7, 654; Pfaff, *Rep. Pharm.*, 1841, 74, 106; Steinberg, *J. prakt. Chem.*, 1842, [1], 25, 384; Jacquelain, *Compt. rend.*, 1843, 16, 30; Segale, *Zeitsch. physiol. Chem.*, 1904, 42, 175.

[7] Schnedermann and Knop, *J. prakt. Chem.*, 1845, [1], 36, 471; Sonnenschein, "*Handbuch der gerichtlichen Chemie*," Berlin, 1869, p. 212; Hodlmoser, *Zeitsch. physiol. Chem.*, 1901, 33, 329; Cerny, *ibid.*, 1902, 34, 408; Ziemke, *Viertelj. Ger. Med.*, 1901, [3], 22, 231; 1902, 23, 51; Mann, "*Forensic Medicine and Toxicology*," London, 1922, p. 380 (Griffin).

[8] Blomendahl, *Arch. Pharm.*, 1909, pp. 246, 599, van Itallie and van Eck, *Proc. Acad. Amsterdam*, 1913, 15, 580.

[9] Gautier, *loc. cit*; Kunkel, *loc. cit.*

[10] Chittenden, *Amer. Chem. J.*, 1884, 5, 8; Marfurt, "*Contribution à la recherche de minimes quantités d'arsenic*," Bâle, 1922.

the intermenstrual period the venous blood of normal women contained, as an average value, $63{\cdot}8 \times 10^{-6}$ g. As per 100 c.c., the range being from 20·5 to 113·4, with little variation in the individual. During menstruation there is an increase of 50 per cent. to an average of 92·5, and during pregnancy it further increases, reaching a maximum value (average 220) between the fifth and sixth months and then gradually falling, although at the full term the value is still above the normal intermenstrual value.

The examination of the urine of a large number of hospital patients subject to the same diet gave the following results:[1] 16 per cent., no arsenic present; 43 per cent., 0·01 to 0·06 mg. As per litre; 33 per cent., 0·07 to 0·20 mg. per litre; 8 per cent., 0·21 to 0·69 mg. per litre. In four cases there was a variation from 0 to 0·23 mg. As per litre over periods of 4 to 6 days. Traces of arsenic may be found in the bones,[2] the skin,[2] and in the hair[3] and nails. The arsenic content of human hair for normal persons not engaged in any arsenical industry or undergoing medication was stated by van Itallie to be 0·01 to 0·03 mg. per 100 grams, and the same observer found that the content in finger and toe nails varies between wide limits. The presence of traces of arsenic in urine, lungs and hair is usual for people living in districts where, owing to industrial operations, the atmosphere is contaminated with arsenic.

Bertrand found arsenic present in hens' eggs, to the extent of 0·005 mg. in one egg chiefly concentrated in the yolk. On the other hand, Gautier could not detect the element in birds' eggs.

The wide distribution of arsenic in so many natural products results in the contamination of a great variety of industrial products. Thus the use of pyrites, or even sulphur which may be slightly arsenical, in the manufacture of sulphuric acid, leaves the element as a common impurity in the acid, and although methods are applied to remove the arsenic as completely as possible (see Vol. VII, Part II, p. 158), traces are still liable to remain. The use of sulphuric acid on an immense scale in the manufacture of hydrochloric and nitric acids, and the further employment of these acids in chemical industry, result in a widespread distribution of arsenic, so that it is frequently found in phosphorus, phosphoric acid and phosphates, hydrobromic acid, calcium chloride, ferric chloride, caustic alkalies, alkali chlorides and carbonates, bismuth compounds, ammonia and ammonium compounds, hydrogen sulphide, chloroform, glycerine, beers, vinegars, flour, sugars and many foodstuffs. The ubiquity of arsenic in artificial materials is undoubtedly a cause of the conflicting evidence, discussed above, as regards its presence as a normal constituent of the organism. It is only in recent years that analytical methods have been sufficiently refined to guard against accidental introduction of the element.

Traces of arsenic may occur in many metals, *e.g.* antimony, bismuth, copper, iron, lead, nickel, tin and zinc, and in alloys derived from such metals. Its presence generally results from the use of arseniferous ores and inadequate purification of the metals. It is found as an impurity in many dyes and colouring matters, and some arsenic compounds

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[1] Bang, *Biochem. Zeitsch.*, 1925, 165, 364, 377.

[2] Mann, *loc. cit.*; Bang, *loc. cit.*

[3] van Itallie, *Pharm. Weekblad*, 1932, 69, 1134, 1145; von Vámossy, *Pharm. Monatsh.*, 1932, 13, 254.

constitute important pigments (see p. 166). Wines coloured with aniline dyes have been found to contain arsenic.[1] Printing inks generally contain it,[2] as do many writing materials. Kappeller[3] examined fourteen samples of violet carbon paper and found arsenic in five; three of German origin contained 0·95 to 3·8 g. As per 100 grams, while two American samples contained 0·9 to 3·0 g. As per 100 grams. Two English violet typewriter ribbons contained 0·5 to 1·1 g. As per 100 grams, or 5·8 to 15·4 mg. per metre. On the other hand, aniline ink powders and violet pencils did not contain arsenic. It is seldom nowadays that arsenic is found in wallpapers[4] and window curtains in excess of the permissible limit of 5 mg. per sq. metre, and the same is to be said of coloured papers and boards used for wrappings,[5] the agreed limit for these being 10 parts per million. Arsenic is sometimes found in wall plaster,[6] however, in dangerous quantity (see p. 292).

[1] Husson, *Compt. rend.*, 1876, 83, 1113.

[2] Barry, *Analyst*, 1927, 52, 217; Morrell and Smyth, *ibid.*, 339.

[3] Kappeller, *Zeitsch. Untersuch. Lebensm.*, 1930, 60, 213.

[4] See Scheringa, *Pharm. Weekblad*, 1928, 65, 677.

[5] Stern, *Analyst*, 1928, 53, 83.

[6] *Analyst*, 1932, 57, 163; Vervloet, *Pharm. Weekblad*, 1933, 70, 578.

CHAPTER III.

ARSENIC AND ITS PROPERTIES.

Symbol, As. Atomic Number, 33. Atomic Weight, 74·91 (O = 16).

History.—Two yellow pigments were used by the ancient Egyptians;[1] the one, a dull yellow, was a natural ochre or hydrated oxide of iron; the other was the bright yellow natural sulphide of arsenic. There is evidence that the latter was employed as early as the 18th Dynasty (1580 to 1350 B.C.) at Tell el Amarna[2] and in the Theban necropolis.[3] Arsenic is frequently found in ancient Egyptian copper and bronze, but the highest amounts recorded[4] (2·3, 3·9 and 5·6 per cent.) are not higher than might have been present as natural impurities in the ores used.

The two naturally occurring sulphides were undoubtedly the first forms in which arsenic was known to the early Greeks, but it is doubtful whether two distinct substances were recognised by them. Aristotle, in the fourth century B.C., used the term *sandarach*; his pupil and successor, Theophrastus, referred to the same material as *arrhenicum*; and in the first century A.D., Dioscorides, a Greek herbalist, writing of *arsenicon*,[5] said that as a remedy for coughs and asthma it "should be burned in combination with resin and the smoke inhaled through a tube." Pliny the Elder (first century A.D.) recommended its use[6] for the same purpose "in the form of a fumigation with cedar dust," and such use probably accounts for the presence of the small quantity of realgar discovered recently in the Roman stratum of the floor in Wookey Hole, Somerset, there being no evidence in the district of its employment as a pigment.[7]

Pliny identified sandarach with arsenicon or *arsenicum*, but he designated that which "resembleth burnished gold in colour," which he considered to be of the best quality, *auripigmentum*, of which term *orpiment*, the present name for the yellow sulphide, As_2S_3, is a contraction. Thus the name *arsenic* appears to be of Greek origin, its meaning being *masculine* or *valiant*, referring to the powerful activity of the sulphide, to which it applied.[8] An Arabic origin of the word has been suggested,[9] possibly from *arsa naki*, but there is doubt as to the authenticity of this term,[10] and a closer relationship may be found in the Persian word for arsenic, *zarnich* or *zirnuk*. The more usual form of

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[1] Lucas, "*Ancient Egyptian Materials*" (Arnold and Co.), 1926.

[2] Flinders Petrie, "*Tell el Amarna*" (Methuen and Co.), 1894, p. 15.

[3] Mackay, "*Ancient Egypt*," 1920, **5**, 37.

[4] Flinders Petrie, "*Ancient Egypt*," 1915, **2**, 17.

[5] "*Dioscorides*," Book V, cap. 122.

sandarach was reddish in colour and was undoubtedly the mineral, more or less pure, now known as *realgar*, As_2S_2, a name derived from the Arabic *Rahj al ghār*, "powder of the mine." The sandarach mines at Pompeiopolis, in Paphlagonia, in which criminal slaves were employed during the first century A.D., are described in the writings of Strabo.[1]

It is evident that white arsenic, in an impure form, must have been observed as a product of the combustion of the sulphides, but although certain medicinal properties were early recognised, no mention appears to have been made of its toxic nature. Nor does its identity as an individual substance appear to have been recognised before the eleventh century, when an Arabian chemist, Avicenna,[2] described it as the product of sublimation of yellow or red arsenic; the thirteenth-century Latin translation of Geber's "*Summa Perfectionis*," supposedly written in Arabic in the eighth or ninth century, contains similar mention, but the origin of this work is not known. Roger Bacon [3] showed that this *arsenicum album* could be obtained by heating orpiment with iron scale—evidently by oxidation of the liberated arsenic vapour. The substance soon became familiar to the mediæval alchemists and *arsenicum* was thought to be of a nature akin to sulphur, and supposed to contain sulphurous earth, salt and a metal.[4] As its poisonous qualities were recognised it became known under various names, such as Goblet-fiend, Bowl-sprite, and the German equivalents Scherbenkobold, Näpchenkobold, also Cobaltum and Fly-poison, while the *arsenicum album* was known as Flowers of Arsenic, Hüttenrauch (arsenical fume), Giftmehl (poison flour) and Rat-poison. Chaucer, however, referred to *arsenicum* as *arsnek*,[5] which later was printed as *arsnecke* and *arsenik*; while Thynne [6] in 1599 explained that "this Resalgar is that which by some is called Ratisbane, a kynde of poysone named Arsenicke."

According to Berthelot,[7] a fragmentary writing attributed to Zosimus (fifth century A.D.) clearly indicates the preparation of metallic arsenic, but such a product does not appear to have been recognised until the thirteenth century, when Albertus Magnus obtained it [8] by fusing *arsenicum* (*i.e.* orpiment) with twice its weight of soap. During the seventeenth and eighteenth centuries it was prepared by reduction of white arsenic by heating with oil [9] or with potash and soap.[10] That the product was not a true metal was soon recognised; Basil Valentine called it [11] a "bastard metal" and Brandt [12] a "semi-metal," and the latter, who early in the eighteenth century made the first discerning experiments on the chemical nature of the arsenical compounds, observed that white arsenic was the calx of metallic arsenic.

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[1] Strabo, *Geographia*, 12, iii, 40.

[2] Bergman, "*De arsenico*," Upsala, 1777.

[3] "*Breve breviarium de dono Dei*," thirteenth century.

[4] Libavius, "*Commentationum metallicarum*," Frankfurt, 1597; Lemery, "*Cours de chymie*," Paris, 1675; Kunckel, "*Philosophia chimica experimentes confirmata*," Amsterdam, 1694; London, 1730.

[5] Chaucer, "*The Chanouns Yemannes Tale*," *circa* 1386.

[6] Thynne, "*Animadversions on Speght's Chaucer*," 1599, p. 36.

[7] Berthelot, *Ann. Chim. Phys.*, 1888, [6], 13, 430.

[8] Albertus Magnus, "*Theatrum chemicum*," 4, 931 (1613 edn.).

[9] Brandt, *Arch. Akad. Upsala*, 1733, 3, 39.

[10] Lemery, "*Cours de chymie*," Paris, 1675.

[11] Valentine, "*Von dem grossen Stein der Uhralten*," Strassburg, 1651

Scheele in 1775 discovered arseniuretted hydrogen and recognised arsenic acid as a chemical entity. The existence of the latter appears to have been suspected by Cavendish, according to his recorded experiments,[1] as early as 1759, whilst the solid product resulting from the oxidation of arsenious oxide by heating with potassium nitrate was observed by the alchemists, Paracelsus describing it as *arsenicum fixum*[2] and Libavius as *butyrum arsenici*;[3] van Helmont called it a "*fiery salt*."[4]

Berzelius in 1817 investigated the stoichiometrical relations of arsenic with other elements and examined the various compounds with sulphur. The physical properties of the element caused it to be classed with the metals, but its non-metallic chemical properties and its similarity in chemical behaviour to nitrogen and phosphorus were gradually recognised.

Preparation.—The element is used only to a small extent in commerce. None at all has been produced in recent years in the United States, where the annual demand rarely exceeds 100 tons.[5] In Europe it is generally produced by the sublimation of native arsenic or by heating arsenopyrite or löllingite. The mineral is heated in the absence of air at 650° to 700° C. in earthenware retorts or in tubes laid horizontally in a long furnace. The arsenide minerals decompose thus:

$$\mathrm{FeS_2.FeAs_2 = 2FeS + 2As}$$
$$\mathrm{4FeAs_2 = Fe_4As + 7As}$$

A furnace usually holds 24 to 30 retorts,[6] about $2\frac{1}{2}$ feet long and 6 inches in diameter, made of clay and powdered bricks, with a glazed exterior which makes them impervious to arsenical vapours, the charge for each retort being about 20 to 25 lbs. of ore. A spiral piece of thin sheet iron is inserted about 4 inches into the mouth of the retort and projects for the same distance into a cylindrical earthen condenser, the joint between the retort and the condenser being luted with clay. A door at the end of the condenser allows access to the retort and enables observation of the operation. On distilling, most of the volatilised arsenic condenses on the iron spirals as nearly white crystalline crusts or as glistening grey scales. Some finely divided arsenic and volatilised sulphide collect on the walls of the condensers, but the volatilisation of sulphide may be minimised by the addition of potash or lime to the charge. The end of the operation, which may take up to 12 hours, is judged by observing the fumes through the condenser door. When cool, the spiral iron sheet is removed and unrolled and the crystalline mass detached. The yield is about 50 per cent. of the arsenic present in the arsenopyrite, while it is somewhat larger in the case of leucopyrite. The residues may be roasted in order to recover the remaining arsenic as arsenious oxide (see p. 125). The arsenic is ready for sale without further treatment, but may be purified by resublimation, after mixing with powdered charcoal.

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[1] Harcourt, *B.A. Reports*, 1840, p. 50; Cavendish, "*Scientific Papers*," Cambridge, 1921, **2**, 298.

[2] Paracelsus, "*The Hermetic and Alchemical Writings*," London, 1895, **2**, 210.

[3] Libavius, "*Alchemia*," Francofurti, 1595.

[4] van Helmont, "*Ortus Medicinæ*," Lugduni, 1656.

[5] Tyler and Petar, *J. Electrochem. Soc.*, 1932, **61**, 125; Gerry and Meyer, "*Mineral Resources, U.S.*" (Bureau Mines), 1931, i, 9; Franke, "*Minerals Year Book*," 1937, p. 713.

[6] Hayward, "*Outline of Metallurgical Practice*," van Nostrand, New York, 1929, p. 316; Schnabel and Louis, "*Handbook of Metallurgy*," Macmillan, 1907, p. 604.

Metallic arsenic is sometimes obtained from arsenious oxide. Thus in Altenberg (Silesia) the oxide is heated at 650° to 700° C. with charcoal in an earthenware crucible covered with a conical iron cap which acts as receiver, while in Chicago[1] retorts composed of steel pipes large enough to take a charge of 450 lbs. were at one time used for the same purpose, the arsenic being collected in water-cooled pipe condensers. This reduction method is not satisfactory, however, as the product is largely amorphous and is not so desirable as the crystalline form, being suitable only for making arsenic compounds. Moreover it always contains arsenious oxide. A Japanese method[2] consists in fixing the vapour of arsenious oxide by means of ferric oxide or alumina at a temperature above 218° C. and then reducing the product with water-gas, Mond gas or producer gas above 100° C.; the arsenic thus freed is then sublimed.

The element may also be prepared by heating the sulphides with carbon and alkali carbonate or cyanide, but in this case also the product is largely amorphous.

Various attempts have been made to employ electrolytic methods for the extraction of arsenic from arsenical minerals. Thus Siemens and Halske[3] suggested the treatment of sulphide ores with sulphides or hydrosulphides of the alkali metals so that the arsenic passed into solution as a double sulphide or thioarsenite, thus:

$$As_2S_3 + 6NaHS = As_2S_3.3Na_2S + 3H_2S$$

Electrolysis of the resulting solution in a diaphragm cell with carbon or platinum cathodes resulted in liberation of arsenic in the cathode compartment. Extraction of the ores with sulphydroxides of the alkaline earth metals and subsequent electrolysis has also been suggested.[4] These methods have little application, however, since the arsenic in the common ores, such as arsenopyrite and leucopyrite, cannot be extracted as sulphide.

Arsenic may be deposited by electrolysis of a solution of arsenic trichloride in glacial acetic acid;[5] it is always obtained in the amorphous form. It has been successfully plated on copper and brass from a solution of arsenious acid containing alkali chlorides.[6]

Pure arsenic has been prepared by reducing carefully purified ammonium dihydrogen arsenate at 1000° C. in a current of ammonia, the arsenic being finally resublimed in a vacuum.[7] The element may also be obtained as an amorphous precipitate by reduction of aqueous arsenious acid, for example, by means of sodium hypophosphite,[8] or by the addition of a few drops of phosphorus trichloride.[9] The reaction in the latter case probably takes the following course:

$$As_2O_3 + 3PCl_3 + 9H_2O = 2As + 3H_3PO_4 + 9HCl$$

A similar reaction occurs also with arsenates and arsenites, and is

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[1] Hayward, *loc. cit.*

[2] Ikebe and Otani, *Japanese Patent*, 94056 (1932).

[3] Siemens and Halske, *German Patent*, 67973 (1892).

[4] Siemens, *English Patent*, 7123 (1896).

[5] Stillwell and Audrieth, *J. Amer. Chem. Soc.*, 1932, 54, 472.

[6] Rodionov, *Russian Patent*, 27546 (1927). See also Gravell, *American Patent*, 1713653 (1929).

[7] de Passillé, *Compt. rend.*, 1934, 198, 1781.

[8] Sazerac and Vaurs, *Compt. rend. Soc. biol.*, 1928, 99, 372.

[9] Sen, *J. Proc. Asiatic Soc. Bengal*, 1919, 15, 263.

sufficiently delicate to reveal the presence of as little as 0·000075 gram of arsenic per cubic centimetre.

Compact pieces of metallic arsenic may be obtained by pressing powdered arsenic at temperatures approaching 500° C., with exclusion of air.[1]

Allotropy of Arsenic.

That arsenic may exist in both crystalline and amorphous forms was observed by Berzelius,[2] who designated them α- and β-arsenic, respectively. Two crystalline allotropes, *metallic arsenic* (the α-form) and *yellow arsenic*, are now recognised, and three amorphous forms, *vitreous arsenic* (the β-form), *grey* and *brown amorphous arsenic*, have been described. The majority of investigators, however, deny the existence of more than one amorphous form, and indeed, as will be seen, it is an open question whether any amorphous form is to be considered as a true allotrope.

Bettendorff[3] showed that when arsenic is sublimed in a current of hydrogen the arsenic vapour condenses first as a crust of vitreous arsenic in the zone nearest the source of heat, beyond this as a crust of crystalline metallic arsenic, and in the coolest zone a yellow deposit forms which rapidly becomes grey and pulverulent. Bettendorff did not examine the unstable yellow deposit, but assumed it to be another allotropic variety; the grey powder, which microscopically resembles flowers of sulphur, he designated γ-arsenic. If the arsenic is sublimed in a glass tube closed at one end, the sublimate contains some arsenious oxide, and between the vitreous and metallic deposits a brown transparent ring is formed which was thought to be a suboxide[4] (see p. 123).

Metallic arsenic is the stable form. It consists of lustrous, steel-grey crystals belonging to the rhombohedral system and isomorphous with α-antimony, with bismuth and, according to Hittorf,[5] probably with red phosphorus, but this is disputed.[6] The crystals are brittle and of density 5·73.[7] They are oxidised slowly in air, the oxidation being marked at 40° C., when the crystals become covered with a layer of arsenious oxide. The metallic arsenic may be purified by resublimation in a vacuum. If resublimed in an open tube there appear in the following order: a mirror-like deposit of vitreous arsenic, dark brown specks, and most remote from the source of heat a grey crust. Erdmann and Reppert[8] regarded the brown deposit, of which the density at 15° C. is 3·70, as amorphous arsenic, and the grey crust of γ-arsenic of density 4·64 as a definite crystalline variety. When heated to 360° C. the latter changed to α-arsenic. The light grey vitreous form, which Bettendorff showed to be always deposited when arsenic vapour is cooled to 210° to 220° C., has density[9] 4·716 to 4·740, and is not oxidised in air even when finely powdered and heated to 80° C. It resembles the γ-form in changing to the α-form at 360° C.

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[1] Schärfe, *German Patent*, 527807 (1928).
[2] Berzelius, *Acad. Handl. Stockholm*, 1843, p. 1.
[3] Bettendorff, *Sitzungsber. Niederrh. Ges. Bonn*, 1867, p. 67.
[4] Retgers, *Zeitsch. anorg. Chem.*, 1893, **4**, 403.
[5] Hittorf, *Ann. Physik*, 1865, **126**, 193.
[6] Linck, *Ber.*, 1899, **32**, 888.
[7] Laschtschenko, *J. Chem. Soc.*, 1922, **121**, 974. Earlier workers give 5·70 to 5·72.
[8] Erdmann and Reppert, *Annalen*, 1908, **361**, 6.

In 1869 Bettendorff recorded[1] the formation of a voluminous brown precipitate when stannous chloride was added to a solution of arsenious oxide, or of magnesium ammonium arsenate, in hydrochloric acid. The precipitate proved to be arsenic (96 to 99 per cent.) with traces of tin which were irremovable. The speed of precipitation depends upon the amount of arsenic present and the temperature. With solutions containing little arsenic, Bettendorff observed, on warming, a yellow colour before the precipitate appeared, but he was unable to prove that the colour was due to arsenic. The reaction involved may be represented thus—

$$2AsCl_3 + 3SnCl_2 = 3SnCl_4 + 2As$$

and when employed for the detection of arsenic is known as Bettendorff's test (see p. 310).

When a mixture of phosphorus and arsenic trichlorides is treated with water, the arsenious acid first formed is rapidly reduced to arsenic, which is deposited[2] as a brownish-black amorphous powder of density 3·7 at 15° C. Engel[3] obtained this brown precipitate by reduction of arsenious acid with stannous chloride, hypophosphorous acid, copper, and by electrolysis. He gave the density as 4·6, however, and maintained that the vitreous β-form, the grey γ-form and the brown precipitate were all identical, the differences in appearance being due only to the state of subdivision. He suggested, therefore, that there were only two allotropic forms, crystalline and amorphous, and these he compared with white and red phosphorus, observing that the ratio between the densities of the two forms, 1·245, was the same as in the case of the two forms of phosphorus (1·244); moreover, the amorphous form sublimes in an inert gas at 280° to 310° C. and after some hours sublimation ceases, leaving a residue of crystalline arsenic which does not sublime below 360° C., the transformation temperature (p. 31). In the same way ordinary phosphorus sublimes at a lower temperature than that at which it is converted to red phosphorus. The analogy may not be pushed too far, however.[4] Attempts to produce a doubly refractive form of arsenic analogous to the doubly refractive form of white phosphorus, obtained by strongly cooling, have not been successful,[5] even at −190° C.

Linck in 1899[6] established the existence of a *yellow* crystalline variety, obtaining it by gently heating ordinary arsenic in a current of carbon dioxide and rapidly cooling the vapour to below 0° C. in a receiver protected from light.[7] The product dissolved readily in carbon disulphide and the solution yielded, on evaporation, microscopic rhombic dodecahedra belonging to the cubic system and strongly smelling of garlic. These change spontaneously to metallic arsenic, especially on heating or on exposure to light; in the latter case the transformation is complete in about three minutes and may be followed

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[1] Bettendorff, *Sitzungsber. Niederrh. Ges. Bonn*, 1869, p. 128.

[2] Geuther, *Annalen*, 1887, 204, 208. See also Sen, *J. Proc. Asiatic Soc. Bengal*, 1919, 15, 263.

[3] Engel, *Compt. rend.*, 1883, 96, 497, 1314; *Bull. Soc. chim.*, 1888, [2], 50, 194; 1895, [3], 13, 721.

[4] Linck, *Ber.*, 1899, 32, 881.

[5] Vorländer, Selke and Kreiss, *Ber.*, 1925, 58 B, 1802.

[6] Linck, *Ber.*, 1899, 32, 888; 1900, 33, 2284.

[7] Haenny, *Helv. Chim. Acta*, 1930, 13, 725.

microscopically. The characteristic garlic odour usually associated with arsenic vapour appears to be evidence of the presence of the yellow variety.[1] Erdmann and von Unruh [2] obtained this allotrope by heating ordinary arsenic in an aluminium tube at a temperature above 360° C. As the hot vapour left the tube to enter a U-tube surrounded by ice-water, it met a current of cooled carbon dioxide and condensed as the yellow form. This was immediately dissolved by carbon disulphide contained in the U-tube. Stock and Siebert [3] obtained a similar solution by an electrical method; a current of about 12 amperes was passed between a carbon anode and a cathode consisting of an alloy of equal parts of arsenic and antimony, both electrodes being immersed in carbon disulphide contained in a vessel cooled by ice-water. The arsenic dissolved, but the antimony, although disintegrated, did not dissolve. From the solution the yellow form of arsenic was obtained either by evaporation or by crystallisation at $-70°$ C. The yellow allotrope was also obtained by subliming arsenic *in vacuo*, the vapour being cooled by liquid air in the dark.

Durrant [4] in 1919 further investigated the reduction of arsenious acid by means of stannous chloride, using solutions of the two chlorides in hydrochloric acid. The anhydrous chlorides do not react, but the addition of a drop of water is sufficient to cause rapid liberation of arsenic. Durrant observed that in the hydrochloric acid solution the appearance of the arsenic precipitate is always preceded by a pale buff tint; the buff-brown precipitate then separates and the pale colour is best observed in mixtures of such dilution that the precipitation is very slow. If the deposit, after washing, is immediately shaken with carbon disulphide, arsenic dissolves, but the amount going into solution is greater if carbon disulphide is vigorously shaken with the solution of the two chlorides while the reaction is in progress. Evaporation of the carbon disulphide leaves a residue of grey arsenic, but during the process pale-coloured particles of arsenic may be seen to rise to the surface and then rapidly darken. Durrant therefore concluded that the yellow allotrope is first deposited but spontaneously changes to the grey amorphous form. Small quantities of arsenic soluble in carbon disulphide may be obtained by reduction of arsenious acid with zinc dust in presence of the solvent.[5]

Yellow arsenic is extremely sensitive to light, especially ultraviolet, quickly darkening in colour as it changes to the grey form even at very low temperatures. It can be preserved for some time if kept away from light and at a temperature below $-60°$ C. According to Erdmann and Reppert,[6] the formation of grey arsenic is an intermediate stage of the transformation of the yellow to metallic arsenic. In red light the formation of the metallic form is extremely slow. In solution in carbon disulphide, the yellow form shows no tendency to change to the metallic,[7] but on standing the solution slowly deposits the brown modification, which is not sensitive to light.

The solubility of yellow arsenic in carbon disulphide is as follows: [7]

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[1] Laschtschenko, *J. Chem. Soc.*, 1922, 121, 974.

[2] Erdmann and von Unruh, *Zeitsch. anorg. Chem.*, 1902, 32, 457.

[3] Stock and Siebert, *Ber.*, 1904, 37, 4572; 1905, 38, 966.

[4] Durrant, *J. Chem. Soc.*, 1919, 115, 134.

[5] Erdmann and von Unruh, *loc. cit.*

Temperature, ° C.	−60	−15	0	12	18–20	46
Grams As in 100 c.c. CS_2	0·8–1·0	2·0–2·5	3·8–4·0	5·5–6·0	7·5–8·0	11

The elevation of the boiling point of carbon disulphide resulting from the dissolution corresponds with the molecular formula As_4.

The significance of the difference in density of the various forms of arsenic has been the subject of much speculation. The density of the yellow allotrope is,[1] at 18° C., 2·026 and at −50° C. 2·35 and, like that of the metallic form, 5·73, is quite definite, whereas the amorphous forms vary considerably in density according to the conditions of formation, the following values being recorded: vitreous 4·71 to 4·74; grey or black, as obtained in arsenical mirrors, 4·60 to 4·74; brown, obtained by reduction of arsenic compounds in solution, 3·7 to 4·7. Watts, as early as 1850,[2] suggested that this difference in the compactness of the constituent matter was the explanation of the supposed allotropic states, while Engel, as stated on p. 28, said that there was only one amorphous allotrope, the different forms being due to the state of subdivision. Erdmann,[3] on the other hand, assumed that differences in molecular constitution explained the relation between the different varieties, thus—

$$\begin{array}{ccccccc} \text{Yellow} & \longrightarrow & \text{Brown} & \longrightarrow & \text{Grey} & \longrightarrow & \text{Metallic} \\ As_4 & & As_8 & & As_2 & & As \end{array}$$

these changes being brought about by light. Geuther [4] had previously observed that the densities of the three last varieties were in the ratio 4 : 5 : 6 and suggested the formulæ $(As_4)_2$, $(As_4 + As_6)$ and $(As_6)_2$. But such molecular formulæ were based on insufficient evidence. The contention that the compactness of the constituent matter was the governing factor was revived by Kohlschütter and his co-workers,[5] who considered that yellow arsenic, specific volume 0·492, passed into the metallic form, specific volume 0·175, merely by a process of condensation, a given amount of matter passing into a much smaller space; also that the grey and brown forms were the same as the metallic but in more diffuse states.

The grey form may be obtained from the yellow in carbon disulphide solution by treating with alcohol, or by cooling with carbon dioxide and ether or with liquid air. It is stable towards atmospheric oxygen, and is oxidised by nitric acid more slowly than the brown and metallic modifications.

The yellow, grey and brown forms do not conduct electricity, whereas metallic arsenic is a conductor. This difference has been made use of in determining the temperatures at which the metallic variety is produced from the other forms at a sensible rate. Bettendorff (1867),

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[1] Erdmann and Reppert, *loc. cit.*

[2] See Gmelin's "*Handbook of Chemistry*" (London), 1850, 4, 251.

[3] Erdmann and Reppert, *Annalen*, 1908, 361, 1; "*Lehrbuch der anorganischen Chemie*," 1910, p. 370.

[4] Geuther, *Annalen*, 1880, 204, 208.

[5] Kohlschütter, Frank and Ehlers, *Annalen*, 1913, 400, 268.

Engel (1883) and Linck [1] (1899) stated that amorphous arsenic is transformed at 360° C., irreversibly and with considerable development of heat, into metallic arsenic ; Erdmann and Reppert gave 303° C. as the transformation temperature, while Jolibois [2] and Gaubeau [3] determined the point of irreversible transformation both of the brown and grey varieties to be 270° to 280° C. Erdmann gave the transition point between the brown form and the grey form as 180° C., but such a critical point has not been substantiated. Jolibois asserted that his thermal observations admitted only two allotropes, the ordinary grey metallic form, stable up to its melting point, 850 ± 10° C., and an unstable yellow amorphous form which undergoes an irreversible transformation into the metallic form at 285° C. The yellow form he considered to be identical with the vitreous modification.

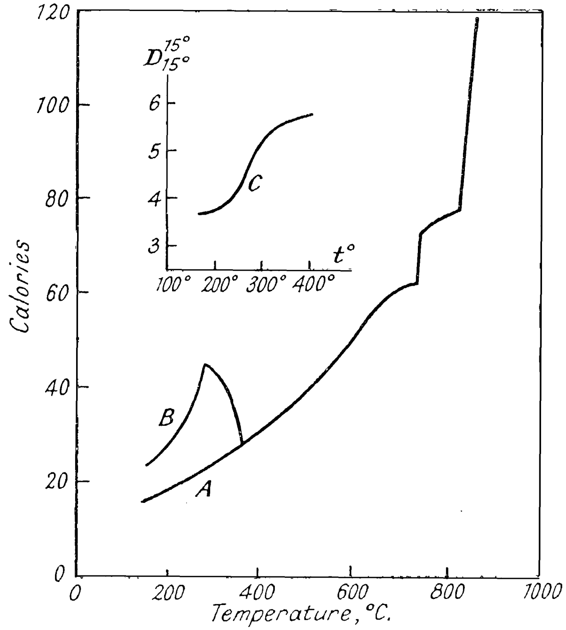

FIG. 1.—Cooling Curves of (A) Metallic Arsenic, (B) Amorphous Arsenic. (C) Density Curve for Amorphous Arsenic.

Thus, while it was generally accepted that the grey metallic and the yellow crystalline forms were true allotropic modifications, there was considerable confusion of thought as regards the so-called amorphous forms. Laschtschenko [4] in 1922 therefore attempted to elucidate the nature of these forms. He measured the amount of heat evolved during cooling from a high temperature of samples of metallic arsenic, purified by sublimation in a vacuum, and of amorphous arsenic prepared by reduction with tin of arsenious oxide dissolved in hydrochloric acid. The operations were carried out in sealed quartz-glass tubes. The cooling curves, fig. 1, showed for metallic arsenic, A, between 868° and

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[1] Linck, *Ber.*, 1899, 32, 888; 1900, 33, 2284.

[2] Jolibois, *Compt. rend.*, 1911, 152, 1767.

[3] Gaubeau, *ibid.*, 1914, 158, 121.

822° C. a sudden increase in the amount of heat evolved owing to solidification, the latter temperature being above the point of fusion of arsenic,[1] and a break at 750° to 738° C., indicating the change to the yellow allotrope. The curve B for the amorphous form is typical of monotropic transformation. It will be seen that the transformation points given above, 270° to 280° C. and 360° C., correspond respectively with the maximum point of B and the point of coincidence of B and A. A series of determinations of density of amorphous arsenic which had been heated in sealed quartz-glass tubes and rapidly cooled to 15° C. showed continuous change (curve C); at 260° to 265° C. the density corresponds with that of the grey modification, and at 360° C., when the curve becomes almost horizontal, with that of the metallic form. The values obtained were:

t° C. . . .	15	175	235	255	275	305	365	400
D_{15}^{15} . . .	3·693	3·698	3·974	4·493	4·947	5·365	5·731	5·729

The density of the pure metallic form at 15° C. was 5·7301. These results suggested that the amorphous forms of arsenic are more probably solid solutions of the yellow and metallic forms rather than true allotropes, the densities depending on the proportions of the two forms present (compare the values given on p. 30). Engel's experiments (p. 28) on the sublimation of arsenic support this contention. The sublimation temperature of amorphous arsenic in a vacuum is about 260° C. and 280° to 310° C. in an inert gas, while that of metallic arsenic is variously given as 450°[2] in hydrogen and 554°[3] and 616° C.[4] at 760 mm. in air. At 360° C. sublimation of the amorphous form ceases, but by sufficiently prolonged sublimation at 310° C. complete transformation of the metastable amorphous phase into the stable metallic modification may be effected. This is in accordance with the distillation of the more volatile component of a solid solution, leaving the component which is non-volatile at the particular temperature. The objection to this conception is that such a change should be reversible, whereas the change of amorphous to metallic arsenic is definitely an irreversible exothermic transformation.

Laschtschenko therefore suggested that the amorphous forms may be of colloidal origin and may thus represent stages in the continuous passage from the colloidal to the crystalline state. The mode of preparation of the brown form by reduction of arsenic compounds in solution is favourable to sol formation, and the view that the various forms differed only in degree of dispersion of the particles has already been mentioned (p. 30). X-ray investigations[5] show that the precipitated

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[1] For other determinations of the melting point of arsenic, see p. 37.

[2] Conechy, *Chem. News*, 1880, 41, 181.

[3] Krafft and Knocke, *Ber.*, 1909, 42, 202.

[4] Jonker, *Chem. Weekblad*, 1908, 5, 783 Preuner and Brockmoller (*Zeitsch. physikal. Chem.*, 1913, 81, 129) give the following sublimation temperatures: at 334 mm., 569° C.; at 430 mm., 580° C.; at 586 mm., 600° C.

[5] Jung, *Centr. Mineral. Geol.*, 1926, A, 107.

brown arsenic, brown translucent arsenic obtained by sublimation, and the arsenic mirror, brown in thin layers by transmitted light, are all amorphous and apparently identical.

A more recent investigation [1] has shown that the product obtained when arsenic vapour condenses below 100° C. in pure hydrogen is amorphous to the X-rays and is a powder of very small particle size. When the vapour is condensed between 100° C. and 130° C. a mixture of powder and coherent sheet is obtained, while between 130° and 250° C. only the coherent sheet or glass is formed. The metallic lustre of the latter increases with the temperature of condensation. It is shown to be amorphous by the X-rays. Above 250° C. the deposit is distinctly crystalline to the X-rays.

The transformation of amorphous arsenic to the crystalline form can be accelerated by the presence of certain catalysts,[2] hydrogen iodide being one of the most active; the transformation temperature is thereby considerably lowered and the change has been induced at 180° C., 90° lower than the temperature previously observed (see p. 31).

Investigation by X-ray methods [3] of the structure of samples of arsenolamprite from two different localities showed only partial agreement with that of metallic rhombohedral arsenic; the differences may be attributed to the presence of impurity in the minerals, but could also be explained by the presence of a second allotropic modification corresponding to black metallic phosphorus (see p. 35).

Colloidal Arsenic.—Arsenic sols may be prepared by the reduction of arsenic compounds under suitable conditions. For example,[4] a mixture containing 1 gram of arsenious oxide and 8 c.c. of hydrochloric acid ($D=1{\cdot}182$) is shaken until dissolution is complete, and then poured into 50 c.c. of warm Paal's liquid [5] acidified with acetic acid. A slight excess of hypophosphorous acid is added and the mixture kept on a water-bath for about 15 minutes until reduction is complete. After cooling, sodium carbonate is added to cause complete precipitation, and the precipitate separated by centrifuging. It is then redissolved in 20 per cent. aqueous sodium hydroxide, and on evaporation a water-soluble product containing 23 to 27 per cent. of arsenic remains. The hydrosol is purified by dialysis; it is negatively charged and fairly stable in air.

Stable hydrosols may be obtained similarly by reduction of arsenious oxide, dissolved in aqueous sodium hydroxide containing some other protective colloid such as gelatin or egg-albumin, by means of alkaline pyrogallol.[6] Salts of metallic acids, such as sodium antimonate or calcium plumbate, with or without the addition of protalbic acid, may also be employed as protective colloids.[7]

Colloidal arsenic is also formed by electrolytic reduction of a cold alkaline solution of arsenious oxide using a platinum cathode and a mercury anode,[8] a small current density being employed; a trace of

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[1] McCormick and Davey, *Phys. Review*, 1935, [2], 47, 330.
[2] Levi and Ghiron, *Atti R. Accad. Lincei*, 1933, 17, 565.
[3] Jung, *loc. cit.*
[4] Gerasimov, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 269.
[5] Paal, *Ber.*, 1902, 35, 2206, 2224. This liquid is an aqueous solution of sodium protalbate or lysalbate; the solute functions as a protective colloid.
[6] Heyden, *German Patent*, 202561 (1908).
[7] Chwala, *American Patent*, 1573375 (1926).
[8] Lecoq, *Compt. rend.*, 1910, 150, 700, 887; Fouard, *ibid.*, 1927, 184, 328.

protective colloid should be present and the solution purified by dialysis. Hydrosols may also be obtained by subjecting dilute aqueous solutions of arsenious oxide to a silent electric discharge[1] in a current of hydrogen, or of a mixture of hydrogen and arsine. Alcosols of arsenic have also been obtained by the latter method, replacing water by ethyl, butyl or amyl alcohol.

The hydrosol is generally brown in colour, and has little toxicity for animals. The element may be precipitated by addition of alcohol[2] or acetone. A sol containing a protective colloid is not affected appreciably by the addition of hydrochloric or sulphuric acid or of sodium or barium chloride; sodium hydroxide or carbonate causes the colour to change to light yellow.[3] Sols having a yellow to bluish-violet colour have been prepared[4] by passing pure arsine through water exposed to light of short wavelengths; the particles are negatively charged and are little affected by electrolytes.[5]

Stable sols of arsenic in glacial acetic acid have been prepared[6] by dissolving yellow arsenic (0·12 g.) in carbon disulphide (333 ml.) and pouring the solution into pure anhydrous glacial acetic acid (667 ml.). The stability of the sols, which are yellow in colour, is decreased on addition of a protective colloid (0·1 g. per l.), and also on attempting to remove carbon disulphide by dialysis or by heating.

General Physical Properties of Arsenic.

Arsenic in the stable metallic form consists of light-greyish lustrous crystals possessing the symmetry of the ditrigonal scalenohedral class (dihexagonal alternating) of the rhombohedral system.[7] This describes both the native and artificial crystals, although the former are usually indistinct. The axial ratio referred to hexagonal axes $a : c$ is, according to Rose,[8] 1 : 1·4025, and to von Zepharovich[9] 1 : 1·4013; if the three edges of the unit rhombohedron which meet in the trigonal axis be taken, the angle θ (100) : (010) is[9] 94° 56′; this corresponds to an angle γ 84° 36′ between the three axes. The crystals, when obtained by sublimation, often twin parallel to the (110) face.[10] Cleavage occurs most readily parallel to the (111) face, but it may occur parallel to the (110) face. Examination of an X-ray spectrograph of powdered metallic arsenic shows that the *crystal structure*[11] consists of two interpenetrating rhombohedral space lattices of axial ratio 2·805, the length of edge of the rhomb being 4·145 A. This is represented in fig. 2, the black circles indicating atoms lying in a single lattice. Regarded as a face-centred lattice the rhombohedron ABCDEF is the unit, the distance AB being

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[1] Miyamoto, *J. Chem. Soc. Japan*, 1934, **55**, 1273.

[2] Auger, *Compt. rend.*, 1907, **145**, 718.

[3] Gutbier and Krautle, *Kolloid-Zeitsch.*, 1917, **20**, 186.

[4] Dede and Walther, *Ber.*, 1925, **58**, 99.

[5] For other methods of obtaining colloidal arsenic, see Auger, *loc. cit.*; Plauson, *English Patents*, 155834, 182696 (1921).

[6] Elder and Burkard, *J. Physical Chem.*, 1937, **41**, 621.

[7] Groth, "*Chemische-Krystallographie*," 1906, 1, 19.

[8] Rose, *Sitzungsber. Akad. Berlin*, 1849, p. 72.

[9] von Zepharovich, *Sitzungsber. K. Akad. Wiss. Wien*, 1875, **71**, 272.

[10] See also Zenger, *ibid.*, 1861, 44, 309; Mugge, *Jahrb. Miner.*, 1886, **1**, 183.

[11] Bradley, *Phil. Mag.*, 1924, [6], **47**, 657; Linck and Jung, *Zeitsch. anorg. Chem.*, 1925, **147**, 288; von Olshausen, *Zeitsch. Krist.*, 1925, **61**, 463; Ewald and Hermann, *ibid.*, 1927, **65**, Suppl., 27.

5·60 A. In each unit rhomb there are four atoms of the first lattice and four of the second lattice, the latter being shown as plain circles. The smaller and more acute rhombohedron AGHDKL is the unit cell of the structure, regarding it as being composed of two simple rhombohedral lattices. The points MNOS of the second lattice correspond to the points AGLR of the first, and A and M constitute a point pair. The general structure is similar to that of antimony[1] and bismuth,[2] but the edge of the unit rhomb, corresponding to AB above, in the case of antimony is 6·20 A. and of bismuth 6·56 A. The shorter interatomic distance of the atoms of the arsenic crystal is stated[3] to be 2·51 A. Various values for the atomic radius of arsenic have been derived, namely: 1·26,[4] 1·36,[5] 1·37[6] and 1·16[7] A.

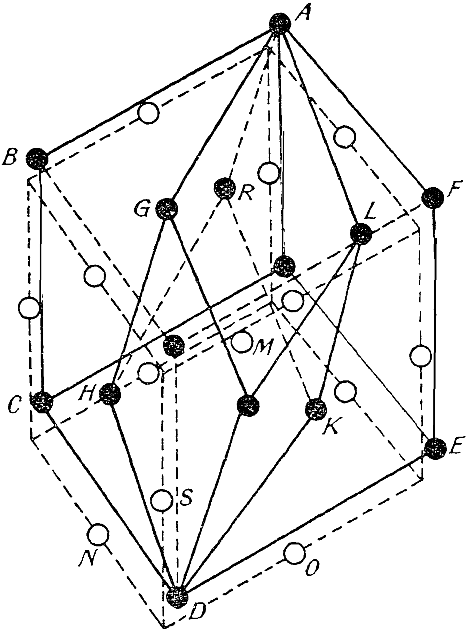

FIG. 2.—The Crystal Structure of Metallic Arsenic.

As already described, other crystalline forms of arsenic besides the rhombohedral are known or suspected to exist. The crystals of the yellow allotrope belong to the cubic system, while native arsenolamprite (p. 8) contains crystals belonging to the rhombic, or possibly to the monoclinic, system. Yellow arsenic is soluble in carbon disulphide.

Metallic arsenic is brittle and of *hardness*[8] 3·5 (Mohs' scale), the Brinell number being[9] 147·0. The *fracture* is uneven and finely granular. The mean *compressibility* at 20° C. between 100 and 500 megabars is[10] $4·5 \times 10^{-6}$. The *specific heat* has been determined over various ranges of temperature and also at specific temperatures. The results are given in the following table, together with the atomic heats at the specific temperatures; unless otherwise stated, the data refer to the metallic form.

The *linear coefficient of thermal expansion*[11] at 40° C. is $5·59 \times 10^{-6}$, and the increase in unit length over the range 0° to 100° C. is $6·02 \times 10^{-4}$.

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[1] James and Tunstall, *Phil. Mag.*, 1920, [6], 40, 233.

[2] James, *ibid.*, 1921, [6], 42, 193.

[3] Bradley, *loc. cit.*

[4] Bragg, *Phil. Mag.*, 1920, [6], 40, 169.

[5] Bozorth, *J. Amer. Chem. Soc.*, 1923, 45, 1621.

[6] Gapon, *Zeitsch. Physik*, 1927, 44, 535; Perlitz, *Scientists' Soc. Tartu*, 1928, 35, 121.

[7] Huggins, *Phys. Review*, 1926, [2], 28, 1086; de Jong and Willems, *Physica*, 1927, 7, 74.

[8] Rydberg, *Zeitsch. physikal. Chem.*, 1900, 33, 353.

[9] Edwards and Herbert, *J. Inst. Metals*, 1921, 25, 175.

[10] Richards, *J. Amer. Chem. Soc.*, 1915, 37, 1643.

[11] Fizeau, *Compt. rend.*, 1869, 68, 1125.

Temperature Range, ° C.	Mean Specific Heat.	Temperature, ° C.	Specific Heat.	Atomic Heat.
21– 66	0·0830[1]	28	0·0772[4]	5·78
0–100	0·0822[2]	– 39	0·0736[4]	5·51
–188– 20	0·0705[3]	–136	0·0619[4]	4·64
21– 65	$0{\cdot}0758_{\text{amorph.}}$[1]	–223 approx.	0·0258[5]	1·93
0–100	$0{\cdot}0840_{\text{grey}}$[2]			

According to Jannettaz,[6] the *thermal conductivity* perpendicular to the (111) face of a crystal of metallic arsenic is nearly twice as great as it is parallel to the chief axis. Little[7] gives the coefficient of thermal conductivity in absolute units at 20° C. to be $3{\cdot}68 \times 10^6$.

When heated under ordinary pressure, arsenic does not melt; the metallic form volatilises at a dull red heat, while amorphous arsenic does so at a lower temperature. The *sublimation temperatures* are given on p. 32. Even at ordinary temperature the element possesses an appreciable vapour pressure, as may be shown[8] by enclosing pieces of arsenic and silver in a vessel, but not in contact with each other; after some months the silver is found to be coated with a film of arsenide. *Vapour pressure* measurements of grey metallic arsenic and its liquid at temperatures up to 853° C. have been made; the results, expressed in atmospheres, are as follows:

Temp., ° C.	Vapour Press. (Solid As). Preuner and Brockmoller.[9]	Temp., ° C.	Vapour Press. (Solid As). Horiba.[10]	Temp., ° C.	Vapour Press. (Liquid As). Horiba.[10]
400	0·008	450	0·026	808	34·2
450	0·025	500	0·076	817	35·7
476	0·042	550	0·222	830	38·1
500	0·080	604	0·785	843	40·5
526	0·171	615·5	0·997	850	41·6
557	0·376	658	2·392	853	42·2
580	0·566	697	4·85		
600	0·771	741	9·7		
(633	1·0)[11]	772	16·9		
		790	22·3		
		815	33·6		

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[1] Bettendorff and Wullner, *Pogg. Annalen*, 1867, 131, 293; see also Regnault, *Ann. Chim. Phys.*, 1840, [2], 73, 39.

[2] Wigand, *Ann. Physik*, 1907, [4], 22, 64, 91.

[3] Richards and Jackson, *Zeitsch. physikal. Chem.*, 1910, 70, 414; see also Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2296.

[4] Ewald, *Ann. Physik*, 1914, [4], 44, 1213.

[5] Dewar, *Proc. Roy. Soc.*, 1913, 89 A, 158.

[6] Jannettaz, *Compt. rend.*, 1892, 114, 1352; *Bull. Soc. franç. Min.*, 1892, 15, 133.

[7] Little, *Phys. Review*, 1926, [2], 28, 418.

[8] Zenghelis, *Zeitsch. physikal. Chem.*, 1906, 57, 90.

[9] Preuner and Brockmoller, *Zeitsch. physikal. Chem.*, 1913, 81, 167. See also Gibson, *Dissertation*, Breslau, 1911.

[10] Horiba, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, 25, 387.

[11] Ruff and Mugdan, *Zeitsch. anorg. Chem.*, 1921, 117, 147.

By extrapolation of the vapour pressure curves (fig. 3) Horiba showed the *melting point* to be 817° to 818° C. at the corresponding pressure of 35·8 atm. Johnston[1] deduced the following *boiling temperatures* at low pressures—

p (mm. Hg) .	10^{-3}	10^{-2}	10^{-1}	1	10	50	100	760
B.pt., ° C. . .	220	260	310	360	430	490	510	610

and calculated the *molar heat of vaporisation* to be 30·5 Cal.[2] The *molar heat of sublimation* was calculated by Horiba to be 33·6 Cal., the *molar heat of fusion* 22·4 Cal., and the *molar heat of vaporisation of the liquid* 11·2 Cal. The boiling point of arsenic was determined by Mott[3] to be 616° C.

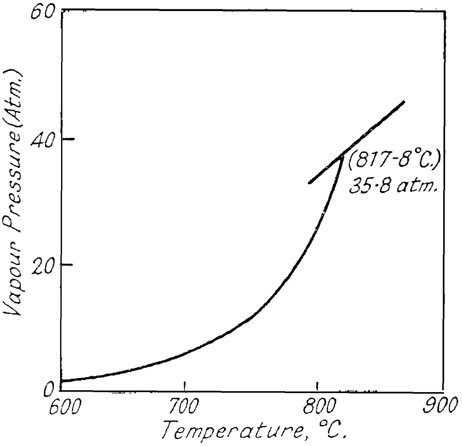

Fig. 3.—Vapour Pressure of Metallic Arsenic and its Liquid.

Much difficulty has been encountered in determining the melting point of arsenic. Landolt[4] in 1859 by prolonged heating to dull redness in a sealed glass tube encased in one of iron obtained liquid globules, and by using similar methods Mallet[5] decided that arsenic melted at a temperature between the melting points of antimony (629° C.) and silver (960° C.). Jonker stated[6] that there was no sign of fusion at 800° C. In 1911, however, Jolibois[7] succeeded in fusing arsenic in a quartz tube and by means of a thermocouple determined the melting point to be 850 ± 10° C. A number of subsequent determinations have been made, with the following results: 814·5 ± 0·5° C.;[8] 817° C.;[9] 818° C.;[10] the two latter values agree with Horiba's value given above, but are somewhat lower than Laschtschenko's value, 822° C., see p. 32. From the crystal lattice data (p. 35) it has been deduced that liquid arsenic should expand during solidification by 5·1 per cent.[11]

The *vapour density* of arsenic varies with the temperature. At

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[1] Johnston, *J. Ind. Eng. Chem.*, 1917, 9, 873.

[2] See also de Forcrand, *Compt. rend.*, 1901, 133, 368, 513; Henglein, *Zeitsch. Elektrochem.*, 1920, 26, 431.

[3] Mott, *Trans. Amer. Electrochem. Soc.*, 1918, 34, 255. See also Ruff and Bergdahl, *Zeitsch. anorg. Chem.*, 1919, 106, 76; Ruff and Mugdan, *ibid.*, 1921, 117, 147.

[4] Landolt, *Neues Jahrb. Min.*, 1859, p. 733. See also Guntz and Broniewski, *Bull. Soc. chim.*, 1907, IV, 1, 977.

[5] Mallet, *Chem. News*, 1872, 26, 97.

[6] Jonker, *Zeitsch. anorg. Chem.*, 1909, 62, 91.

[7] Jolibois, *Compt. rend.*, 1911, 152, 1767; 1914, 158, 121. See also Guertler and Pirani, *Zeitsch. Metallkunde*, 1909, 11, 1.

[8] Heike and Leroux, *Zeitsch. anorg. Chem.*, 1915, 92, 119; Heike, *ibid.*, 1921, 118, 254.

[9] Goubau, *Compt. rend.*, 1914, 158, 121.

[10] Rassow, *Zeitsch. anorg. Chem.*, 1920, 114, 117.

[11] Perlitz, *Scientists' Soc. Tartu*, 1928, 35, 121.

about 600° C. it approximates to the value 10·38 required by As_4.[1] Thus Deville and Troost[2] obtained the values 10·6 at 563° C. and 10·2 at 720° C. As the temperature rises the vapour density decreases and approaches the value for As_2 (5·19);[3] thus the following values have been obtained:[4] 5·543 at 1714° C., 5·451 at 1736° C.; and also[5] 5·4 at 1700° C. Preuner and Brockmöller[6] devised a spiral quartz manometer which enabled them to obtain accurate readings of gas pressures at temperatures from 800° to 1200° C., and so obtained the isothermal curves of arsenic at intervals of 100° between these two temperatures. From their results they concluded that the vapour consists of a mixture of tetratomic, diatomic and monatomic molecules.[7]

The *refractive index*[8] of arsenic vapour for light of wavelength 5893 A. is 1·001550, and for 5460 A. 1·001580. Calthrop[9] observed that the relation between the refractivity and the atomic volume does not correspond with the values obtained for nitrogen and phosphorus, and that whereas the curve obtained by plotting refractivity against atomic volume for elements of a given group is usually a straight line, the value for arsenic is much too low. This is shown by the following data, the estimates of atomic radii being those of Bragg:

	Atomic Radius (A.) r.	Atomic Volume (cubic A.) $\frac{4}{3}\pi r^3$.	Refractivity $(\mu_D - 1) \times 10^{-6}$.	$\frac{\text{Refractivity}}{\text{Atomic Vol.}}$
N . .	0·65	1·152	297·1	257·9
P . .	1·03	4·577	1212·0	264·8
As . .	1·26	8·383	1552·0	185·1

From the determination of the molecular refractions of a large number of organic compounds containing tervalent arsenic, the atomic refraction of arsenic in each compound has been calculated,[10] the values obtained varying from 9·2 to 14·39. Hydrogen, chlorine and alkyl groups in an arsine exert about the same influence on the atomic refraction of arsenic, but replacement of any of these by aryl groups causes an increase in the atomic refraction. The opposite effect results from substitution by a cyanide, oxalate or alkoxyl radical.

Certain organic compounds containing arsenic which are optically active appear to owe their activity to an asymmetric tervalent arsenic atom.[11]

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[1] Mitscherlich, *Ann. Chim. Phys.*, 1833, [2], **55**, 5; Bineau, *Compt. rend.*, 1859, **49**, 799.

[2] Deville and Troost, *ibid.*, 1863, **56**, 891.

[3] Mensching and Meyer, *Ber.*, 1887, **20**, 1833.

[4] Meyer and Biltz, *ibid.*, 1889, **22**, 725.

[5] Biltz, *Zeitsch. physikal. Chem.*, 1896, **19**, 385.

[6] Preuner and Brockmoller, *ibid.*, 1912, **81**, 129.

[7] The equilibrium was also studied by Dushmann, *J. Amer. Chem. Soc.*, 1921, **43**, 397.

[8] Cuthbertson and Metcalfe, *Phil. Trans.*, 1907, A **207**, 135; *Proc. Roy. Soc.*, 1907, A **79**, 202. For early work on the refractive power of arsenic vapour, see Haagen, *Pogg. Annalen*, 1867, **131**, 117; Gladstone, *Proc. Roy. Soc.*, 1868, **16**, 439.

[9] Calthrop, *Phil. Mag.*, 1924, [6], **47**, 772.

[10] Gryszkiewicz-Trochimovski and Sikorski, *Rocz. Chem.*, 1927, **7**, 54; 1928, **8**, 421; *Bull. Soc. chim.*, 1927, [4], **41**, 1570.

[11] Allen and Wells, *J. Amer. Chem. Soc.*, 1933, **55**, 3894.

The action of light on yellow arsenic has been described on p. 29; the rate of change is not affected by radium rays. When placed in the light from a mercury lamp, arsenic exhibits a photoelectric effect, emitting electrons; the longest effective wavelength is λ 2360. At 1100° to 1150° C. a resonance series is excited in the vapour of arsenic [1] by each of the mercury lines λλ 2483, 2536, 2654 and 2804; the fundamental frequency is apparently 410 cm.^{-1}, which gives as the distance As to As in the diatomic molecules 1·94 A., or 77 per cent. of the distance in crystalline arsenic (see p. 35).

Arsenic vapour incident on sodium chloride crystals gives a weak specular beam with much diffuse scattering.[2] Arsenic is also diffusely reflected from crystals of fluorite or orthoclase. Arsenic layers on glass, of such thickness that 10 to 15 per cent. of incident light is transmitted at room temperature, are transparent at liquid air temperatures. Thick layers deposited at liquid air temperatures are black, but on warming become successively, in abrupt changes, deep red, bright yellow, and finally the usual steel grey of metallic arsenic.

The *ionisation potential* for electrons in arsenic vapour has been calculated to be 9·04 volts; [3] the value previously accepted was 11·54 volts.[4] The *inelastic collision potential* is 4·69 volts, and the *resonance potential* 4·7 volts.[5] The *electrical conductivity* of metallic arsenic at 0° C. is 0·00285 mho.[6] The yellow and amorphous forms do not conduct electricity appreciably. The specific resistance of grey arsenic has been determined [7] at various temperatures as follows:

Temperature, ° C. .	Cold	190°	200°	220°	240°	255°
Resistance, ohms .	∞	40,000	30,000	15,000	7000	4100

The effect on the resistivity of maintaining the element at 260° C. is shown in the following results:

After 20 minutes, resistance was 3400 ohms
,, 70 ,, ,, ,, 1000 ,,
,, 90 ,, ,, ,, 250 ,,
,, 170 ,, ,, ,, 11 ,,

According to Matthiessen and von Bose,[8] the electrical resistance at any temperature θ between 12° and 100° C. may be obtained from the equation

$$R_\theta = {}_0(R1 - 0{\cdot}0038996\theta + 0{\cdot}058879\theta^2)$$

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[1] Swings and Migeotte, *Compt. rend.*, 1933, 197, 836.

[2] Ellett and Zahl, *Phys. Review*, 1929, [2], 33, 124.

[3] Piccardi, *Atti R. Accad. Lincei*, 1927, [6], 6, 305.

[4] Foote, Rognley and Mohler, *Phys. Review*, 1919, [2], 13, 59; Ruark, Mohler, Foote and Chenault, *J. Franklin Inst.*, 1924, 198, 541; *Nature*, 1923, 112, 831; *Phys. Review*, 1924, [2], 23, 770.

The pressure coefficient of resistance of arsenic is negative.[1] Little[2] gives the specific resistance at 20° C. as 46,000 ohms and the temperature coefficient of resistance as −0·00435 per degree.

The electrical conductivity of a pure arsenic crystal has been measured[3] at temperatures down to 2·42° Abs. The resistance-temperature curve is similar to those of pure metals. There is evidence of definite residual resistance being maintained at low temperatures, but arsenic does not exhibit the abnormally high residual resistance shown by bismuth, nor does it show superconductivity. The resistance is by no means proportional to the absolute temperature. It has been estimated that the electrical resistance of liquid arsenic at the melting point is about 0·4 of that of the solid phase.[4]

The *single potential* of arsenic in various solutions has been determined.[5] The electrodes used were made in various ways, but the most reliable results were obtained with a solid stick of arsenic; electrodes made by electroplating arsenic on other metals were unsatisfactory. The following combination was used—

Hg | HgCl in 0·5N KCl | Solution of Electrolyte | As

and taking −0·56 for the value of the calomel electrode, the following values were obtained with standard solutions of various electrolytes:

SINGLE POTENTIALS OF ARSENIC IN SOLUTIONS OF ELECTROLYTES.

Electrolyte.	Concentration.	Volts.	Electrolyte.	Concentration.	Volts.
$AsCl_3$	1 g. equiv. per l.	−0·554	K_3AsO_4	0·5 g. equiv. per l.	−0·381
AsI_3	,,	−0·540	Na_3AsO_4	,,	−0·381
NaCl saturated with As_2O_3	,,	−0·365	Na_3AsO_3	,,	−0·054
KCl saturated with As_2O_3	,,	−0·365			

Using the scale in which hydrogen is zero, the electrode potential of arsenic in contact with normal arsenious chloride is −0·27 volt.[6] Using an electrode formed by plating arsenic on copper, Marquis[7] made a series of potential measurements in an alcoholic solution of arsenious chloride and from his results concluded that arsenic should be placed between hydrogen and copper in the electromotive series; the nature of the electrolyte used, however, influences the relative positions of

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[1] Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1921, 56, 61; 1929, 64, 51; 1933, 68, 27, 95.

[2] Little, *Phys. Review*, 1926, [2], 28, 418. See also Bridgman, *loc. cit.*

[3] McLennan, Niven and Wilhelm, *Phil. Mag.*, 1928, [7], 6, 666.

[4] Perlitz, *Scientists' Soc. Tartu*, 1928, 35, 121.

[5] Kahlenberg and Steinle, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 493. See also Neumann, *Zeitsch. physikal. Chem.*, 1894, 14, 220; von Zawidzki, *Ber.*, 1903, 36, 1435; Le Blanc and Reichenstein, *Zeitsch. Elektrochem.*, 1909, 15, 261.

[6] Neumann, *loc. cit.*; Wilsmore, *Zeitsch. physikal. Chem.*, 1900, 35, 318.

[7] Marquis, *J. Amer. Chem. Soc.*, 1920, 42, 1569. See also Schuhmann, *ibid.*, 1924, 46, 1444.

metals in the series,[1] and arsenic is generally placed between bismuth and copper thus : Pb, H, Sb, Bi, As, Cu, Hg, Ag, Pd. Thus arsenic is able to replace copper, mercury and silver from solutions of their salts. The reaction which takes place in these cases may be represented thus—

$$6MX + 2As + 3H_2O = 6M + 6HX + As_2O_3$$

M being a univalent metal and X a univalent acid radical. Arsenic may similarly be replaced by metals, but the replacement cannot always be predicted from the position of arsenic in the electrochemical series, this power of replacement being a highly specific property which depends on the nature of the metal and the conditions of the experiment. Such reactions in liquid ammonia solutions show that in the following series an element will in general replace any subsequent element, if it is present in an analogous anion : [2] I, S, Se, Te, As, Sb, Sn, Bi, Pb.

The *overvoltage* of hydrogen on an arsenic electrode has been determined [3] by measuring the back e.m.f. or polarisation of a cell consisting of a platinum anode and an arsenic cathode in normal sulphuric acid. By the open-circuit method the value obtained was 0·379 volt, and by the closed-circuit method 0·478 volt. With 2N sulphuric acid the value at 25° C. is [4] 0·369 ± 0·014 volt. According to Grube and Kleber,[5] the electrolytic discharge of hydrogen ions at an arsenic cathode yields arsine as the primary product, and gaseous hydrogen is formed by decomposition of this hydride. Lloyd,[6] however, studied the electrolysis of sulphuric, hydrochloric, phosphoric, oxalic and tartaric acids, using various concentrations and employing a cathode of polished compact arsenic, with the following conclusions: Initial polarisation at low c.d.'s yields a high overpotential which is not maintained at high c.d.'s. A maximum is reached so long as no arsine is produced ; in the event of the presence of arsine there is a decrease in the overpotential. The percentage of arsine produced at a fixed c.d. is approximately the same for the different acids and does not greatly vary with the concentration.

The cathodic deposition of arsenic at the dropping mercury cathode has been studied [7] and appears to be complex both in acid and in alkaline solutions ; the polarisation curves do not show reversible shifts. From acid solutions the deposition of antimony or bismuth proceeds reversibly.

The *thermal e.m.f.* of arsenic against copper is $+(7{\cdot}91t + 0{\cdot}051t^2)$ microvolts between 0° and 170° C. ; [8] that of arsenic against lead is $-13{\cdot}56$ microvolts.[9]

Arsenic exhibits *triboelectricity*,[10] becoming negatively charged when rubbed on glass under suitable conditions.

From measurements of the *magnetic susceptibilities* of a large number of arsenic compounds it is found [11] that combined arsenic has two

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[1] Kahlenberg and Steinle, *loc. cit.*

[2] Bergstrom, *J. Amer. Chem. Soc.*, 1925, 47, 1503.

[3] Marquis, *loc. cit.*

[4] Thiel and Hammerschmidt, *Zeitsch. anorg. Chem.*, 1923, 132, 15.

[5] Grube and Kleber, *Zeitsch. Elektrochem.*, 1925, 30, 517.

[6] Lloyd, *Trans. Faraday Soc.*, 1930, 26, 15.

[7] Bayerle, *Rec. Trav. chim.*, 1925, 44, 514.

[8] Little, *Phys. Review*, 1926, [2], 28, 418.

[9] Matthiessen, *Pogg. Annalen*, 1858, 103, 412.

[10] Shaw and Jex, *Proc. Roy. Soc.*, 1928, A 118, 97, 108.

[11] Pascal, *Compt. rend.*, 1922, 174, 1698.

atomic susceptibilities, according to the degree of saturation of it compounds, and the results support the rule that the logarithm of th atomic susceptibility is a function of the atomic number in each natura family. This is the case for the quinquevalent group P, As, Sb, and fo the tervalent group As, Sb, Bi.

From the results of an investigation of thermomagnetic and galvano magnetic effects in arsenic, Little[1] has recorded the following coefficient in absolute e.m.u. at 20° C. :

Specific resistance,	$4·60 \times 10^{4}$
Thermal conductivity,	$3·68 \times 10^{6}$
Peltier heat against lead,	$3·80 \times 10^{5}$
Thomson heat,	$3·33 \times 10^{3}$
Hall coefficient.	$4·52 \times 10^{-2}$
Nernst coefficient,	$2·25 \times 10^{-3}$
Ettingshausen coefficient,	$1·75 \times 10^{-7}$
Righi-Leduc coefficient,	$4·15 \times 10^{-7}$

None of the coefficients varies with the strength of the magnetic field When a plate of arsenic was subjected to a temperature gradient of 10 per cm., a field of 8000 gauss caused a fall in temperature of 0·4°. Th value of the coefficient provisionally defined by the equation

$$\text{Temperature change} = \text{Coefficient} \times (\text{Temperature gradient})^2 \times (\text{Field strength})$$

is, for arsenic, $-6·25 \times 10^{-10}$ at 20° C.

Arsenic may be obtained in a radioactive state by bombardmen with deuterons or neutrons.[2] The activity is accompanied by th emission of γ-rays, β-particles and a few positrons.

Spectrum.—The *line emission spectrum* of arsenic has been th subject of much investigation[3] throughout the whole range of radiation accessible to photography and under varying conditions of excitation It is characterised by a great number of lines and is difficult to analys because many important lines lie in the far ultraviolet or in the infra-red

In the *arc spectrum* there are no lines in the visible region, but man

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[1] Little, *loc. cit.*

[2] Thornton, *Phys. Review*, 1936, [2], 49, 207; Brown and Mitchell, *ibid.*, 1936, [2 50, 593; Harteck and others, *Naturwiss.*, 1937, 25, 477.

[3] For earlier work, see Kirchhoff, *Sitzungsber. K. Akad. Wiss. Berlin*, 1861, p. 63 1863, p. 227; Miller, *Phil. Trans.*, 1862, 152, 861; Robinson, *ibid.*, 1862, 152, 939; Volpicell *Atti R. Accad. Lincei*, 1862, [1], 16, 91; Huggins, *Phil. Trans.*, 1864, 154, 139; Plücker an Hittorf, *ibid.*, 1865, 155, 1; Thalén, *Ann. Chim. Phys.*, 1869, [4], 18, 244; Ditte, *Comp rend.*, 1871, 73, 738; Capron, "*Photographed Spectra*," London, 1877; Ciamician, *Sit zungsber. K. Akad. Wiss. Wien*, 1878, 78, 867; 1880, 82, 425; Huntington, *Amer. J. Sci* 1881, [3], 22, 214; Hartley, *Phil. Trans.*, 1884, 175, 325; 1894, A 185, 161; *Trans Roy. Dublin Soc.*, 1882, [2], 1, 231; *Proc. Roy. Soc.*, 1907, 78, 403; Hartley and Moss *ibid.*, 1912, A 87, 38; Hartley and Adeney, *Phil. Trans.*, 1884, 175, 63; Hartley an Ramage, *Trans. Roy. Dublin Soc.*, 1901, [2], 7, 339; Schumann, *Phot. Runds.*, 1890, 41 71; Kayser and Runge, *Sitzungsber. K. Akad. Wiss. Berlin*, 1893, p. 3; de Gramont *Compt. rend.*, 1894, 118, 591, 746; 1902, 134, 1205, 1908, 146, 1260; "*Analyse spectral directe des minéraux*," Paris, 1895; Demarçay, "*Spectres électriques*," Paris, 1895; Exne and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1901, 110, 964; "*Die Spektren de Elemente bei normalen Druck*," Wien and Leipzig, 1912, Hagenbach and Konen, "*Atla der Emissionsspektra*," Jena, 1905; Konen, *Arch. Sciences Genève*, 1914, [4], 37, 262 Herpertz, *Zeitsch. wiss. Photochem.*, 1906, 4, 175; de Watteville, *ibid.*, 1909, 7, 279 Eder and Valenta, "*Atlas typischer Spektren*," Wien, 1911; Eder, *Sitzungsber. K. Akad Wiss. Wien*, 1913, 122, 607; Pollock, *Proc. Roy. Dublin Soc.*, 1912, [2], 13, 202.

occur between λλ 3000 and 2000 A. The method employed to obtain the arc spectrum is usually to place metallic arsenic in the hollowed ends of carbon or metal poles. Thus Rao [1] used arsenic contained in carbon or aluminium poles and photographed the spectrum between 8800 and 1370 A.; he used the arc in nitrogen for investigating the Schumann region down to 1650 A., and below this the arc in vacuum between carbon poles containing arsenic, and the spark between metallic arsenic electrodes in hydrogen; [2] later [3] the arc in helium and neon enabled him to obtain measurements from 2800 to 500 A. Meggers and de Bruin [4] vaporised arsenic in graphite or copper arcs and by means of concave grating and quartz prism spectrographs measured wavelengths ranging from 10,023·98 to 1889·85 A. Hartley,[5] using solutions of arsenious chloride to moisten graphite electrodes, arranged as shown in fig. 4, found the following to be the most persistent lines :

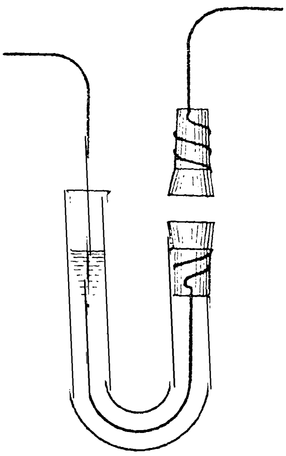

Fig. 4.—Hartley's Apparatus.

Solution $AsCl_3$				
1 per cent. .	2859·7	2779·5	2350·1	2288·9
0·1 ,, ,, .	. .	2779·5	. .	. .

Using the condensed spark, de Gramont [6] gave the following as the *raies de grande sensibilité*, those marked with an asterisk being the *raies ultimes* :

2860·5   2780·2*   2745·0   2349·8*   2288·1

Rao [7] observed a strong ultraviolet triplet at 1972·6, 1937·7 and 1890·5 A., which he stated constitutes the *raies ultimes* of the whole emission spectrum.

The *spark spectrum* exhibits a great many lines throughout the whole range of wavelengths. It includes the lines of the arc spectrum, but the relative intensities are different. Many of the lines have fine structures, and careful analysis of these has made possible a classification of a number of the lines according to whether they belong to the neutral atom (As I), to an atom simply ionised (As II), doubly ionised (As III) or in a higher state of ionisation (As IV, As V, etc.), and the electronic configurations and transitions involved have been derived.[8] The

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[1] Rao, *Proc. Roy. Soc.*, 1929, A 125, 238. See also L. and E. Bloch, *Compt. rend.*, 1914, 158, 1416; 1920, 171, 709; *J. Phys. Radium*, 1921, [6], 2, 229.

[2] See also Rydberg, *Nature*, 1932, 129, 167; Kimball and Bates, *ibid.*, 1931, 128, 969.

[3] Rao, *Proc. Phys. Soc.*, 1932, 44, 594.

[4] Meggers and de Bruin, *Bureau Standards J. Research*, 1929, 3, 765.

[5] Hartley, *J. Chem. Soc.*, 1882, 41, 90; *Phil. Trans.*, 1884, 175, [2], 327.

[6] de Gramont, *Compt. rend.*, 1920, 171, 1106. See also Hulburt, *Phys. Review*, 1925, [2], 25, 888.

[7] Rao, *loc. cit.*

[8] See Lang, *Phil. Trans.*, 1924, p. 396; *Phys. Review*, 1928, [2], 32, 737; McLennan and McLay, *Trans. Roy. Soc. Canada*, 1927, iii, 21, III, 63; Gartlein, *Phys. Review*, 1928, [2], 32, 320; Sawyer and Humphreys, *ibid.*, 32, 583; Rao, *Proc. Roy. Soc.*, 1929, A 125, 238; 1932, A 134, 604; *Nature*, 1929, 123, 244; 1932, 130, 1630; *Proc. Phys. Soc.*, 1931, 43, 68; 1932, 44, 343, 594; *Current Science*, 1932, 1, 42; *Indian J. Physics*, 1933, 7, 561;

classification has been facilitated by photographing the spectrum obtained from an electrodeless discharge in arsenic vapour.[1] Gartlein[2] photographed the spark spectrum using various amounts of inductance in series with the spark and observed the presence of As II lines even with large amounts of inductance, but increase in the inductance resulted in a decrease in the intensity of lines from the higher states of ionisation; the spectrum was also characterised by "long lines" due to glowing arsenic vapour. The nuclear moment of the arsenic atom has been calculated[3] to be 3/2.

The table on p. 45 gives the more intense lines of the emission spectrum, the wavelengths given being the weighted mean values derived from the most reliable data available.[4] The lines present in the arc spectrum and those due to the un-ionised atom are indicated. The scale of relative intensities is an arbitrary one—1 weakest, 10 strong, 15, 20, etc. very strong.

Most of the lines in the arc spectrum are easily reversed. In order to differentiate the arc and spark spectra Buffam and Ireton[5] used an under-water oscillatory condenser discharge with a suitable condenser capacity in the circuit; the spectra were produced between poles of metallic arsenic in a vessel through which water circulated continuously, and were photographed by means of Hilger spectrographs. The arc lines were inverted on a dark continuous background, while the spark lines were not.

It has been found that in spectral analytical investigation the interrupted and flaming arc methods are respectively 100 and 10 times more sensitive than the condensed spark method.[6] As little as 2×10^{-5} mg. of arsenic can thus be detected in solid alloy electrodes and, in solutions free from heavy metals, 0·01 per cent. of arsenic can be detected.[7] Micro-methods for the spectrographic determination of small amounts of arsenic have been described.[8]

The emission spectrum of arsenic vapour shows a group of bands, attributable to As_2 molecules, in the region 2700 to 4200 A., whilst several bands in the region 2148 to 3047 A. appear to be due to As atoms.[9] The extinction coefficient of arsenic vapour at various temperatures and over the range 3000 to 3900 A., has been measured.[10]

Zeitsch. Physik, 1933, 84, 236; Rao and Narayan, *ibid.*, 1929, 53, 587; 57, 865; *Proc. 15th Indian Sci. Cong.*, 1928, p. 80; *Nature*, 1929, 124, 229; Pattabhiramiah and Rao, *Indian J. Physics*, 1929, 3, 437; Queney, *Compt. rend.*, 1929, 189, 158; Meggers and de Bruin, *Bureau Standards J. Research*, 1929, 3, 765; Borg and Mack, *Phys. Review*, 1931, [2], 37, 470; Tolansky, *Proc. Roy. Soc.*, 1932, A 137, 541; *Nature*, 1932, 129, 652; *Zeitsch. Physik*, 1933, 87, 210; Crawford and Crooker, *Nature*, 1933, 131, 655; Hicks, *Phil. Mag.*, 1933, [7], 15, 1080; Schlapp, *Proc. Roy. Soc. Edin.*, 1934, 54, 109.

[1] Ram, *Indian J. Physics*, 1932, 7, 299. See also Queney, *J. Phys. Radium*, 1929, [6], 10, 448; Balasse, *Bull. Acad. roy. Belg.*, 1934, [5], 20, 563.

[2] Gartlein, *Phys. Review*, 1928, [2], 32, 320.

[3] Tolansky, *loc. cit.*; Rao, *Current Science*, 1932, 1, 42, 163; *Zeitsch. Physik*, 1933, 84, 236. Crawford and Crooker (*Nature*, 1933, 131, 655) give $1{\cdot}5 \times h/2\pi$ (h=Planck's constant). See also Schüler and Westmeyer, *Zeitsch. Physik*, 1933, 81, 565; Goudsmit, *Phys. Review*, 1933, [2], 43, 636; Malone, *J. Chem. Phys.*, 1933, 1, 197; Tolansky and Heard, *Proc. Roy. Soc.*, 1934, A 146, 818.

[4] *International Critical Tables*, 1929, 5, 281, 394.

[5] Buffam and Ireton, *Trans. Roy. Soc. Canada*, 1925, [3], 19, 113.

[6] Gerlach and Ruthardt, *Zeitsch. anorg. Chem.*, 1932, 209, 337.

[7] Riedl, *Zeitsch. anorg. Chem.*, 1932, 209, 356.

[8] Riedl, *loc. cit.*; Spath, *Monatsh.*, 1932, 61, 107.

[9] Winand, *Bull. Acad. roy. Belg.*, 1932, [5], 18, 422. See also Almy and Kinzer, *Phys. Review*, 1935, [2], 47, 199.

[10] Winand, *loc. cit.*

EMISSION SPECTRUM OF ARSENIC.

Wavelength λ (A.).	Relative Intensity Spark.	Wavelength λ (A.).	Relative Intensity		Wavelength λ (A.).	Relative Intensity Spark.
			Spark.	Arc.		
6170	6	I 3119·6	7	4	* 1972	4 R
6110	6	I 3075·32	5	2	* 1936·9	5
6023	6	I 3032·84	8	4	* 1889·9	4 R
5651·3	10	I 2990·99	4	2	1742·9	20
5558·1	10	2959·6	7	..	1733·0	15
5497·8	10	I 2898·73	10	4 R	1700·2	10
5496·9	5	I * 2860·46	8	4 R	1287	10
5331·3	8	2830·4	4	..	1267	40
5161·1	7	I * 2780·23	10	8 R	1208	30
5107·6	8	I 2745·00	5	6 R	1171	15
5105·5	8	2492·91	5	2	1106	10
4985·4	5	2456·52	7	4 R	1093	20
4474·4	4	2437·22	5	1	1081	50
4431·6	4	I 2381·20	5	4 R	1009	10
4371	5	2370·77	5	4 R	1001	10
4352·1	5	2369·67	5	4 R	984	10
4336·7	5	I * 2349·84	6	10 R	963	10
4037·0	6	I * 2288·14	3	10 R	956	8
3922·5	10	2271·39	1	4	952	8
3842·9	4	2228·7	1	2	926	8
		2165·5	2	4	878	8
		2144·2	1	4	873	8
		2074	12	..	827	5
		2031	10	..	529	1

I = Lines emitted by neutral atom. R = Easily reversed. * = Most persistent lines.

The Zeeman effect of arsenic spectra has been studied,[1] and wavelengths, classifications and Zeeman patterns have been determined for 11 lines in As I, 64 lines in As II and 2 lines in As III.

A fluorescence spectrum of arsenic vapour, after exposure to a mercury lamp at a high temperature has been observed (see p. 39).[2]

The absorption spectrum of arsenic vapour has been examined by passing the light from the arc or spark of arsenic through the non-luminous vapour.[3] Eighty absorption bands between 2200 and 2750 A. have been enumerated [4] in the spectrum obtained by passing ultraviolet light through the vapour heated to 1100° C., and can be assigned to the diatomic molecule.

The ultraviolet absorption spectrum [5] of arsine gives an absorption

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[1] Green and Barrows, Jun., *Phys. Review*, 1935, [2], 47, 131.

[2] *Cf.* Winand, *loc. cit.*

[3] McLennan and McLay, *Trans. Roy. Soc. Canada*, 1925, [3], 19, 89; 1927, [3], 21, 407; McLennan, Young and Ireton, *ibid.*, 1919, [3], 13, 7. See also Lockyer, *Proc. Roy. Soc.*, 1874, 22, 374; *Phil. Mag.*, 1875, [4], 49, 320; Humphreys, *Astrophys. J.*, 1897, 6, 169; Dobbie and Fox, *Proc. Roy. Soc.*, 1920, A 98, 147; Ruark and others, *Nature*, 1923, 112, 831; *J. Franklin Inst.*, 1924, 198, 541; Rosen, *Naturwiss.*, 1926, 14, 978; *Zeitsch. Physik*, 1927, 43, 69. For the band spectrum of AsO, see Connelly, *Proc. Roy. Soc.*, 1934, 46, 790; Jenkins and Strait, *Phys. Review*, 1935, [2], 47, 136.

[4] Gibson and Macfarlane, *Nature*, 1934, 133, 951; *Phys. Review*, 1934, [2], 46, 1059; see also Terenin, *Zeitsch. Physik*, 1925, 31, 26; 1926, 37, 98.

[5] Cheesman and Emeléus, *J. Chem. Soc.*, 1932, p. 2847.

limit at 2390 A. There appears to be a definite gradation in the absorption spectra of the hydrides of nitrogen, phosphorus, arsenic and antimony; the ammonia spectrum has well-defined predissociation bands, that of phosphine weak ones, while arsine and stibine show only continuous absorption. The infra-red absorption spectra [1] of the first three of these gases are similar in that each has two sequences of harmonic oscillation bands, but arsine and phosphine also exhibit a third sequence peculiar to themselves. Thus while the structure of the three molecules appears to be essentially similar, each possesses distinctive features.

The Raman spectra of arsenious chloride,[2] in the liquid and gaseous states, of "light" and "heavy" arsine [3] and of sodium arsenite and sodium arsenate,[4] have been examined and frequencies obtained. The Raman spectra of the chloride and bromide in solution in ether or benzene consist of the spectra of the pure solute and pure solvent only, indicating that chemical combination does not occur in the solution.[5] With solutions in methyl and ethyl alcohols, the frequencies of the latter are unchanged, but those of arsenious chloride are lowered somewhat.[6]

The X-ray and series spectra,[7] and also the β-ray spectrum of radioactive arsenic,[8] have been examined.

Chemical Properties of Arsenic.

Arsenic does not combine directly with molecular hydrogen,[9] and the element may be purified by sublimation in that gas. Hydrides, however, may be obtained by indirect methods (see pp. 79–84). Arsenic may be displaced by the gas from solutions of its salts at high temperatures and pressures. Thus arsenic separates in large well-defined crystals when a solution of sodium arsenate is subjected to the action of hydrogen at 25 atm. pressure; [10] the action commences at 300° C., 15 per cent. of the arsenic being precipitated at this temperature, but it increases rapidly with rising temperature and at 350° C. 77 per cent. of the arsenic is liberated. Arsine is not produced in the reaction.

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[1] Robertson and Fox, *Nature*, 1928, 122, 774.

[2] Daure, *Compt. rend.*, 1928, 187, 826, 940; 1929, 188, 1605; Bhagavantam, *Indian J. Physics*, 1930, 5, 35, 59; Braune and Engelbrecht, *Zeitsch. physikal. Chem.*, 1932, B, 19, 303; Cabannes and Rousset, *Ann. Phys.*, 1933, 19, 229; Yost and Anderson, *J. Chem. Physics*, 1935, 3, 754.

[3] Delfosse, *Nature*, 1936, 137, 868.

[4] Ghosh and Das, *J. Phys. Chem.*, 1932, 36, 586.

[5] Finkelstein and Kurnossova, *Acta Physico-chim.* (*U.S.S.R.*), 1936, 4, 123. See also Trevedi, *Bull. Acad. Sci. Agra and Oudh*, 1934, 3, 229; *Chem. Zentr.*, 1935, i, 2946; Allsopp, *Proc. Roy. Soc.*, 1937, A 158, 167.

[6] Sack and Brodskii, *Acta Physico-chim.* (*U.S.S.R.*), 1935, 2, 215.

[7] Wagner, *Phys. Zeit.*, 1917, 18, 405, 432, 461, 488; Robinson, *Phil. Mag.*, 1925, [6], 50, 241; Robinson and Cassie, *Proc. Roy. Soc.*, 1926, A 113, 282; Woo, *Phys. Review*, 1926, [2], 28, 427; Sawyer and Humphreys, *ibid.*, 1928, [2], 32, 583; Edlen, *Zeitsch. Physik*, 1928, 52, 364; Mukherjee and Ray, *ibid.*, 1929, 57, 345; Hicks, *Phil. Mag.*, 1933, [7], 15, 1080; Kruger and Shoupp, *Phys. Review*, 1934, [2], 45, 759; Hulubei, *Compt. rend.*, 1935, 201, 544.

[8] Brown and Mitchell, *Phys. Review*, 1936, [2], 50, 593; Harteck and others, *Naturwiss.*, 1937, 25, 477.

[9] Vandervelde, *Bull. Acad. roy. Belg.*, 1895, [3], 30, 78; Reckleben and Scheiber, *Zeitsch. anorg. Chem.*, 1911, 70, 255.

[10] Ipatiev and co-workers, *Ber.*, 1930, 63, B, 166.

The reduction in presence of alkali occurs in two stages :[1]

$$Na_2HAsO_4 + 2H \longrightarrow Na_2HAsO_3 + H_2O$$
$$Na_2HAsO_3 + 3H \longrightarrow As + 2NaOH + H_2O$$

With hydrogen at 45 atm. pressure and at 200° C. only the first reaction takes place, but at 250° C. the arsenic begins to separate and at 350° C. the maximum separation, 96 per cent., is observed. The yield varies slightly with the amount of alkali present, but the maximum at this temperature (350° C.) can occur in the absence of alkali. Complete displacement has not been observed.

With pressures up to 150 atm. the quantity of arsenic displaced by hydrogen from solutions of arsenic trichloride in hydrochloric acid is proportional to the pressure. Between 15 and 250 atm., and with solutions not exceeding normal concentration, the reaction is one of the first order ;[2] between 125° and 175° C. log K is a linear function of $\frac{1}{T}$. The activating energy of the replacement is calculated to be 28,000 ± 2000 calories. It is estimated that the displacement of 1 per cent. of arsenic from a normal solution of arsenic trichloride at room temperature and 100 atm. of hydrogen would require 1140 years. Increase in the concentration of hydrochloric acid accelerates the reaction, which is inhibited by the presence of sodium chloride, and the reaction appears to be ionic rather than molecular.[3]

Arsenic is not attacked by dry air,[4] but in moist air the element, in the crystalline form, is superficially oxidised, acquiring a bronze tinge or even disintegrating to a black powder. The change is accelerated by exposure to light[5] or by gently warming to 30° to 40° C. Amorphous arsenic is not attacked. At a higher temperature arsenic burns with a smouldering flame, emitting a reddish fume which has an odour of garlic and forming arsenious oxide ; at a still higher temperature the flame is pale blue. Combustion is vigorous in oxygen,[6] and the presence of moisture does not appear to be necessary for this reaction.

Arsenic, when gently heated in the presence of air or oxygen, exhibits *phosphorescence*[7] which, as with phosphorus and sulphur, is accompanied by oxidation, arsenious oxide containing about 3 per cent. of arsenic oxide being produced. No ozone is formed, nor is there ionisation, as in the phosphorescence of the two elements mentioned. The arsenic oxide appears to be a primary product formed directly from the arsenic, as the lower oxide does not yield it under such conditions. Arsenious oxide is formed slowly below 200° C. without luminescence, but between 250° and 310° C. the glow appears suddenly[8] so long as the pressure is between certain limits,[9] outside of which no luminescence is observed. The lower limit, 4 to 10 mm. Hg, falls with increasing temperature, while the upper limit, 200 to 700 mm. Hg, rises

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[1] Ipatiev and co-workers, *Ber.*, 1930, 63, B, 2812.

[2] Ipatiev and co-workers, *Ber.*, 1931, 64, B, 1959.

[3] Ipatiev, Jun., *Ber.*, 1931, 64, B, 2725.

[4] Bergman, "*De arsenico*," Upsala, 1777; von Bonsdorff, *L'Inst.*, 1835, 3, 99; Panzer, *Verh. Vers. deut. nat. Aerzte*, 1902, 2, i, 79.

[5] Panzer, *loc. cit.*

[6] Baker and Dixon, *Proc. Roy. Soc.*, 1888, 45, 1.

[7] Joubert, *Compt. rend.*, 1874, 78, 1853.

[8] Emeléus, *J. Chem. Soc.*, 1927, p. 783.

[9] Damerell and Emeléus, *J. Chem. Soc.*, 1934, p. 974.

with temperature. On appearance of the glow the temperature rises about 7° C. The glow appears at lower temperatures (220° to 245° C.) with flowing oxygen than with the stationary gas at the same pressure ; also the glow temperature is 10° lower in air than in oxygen. The appearance of the glow is favoured by a rapid removal of the arsenious oxide formed. The introduction of a small quantity of carbon tetrachloride, nitrobenzene or sulphur dioxide into the oxygen does not affect the glow temperature, although the analogous glow of phosphorus is inhibited by this means. The arsenic glow may be completely extinguished at a given temperature by saturating the oxygen with the vapour of benzene, methyl or ethyl alcohol, hexane, acetone, chloroform, amyl or ethyl acetate, or chlorobenzene ;[1] the glow reappears on removal of the organic vapour or on raising the temperature by 12° to 30°. The spectrum of the phosphorescent flame consists of an apparently continuous band between 4300 and 4900 A., with a maximum intensity at about 4600 A. ; there was no evidence of bands in the ultraviolet. The ordinary flame of arsenic burning in oxygen gives a similar spectrum. The non-luminescent reaction below 200° C. is a surface one, but the chemi-luminescent reaction occurs in the vapour phase.[2] When arsenic is burned in oxygen at 15 to 40 atm. pressure, the ratio $As_2O_5 : As_2O_3$ in the product increases with the concentration of the oxygen.[3] Arsenic is oxidised to arsenic acid by ozone or by ozonised ether or turpentine.[4]

At ordinary temperature pure water, free from air, has no action upon arsenic, even after ten years' contact in a sealed glass tube.[5] In the presence of dissolved oxygen, absorbed by exposure to air, oxidation occurs, arsenious acid being formed, but no arsine.[6] Under ordinary conditions oxidation is slight, and not more than 7 per cent. of arsenious acid is formed at 350° C.[7] In the presence of alkali hydroxide, however, oxidation is more vigorous, arsenite, accompanied by a small amount of arsenate, being formed in quantity. Increase in the concentration of the alkali facilitates oxidation up to a point, beyond which further increase causes a marked decrease in the amount of arsenic oxidised. The reaction commences at about 200° C. and the rate increases rapidly up to 350° C., then decreases sharply. Complete oxidation does not occur and the reaction appears to be a balanced one, thus :

$$2As + 3H_2O \rightleftharpoons As_2O_3 + 3H_2$$

This view is supported by the following facts. If the hydrogen is removed periodically, the oxidation of arsenic becomes nearly quantitative ; if, on the other hand, the apparatus is filled initially with hydrogen at 30 atm., the quantity of arsenic oxidised is diminished from 58 per cent. to 15 per cent. The amount of quinquevalent arsenic produced is, in general, approximately one-sixth of the amount of tervalent arsenic formed.

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[1] Emeléus, *J. Chem. Soc.*, 1929, p. 1846.

[2] Damerell and Emeléus, *J. Chem. Soc.*, 1934, p. 974.

[3] de Passillé, *Ann. Chim.*, 1936, [11], 5, 83.

[4] Schonbein, *Pogg. Annalen*, 1849, 78, 514; *Verh. nat. Ges. Basel*, 1857, 1, 237.

[5] Mellor, "*A Comprehensive Treatise on Inorganic and Theoretical Chemistry*" (Longmans), 1929, 9, 33. See also von Bonsdorff, *loc. cit.*; Cooke, *Proc. Roy Soc.*, 1906, A 77, 148; *Chem. News*, 1903, 88, 290; *Proc. Chem. Soc.*, 1903, 19, 243.

[6] Orfila, *J. Chim. Méd.*, 1830, [1], 6, 6. *Cf.* Elsey, *Science*, 1927, [2], 66, 300.

[7] Ipatiev and co-workers, *Ber.*, 1930, 63, B, 166.

Hydrogen peroxide reacts vigorously with arsenic to form arsenic pentoxide.[1]

Fluorine[2] and chlorine[3] react vigorously with arsenic to form the trihalides and, in the case of fluorine, some pentafluoride. The reactions are accompanied by incandescence. Bromine[4] and iodine[5] also yield the trihalides, but the reactions occur much less readily and it is necessary to warm the powdered mixture of arsenic and iodine. The hydracids do not react readily; hydrogen fluoride and hydrogen chloride react in the presence of air,[6] and hydrogen bromide and hydrogen iodide act the more rapidly as the halogen element is liberated by the ready dissociation of the gas. Arsenic is readily oxidised to arsenic acid by chloric or bromic acid,[7] and to arsenate by boiling aqueous potassium chlorate.[8] A mixture of powdered arsenic and potassium chlorate detonates on percussion.[9] Iodine fluoride reacts energetically with arsenic.[10]

Arsenic unites directly with sulphur when a mixture of the two elements is heated (see p. 237). When a solution of sulphur and arsenic in carbon disulphide is exposed to light, a powder, the colour of which varies from yellow to orange, is slowly deposited.[11] After prolonged extraction with carbon disulphide, the powder contains the two elements in a proportion which depends on that in the original solution, and appears to consist of a mixture of sulphides, the composition of which, however, remains obscure. When arsenic is heated at 230° C. in hydrogen sulphide it gradually forms arsenic trisulphide;[12] the reaction takes place more readily in the presence of aluminium chloride,[13] hydrogen chloride also being formed. A precipitate of the sulphide is formed when hydrogen sulphide is passed into a solution of yellow arsenic in carbon disulphide.[14] Sulphur dioxide deposits a small quantity of brown arsenic from such a solution. This gas does not react with solid arsenic, but with the vapour arsenious oxide and sulphide are formed.[15] Aqueous sulphurous acid, heated with arsenic in a sealed tube at 200° C., produces a mixture of arsenious oxide, sulphuric acid and free sulphur.[16] Sulphur trioxide[17] and boiling concentrated sulphuric acid[18] oxidise arsenic to arsenious oxide; in the latter case the reaction commences at about 110° C. and sulphur dioxide is evolved. Chlorsulphonic acid yields[19] arsenic trichloride, sulphur dioxide and sulphuric acid. Aqueous solutions of alkali

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[1] Moissan, *Compt. rend.*, 1884, 99, 874; 1902, 135, 563.

[2] Davy, *Phil. Trans.*, 1812, 102, 169.

[3] Dumas, *Ann. Chim. Phys.*, 1826, [2], 33, 351; Thomas and Dupuis, *Compt. rend.*, 1906, 143, 282.

[4] Sérullas, *Ann. Chim. Phys.*, 1828, [2], 38, 319; Linck, *Ber.*, 1899, 32, 892; 1900, 33, 2284.

[5] Plisson, *Ann. Chim. Phys.*, 1828, [2], 39, 265; Linck, *loc. cit.*

[6] Napoli, *Amer. J. Sci.*, 1854, [2], 18, 190; *J. prakt. Chem.*, 1854, [1], 64, 93; Thiele, *Thesis*, Berlin, 1910.

[7] Gooch and Blake, *Amer. J. Sci.*, 1902, [4], 14, 285; Hendrixson, *J. Amer. Chem. Soc.*, 1904, 26, 747.

[8] Slater, *J. prakt. Chem.*, 1853, [1], 60, 247.

[9] de Fourcroy and Vauquelin, *Ann. Chim. Phys.*, 1797, [1], 21, 237.

[10] Moissan, *loc. cit.*

[11] Haenny, *Helv. Chim. Acta*, 1930, 13, 725.

[12] Brunn, *Ber.*, 1888, 21, 2546; 1889, 22, 3205.

[13] Ruff, *Ber.*, 1901, 34, 1749.

[14] Thiele, *loc. cit.*

[15] Schiff, *Annalen*, 1861, 117, 95.

[16] Geitner, *ibid.*, 1864, 129, 250.

[17] Aimé, *J. Pharm. Chim.*, 1852, [3], 21, 84.

[18] Adie, *Proc. Chem. Soc.*, 1899, 15, 133.

[19] Heumann and Köchlin, *Ber.*, 1882, 15, 418, 1736.

persulphates[1] bring about the oxidation of arsenic to arsenic acid. Selenium and tellurium and their hydrides readily attack arsenic to form the selenide or telluride;[2] the element is also dissolved by hot aqueous telluric acid.[3]

Nitrogen does not react with arsenic. The latter dissolves in aqueous ammonia, apparently forming a complex compound.[4] In anhydrous liquid ammonia it dissolves without reaction[5] and from the solution the arsenic may be successfully electrodeposited.[6] This is not the case with antimony or bismuth. The solution of arsenic in liquid ammonia does not react with metallic cyanides.[7]

Arsenic is oxidised, mainly to arsenious oxide, when heated in nitrous oxide;[8] the reaction becomes appreciable at 250° to 270° C. and ignition occurs at 400° to 450° C. This reaction takes place specifically between arsenic and the nitrous oxide and is not due to reaction with oxygen after thermal decomposition of the nitrous oxide, as such decomposition does not occur below 400° C. and is very slight at 460° C. Nor does the reaction resemble that which occurs in oxygen, except that, like the reaction in the dark with the latter gas (see p. 47), it is a surface reaction. No chemi-luminescence is observed, however, and there is no upper critical oxidation pressure. At 360° C. the product contains at least 99 per cent. of pure arsenious oxide, and at 420° C. it contains about 5·8 per cent. of arsenic pentoxide.

Aqueous nitric acid up to 50 per cent. concentration has little action on arsenic,[9] but the concentrated acid or aqua regia causes rapid oxidation to arsenious and arsenic acids. When the acid is more dilute some ammonia may be formed.[10] A mixture of arsenic and potassium nitrate detonates on ignition.[11] Solutions of ammonium[12] and barium[13] nitrates slowly dissolve arsenic to form arsenite and arsenate. Hydrazoic acid dissolves the element with evolution of hydrogen, and the solution on evaporation deposits arsenious oxide.[14] Nitrosyl chloride[15] and potassium amide[16] also react with arsenic.

Phosphorus, when heated to redness with arsenic, combines to form arsenic phosphide (see p. 286). When phosphorus pentoxide and arsenic are heated together at 290° C. the latter is oxidised to arsenious oxide and phosphorus is liberated.[17] Phosphorus trichloride converts arsenic quantitatively into arsenic trichloride when the mixture is

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[1] Levi and co-workers, *Gazzetta*, 1908, 38, i, 598.

[2] Berzelius, *Schweigger's J.*, 1812, 6, 311; 1818, 23, 309, 430; 1823, 34, 78; *Pogg. Annalen*, 1826, 7, 242; 8, 423.

[3] Hutchins, *J. Amer. Chem. Soc.*, 1905, 27, 1157.

[4] Kraus, *ibid.*, 1922, 44, 1216.

[5] Hugot, *Ann. Chim. Phys.*, 1900, [7], 21, 5.

[6] Booth and Merlub-Sobel, *J. Physical Chem.*, 1931, 35, 3303.

[7] Bergstrom, *J. Amer. Chem. Soc.*, 1926, 48, 2319.

[8] Damerell and Emeléus, *J. Chem. Soc.*, 1934, p. 974.

[9] Askenasy and co-workers, *Zeitsch. anorg. Chem.*, 1927, 162, 161; Palit and Dhar, *J. Physical Chem.*, 1926, 30, 1125.

[10] Personne, *Bull. Soc. chim.*, 1864, [2], 1, 163; *Chem. News*, 1864, 9, 242; Maumené, *Ann. Chim. Phys.*, 1864, [4], 3, 349.

[11] Slater, *J. prakt. Chem.*, 1853, [1], 60, 247.

[12] Bergstrom, *J. Physical Chem.*, 1925, 29, 165; 1926, 30, 15.

[13] Slater, *loc. cit.*

[14] Curtius and Darapsky, *J. prakt. Chem.*, 1900, [2], 61, 408.

[15] Sudborough, *J. Chem. Soc.*, 1891, 59, 655.

[16] Bergstrom, *loc. cit.*

[17] Krafft and Neumann, *Ber.*, 1901, 34, 566.

heated for 12 hours at 200° C.;[1] phosphorus pentachloride yields a mixture of the trichlorides.[2]

Arsenic does not combine directly with carbon, silicon or boron. The reaction with metals to form definite arsenides or alloys is described no pp. 57–78. The presence of small quantities of arsenic or of its compounds in certain catalysts has a poisoning effect. The first traces added to the catalyst have the greatest effect; thus the activity of 0·35 g. of platinum was reduced linearly by the addition of arsenic up to 0·7 mg., this quantity reducing the catalytic activity to 45 per cent. of its original value; the addition of 10 mg. of arsenic, however, depressed the activity only to 26 per cent. of the original value.[3] Vanadium catalysts are poisoned by the presence of arsenic, although the action is slow; arsenic pentoxide is formed.[4]

Arsenic and many of its compounds exhibit catalytic properties, which may be positive or negative, especially in organic reactions. Thus the element itself in concentrations up to 1 per cent. inhibits the oxidation of acraldehyde for several hours and then accelerates it, while for *l*-pinene the order is reversed.[5] The activity of arsenic and its oxides is relatively low on account of their insolubility, but the activities of the halogen derivatives are considerably higher.

The ability of arsenic to replace certain metals from solution has already been referred to (p. 41). When finely divided arsenic is added to a 10 per cent. aqueous solution of silver nitrate, an immediate deposition of silver occurs, accompanied by the evolution of brown fumes of nitrogen dioxide.[6] The main reaction may be represented by the equation:

$$3AgNO_3 + 4As = 3Ag + 2As_2O_3 + 3NO$$

If the arsenic is added as a piece the silver is deposited in the form of a dull, white, smooth plating. The reaction does not go to completion even after several months' contact. On the other hand, silver is completely displaced within a few hours from solutions saturated with silver nitrite or sulphate, and after a longer time from saturated aqueous solutions of silver acetate and tartrate. In each case arsenic goes into solution as the trioxide. With a solution of silver cyanide in aqueous potassium cyanide the reaction takes a different course, probably following the equation:

$$3KAg(CN)_2 + As = K_3As(CN)_6 + 3Ag$$

Only a small proportion of the silver is precipitated, however. Arsenic also replaces silver from some non-aqueous solutions, such as solutions of the nitrate or chloride in pyridine; in others, such as silver palmitate in ether or in acetone, there is no action.

The reaction with salts of mercury is similar, but with mercuric salts a precipitate of the mercurous salt first appears, which gradually disappears, leaving a deposit of mercury. The arsenic passes into solution as the trioxide. Similarly, copper is deposited from solutions of its common salts; with cupric chloride some cuprous chloride is precipitated. The reactions generally are incomplete.

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[1] Krafft and Neumann, *loc. cit.*

[2] Reinitzer and Goldschmidt, *ibid.*, 1880, 13, 850.

[3] Maxted and Dunsby, *J. Chem. Soc.*, 1928, p. 1600.

[4] Adadurov and Guminskaya, *J. Applied Chem.* (*U.S.S.R.*), 1932, 5, 722.

[5] Moureu, Dufraisse and Badoche, *Compt. rend.*, 1928, 187, 917.

Platinum and gold are slowly replaced from solutions of their chlorides, thus :

$$3PtCl_4 + 4As + 6H_2O = 3Pt + 2As_2O_3 + 12HCl$$
$$2AuCl_3 + 2As + 3H_2O = 2Au + As_2O_3 + 6HCl$$

No reaction occurs between arsenic and solutions of antimony and bismuth chlorides. Ferric chloride is reduced thus—

$$6FeCl_3 + 2As + 3H_2O = 6FeCl_2 + As_2O_3 + 6HCl$$

while cadmium sulphate is reduced to the yellow sulphide :

$$3CdSO_4 + 8As = 3CdS + 4As_2O_3$$

Atomic Weight of Arsenic.

The earliest attempts to determine the atomic weight of arsenic were made prior to 1826 by Berzelius.[1] By oxidising the element to arsenious oxide he first obtained the value 80·2 ($O = 16$), and later by reduction of the oxide by means of sulphur he arrived at the figure 75·02. In 1845 Pelouze,[2] and in 1859 Dumas,[3] applied the method of titration of known quantities of pure silver to the analysis of arsenic trichloride and both obtained values slightly lower than that of Berzelius, the mean value from the two series of experiments being 74·91. A lower figure, however, was obtained in 1859 by Wallace,[4] who used the same method of titration on the bromide, his value being 74·19. Kessler [5] in 1861, after investigating the oxidation of arsenious oxide by means of potassium chlorate and potassium dichromate, deduced the molecular weight of the oxide and calculated the atomic weight of arsenic to be 75·13. That the value should be near to 75 was in accord with the periodic law and with the physical and chemical properties of the element, and the generally accepted value up to 1896 was 74·9.

In the latter year the problem was again attacked with much improved experimental methods. Hibbs,[6] by heating sodium pyroarsenate in hydrogen chloride at a temperature well below the fusion point of sodium chloride, obtained the latter as a pure product, and from the ratio $Na_4As_2O_7 : 4NaCl$ obtained [7] as the mean value from ten experiments 74·876. Ebaugh [8] made three series of somewhat similar experiments ; in the first, silver arsenate was heated in hydrogen chloride and the silver chloride formed, after weighing, was reduced to silver in a stream of hydrogen ; in the second and third series lead arsenate was converted similarly into lead chloride and lead bromide respectively. The following are the mean values obtained and the ratios from which they were derived :

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[1] Berzelius, *Ann. Chim. Phys.*, 1817, [2], 5, 174; *Pogg. Annalen*, 1826, 8, 1.

[2] Pelouze, *Compt. rend.*, 1845, 20, 1047.

[3] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 174.

[4] Wallace, *Phil. Mag.*, 1859, [4], 18, 270.

[5] Kessler, *Pogg. Annalen*, 1855, 95, 204; 1861, 113, 134.

[6] Hibbs, *J. Amer. Chem. Soc.*, 1896, 18, 1044; *Thesis*, Univ. Pennsylvania, 1896.

[7] The values for the atomic weight given here are not necessarily those given originally by the authors, but have been recalculated using the following antecedent data: $O = 16·000$; $Ag = 107·880$; $Cl = 35·457$; $N = 14·008$; $C = 12·000$; $Na = 22·997$; $Pb = 207·22$; $Br = 79·916$.

[8] Ebaugh, *J. Amer. Chem. Soc.*, 1902, 24, 489; *Thesis*, Univ. Pennsylvania, 1901.

$Ag_3AsO_4 : 3AgCl$	As = 74·90
$Ag_3AsO_4 : 3Ag$	As = 75·06
$Pb_3(AsO_4)_2 : 3PbCl_2$	As = 74·93
$Pb_3(AsO_4)_2 : 3PbBr_2$	As = 74·84

Baxter and Coffin,[1] in 1909, also heated silver arsenate in hydrogen chloride. Samples of different origin were used, with slightly different results. They also dissolved the arsenate in nitric acid and precipitated the silver as chloride or bromide. The following mean values were obtained :

$Ag_3AsO_4 : 3AgCl$	(1st series)	As = 75·05
	(2nd series)	As = 74·93
$Ag_3AsO_4 : 3AgBr$		As = 74·92

The value internationally accepted up to 1928 was 74·96. However, in 1929 the British Sub-committee on Atomic Weights proposed that 74·934, the value obtained by Aston [2] from calculations based upon mass spectrograms, should be accepted, it being considered that Aston's method was less liable to error than any other. Křepelka,[3] from analyses of especially purified arsenic trichloride, obtained as the mean of 13 determinations 74·936 ± 0·001, a result which nearly coincides with that of Aston. The value 74·93 was adopted internationally in 1930.[4]

Later work by Aston [5] on the mass spectrum of gaseous arsenic hydride led to the lower figure 74·92, and in 1933 Baxter and his co-workers [6] analysed arsenic trichloride and arsenic tribromide by comparison with silver. The compounds were prepared from arsenic and the pure halogens, and were subjected to prolonged fractionation in exhausted glass apparatus. They were then converted to ammonium halide and arsenite and the former precipitated with silver nitrate. The trichloride was also compared with iodine pentoxide [7] by hydrolysing weighed quantities of the former with sodium hydroxide in a vacuum, then after neutralisation adding a weighed, nearly equivalent, quantity of iodine pentoxide and finding the end-point in the presence of starch by neutralising with phosphate and adding standard dilute iodine or arsenite solutions. The weights of iodine pentoxide were corrected for retained moisture and adsorbed air. The following results were obtained (see p. 54).

The average value for the atomic weight of arsenic from all the above experiments is 74·908 and, in view of the concordance of the results, the value adopted by the International Union of Chemistry [8] in 1934 was **74·91**, this value remaining unchanged [9] in 1938.

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[1] Baxter and Coffin, *J. Amer. Chem. Soc.*, 1909, 31, 297.

[2] Aston, *Nature*, 1927, 120, 958; *Proc. Roy. Soc.*, 1927, A 115, 504.

[3] Křepelka, *Nature*, 1929, 123, 944; *Collection Czech. Chem. Communications*, 1930, 2, 255.

[4] 36th Ann. Report At. Wts., Baxter, *J. Amer. Chem. Soc.*, 1930, 52, 857.

[5] Aston, "*Mass Spectra and Isotopes*," Arnold and Co., 1933, p. 139.

[6] Baxter, Schaefer, Dorcas and Scripture, *J. Amer. Chem. Soc.*, 1933, 55, 1054.

[7] Baxter and Schaefer, *ibid.*, 1933, 55, 1957.

[8] Fourth Report of the Committee on Atomic Weights of the International Union of Chemistry, *J. Chem. Soc.*, 1934, p. 504; *J. Amer. Chem. Soc.*, 1934, 56, 753; *Ber.*, 1934, 67, [A], 47.

[9] Eighth Report of the Committee on Atomic Weights of the International Union of Chemistry, *J. Amer. Chem. Soc.*, 1938, 60, 744.

No. of Experiments.	Ratio.	At. Wt. of As.
3	$AsBr_3 : 3Ag$	74·919
14	$AsBr_3 : 3Ag$	74·897
13	$AsCl_3 : 3Ag$	74·909
6	$AsCl_3 : 3Ag$	74·900
6	$AsCl_3 : 3Ag$	74·905
6	$AsCl_3 : 3Ag$	74·907
6	$AsCl_3 : 3AgCl$	74·917
8	$6AsCl_3 : I_2O_5$	74·911

In 1935, Baxter and Frizzell [1] determined the ratio of arsenic trichloride to iodine, using the value 126·917 for the atomic weight of iodine. Weighed quantities of arsenic trichloride, purified as described above, were hydrolysed with disodium hydrogen phosphate, and the arsenious acid formed allowed to react with weighed, very nearly equivalent, quantities of pure iodine in nearly neutral solution. A slight deficiency of one or the other was then made up with dilute solutions of arsenious acid or iodine. The reactions were carried out without contact with oxygen by working in exhausted vessels up to the final determination of the end-point. The weights were corrected to vacuum, and the following values obtained :

No. of Experiments.	Ratio $AsCl_3 : I_2$.	At. Wt. of As.
10	0·714221	74·923
5	0·714183	74·913
13	0·714192	74·915
Average of all	0·714200	74·917

These results suggest a slightly higher figure than the International value,[2] 74·91, and more recent work also points in the same direction. Křepelka and Kočnar [3] in 1936 synthesised arsenic tribromide from highly purified bromine and arsenic and from determinations of the ratios $AsBr_3 : 3Ag$ and $AsBr_3 : 3AgBr$ arrived at the value 74·923, which closely approaches Aston's value derived from the mass spectrum of arsine (p. 53).

The evidence would justify, therefore, the value 74·92 for the atomic weight of arsenic.

There are no isotopes of arsenic.[4]

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[1] Baxter and Frizzell, *J. Amer. Chem. Soc.*, 1935, **57**, 851.

[2] Eighth Report of the Committee on Atomic Weights of the International Union of Chemistry, *ibid.*, 1938, **60**, 741; *J. Chem. Soc.*, 1937, p. 1893.

[3] Křepelka and Kočnar, *Coll. Czech. Chem. Comm.*, 1936, **8**, 485; see *Nature*, 1937, **139**, 76.

[4] First Report of the Committee on Atoms of the International Union of Chemistry, *J. Chem. Soc.*, 1937, p. 1910.

Uses of Arsenic.

Arsenic in elementary form finds limited application in industry. It is sometimes employed in the manufacture of arsenic compounds, and it is a useful constituent of certain alloys.[1] Small quantities, 0·1 to 0·2 per cent., are added to lead in the production of lead shot, which is obtained by allowing drops of the molten metal to fall into water. Pure melted lead, when dropped from a height, forms tailed drops, but the addition of arsenic leads to the formation of nearly spherical pellets. The effect appears to be due to the fluxing of the film of lead oxide which forms and surrounds the liquid particle as it falls.[2] Alloys of lead containing small amounts of arsenic are used for making bearings, sheaths for electric cables and battery grids. Examples of such alloys are : (1) lead with not more than 4 per cent. Sb and not more than 1 per cent. As,[3] (2) lead with Sn 9 to 11, Sb 9 to 11, Cd 1·4 to 1·8, Cu 1·2 to 1·6, As 0·9 to 1·7.[4] The addition of more than 1 per cent. of arsenic to alloys of lead and tin causes increased hardness and compressive strength but the toughness is diminished ; such alloys are useful for bearings to withstand high bearing pressure free from impact.[5] Lead anodes containing arsenic (less than 0·5 per cent.) are used in the electrolytic preparation of zinc.

Small amounts of arsenic in iron permit the latter to take a brilliant polish and such metal is used for making chains and ornaments. A film of arsenic electrolytically deposited on iron provides a resistant protective coating against subaqueous corrosion.[6] Alloys of arsenic with iron, manganese, molybdenum or tungsten, separately or mixed, are resistant to acids, particularly hydrochloric acid.[7] The presence of arsenic in steels is not desirable. Small quantities (up to 0·05 per cent.) have no appreciable effect on the mechanical properties, even on impact, but larger quantities (up to 0·46 per cent.), although slightly increasing the elastic limits and ultimate strength, decrease ductility, elongation and impact resistance, especially for medium-carbon steels.[8] There is a slight embrittling effect, and while the weakening is less than that caused by phosphorus or sulphur, it intensifies the effects of these elements if present. Arsenic appears to promote in steel the development of a dendritic heterogeneous structure which easily cracks under dynamic tests. It adversely affects hot malleability and tool life of high-speed tool steel, although the hardness is not appreciably affected.[9]

Copper containing small quantities of arsenic (up to 1 per cent.) in the absence of other impurities shows remarkable malleability and ductility and can be worked hot or cold to any desired extent.[10] The

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[1] The alloys and arsenides of the metals are described on p. 57–78.

[2] Tammann and Dreyer, *Zeitsch. Metallkunde*, 1933, 25, 64.

[3] Seljesaeter, *U.S. Patent*, 1722358 (1929).

[4] Deiches, *Austrian Patent*, 130903 (1931).

[5] Anon, *Zeitsch. Metallkunde*, 1932, 24, 306.

[6] Carrick, *J. Amer. Water Works Assocn.*, 1928, 19, 704; Tammann and Warrentrup, *Zeitsch. anorg. Chem.*, 1936, 228, 92.

[7] Frischer, *French Patent*, 725448 (1931).

[8] Cameron and Waterhouse, *J. Iron and Steel Inst.*, 1926, 113, 355; Cameron, *Trans. Can. Inst. Mining and Met.*, 1927, 30, 858: Hoffman, *Proc. Amer. Soc. Testing Materials*, 1929, 29, Part I; Bauer, *Metals and Alloys*, 1930, 2, 89; Burago, *Metallurg.*, 1933, No. 261.

[9] French and Digges, *Trans. Amer. Soc. Steel Treating*, 1928, 13, 919.

[10] Hanson and Marryat, *J. Inst. Metals*, 1927, 37, 121.

effect is enhanced if antimony is also added (up to 5 per cent. of each element).[1] The electrical conductivity of copper is reduced by the addition of arsenic. The presence of arsenic is useful in copper which is to be subject to reducing conditions at high temperature. Boiler tubes and plates for locomotive fireboxes are generally made of such copper. Arsenical copper is frequently brittle, but the brittleness develops only after heat treatment below 650° C.; the critical temperature for its development appears to be 500° C.[2] Up to 2 per cent. of arsenic is beneficial in certain bronzes and speculum metals; Britannia metal also, and brasses for high temperature work, may advantageously contain arsenic.[3] In ordinary brass (60 : 40), however, as little as 0·12 per cent. of arsenic halves the ductility. The element is also contained in certain corrosion-resisting alloys of aluminium[4] and of silver.[5]

Arsenic in the form of an amalgam is used to a small extent in medicine. It also finds application as a poison in fly-traps.[3]

For the uses of white arsenic, arsenites and arsenates, see p. 159.

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[1] Archbutt and Prytherch, *J. Inst. Metals*, 1931, 45, 265.

[2] Blazey, *J. Inst. Metals*, 1927, 37, 51. See also Sachs and Burkhardt, *German Patent*, 571749 (1933).

[3] Smith, "*Liddell's Handbook of Non-Ferrous Metallurgy*" (McGraw-Hill Book Co., N.Y.), 1926, 2, 804.

[4] Bosshard, *U.S. Patent*, 1899133 (1933).

[5] Assmann, *German Patents*, 496348–9 (1926).

CHAPTER IV.

THE METALLIC ARSENIDES.

As mentioned in Chapter II, many metallic arsenides are found in Nature. Arsenic combines directly with most metals to form stable compounds, those of the heavy metals being the most stable. The latter may be obtained by allowing an aqueous solution of a salt of the appropriate metal to drop into an atmosphere of arsine, air being completely absent, and the vessel continually shaken.[1] Precipitation by passing arsine into the salt solution is not satisfactory as, in the case of copper, silver, gold, mercury and lead, a secondary reaction with the excess of metallic ions occurs :

$$M_3As + 3M^+ + 3H_2O = 6M + 3H^+ + As(OH)_3$$

With polyvalent metals, the lowest oxide of the metal is formed.

With iron, cobalt and nickel, alcoholic solutions of the salts should be used, since with aqueous solutions the resulting arsenide is contaminated with free arsenic. Zinc and manganese arsenides are readily hydrolysed and cannot be obtained by the above method, but are prepared by combination of the elements.

The arsenides of the heavy metals are usually black and readily oxidisable. On exposure to moist air they are converted into the metal and arsenious acid. In the dry finely divided state they may ignite spontaneously at ordinary temperatures. At higher temperatures, in absence of air, the arsenides of the noble metals lose nearly all their arsenic, while other heavy metal arsenides form lower arsenides. The arsenides are more stable than the corresponding phosphides.

The metallic arsenides generally melt between 800° and 1200° C., many with decomposition,[2] volatilisation of arsenic occurring below the melting point. The majority of mineral sulpharsenides melt between 400° and 600° C. Arsenopyrite decomposes to arsenic, sulphur and ferrous sulphide at 675° to 685° C., while löllingite (p. 10) loses 23·83 per cent. of arsenic at 735° C.[3]

Aluminium Arsenide, Al_3As_2.—When a mixture of powdered aluminium and arsenic is heated, no reaction occurs up to 600° C., but above 750° C., if the pressure of the arsenic vapour is kept low, combination takes place with incandescence and results in the formation of a brown microcrystalline powder[4] of composition Al_3As_2. The

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[1] Brukl, *Zeitsch. anorg. Chem.*, 1923, **131**, 236.

[2] Borgstrom, "*Nord. Kemistmötet*," Finland, 1928, p. 169.

[3] Monclova, *Bull. Soc. franç. Min.*, 1930, **53**, 491.

[4] Wohler, *Pogg. Annalen*, 1827, **11**, 161; Mansuri, *Metal Ind.*, 1912, **21**, 388; *J. Chem. Soc.*, 1922, **121**, 2272. See also Winkler, *J. prakt. Chem.*, 1864, [1], **91**, 193; Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314; Lorentz, *Bureau of Standards, Circ. No.* 346, 1927, p. 101.

product is stable at high temperatures and Mansuri stated that it is infusible up to 1600° C. Natta and Passerini,[1] however, found the melting point of the pure arsenide to be 1200° C. It is less stable at ordinary temperatures, a little arsenic being slowly liberated. When freshly prepared it is completely soluble in acid, but after keeping, a slight residue of arsenic remains after dissolution in hydrochloric acid. X-ray analysis by the powder method suggests that the crystals belong to the cubic system and resemble the blendes. The density calculated from the crystallographic data is 3·81 ; the observed density is 3·60. The compound reacts readily with water, evolving arsine, and is consequently unstable in moist air. With alcohols it reacts to yield alkyl arsines.[2] When heated in air it is oxidised to alumina and arsenious oxide.

Antimony Arsenides.—A crystalline arsenide of composition Sb_2As was described by Descamps,[3] who heated a mixture of the elements under fused boric oxide. A thermal investigation of the system antimony–arsenic shows, however, that the two elements alloy in all proportions, forming a continuous series of solid solutions, no chemical compound being formed. The alloys freeze over a range of temperature and do not have a single sharp melting point ; this is shown by the freezing point curves (fig. 5) obtained by Mansuri,[4] who found that the alloy of lowest freezing point (605° C.) contained 13 per cent. of arsenic. Parravano and de Cesaris [5] found the minimum on the liquidus curve to be at 612° C. corresponding with 17·5 per cent. of arsenic. Padoa [6] examined the electrical conductivity of alloys at various temperatures and observed a pronounced maximum shown by

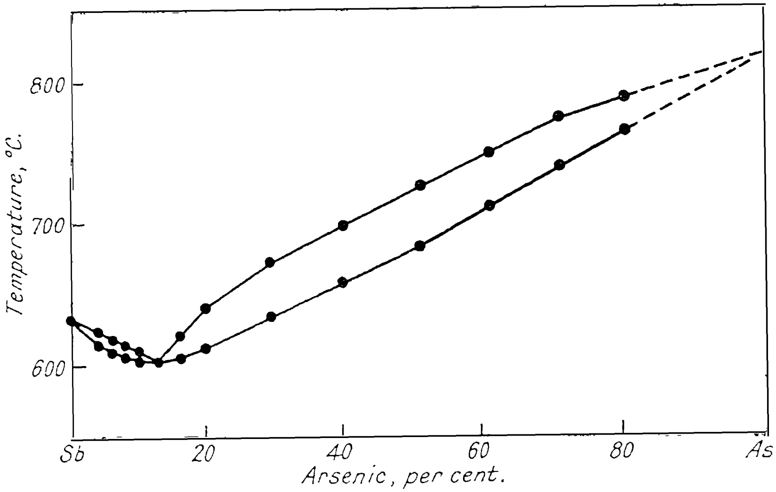

FIG. 5.—Equilibrium Diagram of the System Sb–As.

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[1] Natta and Passerini, *Gazzetta*, 1928, 58, 458.
[2] Natta, *Giorn. Chim. Ind. Appl.*, 1926, 8, 367.
[3] Descamps, *Compt. rend.*, 1878, 86, 1066.

an alloy of composition Sb_2As at $-10°$ C. At high temperatures alloys of antimony and arsenic have a gel-like structure which is retained after rapid cooling.[1]

Antimony and arsenic frequently occur associated in Nature, the most important mineral rich in arsenic being *allemontite* [2] (see p. 8), the composition of which approximates to $SbAs_3$.

The ternary system Pb–Sb–As has been investigated [3] by thermal and metallographic methods; the antimony and arsenic form a continuous series of solid solutions which are insoluble in the lead but form eutectics with it. For the alloys rich in arsenic the eutectic melts at 294° C., while for those rich in antimony the temperature is 252° C.

Barium Arsenide, Ba_3As_2.—By passing arsine over barium oxide at red heat Soubeiran [4] obtained a mixture of arsenide and arsenite. Lebeau [5] prepared the pure arsenide by reduction of barium arsenate with carbon in an electric furnace. Barium arsenide is very similar in properties to the arsenides of calcium and strontium; it is slightly darker in colour, more readily fusible and more reactive chemically. Its density at 15° C. is 4·1. It burns spontaneously in fluorine, chlorine or bromine vapour. In oxygen it burns at about 300° C. and in sulphur vapour at dull red heat.

Beryllium Arsenide is formed [6] when a mixture of beryllium and arsenic is heated; the reacting mixture becomes incandescent. The arsenide is decomposed by water with evolution of arsine.

Bismuth Arsenides.—When bismuth and arsenic are melted together there is no evidence of chemical combination. The two elements are only slightly miscible in the molten state [7] and separate completely on solidification if an open vessel is used, but according to Heike [8] they are perfectly miscible if melted in a sealed tube. Descamps [9] melted a mixture of bismuth and excess of arsenic under fused boric oxide, keeping the temperature as low as possible, and obtained a product of density 8·45 and approximate composition Bi_3As_4, but it is doubtful whether this was a definite compound.

Bismuth Monarsenide, BiAs, may be obtained by passing arsine through a solution of bismuth trichloride containing a minimum quantity of hydrochloric acid.[10] It is a black substance unattacked by water, dilute acids or alkalis, but decomposed by concentrated hydrochloric acid with formation of arsine.

Cadmium Arsenides.—The freezing point, density and atomic volume curves indicate the existence of two arsenides, Cd_3As_2 and $CdAs_2$.[11] The freezing point curve was obtained by cooling mixtures of the elements melted under fused alkali chloride; no mixed crystals were observed. Two other arsenides have been described: Cd_6As, said to

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[1] Kalb, *Metall Erz*, 1926, 23, 113; *Zeitsch. Kryst.*, 1922, 57, 572.

[2] Haidinger, "*Handbuch der bestimmenden Mineralogie*," Wien, 1845, p. 557.

[3] Abel and Redlich, *Zeitsch. anorg. Chem.*, 1927, 161, 221.

[4] Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 415.

[5] Lebeau, *ibid.*, 1902, [7], 25, 470; *Compt. rend.*, 1899, 129, 47.

[6] Wohler, *Pogg. Annalen*, 1828, 13, 577.

[7] Friedrich and Leroux, *Metallurgie*, 1908, 5, 148.

[8] Heike, *Internat. Zeitsch. Metallog.*, 1914, 6, 209.

[9] Descamps, *Compt. rend.*, 1878, 86, 1065.

[10] Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[11] Schemtschuschny, *Int. Zeitsch. Metallographie*, 1913, 4, 228; *J. Russ. Phys. Chem. Soc.*, 1913, 45, 1137. See also Heycock and Neville, *J. Chem. Soc.*, 1892, 61, 888; *Chem. News*, 1890, 62, 280.

be formed when cadmium and arsenic were melted together,[1] and Cd_3As, obtained by reducing cadmium arsenate with fused potassium cyanide,[2] the product being white, with a slight reddish tinge and a metallic lustre, and of density 6·26. The reddish tinge is common to alloys containing 22 to 50 atoms As per cent.; those with more arsenic exhibit a bluish tinge.

Cd_3As_2 has been prepared by subjecting a mixture of powdered cadmium and arsenic, in appropriate proportions, to a pressure of 6500 atmospheres,[3] by passing arsenic vapour mixed with hydrogen or an inert gas over heated cadmium,[4] by fusing a mixture of the elements under a layer of fused lithium and potassium chlorides,[5] and by slowly dropping an ammoniacal solution of cadmium sulphate into a globe filled with arsine.[6] It forms reddish octahedra and cubes of density 6·25 at 20° C. and of hardness nearly 3·5 (Mohs' scale). From an X-ray analysis by the powder method Passerini [7] concluded that the crystals belong to the cubic system, with a non-ionic structure, but von Stackelberg and Paulus [8] state that the arsenide crystallises in the tetragonal system, with 8 molecules in the unit cell, and space group D_{4h}^{15}. In the co-ordinated lattice the arsenic atoms constitute a slightly deformed closest cube packing in the tetrahedral interstices of which are the cadmium atoms. According to Schemtschuschny, the arsenide undergoes some form of reversible transformation at 578° C. The melting point is 721° C. It dissolves slowly in cold dilute acids yielding arsine. Halogens and oxidising agents such as concentrated nitric acid or aqua regia vigorously attack it, sometimes with incandescence.[9]

$CdAs_2$, obtained by fusing the elements in the requisite proportions under fused alkali chloride,[10] is bluish-grey in colour, of density 5·86 at 20° C., and of hardness 3·5 to 4·0 on Mohs' scale. It melts at 621° C.

Calcium Arsenide, Ca_3As_2, is formed by the direct combination of calcium with arsenic vapour at dull red heat.[11] When a mixture of hydrogen and arsenic vapour is passed over heated quicklime the product is mainly arsenite, only a little arsenide being formed.[12] It is best prepared by the reduction of calcium arsenate by carbon in an electric furnace.[13] Lebeau used a mixture of 100 parts of the arsenate with 31 parts of petroleum coke and employed a current of 950 to 1000 amperes at 45 volts, the heating being continued for 2 to 3 minutes. Guérin [14] has shown that calcium arsenate is reduced by carbon slowly at 800° C. and rapidly at 850° C., the arsenite being first produced and

[1] Spring, *Ber.*, 1883, 16, 325.

[2] Descamps, *Compt. rend.*, 1878, 86, 1022, 1065.

[3] Spring, *loc. cit.*

[4] Granger, *Compt. rend.*, 1904, 138, 574; *Bull. Soc. chim.*, 1904, [3], 31, 568.

[5] Schemtschuschny, *loc. cit.*

[6] Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 242.

[7] Passerini, *Gazzetta*, 1928, 58, 775.

[8] von Stackelberg and Paulus, *Zeitsch. physikal. Chem.*, 1935, B, 28, 427.

[9] Granger, *loc. cit.*; Spring, *loc. cit.*; Brukl, *loc. cit.*

[10] Schemtschuschny, *loc. cit.*

[11] Moissan, *Ann. Chim. Phys.*, 1899, [7], 18, 289; *Compt. rend.*, 1898, 127, 584. Riedel describes an alloy obtained by heating Ca and As with sand as a diluent, see *German Patent*, 300152 (1916).

[12] Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 407.

[13] Lebeau, *ibid.*, 1902, [7], 25, 470; *Compt. rend.*, 1899, 129, 95.

[14] Guérin, *ibid.*, 1935, 200, 1210.

finally calcium oxide and arsenic; in order to obtain the arsenide, rapid heating to 1500° to 1600° C. is necessary. If the heating is slow, loss of arsenic occurs.

The arsenide is obtained as a crystalline mass, small fragments of which are transparent and reddish-brown in colour. Its density is 2·5, and it is harder than calcite. It is readily attacked by the halogens, but the higher the atomic number of the latter, the higher the temperature necessary for reaction to occur. It remains unchanged in dry air or oxygen at the ordinary temperature, but when heated in the latter it burns brilliantly to form arsenate; if the oxygen supply is limited, however, arsenious oxide and arsenic may be produced. With oxidising agents there is vigorous heat evolution. Hydrogen does not attack the arsenide, even at 700° to 800° C. Water decomposes it in the cold with formation of calcium hydroxide and evolution of arsine; it is consequently unstable in moist air. It is attacked by sulphur or hydrogen sulphide at dull red heat. Cold concentrated sulphuric acid is reduced to sulphurous acid. The gaseous halogen acids react at red heat giving arsenic and a calcium salt. Fuming nitric acid does not attack it in the cold, but there is a rapid reaction on heating. Carbon and boron are without action at 1000° C., but the former can decompose it completely at the temperature of the electric furnace. Many metallic salts are decomposed when heated with the arsenide.

The presence of small amounts of arsenic in calcium retards the absorption of nitrogen by the latter.[1]

Cerium Arsenide.—Hirsch[2] obtained an alloy of cerium and arsenic by adding the latter in small amounts to cerium melted under a layer of sodium chloride. The reaction appeared to be exothermic and a soft, somewhat pyrophoric alloy remained, which did not decompose on being kept.

Chromium Arsenides.—Two arsenides, of composition CrAs and Cr_2As_3, respectively, have been obtained.[3] The *monarsenide* is formed when the sesquiarsenide is heated in hydrogen at 480° to 500° C. Its density at 16° C. is 6·35, and X-ray examination shows that it is hexagonal in structure.[4] It is insoluble in acids. The *sesquiarsenide* is prepared by heating finely divided chromium with excess of arsenic at 700° C. in a sealed exhausted tube, the product being powdered and again heated. The resulting compound is not changed in composition by prolonged heating in hydrogen at 400° C., but above that temperature it loses arsenic and passes to the monarsenide. Chromium sesquiarsenide is a grey powder, of density 6·2 at 22° C.; it is insoluble in acids.

Cobalt Arsenides.—Cobalt alloys readily with arsenic and several compounds have been prepared. On the freezing point curve[5] there is a eutectic point at 916° C. and 30 per cent. As, and maxima occur at 926° C., 959° C. and 1180° C., corresponding respectively with Co_5As_2 (33·7 per cent. As), Co_2As (38·9 per cent. As) and CoAs (about 55 per

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[1] Ruff and Hartmann, *Zeitsch. anorg. Chem.*, 1922, 121, 167.

[2] Hirsch, *Trans. Amer. Electrochem. Soc.*, 1911, 20, 57; *J. Ind. Eng. Chem.*, 1911, 3, 880; 1912, 4, 65.

[3] Dieckmann and Hanf, *Zeitsch. anorg. Chem.*, 1914, 86, 291. See also Dieckmann, "*Ueber einige Mono- und Bi-Arsenide des Eisens, Mangans und Chroms*," Berlin, 1911.

cent. As). The curve cannot be obtained for higher percentages of arsenic owing to volatilisation of the latter. The existence of a fourth arsenide, Co_3As_2, which dissociates without melting at 1014° C., is also indicated. Alloys containing from 12 to 46 per cent. As undergo a transformation on cooling, heat being evolved at temperatures ranging from 250° to 350° C., and a maximum heat development occurs at the composition Co_2As, when the transformation point is 352° C. The change is accompanied by a considerable increase in volume and the alloy is sometimes disrupted. The transformation temperatures for the definite arsenides Co_5As_2 and Co_3As_2 are respectively 828° and 915° C. Alloys containing up to 38 per cent. arsenic are magnetic; with more than this proportion they are non-magnetic. The addition of arsenic to cobalt causes increased hardness. Other arsenides of composition Co_2As_3, $CoAs_2$, Co_2As_5 and $CoAs_3$ have been described.[1]

Tri-cobalt Di-arsenide, Co_3As_2, may be prepared[2] by the action of arsenic trichloride on metallic cobalt at 800° to 1400° C.; or by heating mixtures of arsenic and cobalt in hydrogen or carbon monoxide at this temperature. It is also formed when powdered cobalt is heated in hydrogen containing arsenic vapour, and when cobalt arsenate or arsenite is reduced by hydrogen at 900° C. Its density is 7·82 at 0° C. When strongly heated it loses arsenic. It is only slowly attacked by fused alkali, or by hot concentrated hydrochloric or sulphuric acid. It dissolves readily in nitric acid or aqua regia, and reacts vigorously with oxygen, sulphur or chlorine.

Cobalt Monarsenide, CoAs, is obtained when the previous compound is heated at 600° to 800° C.,[3] when cobalt is heated to 275° to 335° C. in arsenic vapour,[4] or when the elements in equal molecular proportions are heated for not less than a day at 730° C.[5] It is a grey crystalline powder, of density 7·62 at 0° C., tarnishing slightly in the air.[6] It melts at 1180° C. When strongly heated in hydrogen it loses arsenic. It resembles the arsenide Co_3As_2 in chemical properties. The lattice structure resembles that of the corresponding manganese and iron arsenides, the metal atoms forming zigzag chains, thus differing from nickel monarsenide, in which the metal atoms form straight rows.[7]

Di-cobalt Tri-arsenide, Co_2As_3, is formed when cobalt monarsenide is heated at 400° to 600° C., or when cobalt is heated with arsenic trichloride at the same temperature. According to Beutell and Lorenz,[8] it is formed when cobalt is heated in arsenic vapour at 345° to 365° C., but it slowly undergoes decomposition below 400° C. to form the di-arsenide, $CoAs_2$. It also decomposes when heated above 600° C. The density is 7·35 at 0° C.

Cobalt Di-arsenide, $CoAs_2$, is formed when cobalt is heated in arsenic vapour at 385° to 405° C.[8] Its density is 6·97 at 0° C. It is grey in colour, slightly oxidised by air, and decomposes above 400° C. This

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[1] Beutell and Lorenz, *Centr. Min.*, 1916, pp. 10, 49. See also Gehlen, *Schweigger's J.*, 1815, 15, 501; 1817, 20, 353; Berthier, *Ann. Chim. Phys.*, 1836, [2], 62, 113; Kopp, *Annalen (Suppl.)*, 1864, 3, 289; Rammelsberg, *Pogg. Annalen*, 1866, 128, 441; *Neues Jahrb. Min.*, 1897, ii, 45.

[2] Ducelliez, *Compt. rend.*, 1908, 147, 424.

[3] Ducelliez, *loc. cit.*

[4] Beutell and Lorenz, *loc. cit.*

[5] Fylking, *Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 18, 1.

[6] See Tammann and Bredemeier, *Zeitsch. anorg. Chem.*, 1924, 136, 337.

[7] Fylking, *loc. cit.* See also de Jong and Willems, *Physica*, 1927, 7, 74.

[8] Beutell and Lorenz, *loc. cit.*

arsenide occurs in two forms in Nature, *smaltite* (cubic, p. 10), an important ore of cobalt, and *safflorite* (rhombic, p. 12).[1]

Cobalt Tri-arsenide, $CoAs_3$, is found in Nature as the mineral *skutterudite* (p. 10), and is formed when cobalt is heated in arsenic vapour at 450° to 618° C.[2]

Copper Arsenides.—Investigation of the freezing point curve of the system Cu–As confirms the existence of the two arsenides, Cu_3As and Cu_5As_2,[3] and there is evidence of the formation of the arsenide Cu_2As. An arsenide of composition Cu_3As_2 is also known. The addition of arsenic to copper lowers the freezing point uniformly up to 14 per cent. As, when a steep fall occurs, reaching a minimum at 685° C. and yielding a eutectic mixture with 19·2 per cent. As corresponding approximately with Cu_5As. As the proportion of arsenic is increased, the curve rises until, at 747° C., the first compound, Cu_3As, containing 28·4 per cent. As, crystallises out. This is soon followed by the crystallisation at 807° C. of a second compound, Cu_5As_2, with 32·2 per cent. As. The freezing temperature then falls to a minimum at about 695° C., the eutectic mixture containing approximately 35 per cent. of As. With more arsenic the curve rises to 740° C. and, according to Hiorns, the arsenide, Cu_2As, with 37·34 per cent. As, separates; Friedrich, however, could not obtain this compound. Beyond this point the curve begins to fall, but with more than 43 to 44 per cent. As, alloys could not be obtained by fusion, the excess of arsenic rapidly burning off.[4]

Many arseniferous minerals contain arsenides of copper in a more or less pure state. They are found in various localities, but especially in Michigan and Chile. The more important are *domeykite*, Cu_3As, and the allied minerals *argento-domeykite*, $(Cu, Ag)_3As$, *mohawkite*, $(Cu, Ni, Co)_3As$, and *stibio-domeykite*, $Cu_3(As, Sb)$; also *algodonite*, Cu_6As, *whitneyite* and *darwinite*, Cu_9As (see pp. 10, 12).

The influence of small quantities of arsenic on copper has already been described (p. 55). The thermal conductivity of Cu–As alloys has been investigated,[5] as also has the electrical behaviour at temperatures as low as 1·26° Abs., obtained by means of liquid helium; [6] whether or not the alloys are supraconductive at these temperatures has not been definitely determined. The structure of various Cu–As alloys has been investigated by means of the X-rays.[7]

Tri-copper Arsenide, Cu_3As, has been prepared by melting a mixture of copper and arsenic under a layer of fused boric acid; [8] by subjecting an intimate mixture of the elements in the required proportions to a pressure of 6500 atm.; [9] by heating copper in arsenic vapour; [10] by

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[1] For other minerals containing cobalt arsenides, see p. 13.

[2] Beutell and Lorenz, *loc. cit.*

[3] Hiorns, *J. Soc. Chem. Ind.*, 1906, 25, 617; Friedrich, *Metallurgie*, 1905, 2, 477; 1908 5, 530.

[4] See also Bergman, "*De arsenico*," Stockholm, 1777; Berthier, *Ann. Chim. Phys.*, 1836, [2], 62, 113; Weiss, *ibid.*, 1923, [9], 20, 131; Kordes, *Zeitsch. anorg. Chem.*, 1926, 154, 97.

[5] Hanson and Rodgers, *J. Inst. Metals*, 1932, 48, 37; *Engineering*, 1932, 133, 354.

[6] Wilhelm, *Phil. Mag.*, 1930, [7] 10, 500; Meissner, Franz and Westerhoff, *Ann. Physik*, 1933, 17, 593.

[7] Katoh, *Zeitsch. Krist.*, 1930, 76, 228; *Bull. Chem. Soc. Japan*, 1930, 5, 275.

[8] Descamps, *Compt. rend.*, 1878, 86, 1023.

[9] Spring, *Bull. Acad. roy. Belg.*, 1883, [3], 5, 234; *Ber.*, 1883, 16, 324.

[10] Koenig, *Amer. J. Sci.*, 1900, [4], 10, 439; 1902, [4], 14, 414, *Proc. Amer. Phil. Soc.*, 1903, 42, 219; *Zeitsch. Kryst. Min.*, 1901, 34, 67; 1903, 38, 529.

heating a mixture of copper and the hemi-arsenide, Cu_2As ;[1] by the action of arsine on an aqueous solution of potassium cuprochloride, excess of Cu^+ ion being avoided, otherwise precipitation of copper occurs ;[2] and by the action of hydrogen at high temperature and pressure on copper arsenate.[3] By heating copper or a suitable alloy at about 600° C. in arsenic vapour Koenig[4] obtained brilliant crystals corresponding in composition with the various forms of domeykite enumerated above.

The density of Cu_3As is 6·7 to 7·7 ; the density calculated from crystallographic data[5] is 8·22. The hardness is 3·0 to 3·5 on Mohs' scale. The specific heat is[6] 0·0919. On heating, sublimation occurs at 345° to 370° C.[7] The arsenide decomposes on strong heating.[8] It is completely reduced when heated in hydrogen.[9] It is stable towards hydrochloric acid, but is attacked by nitric acid.[10]

The arsenide Cu_5As_2 has been prepared by passing a current of carbon dioxide and arsenic vapour over finely divided copper heated to the temperature of boiling sulphur ;[11] by the action of copper on arsenic trichloride or on arsenic dissolved in hydrochloric acid ;[12] and by the action of cuprous chloride on arsenic. Lustrous regular crystals of density 7·56 are obtained. These tarnish on exposure to air. When heated it loses arsenic and yields Cu_3As, which at a higher temperature also decomposes. Cu_5As_2 dissolves in nitric acid. It is readily attacked by chlorine or bromine.[13]

The *hemi-arsenide*, Cu_2As, was described by Descamps[14] as being formed when the black precipitate, resulting from the addition of arsenic to a solution of a copper salt, was fused under borax ; according to Koenig,[15] it is formed, with Cu_3As, when arsenic vapour is passed over heated copper. Hiorns described it as being formed by fusing the elements together (see above),[16] but Friedrich did not observe this to be the case. Koenig described it as a grey crystalline mass of density 7·71 at 21° C.

Tri-copper Di-arsenide, Cu_3As_2, is formed when arsine acts on a solution of copper sulphate,[17] or on dry copper sulphate or chloride ;[18] by subjecting a suitable mixture of the powdered elements to a pressure of 6500 atm. ;[19] by reducing cupric arsenite with fused potassium

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[1] Koenig, *loc. cit.*

[2] Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[3] Ipatiev and Nikolaiev, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 664, 686, 692, 698.

[4] Koenig, *loc. cit.*

[5] Katoh, *loc. cit.*

[6] Sella, *Ges. Wiss. Gött.*, 1891, p. 311.

[7] Joly, *Chem. News*, 1913, 107, 341 ; *Phil. Mag.*, 1914, [6], 27, 1.

[8] Granger, *Compt. rend.*, 1903, 136, 1397 ; *Bull. Soc. chim.*, 1903, [3], 29, 729.

[9] Cornu and Redlich, *Centr. Min.*, 1908, p. 277.

[10] Wright, *Proc. Amer. Phil. Soc.*, 1903, 42, 237.

[11] Granger, *loc. cit.*

[12] Reinsch, *J. prakt. Chem.*, 1841, [1], 24, 244 ; Paul and Cownley, *Pharm. J.*, 1901, [4], 12, 136.

[13] Granger, *loc. cit.*

[14] Descamps, *loc. cit.*

[15] Koenig, *loc. cit.*

[16] See also Gehlen, *Schweigger's J.*, 1815, 15, 89.

[17] Dumas, *Ann. Chim. Phys.*, 1826, [2], 33, 355 ; 1830, [2], 44, 289.

[18] Kane, *Proc. Irish Acad.*, 1840, 1, 182 ; Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[19] Spring, *loc. cit.*

cyanide;[1] or by the action at 100° C. of a solution of arsenic trichloride in hydrochloric acid on copper. It is obtained as a brittle bluish-grey crystalline mass of density 6·94.

Arsenides of **gallium** and **germanium** have not been prepared.

Gold Arsenides.—Alloys containing up to 25 atoms per cent. of arsenic have been prepared by fusing together gold and an alloy rich in arsenic.[2] The freezing point curve reveals a eutectic point at 665° C. with about 46 atoms As per cent. Several arsenides have been described. Descamps,[1] by adding metallic arsenic to a solution of auric chloride, obtained a dark red deposit somewhat richer in arsenic than corresponds to the composition Au_3As. This product when fused with potassium cyanide is converted into a yellow arsenide, Au_4As_3, of density 16·2. The *monarsenide*, AuAs, was prepared by Brukl[3] by dropping a solution of sodium chloraurate into an atmosphere of arsine. This arsenide is stable towards dilute acids and alkalis. Concentrated nitric acid reduces it to spongy gold. At high temperatures it decomposes with almost complete loss of arsenic.

Indium arsenides have not been reported.

Iridium Arsenide, $IrAs_2$, has been obtained in a pure form by heating iridium chloride with an excess of arsenic in a current of hydrogen.[4] It is also formed when an intimate mixture of the finely divided metal and excess of arsenic is heated in an indifferent atmosphere. The arsenide may be analysed by the method described under palladium arsenide (p. 73).

Iron Arsenides.—The system Fe–As has been investigated by Friedrich,[5] alloys containing up to 56 per cent. As having been examined. The following compounds are indicated on the freezing point curve: Fe_2As, Fe_3As_2, FeAs, and possibly Fe_5As_4. Thus the curve falls from the freezing point of iron (1535° C.) to a eutectic point at 30 per cent. As[6] and 835° C., and rises to a maximum at 40·1 per cent. (Fe_2As) and 919° C. Less distinct maxima occur at 51·7 per cent. As (*i.e.* Fe_5As_4) and 964° C., and at 57·3 per cent. As (*i.e.* FeAs) and 1031° C., the latter point being obtained by extrapolation of the curve of solidification times. A reaction between the solid products occurs at 800° C. in all alloys containing 40 to 56 per cent. As, the maximum development of heat taking place with 47·2 per cent., corresponding with the formation of Fe_3As_2.

The above conclusions were confirmed by micrographic examination of the alloys, which were etched by means of a hot solution of iodine in potassium iodide. Alloys containing more than 40 per cent. As were non-magnetic. Those formed in the neighbourhood of a maximum were brittle. A study of the E.M.F. diagram[7] of Fe–As alloys containing 6 to 56 per cent. As indicated the formation of Fe_2As and Fe_5As_4. The effect of adding small quantities of arsenic (up to 8 per cent.) to

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[1] Descamps, *loc. cit.*

[2] Schleicher, *Intern. Zeitsch. Metallographie*, 1914, 6, 18. See also Bergman, "*De arsenico*," Stockholm, 1777; Hatchett, *Phil. Trans.*, 1803, 93, 43; Liversidge, *Chem. News*, 1894, 69, 152; Arnold and Jefferson, *Engineering*, 1896, 61, 176.

[3] Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[4] Wohler and Ewald, *Zeitsch. anorg. Chem.*, 1931, 199, 57.

[5] Friedrich, *Metallurgie*, 1907, 4, 129.

[6] Oberhoffer and Gallaschik (*Stahl u. Eisen*, 1923, 43, 398) observed the eutectic point to be at 30·3 per cent. As.

iron was examined by Oberhoffer and Gallaschik,[1] who observed that on cooling the change point of the δ mixed crystals with liquid to γ mixed crystals (which they recorded as 1440° C.) was depressed 80° by the presence of 0·5 per cent. As and remained constant with further addition. The change point on heating was not affected. With more than 3 per cent. As no change point could be detected. The maximum solubility of arsenic in δ-iron is 0·9 per cent. and in γ-iron 6·8 per cent. Micro-examination confirmed the thermal data and revealed homogeneous mixed crystals up to 6·67 per cent. As. The alloy with 7·29 per cent. As showed traces of eutectic.

A comprehensive X-ray investigation has been made of Fe–As alloys containing up to 56·9 per cent. As,[2] the highest content obtainable. The alloys were prepared by dropping pellets of arsenic into molten pure iron contained in a magnesia crucible in an atmosphere of nitrogen. The displacement of Fe lines indicated that α-iron will hold approximately 5 per cent. of arsenic in solution at room temperature. With increasing arsenic the first compound indicated, Fe_2As, has a simple tetragonal lattice with $a=3{\cdot}627$ A. and $c=5{\cdot}973$ A., two molecules forming the unit cell. The As atom is surrounded by 4Fe at 2·40 A., 4Fe at 2·60 A. and 1Fe at 2·41 A. The Fe–As distances are less than those calculated from the normal atomic radii. The arsenide Fe_3As_2 could not be found in slowly cooled alloys, but quenched alloys of the proper composition, when examined microscopically, presented an appearance suggesting high-temperature stability (above 795° C.) for Fe_3As_2, the compound breaking down at lower temperatures into Fe_2As and FeAs. The arsenide FeAs has a simple orthorhombic lattice with $a=3{\cdot}366$ A., $b=6{\cdot}016$ A. and $c=5{\cdot}428$ A., each unit cell containing four molecules. The lattice structure resembles that of the corresponding cobalt arsenide. The crystal structure of various minerals containing iron arsenide, for example, löllingite, $FeAs_2$, safflorite (Co, Fe)As_2, rammelsbergite (Ni, Co, Fe)As_2, and certain arseno-sulphides, including arsenopyrite, has been investigated.[3] The conclusions as regards löllingite are not in agreement, and further study is desirable. Buerger gives the following structure: space group, V_h^{12}; two molecules in unit cell, with dimensions $a=2{\cdot}85$, $b=5{\cdot}25$ and $c=5{\cdot}92$ A.; the effective As radius 1·23 A.; Fe–As = 2·35 and Fe radius 1·12 A., as in marcasite, with which mineral löllingite is isomorphous.

A metallographic and analytical examination[4] of the ternary system Ni–Fe–As shows the formation of the crystalline double arsenides $2Fe_2As.Ni_5As_2$ and $4Fe_2As.Ni_5As_2$.

Iron Subarsenide, Fe_2As, is formed by melting a mixture of the two elements in the requisite proportions.[5] It melts at 919° C. A product of the same composition is obtained when a mixture of borax and arsenopyrite is heated in a carbon crucible and the product digested with hydrochloric acid.[6]

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[1] Oberhoffer and Gallaschik, *loc. cit.*

[2] Hagg, *Zeitsch. Krist.*, 1928, 68, 470; 1929, 71, 134; *Chem. Zentr.*, 1929, ii, 1889; *Nova Acta Soc. Sci. Upsaliensis*, 1929, [4], 7, 1. See also Fylking, *Arkiv Kemi, Min., Geol.*, 1935, 11, B, No. 18, 1; Elander, Hägg and Westgren, *ibid.*, 1936, 12, B, No. 1, 1.

[3] de Jong, *Physica*, 1926, 6, 325; Buerger, *Zeitsch. Krist.*, 1932, 82, 165.

[4] Guertler and Savelsberg, *Metall u. Erz*, 1932, 29, 84.

[5] Friedrich, *Metallurgie*, 1907, 4, 129. See also Percy, "*Metallurgy of Iron and Steel,*" London, 1864, p. 74.

[6] Berthier, *Ann. Chim. Phys.*, 1836, [2], 62, 113; *Ann. Mines*, 1837, [3], 11, 501.

The conditions under which the formation of the arsenides Fe_3As_2 and Fe_5As_4 may occur are indicated on p. 65. The former was obtained by Brukl [1] as a black precipitate by the action of arsine on an alcoholic solution of ferrous ammonium sulphate. The product was only slightly attacked by concentrated hydrochloric or sulphuric acid but was soluble in nitric acid, aqua regia and bromine water.

Iron Monarsenide, FeAs, may be obtained by heating iron in a current of arsenic vapour at 335° to 380° C.; [2] by heating a mixture of the elements in a bomb tube at 680° C.,[3] or a mixture of iron, arsenious oxide and carbon in an electric arc furnace; [4] by the action of fused potassium cyanide on iron arsenate; [5] by reduction of the di-arsenide at 680° C. in a current of hydrogen; [3] or by dropping a solution of a ferrous salt into an atmosphere of arsine.[6]

It forms silver-white, rhombic crystals,[7] of density 7·83, and melting point 1020° C. according to Hilpert and Dieckmann [8] or 1031° C. according to Friedrich.[9] It is non-magnetic. Steel-grey crystals of the arsenide of density 7·94 have been found associated with tin sulphide in the hearth of an old tin smelting furnace in Cornwall.[10]

The product, of density 7·22, which results when iron is heated in arsenic vapour at 395° to 415° C.[11] agrees in composition with the formula Fe_2As_3. The existence of such an arsenide has not been confirmed, however, although some forms of löllingite approach this composition.

Iron Di-arsenide, $FeAs_2$, occurs as the minerals löllingite and arsenoferrite (see p. 10), and may be made artificially by heating iron in arsenic vapour at 480° to 618° C.,[12] or by heating a finely powdered mixture of the elements in a bomb tube at 700° to 750° C.[13] After treatment with dilute hydrochloric acid the pure di-arsenide is obtained as a silver-grey microcrystalline powder of density 7·38. It melts at 980° to 1040° C. It is insoluble in hydrochloric acid, whether dilute or concentrated, but is slowly oxidised by nitric acid, yielding arsenic acid. Heated with concentrated sulphuric acid, sulphur dioxide is evolved. When heated in air it burns, yielding arsenious oxide and ferric oxide. It is non-magnetic.

When the mineral löllingite is heated *in vacuo* it loses 23·8 per cent. of arsenic, the residue containing two unidentified constituents.[14] Arsenopyrite, treated similarly, decomposes at 675° to 685° C.

Lead Arsenides.—An investigation of the system Pb–As reveals no evidence of the existence of any definite compounds.[15] At its melting

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[1] Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[2] Beutell and Lorenz, *Centr. Min.*, 1916, pp. 10, 49.

[3] Hilpert and Dieckmann, *Ber.*, 1911, 44, 2378, 2831.

[4] Lebeau, *Compt. rend.*, 1899, 129, 47.

[5] Descamps, *ibid.*, 1878, 86, 1066.

[6] Brukl, *loc. cit.*

[7] de Jong, *Physica*, 1926, 6, 325; de Jong and Willems, *ibid.*, 1927, 7, 74; Hagg, *Zeitsch. Krist.*, 1929, 71, 134; *Chem. Zentr.*, 1929, ii, 1889.

[8] Hilpert and Dieckmann, *loc. cit.*

[9] Friedrich, *loc. cit.*

[10] Headden, *Amer. J. Sci.*, 1898, (4), 5, 93.

[11] Beutell and Lorenz, *loc. cit.*

[12] Beutell and Lorenz, *loc. cit.*

[13] Hilpert and Dieckmann, *loc. cit.* See also Bergman, "*De arsenico*," Stockholm, 1777; Gehlen, *Schweigger's J.*, 1815, 15, 501; 1817, 20, 353.

[14] Monclova, *Bull. Soc. franç. Min.*, 1930, 53, 491.

[15] Friedrich, *Metallurgie*, 1906, 3, 41; *cf.* Heycock and Neville, *Chem. News*, 1890, 62, 280; Descamps, *Compt. rend.*, 1878, 86, 1022.

point lead does not dissolve any arsenic, but at higher temperatures two layers are formed ;[1] the lower layer consists of lead containing a small quantity of arsenic dissolved in it, and the upper layer is arsenic containing a small quantity of lead. At atmospheric pressure only up to 35 per cent. of arsenic can be alloyed with lead.[2] There is a eutectic at 290° C. with 2·6 per cent. of arsenic. At this temperature the lead retains in solution 0·045 to 0·05 per cent. As. The solubility of arsenic in lead diminishes rapidly as the temperature is lowered and at room temperature it is probably less than 0·01 per cent. As. With arsenic-rich alloys the primary crystals are almost pure arsenic, so that the solubility of lead in arsenic is practically nil.

The addition of small quantities of arsenic reduces the shrinkage of lead during solidification and increases the hardness and, in small degree, the compressive strength.[3] It has no effect on the rate of corrosion in water.

The following arsenides have been described in the literature: Pb_9As, a malleable crystalline alloy obtained by heating arsenic with molten lead for 20 hours ;[4] Pb_6As, crystalline plates found associated with tin in Cornwall ;[5] Pb_2As, obtained by melting excess of arsenic with lead under fused boric acid and heating to a moderate temperature ;[6] if the temperature in the latter case is kept as low as possible the product has the composition Pb_3As_4 ; if the mixture is heated strongly, Pb_3As_2 is formed ;[7] finally PbAs, obtained by reduction of lead arsenate under fused potassium cyanide.[6] The existence of none of these as a true compound has been confirmed, however.

Lithium Arsenide, Li_3As, is formed when a mixture of the elements in suitable proportions is heated to redness, or when lithium arsenate is reduced by heating with charcoal in an electric furnace.[8] It is a dark brown crystalline substance of great reactivity. It is attacked by the halogen elements at the ordinary temperature with incandescence. It burns vividly when heated in oxygen; it reacts violently with nitric acid, and at a comparatively low temperature it reduces many metallic oxides.

Magnesium Arsenide, Mg_3As_2, may be prepared by heating magnesium powder with a slight excess of arsenic in the absence of air ;[9] it is obtained as a grey, metallic, microcrystalline powder, of density 3·165 and melting point 800° C. It has also been obtained by heating arsenic and magnesium filings in hydrogen [10]—this product was described

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[1] Faruq, *Proc. 15th Indian Sci. Congress*, 1928, 176.

[2] Bauer and Tonn, *Zeitsch. Metallk.*, 1935, 27, 183.

[3] Bauer and Tonn, *loc. cit.* For recent work on the influence of As on Pb and Pb alloys, see Anon, *ibid.*, 1932, 24, 306; Tammann and Dreyer, *ibid.*, 1933, 25, 64; Wegner, *Metals and Alloys*, 1932, 3, 116; and for the preparation and uses of such alloys, see Amer. Smelting and Refining Co., *British Patent*, 390330 (1933), *Canadian Patent*, 334295 (1933); Deisches, *Austrian Patent*, 130903 (1931); Seljesaeter, *U.S. Patent*, 1722358 (1929); *Canadian Patent*, 311353 (1931).

[4] Koenig, *Proc. Amer. Phil. Soc.*, 1903, 42, 219; *Zeitsch. Kryst. Min.*, 1903, 38, 529.

[5] Headden, *Amer. J. Sci.*, 1898, [4], 5, 95; *Proc. Colorado Scient. Soc.*, 1901, 6, 80; Stevanovic, *Zeitsch. Kryst. Min.*, 1905, 40, 326.

[6] Descamps, *Compt. rend.*, 1878, 86, 1065.

[7] Descamps, *loc. cit.*; see also Stead, *J. Inst. Metals*, 1919, 22, 127; *Engineering*, 1919, 108, 663; Spencer, *Mining Mag.*, 1921, 19, 113; Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[8] Lebeau, *Compt. rend.*, 1899, 129, 49; 1900, 130, 502.

[9] Natta and Passerini, *Gazzetta*, 1928, 58, 541.

[10] Parkinson, *J. Chem. Soc.*, 1867, 20, 125, 309.

as a brittle, chocolate-brown mass with a metallic lustre: by heating a mixture of arsenic, magnesium and sand;[1] and by igniting the mixed elements[2]—the reaction in this case being very violent.

Magnesium arsenide decomposes rapidly on exposure to air. It reacts with water and acids to yield arsine;[3] with ethyl alcohol at the boiling point it also gives arsine, and at 280° to 295° C. ethyl- and diethyl-arsines, with a trace of triethylarsine, are formed.[4] The crystal structure of the arsenide has been investigated by the X-ray powder method.[5] It resembles the corresponding zinc arsenide and has a cubic lattice containing two molecules of Mg_3As_2 in the unit cell, the side of which is 6·10 A., the calculated density being 3·26. The arrangement of the atoms in the lattice represents an unusual type of structure which is defined by the co-ordinates As $= (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), (\frac{3}{4}, \frac{3}{4}, \frac{3}{4}), (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}), (\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$; and Mg $= (\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, 0)$. The distance Mg–Mg is 3·05 A., that of As–Mg, 2·64 A., while that of As–As is 4·31 A. From these data the radius of the Mg atom is calculated to be 1·525 A., and the atomic diameter of As 1·02 A.; these values correspond roughly to the values for the neutral atoms (1·62 and 1·16 A., respectively) calculated by Goldschmidt. The structure of magnesium arsenide is not ionic.

Manganese Arsenides.—Three of these have been described: Mn_2As, Mn_3As_2 and MnAs. The *hemi-arsenide*, Mn_2As, is prepared, according to Arrivaut,[6] by heating a mixture of arsenic and manganese at 500° C.; combination occurs with incandescence. It is also formed when the monarsenide is heated in the absence of air.[7] Hilpert and Dieckmann[8] could not obtain the hemi-arsenide, but Arrivaut,[9] in an investigation of the E.M.F. diagram of Mn–As alloys containing 6 to 53 per cent. As, showed the presence of the two arsenides Mn_2As and Mn_3As_2. The former is grey and non-magnetic and is stable at high temperatures. The latter, *trimanganese di-arsenide*, Mn_3As_2, is obtained by heating the mixture of elements in a current of hydrogen at 700° to 800° C.[10] When freshly prepared, this arsenide is ferromagnetic, but on heating to about 45° C. it becomes paramagnetic; on cooling it returns to the ferromagnetic state.[11] Each subsequent transition from the ferromagnetic to the paramagnetic state increases the intrinsic magnetisation, and the thermal properties are also affected. Thus the specific heat of a specimen of the arsenide was observed[12] to change as shown in fig. 6; the value increased slowly from 0·122 at 28° C. to 0·14 at 36° C., then rapidly rose to a maximum of about 0·8 at 42·2° C., falling steeply to 0·13 at 45° C. (the critical temperature) and reaching a minimum at about 46·5° C. Thus heat is rapidly absorbed as the substance passes from the ferromagnetic to the paramagnetic state. In the figure, the curve B shows, in arbitrary units, the effect of temperature on the

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[1] Riedel, *German Patent*, 300152 (1916).

[2] Natta, *Giorn. Chim. Ind. Appl.*, 1926, 8, 367.

[3] Parkinson, *loc. cit.*

[4] Natta, *loc. cit.*

[5] Natta and Passerini, *loc. cit.*

[6] Arrivaut, *7th Intern. Cong. Appl. Chem.*, 1909, sect. ii, 100.

[7] Wedekind and Veit, *Ber.*, 1911, 44, 2663.

[8] Hilpert and Dieckmann, *ibid.*, 1911, 44, 2378.

[9] Arrivaut, *Chim. et Ind.*, Spec. Nos. 284–5, Sept. 1925.

[10] Arrivaut, *7th Intern. Cong. Appl. Chem.*, 1909, sect. ii, 100.

[11] Shoen, *Metallurgie*, 1911, 8, 739; Bates, *Phil. Mag.*, 1928, [7], 6, 593; 1932, [7], 13, 393; 1933, [7], 16, 657; 1934, [7], 17, 783.

[12] Bates, *Proc. Roy. Soc.*, 1928, A 117, 680.

nagnetic induction, and the curve C the rate of change of magnetic nduction with temperature, also in arbitrary units. The latter shows a naximum at 42·2° C. and corresponds closely to the specific heat curve. Bates suggests that the changes are due to interaction between the spin noment of one atom and the orbital moment of another. The density lso changes[1] from 6·26 to 6·20, and the course of the volume-emperature curve between 15° and 50° C. resembles those of the ntensity of magnetisation-temperature and the specific heat-temperature curves. The change is gradual and there is a temperature

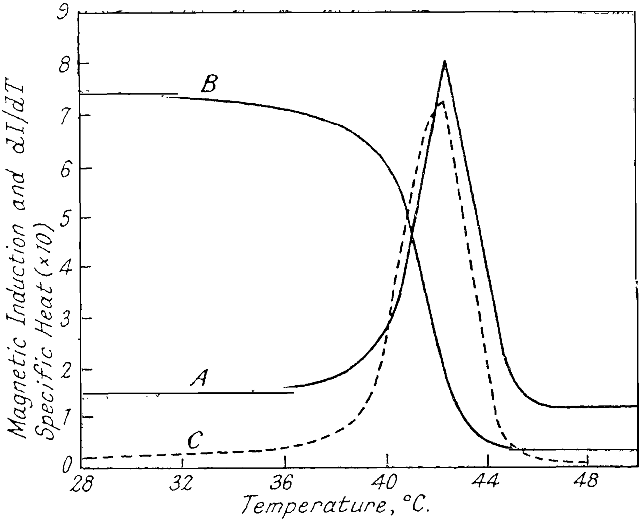

FIG. 6. The Effect of Temperature on (A) Specific Heat and (B) Magnetic Induction of Trimanganese Di-arsenide, and (C) the Rate of Change of the Magnetic Induction with Temperature.

hysteresis. The transition from the paramagnetic to the ferromagnetic form appears to involve a series of irreversible metastable conditions. No volume change results from the application of a magnetic field.

Manganese Monarsenide, MnAs, was described by Wedekind[2] as a black crystalline powder formed by heating together manganese and arsenic, the product being freed from excess of the former by treatment with dilute hydrochloric acid, and of the latter by heating in chlorine. Its density was 5·5 and it was stable only below 400° to 450° C., further heating causing loss of arsenic. A similar product may be obtained by the action of arsenic trichloride on manganese. Hilpert and Dieckmann heated pure manganese in arsenic vapour under pressure,[3] but Bates,[4] using the same method, found that the product contained nearly equal parts of manganese and arsenic and therefore corresponded with Mn_3As_2. Arrivaut[5] was unable to prepare the monarsenide, as the

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[1] Smits, Gerding and Vermast, *Zeitsch. physikal. Chem.*, *Bodenstein Festband*, 1931, p. 357; *Rec. Trav. chim.*, 1932, 51, 1178.

[2] Wedekind, *Zeitsch. Elektrochem.*, 1906, 11, 850; *Ber. deut. physikal. Ges.*, 1907, 4, 412; *Physikal. Zeitsch.*, 1907, 7, 805; *Zeitsch. physikal. Chem.*, 1909, 66, 614.

[3] Hilpert and Dieckmann, *Ber.*, 1911, 44, 2378, 2831.

[4] Bates, *Proc. Roy. Soc.*, 1928, A 117, 680.

[5] Arrivaut, *Chim. et Ind.*, Spec. Nos. 284–5, Sept. 1925.

mixture (containing 57 per cent. As) decomposed on fusion. There is consequently some confusion in the literature. Wedekind's product was non-magnetic. The crystal structure of the so-called monarsenide has been investigated.[1]

Mercury Arsenides.—Arsenic does not dissolve in mercury even at the boiling point,[2] nor has an amalgam been obtained by the action of sodium amalgam on moist arsenious oxide [3] or by electrolysis of a solution of arsenic trichloride using a mercury cathode ; [4] in the latter case arsenic is deposited on the surface of the mercury but does not dissolve. Nevertheless, two arsenides of mercury, which appear to be definite compounds, have been prepared.

Mercuric Arsenide, Hg_3As_2, may be obtained by passing arsine, largely diluted with hydrogen, into an alcoholic solution of mercuric chloride ; [5] the yellow chloromercurarsine, $AsH_2.HgCl$, is first formed, followed by the orange di- and brown tri-chloromercurarsines $AsH(HgCl)_2$ and $As(HgCl)_3$, and finally the arsenide is obtained as a black microcrystalline powder. It may also be prepared as follows : [6] 10 g. of arsenious oxide are dissolved in 100 g. of concentrated hydrochloric acid and the solution treated with 40·65 g. of mercuric chloride in 700 to 800 g. of dilute hydrochloric acid (1 : 5). After filtration, 60 g. of sodium hypophosphite are added and the mixture, shaken from time to time, is kept for several hours; on heating to boiling, the black precipitate of mercuric arsenide appears. Vortmann [7] electrolysed a hydrochloric acid solution of mercuric and arsenic chlorides after adding potassium iodide to prevent the formation of basic salts ; much arsine was evolved and a brownish-black amalgam was obtained.

Mercuric arsenide forms microscopic mamellated crystals. When dry it oxidises readily in the air to arsenious oxide and mercury. On heating it volatilises without melting, forming a sublimate of arsenic and mercury and a little arsenious oxide. The arsenide is therefore dried under diminished pressure. When heated with an alkyl iodide, a diarsonium mercuriodide of the type $As_2R_6I_2.2HgI_2$ is formed.[8]

Mercurous Arsenide, Hg_3As, was obtained by Brukl [9] as a black precipitate by dropping an aqueous solution of a mercurous salt into an atmosphere of arsine in complete absence of air. It is readily oxidised, and on keeping in air it yields mercury and arsenious oxide. It dissolves in nitric acid.

Molybdenum Arsenide, $MoAs_2$, is formed [10] by heating powdered molybdenum for 36 hours with arsenic at 570° C., the excess of arsenic then being removed by sublimation. It is a black powder of density

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[1] de Jong and Willems, *Physica*, 1927, 7, 74; Oftedal, *Zeitsch. physikal. Chem.*, 1928, 132, 208.

[2] Ramsay, *J. Chem. Soc.*, 1889, 55, 531; *cf.* Bergman, "*De arsenico*," Stockholm, 1777.

[3] Bottger, *J. prakt. Chem.*, 1834, [1], 3, 283; Lassaigne, *J. Chim. Méd.*, 1836, [2], 2, 650; *cf.* Dranty, *ibid.*, p. 650.

[4] Tammann and Hinnuber, *Zeitsch. anorg. Chem.*, 1927, 160, 256; Ramsay, *loc. cit.*

[5] Partheil and Amort, *Arch. Pharm.*, 1899, 237, 121; *Ber.*, 1898, 31, 594; Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236. See also Stromeyer, *Comment. Soc. Gött.*, 1808, 16, 141; Rose, *Pogg. Annalen*, 1840, 51, 423.

[6] Dumesnil, *Compt. rend.*, 1911, 152, 868.

[7] Vortmann, *Ber.*, 1891, 24, 2764.

[8] Partheil, Amort and Gronover, *Arch. Pharm.*, 1899, 237, 127.

[9] Brukl, *loc. cit.*

8·07 at 25° C. It resembles molybdenum phosphide in being insoluble in concentrated hydrochloric acid or ammoniacal hydrogen peroxide, but it is readily soluble in nitric acid, hot concentrated sulphuric acid or aqua regia.

Nickel Arsenides.—The freezing-point curve of Ni–As alloys containing up to 57·4 per cent. As has been studied.[1] The freezing point of nickel is lowered by addition of arsenic until with 27·8 per cent. of the latter a eutectic point is reached at 900° C. With 34·3 per cent. of arsenic there is a maximum at 998° C., corresponding with the arsenide Ni_5As_2. A second eutectic point is reached at 804° C. with 43·3 per cent. of arsenic, and the curve then rises to another maximum at 968° C. and 56·0 per cent. of arsenic, corresponding with the arsenide NiAs. Solid solutions are formed between the limits 0 to 5·5 per cent. and 33·5 to 35·7 per cent. of arsenic. Alloys containing 35·7 to 56 per cent. of arsenic undergo a transformation on cooling, with evolution of heat, the maximum development occurring at 45·5 per cent. of arsenic, thus indicating the formation of a third arsenide, Ni_3As_2. In addition, the diarsenide, $NiAs_2$, is known to exist, and a product obtained by heating nickel in arsenic trichloride vapour approximated in composition to the hemi-arsenide,[2] Ni_2As, but its identity as a definite compound has not been confirmed.

Pentanickel Di-arsenide, Ni_5As_2, prepared by fusing together the elements in the required proportions, is a hard, brittle compound.[3] It is non-magnetic.

Trinickel Di-arsenide, Ni_3As_2, is formed by reducing nickel arsenate, or a mixture of nickel oxide and arsenious oxide, with fused potassium cyanide;[4] when reduced nickel is heated at 800° to 1400° C. in vaporised arsenic chloride;[5] or when an alcoholic solution of nickel ammonium sulphate is dropped into an atmosphere of arsine completely free from air, the reaction vessel being repeatedly shaken.[6] The arsenide is a grey substance which melts at 1000° C.[7] Its density is 7·86 at 0° C. The crystals are tetragonal with $a = 3·45$ A. and $c = 21·7$ A., and a superposed 2-dimensional overstructure having $a = 6·9$ A.[8] The arsenide is very stable and is only slightly decomposed at 1400° C. It is attacked when heated in oxygen, chlorine or sulphur vapour. It readily dissolves in acids and is attacked more slowly by alkalis. According to Descamps,[9] when heated under fused boric oxide it loses arsenic to yield an arsenide Ni_3As, but the existence of this arsenide has not been confirmed.

Nickel Monarsenide, NiAs, is formed when reduced nickel is heated at 400° to 800° C. in arsenic chloride vapour.[10] It is identical with the mineral *niccolite* or *nickeline* (p. 12), and has, like it, a red colour. Its density is 7·57 at 0° C. When heated it commences to lose arsenic at

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[1] Friedrich and Bennigson, *Metallurgie*, 1907, 4, 200.

[2] Granger, *Arch. Sci. Genève*, 1898, [4], 6, 391.

[3] Friedrich and Bennigson, *loc. cit.*

[4] Descamps, *Compt. rend.*, 1878, 86, 1022, 1065.

[5] Vigouroux, *Compt. rend.*, 1908, 147, 426; Friedrich and Bennigson, *loc. cit.*; Granger and Didier, *Compt. rend.*, 1900, 130, 914; *Bull. Soc. chim.*, 1900, [3], 23, 506; Wohler, *Ann. Chim. Phys.*, 1832, [2], 51, 208.

[6] Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[7] Vigouroux, *loc. cit.*

[8] Laves, *Fortschr. Min.*, 1935, 19, 33.

[9] Descamps, *loc. cit.*

[10] Vigouroux, *loc. cit.*

100° C. and is gradually converted into Ni_3As_2. The crystal structure of nickeline has been examined, but the results obtained are not concordant.[1]

Nickel Di-arsenide, $NiAs_2$, occurs in Nature as *chloanthite* and *rammelsbergite* (p. 12). It may be prepared by heating either of the two previously described arsenides with arsenic in an atmosphere of hydrogen at decreasing temperatures; the arsenic is absorbed and the di-arsenide forms as a grey powder as the temperature falls below 400° C.[2]

Rammelsbergite is readily oxidised by aerated waters, the oxidation proceeding much more rapidly than in the case of niccolite and other arsenide minerals;[3] the oxidation is accelerated by the presence of iron pyrites, manganese dioxide or platinum black.[4]

Niobium Arsenide, $NbAs_2$, has been prepared[5] by heating the elements together in a sealed tube at 500° C. The product, the composition of which corresponded more exactly with $NbAs_{1.80}$, had density 7·28 at 25° C.

Palladium Di-arsenide, $PdAs_2$.—It was early observed[6] that palladium combines with arsenic with evolution of heat, a brittle fusible alloy being formed. The di-arsenide may be prepared[7] in a pure form by heating a mixture of palladium chloride with an excess of arsenic in a current of hydrogen. It melts at 680° C. with loss of arsenic. The crystals have the pyrites structure, with $a = 5{\cdot}970 \pm 0{\cdot}004$ A. It is not ferromagnetic.[8] By repeated oxidation and reduction at 400° to 500° C. the arsenic is removed as arsenious oxide, leaving a residue of palladium; this method may be used for the analysis of the arsenides of any of the metals of the platinum group.

Platinum Arsenides.—Platinum and arsenic combine readily on heating; Gehlen observed[9] deflagration when the spongy metal was heated with excess of arsenic. The system Pt–As, up to about 28 per cent. of arsenic, has been studied.[10] There is a eutectic containing 13 per cent. of arsenic solidifying at 597° C., and from the times of eutectic solidification indications of the probable existence of the arsenide Pt_2As_3 were obtained. The formation of an arsenide of composition Pt_3As_2 was described by Tivoli[11] who, by the action of arsine on aqueous platinic chloride, obtained black crystalline scales which he considered to be a hydroxyarsenide, PtAs(OH). This substance could be dried at 130° C. without decomposition, but above that temperature it yielded the arsenide in accordance with the equation:

$$6PtAs(OH) = As_2O_3 + 2Pt_3As_2 + 3H_2O$$

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[1] Aminoff, *Zeitsch. Krist.*, 1923, 58, 212; de Jong, *Physica*, 1925, 5, 194; *Chem. Zentr.*, 1925, ii, 2306.

[2] Vigouroux, *loc. cit.*; Beutell, *Centr. Min.*, 1916, p. 49.

[3] Walker and Parsons, *Univ. Toronto Geol. Studies*, 1921, p. 12; 1925, p. 20.

[4] Carmichael, *ibid.*, 1927, No. 24, p. 47.

[5] Heinerth and Biltz, *Zeitsch. anorg. Chem.*, 1931, 198, 168.

[6] Chenevix, *Phil. Trans.*, 1803, 93, 4; Fischer, *Schweigger's J.*, 1827, 51, 192; *Phil. Mag.*, 1828, [2], 4, 230; *Pogg. Annalen*, 1847, 71, 431.

[7] Wohler and Ewald, *Zeitsch. anorg. Chem.*, 1931, 199, 57.

[8] Thomassen, *Zeitsch. physikal. Chem.*, 1929, B, 4, 277.

Wöhler,[1] however, has shown that the product of the interaction of arsine and an aqueous solution of platinic chloride or potassium chlorplatinite is a mixture of variable composition, and he was unable to obtain the hydroxyarsenide.

Platinum Di-arsenide, $PtAs_2$, occurs in Nature as the rare mineral *sperrylite* (p. 12), and may be prepared in the laboratory by heating a mixture of the elements in a sealed tube at 270° C.[2] The reaction is explosive, but can be moderated by using a large excess of arsenic, which is afterwards removed in a stream of carbon dioxide at 500° C. The residual grey powder resembles natural sperrylite, and is attacked with difficulty by concentrated nitric acid or aqua regia. The di-arsenide has also been obtained [3] in a pure form by heating platinic chloride with an excess of arsenic in a current of hydrogen. The crystal structure has been investigated [4] by the powder method ; $a = 5{\cdot}957 \pm 0{\cdot}003$ A.

Potassium Arsenides.—Potassium combines with arsenic with incandescence,[5] and the arsenide K_3As may be obtained by heating the elements in the correct proportions in a glass tube. The pure arsenide is prepared [6] by heating to redness in a closed iron vessel a mixture of the elements containing an excess of potassium, the uncombined metal being subsequently removed from the cooled product by means of liquid ammonia ; the arsenide remains in the form of black crystals after removing ammonia by heating in nitrogen. Another method of preparation consists [7] in treating arsenic with an excess of potassammonium, NH_3K, when a brick-red compound, $K_3As.NH_3$, results ; this, when heated at 300° C. *in vacuo*, yields the black arsenide. The latter, like other alkali arsenides, reacts with water to yield solid arsenic monohydride and some arsine (see p. 79). If the potassammonium is heated with excess of arsenic, the product is an orange-coloured solid, $K_2As_4.NH_3$, which when heated *in vacuo* a little below 300° C. yields a cinnabar-red arsenide K_2As_4.

Rhodium Arsenide, $RhAs_2$, has been prepared in a pure form by heating rhodium chloride with an excess of arsenic in an atmosphere of hydrogen.[8] If finely divided rhodium is heated with excess of arsenic in an atmosphere of an indifferent gas, the arsenide produced is not pure.[9]

Ruthenium Arsenide, $RuAs_2$, may be prepared in an exactly similar manner to rhodium arsenide. The method of analysis described under palladium arsenide (p. 73) may be applied to both of these arsenides.

Silver Arsenides.—A study of the system Ag–As gives no evidence of the existence of any definite compound of the two elements.[10] When the mixtures were heated in sealed tubes it was observed that the addition of silver lowered the melting point of arsenic to a eutectic point

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[1] Wöhler, *Zeitsch. anorg. Chem.*, 1930, 186, 324.

[2] Wöhler, *loc. cit.*

[3] Wöhler and Ewald, *Zeitsch. anorg. Chem.*, 1931, 199, 57.

[4] Thomassen, *Zeitsch. physikal. Chem.*, 1929, B, 4, 277.

[5] Davy, *Phil. Trans.*, 1810, 100, 31; Gay-Lussac and Thénard, *Ann. Chim. Phys.*, 1810, [1], 73, 229; Gehlen, *Schweigger's J.*, 1815, 15, 501; Soubeiran, *J. Pharm. Chim.*, 1830, [2], 16, 353.

[6] Lebeau, *Compt. rend.*, 1900, 130, 502; *Bull. Soc. chim.*, 1900, [3], 23, 250.

[7] Hugot, *Compt. rend.*, 1899, 129, 603.

[8] Wöhler and Ewald, *Zeitsch. anorg. Chem.*, 1931, 199, 57.

[9] Wöhler and Ewald, *loc. cit.*; *cf.* Wollaston, *Phil. Trans.*, 1804, 94, 419; 1829, 119, 1.

[10] Friedrich and Leroux, *Metallurgie*, 1906, 3, 193; Heike and Leroux, *Zeitsch. anorg. Chem.*, 1915, 92, 119. See also Hilpert and Herrmann, *Ber.*, 1913, 46, 2220.

at 540° C. and 25·1 atoms per cent. of arsenic. Solid solutions only formed with from 0 to 6 atoms per cent. of arsenic. Alloys between this composition and the eutectic undergo a transformation at 595° C. due to a reaction between the solid and liquid phases, forming a new solid solution with a limiting concentration of 10·5 atoms per cent.; a second transformation occurs at 374° C. over almost the whole range of composition and is due to a eutectoid decomposition of the solid solution. There is a marked tendency to undercooling, which may suppress these changes. The alloys obtained are grey and brittle.

The arsenide Ag_3As occurs in an impure form in Nature as *huntilite* (p. 12). It may be prepared artificially by dropping an aqueous solution of silver nitrate or acetate into an atmosphere of arsine.[1] Spring[2] obtained products of composition Ag_6As and Ag_3As by compressing mixtures of the two elements in powder form at 6500 atmospheres. Descamps[3] gently fused silver arsenate with potassium cyanide and obtained hard, brittle, white crystals of density 8·51 and of composition AgAs, which lost arsenic on heating. When fused under a layer of boric acid at a high temperature this substance was converted into Ag_3As, the density of which was 9·51. Products of composition $AgAs_3$ and $AgAs_4$ have also been described,[4] but it is doubtful whether any arsenide other than Ag_3As exists as a chemical individual.

An X-ray study of the structure of Ag–As alloys has been made,[5] and the results support those obtained by thermal examinations as stated above.

Sodium Arsenide, Na_3As, has been obtained in an impure state by heating together sodium and arsenic,[6] or sodium and arsenious oxide;[7] by the action of arsine on dry sodium or on a solution of sodium in liquid ammonia;[8] and by heating the product obtained by the action of liquid ammonia on a mixture of the two elements.[9] Lebeau heated a mixture of sodium and arsenic to redness, digested the product with liquid ammonia to remove excess of sodium, and finally removed the ammonia by heating in nitrogen. Hugot treated the mixture of elements with liquid ammonia and obtained a reddish-brown compound of approximate composition $Na_3As.NH_3$. This, after heating in a vacuum at 300° C., left the impure arsenide, some sodamide remaining in the product.

Strontium Arsenide, Sr_3As_2, may be prepared by reduction of strontium arsenate. This is best accomplished by rapidly heating with carbon[10] to 1500° to 1600° C. If the heating is slow, reduction begins at about 800° C. yielding first the arsenite, arsenic then being lost and strontium oxide formed. Calcium arsenate behaves similarly (p. 60). Strontium arsenide forms reddish-brown crystals, transparent in thin

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[1] Brukl, *Zeitsch. anorg. Chem.*, 1923, 131, 236.

[2] Spring, *Bull. Acad. roy. Belg.*, 1883, [3], 5, 229; *Ber.*, 1883, 16, 324.

[3] Descamps, *Compt. rend.*, 1878, 86, 1022.

[4] Hilpert and Herrmann, *loc. cit.*

[5] Broderick and Ehret, *J. Phys. Chem.*, 1931, 35, 3322.

[6] Gay-Lussac and Thénard, *Ann. Chim. Phys.*, 1810, [1], 73, 229; Landolt, *J. prakt. Chem.*, 1853, [1], 40, 385; *Annalen*, 1854, 89, 301; Janowsky, *Ber.*, 1873, 6, 220.

[7] Saunders, *Chem. News*, 1899, 79, 66.

sections, and of density 3·6 at 15° C. It decomposes in contact with water, forming strontium hydroxide with liberation of arsine. It burns brilliantly when heated in oxygen or sulphur vapour. It reacts with fluorine at ordinary temperature with incandescence and formation of arsenic trifluoride. Similar reactions occur with chlorine at 160° C., with bromine at 200° C., and with iodine vapour at a higher temperature. It is a powerful reducing agent and attacks most metallic oxides and oxidising agents. When heated with carbon in an electric furnace it yields strontium carbide.

Thallium Arsenide.—The freezing point curve of the thallium-arsenic system was investigated by Mansuri,[1] who was unable to isolate any definite arsenide. The two elements alloy in all proportions, but do not react chemically with each other and do not form any solid solutions. By fusing together thallium and arsenic in suitable proportions, Carstanjen [2] obtained a white crystalline mass which he considered to be the arsenide Tl_2As. The product was soft enough to be cut with a knife. It acquired a yellow tinge when exposed to the air, and was readily decomposed by cold acids, arsine being evolved.

Tin Arsenides.—A study of the system Sn–As has been made [3] over the complete range from pure tin to almost pure arsenic. The elements alloy in all proportions and form two definite compounds, Sn_3As_2 and SnAs, as shown by two distinct maxima on the fusion curves and by photomicrographs. Crystals of the former have been isolated.[4] The melting point of tin is not lowered by the addition of arsenic. Gehlen observed [5] a vigorous action when powdered arsenic was stirred into the molten metal, heat and light being evolved. He also obtained alloys by heating white arsenic with tin.[6] Arsenides other than the above have been described: for example, Sn_2As_3, obtained by heating a mixture of the two elements under fused boric acid; [7] Sn_3As_4, by subjecting the mixture of elements to high pressure; [8] Sn_4As_3 [9] and Sn_6As.[10] The existence of none of these as chemical compounds has been confirmed, however.

The alloys of tin and arsenic are very hard and readily crystallise.[11] When the arsenic is not present in excess they are white, sonorous and brittle, and attacked by hydrochloric acid with liberation of arsine. When heated strongly, arsenic volatilises. The electrical conductivity of thin rods, of composition Sn_2As_3, SnAs and Sn_3As_2, has been measured [12] between −81° and 400° C. In each case it passes through a maximum, at 25°, 0° and −25° C. respectively.

Tungsten Arsenide, WAs_2.—When tungsten and arsenic are

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[1] Mansuri, *J. Inst. Metals*, 1922, 28, 453.

[2] Carstanjen, *J. prakt. Chem.*, 1867, [1], 102, 65, 129.

[3] Mansuri, *J. Chem. Soc.*, 1923, 123, 214; Parravano and de Cesaris, *Atti R. Accad. Lincei*, 1911, [5], 20, i, 593; *Intern. Zeitsch. Metallog.*, 1912, 2, 1; Kordes, *Zeitsch. anorg. Chem.*, 1926, 154, 93.

[4] Stead, *J. Soc. Chem. Ind.*, 1897, 16, 200; *J. Inst. Metals*, 1919, 22, 127.

[5] Gehlen, *Schweigger's J.*, 1815, 15, 501. See also Vogel, *J. prakt. Chem.*, 1835, [1], 6, 345; Bergman, "*De arsenico*," Stockholm, 1777.

[6] See also Bulles, *German Patent*, 46214 (1889).

[7] Descamps, *Compt. rend.*, 1878, 86, 1065.

[8] Spring, *Ber.*, 1883, 16, 324; *Bull. Acad. roy. Belg.*, 1883, [3], 5, 229.

[9] Jolibois and Dupuy, *Compt. rend.*, 1911, 152, 1312.

[10] Headden, *Amer. J. Sci.*, 1898, [4], 5, 95; *Proc. Colorado Sci. Soc.*, 1901, 6, 80.

[11] Puschin, *J. Russ. Phys. Chem. Soc.*, 1906, 39, 528.

[12] Padoa, *Gazzetta*, 1925, 55, 975; 1927, 57, 399.

heated together in a sealed tube at 620° for 5 days, a product of composition $WAs_{1\cdot95}$ and of density 10·95 at 25° C. is obtained.[1] Defacqz[2] described the di-arsenide as a black crystalline mass of density 6·9 at 18° C. This product he obtained by heating pure tungsten hexachloride in a current of arsine, the temperature being maintained at 150° to 200° C. for a time and then gradually raised to 350° C. The arsenide is stable in air at the ordinary temperature; at red heat it is readily oxidised, leaving a residue of yellow tungstic anhydride. It readily combines with chlorine, sulphur and phosphorus when heated. It is quite insoluble in water, carbon disulphide and the usual organic solvents; solutions of hydrofluoric and hydrochloric acids have no action upon it, but nitric acid and aqua regia oxidise it on warming. Fused alkalis and alkali carbonates act upon it, forming arsenate and tungstate. Tungsten chlorarsenide, W_2AsCl_9, is obtained by heating a mixture of tungsten hexachloride and liquid arsine in a sealed tube at 60° to 75° C.[3] It forms bluish-black, hygroscopic crystals, and is readily decomposed by water, acids and alkalis.

Uranium Arsenide, U_3As_4, may be obtained[4] by passing hydrogen over a fused mixture of sodium uranous chloride and sodium arsenide. It is a greyish powder which readily burns in the air. Sometimes it is obtained in a pyrophoric condition. An aluminium-containing product results when the aluminothermic process, using an oxide of uranium and arsenious oxide, is employed. The purest arsenide is obtained, in the crystalline form, when a mixture of hydrogen and arsenic vapour is passed over sodium uranium chloride. It is rapidly decomposed by nitric acid.

Zinc Arsenides.—Arsenic readily alloys with zinc, and arsenides of composition Zn_3As,[5] Zn_2As,[6] Zn_3As_2, $ZnAs$[7] and $ZnAs_2$ have been described. A thermal study of the system Zn–As has shown, however, that only Zn_3As_2 and $ZnAs_2$ exist.[8] Both are brittle and they melt at 1015° and 771° C., respectively. *Trizinc diarsenide* may be prepared by melting zinc in arsenic vapour and hydrogen,[9] by subjecting zinc and arsenic in appropriate proportions to a pressure of 6500 atmospheres,[10] or by heating the mixture of elements at 800° C. out of contact with air.[11] A compact but fragile crystalline mass, of density 5·578, is obtained. The crystal structure has been investigated by the X-ray powder method,[12] and is found to resemble that of magnesium arsenide (p. 69). According to Natta and Passerini, it has a cubic lattice containing two molecules of Zn_3As_2 in the elementary cell, with $a = 5\cdot81$ Å. and a calculated density of 5·854. The arrangement of the atoms in the lattice is the same as in the case of the magnesium compound. The distance

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[1] Heinerth and Biltz, *Zeitsch. anorg. Chem.*, 1931, 198, 168.

[2] Defacqz, *Compt. rend.*, 1901, 132, 138.

[3] Defacqz, *loc. cit.*

[4] Colani, *Compt. rend.*, 1903, 137, 382; *Ann. Chim. Phys.*, 1907, [8], 12, 59.

[5] Descamps, *Compt. rend.*, 1878, 86, 1065.

[6] Koenig, *Proc. Amer. Phil. Soc.*, 1903, 42, 219.

[7] Vogel, *J. prakt. Chem.*, 1835, [1], 6, 345.

[8] Friedrich and Leroux, *Metallurgie*, 1906, 3, 477; Heike, *Zeitsch. anorg. Chem.*, 1921, 118, 264; Kordes, *ibid.*, 1926, 154, 93.

[9] Descamps, *loc. cit.*

[10] Spring, *Ber.*, 1883, 16, 324.

[11] Natta and Passerini, *Gazzetta*, 1928, 58, 541.

[12] Natta and Passerini, *loc. cit.*; von Stackelberg and Paulus, *Zeitsch. physikal. Chem.*,

Zn–Zn is 2·90 A., that of Zn–As 2·52 A. and of As–As 4·11 A. The atomic radius of zinc is calculated to be 1·45 A. and the atomic diameter of arsenic 1·19 A., values which correspond roughly with those for the neutral atoms, it being concluded that the structure of the arsenide is non-ionic, a conclusion which is confirmed by the value of the heat of formation, which is 30·3 calories per mole. This is low in comparison with that of zinc blende which, though containing only one atom of zinc in the molecule, has a heat of formation of 43 calories per mole. According to von Stackelberg and Paulus, the arsenide crystallises in the tetragonal system, with eight molecules in the unit cell, and space group D_{4h}^{15}.

The hardness of Zn_3As_2 is approximately 3 (Mohs' scale). At 672° C. it undergoes a reversible transformation,[1] $\alpha\text{-}Zn_3As_2 \rightleftharpoons \beta\text{-}Zn_3As_2$. With dilute sulphuric acid arsine is evolved.

Zinc Di-arsenide, $ZnAs_2$, is prepared by heating zinc and arsenic together in suitable proportions. It is grey in colour and of hardness approximately 3. It dissolves in acids with evolution of arsine.[2]

[1] Heike, *loc. cit.*

[2] Vogel, *loc. cit.* See also Fischer, *Zeitsch. Elektrochem.*, 1929, 35, 502.

CHAPTER V.

ARSENIC AND HYDROGEN.

UNDER ordinary conditions of temperature and pressure, arsenic does not combine directly with hydrogen unless the latter is in an activated or nascent condition. Three hydrides are known, however, two of which, hydrogen monarsenide, AsH or As_2H_2, and the di-arsenide, As_2H or As_4H_2, are solid at ordinary temperatures, the third being the gaseous hydride, arsine, AsH_3, which is the most stable.

Arsenic Subhydride (or **Hydrogen Di-arsenide**), As_2H or As_4H_2, was obtained by Moser and Brukl [1] as a red amorphous powder by the oxidation of arsine by means of stannic chloride in the presence of hydrochloric acid. It appears to be more stable than the monarsenide, but in the presence of moist air it gradually decomposes. It is insoluble in water, even when boiling, and is unaffected by hydrochloric acid, but it decomposes yielding arsenic when boiled with concentrated alkali solution or when heated with the fused alkali. When heated alone, it breaks up into arsenic, hydrogen and arsine. It is oxidised to arsenic acid by hydrogen peroxide, bromine or nitric acid.

Arsenic Monohydride (or **Hydrogen Monarsenide**), AsH or As_2H_2.—The formation of a solid product, which was apparently an arsenide of hydrogen, during the electrolysis of water using an arsenic cathode, was first observed by Davy.[2] Other observers,[3] however, could not obtain more than a trace of such a product by this means. Olszewsky [4] obtained it by employing platinum electrodes in an aqueous solution of arsenious oxide. Weeks and Druce [5] produced it in more satisfactory yield as a brown amorphous powder by electrolysis of a normal solution of sodium hydroxide, using a platinum anode and an arsenic cathode, the latter being suspended in a porous pot. The current density was 100 milliamperes per sq. cm. and the monarsenide was deposited around the cathode, arsine being simultaneously evolved.

Similar brown products may be obtained by the action of water on sodium,[6] potassium [7] or calcium [8] arsenide, thus :

$$2Na_3As + 6H_2O = 6NaOH + As_2H_2 + 2H_2$$

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[1] Moser and Brukl, *Monatsh.*, 1924, 45, 25.

[2] Davy, *Phil. Trans.*, 1810, 100, 31.

[3] Magnus, *Pogg. Annalen*, 1829, 17, 526; Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 407.

[4] Olszewsky, *Arch. Pharm.*, 1878, [3], 13, 563.

[5] Weeks and Druce, *Rec. Trav. chim.*, 1925, 44, 970.

[6] Gay-Lussac and Thénard, "*Recherches physico-chimiques,*" Paris, 1811, 1, 232. See Janowsky, *Ber.*, 1873, 6, 216.

[7] Reckleben and Scheiber, *Zeitsch. anorg. Chem.*, 1911, 70, 255.

[8] Thoms and Hess, *Ber. deut. Pharm. Ges.*, 1920, 30, 483.

Arsine is also evolved. When dilute mineral acids are used, the resulting solid appears to be mainly arsenic.[1]

The hydride is frequently obtained by partial decomposition of arsine, as by the atmospheric oxidation of an aqueous solution,[2] or by the influence on the gas of the silent electric discharge.[3] Gaseous arsine may also undergo decomposition by the prolonged action of air,[4] chlorine,[5] nitric oxide,[6] nitric or sulphuric acid,[7] mercuric chloride [8] or phosphorus pentachloride.[9] In the last case the reaction may be represented by the equation:

$$2AsH_3 + 2PCl_5 = 2PCl_3 + 4HCl + As_2H_2$$

This reaction does not proceed in carbon tetrachloride solution.[10] Retgers [11] stated that the solid hydride resulted when arsine was heated or when the flame of arsine impinged on a cold plate; but other observers [12] maintain that arsenic alone is produced. A solid hydrogen-containing product has also been obtained by the action of zinc, in the presence of sulphuric and nitric acids, on arsenious oxide,[13] and by the action of arsine on solid potassium hydroxide,[14] followed by the addition of water. A good yield (up to 93 per cent.) of the hydride in a comparatively pure state may be obtained by mixing an ether solution of stannous chloride with a solution of arsenic trichloride in dilute hydrochloric acid.[15] The reaction is:

$$2AsCl_3 + 4SnCl_2 + 2HCl = As_2H_2 + 4SnCl_4$$

The composition of the solid products obtained by the earlier investigators varied within wide limits, and various formulæ, for example AsH_2,[16] AsH [17] and As_2H,[18] were suggested. The products were undoubtedly indefinite mixtures containing arsenic, and later workers have found considerable difficulty in obtaining the hydride in a pure state. That the composition of the latter corresponds to the empirical formula AsH was established by Janowsky [17] and has been confirmed.[19] As_2H_2 is usually taken as the molecular formula in order to conform with valency considerations, the structure H.As : As.H being assumed.

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[1] Wiederhold, *Pogg. Annalen*, 1863, 118, 615; Engel, *Compt. rend.*, 1873, 77, 1547.

[2] Moser and Brukl, *Monatsh.*, 1924, 45, 26.

[3] Ogier, *Ann. Chim. Phys.*, 1880, [5], 20, 17.

[4] Brunn, *Ber.*, 1889, 22, 3205.

[5] Gay-Lussac and Thénard, *loc. cit.*; Wiederhold, *loc. cit.*; Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 407.

[6] Brunn, *loc. cit.*

[7] Humpert, *J. prakt. Chem.*, 1865, [1], 94, 392.

[8] Dumas, *Ann. Chim. Phys.*, 1826, [2], 33, 355.

[9] Janowsky, *Ber.*, 1875, 8, 1636.

[10] Moser and Brukl, *Monatsh.*, 1924, 45, 26.

[11] Retgers, *Zeitsch. anorg. Chem.*, 1893, 4, 429.

[12] Reckleben and Scheiber, *loc. cit.*

[13] Blondlot, *Ann. Chim. Phys.*, 1862, [3], 64, 486.

[14] Reckleben and Scheiber, *loc. cit.*

[15] Weeks and Druce, *Chem. News*, 1924, 129, 31; Weeks, *ibid.*, 1924, 128, 54; Druce, *Chem. Listy*, 1925, 19, 156; Montignie, *Bull. Soc. chim.*, 1935, [5], 2, 1020.

[16] Soubeiran, *loc. cit.*

[17] Janowsky, *loc. cit.*

[18] Ogier, *Ann. Chim. Phys.*, 1880, [5], 20, 17; Wiederhold, *Pogg. Annalen*, 1863, 118, 615.

[19] Reckleben and Scheiber, *Zeitsch. anorg. Chem.*, 1911, 70, 255; Moser and Brukl, *loc. cit.*; Weeks and Druce, *loc. cit.*

The properties of hydrogen monarsenide are little known, many of those ascribed to it being really the properties of elementary arsenic. It is a brown, amorphous powder, stable in air at ordinary temperatures, but undergoing oxidation on heating at 70° to 80° C.; it cannot therefore be dried in an oven and a vacuum desiccator is generally used. It is only slightly soluble in water, 1 litre at 20° C. dissolving 0·35 gram.[1] It is oxidised by boiling water. It is insoluble in alcohol and ether and also in hydrochloric and sulphuric acids. It dissolves in hot dilute nitric acid, in hot or cold concentrated nitric acid, or in aqua regia, arsenic acid being formed. When heated *in vacuo* it decomposes into arsenic and hydrogen. On boiling with ammoniacal silver nitrate, out of contact with air, silver is precipitated according to the equation :[2]

$$As_2H_2 + 6Ag_2O = As_2O_5 + 12Ag + H_2O$$

This reduction is accomplished also by arsine, arsenious oxide and arsenic itself. The monarsenide also reduces Fehling's solution.[3] It reacts with the halogens, sulphur and phosphorus. With phosphorus trichloride it yields arsenic trichloride and phosphide, thus—

$$3As_2H_2 + 4PCl_3 = 6HCl + 2AsCl_3 + 4AsP$$

and with sodium, hydrogen is liberated :

$$As_2H_2 + 6Na = 2Na_3As + H_2$$

Arsenic Trihydride (Arsine, Arseniuretted Hydrogen), AsH_3.

This gaseous hydride of arsenic was discovered in 1775 by Scheele,[4] who obtained it by the action of aqueous arsenic acid on zinc. In 1798 Proust[5] observed the reaction, which soon became the basis of the most important method[6] of arsenic detection and estimation, namely, the liberation of arsine, admixed with hydrogen, upon the addition of dilute sulphuric or hydrochloric acid to zinc in the presence of arsenious acid. The zinc may be replaced by magnesium,[7] and it is evident that the reaction is between the nascent hydrogen produced and the arsenic compound. The reaction is inhibited by the presence of mercuric chloride.[8] If the zinc is replaced by iron, very little arsine is produced, and it has been stated that, with iron, the gas is not formed at all,[9] especially if commercial sulphuric acid containing nitric acid is employed. Investigations of a large number of cases of poisoning in the steel industry, however, reveal[10] that arsine is generated by the action of 5 per cent. sulphuric acid on steel, the arsenic being derived from impurities in both the acid (especially when made from sulphide ores) and the steel. A sample of air (25 litres) taken at the surface of the acid in a pickling tank contained 0·006 mg. AsH_3, while 10 feet away

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[1] Weeks and Druce, *loc. cit.*

[2] Reckleben and Scheiber, *loc. cit.*

[3] Montignie, *loc. cit.*

[4] Scheele, "*Opuscule,*" 1775, 2, 26.

[5] Proust, *Ann. Chim. Phys.*, 1798, [1], 28, 213.

[6] Marsh, *Edin. Phil. J.*, 1836, 21, 229.

[7] Draper, *Dingl. poly. J.*, 1872, 204, 320; *Amer. Chemist*, 1872, 2, 456.

[8] Vitali, *Boll. Chim. Farm.*, 1905, 44, 49.

[9] Buchner, *Repert. Pharm.*, 1835, 50, 234; 1837, 59, 23; Dupasquier, *Compt. rend.*, 1842, 14, 511.

[10] See *J. Ind. Hyg.*, 1928, 10, 137.

the quantity present was negligible. Laboratory experiments show[1] that crude dilute sulphuric acid acts on iron in the presence of reducible arsenic compounds, even at atmospheric temperatures, to produce arsine, and at higher temperatures extremely dilute acid will so react; moreover, the small amounts of nitric acid present in technical sulphuric acid do not prevent the reaction. Thiele[2] found that the yield of arsine is much increased in this reaction by the addition of a little antimony trichloride, and stibine, SbH_3, is not formed.

It was soon found that arsenic itself in the presence of zinc and dilute sulphuric or hydrochloric acid gives a mixture of arsine and hydrogen,[3] and that the yield of the former is increased if an alloy of zinc and arsenic, or zinc arsenide, is used, it being possible to obtain a gas containing as much as 99 per cent. arsine[4] (see p. 84). Other metallic arsenides or alloys with arsenic yield arsine on reacting with water or dilute acids; thus the action of water is sufficient in the case of the arsenides of the alkali metals,[5] calcium arsenide,[6] Ca_3As_2, or aluminium arsenide,[7] Al_3As_2, almost pure arsine being produced. An alloy of potassium, antimony and arsenic has been used successfully.[8] Less pure products are obtained by warming arsenic alloys with tin or iron and dilute acids.[9]

The reduction of arsenic compounds to arsine by nascent hydrogen may also be effected in alkaline medium; thus in the presence of caustic alkali with zinc,[10] aluminium[11] or sodium amalgam,[12] and also in ammonia or ammonium chloride with zinc.[13]

The combination of arsenic with dry nascent hydrogen was observed by Vournazos,[14] who obtained a mixture of hydrogen and arsine by heating rapidly to 400° C. in a round-bottomed flask a mixture of three parts of powdered arsenic with eight parts of dry sodium formate. The addition of sodium hydroxide or lime to the mixture prevents the formation of sodium oxalate and hence of carbon monoxide. Arsenious oxide, sodium arsenite or arsenic acid may be used in place of arsenic, but the yields are small. The gas is also formed if arsenic vapour is passed over heated sodium formate. Also, if the sulphide or phosphide of arsenic is heated with the formate, hydrides of both components of the arsenic compound are formed; but with metallic arsenides the hydride of the non-volatile component is not formed.

The hydride is also produced by the action of activated hydrogen

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[1] Leymann and Weber, *Chimie et Industrie*, 1930, 24, 832.

[2] Thiele, *Apoth. Zeit.*, 1890, 5, 86; "*Analytische Beitrage zur Kenntnis von Antimon und Arsen*," Halle, 1890, p. 25.

[3] Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 407; Thiele, *loc. cit.*

[4] Vogel, *J. prakt. Chem.*, 1835, [1], 6, 345.

[5] Davy, *Phil. Trans.*, 1810, 100, 31; Gay-Lussac and Thénard, *Ann. Chim. Phys.*, 1810, [1], 73, 229; "*Recherches physico-chimiques*," Paris, 1811, 1, 232; Janowsky, *Ber.*, 1873, 6, 216; 1875, 8, 1638.

[6] Lebeau, *Ann. Chim. Phys.*, 1902, [7], 25, 470; Moissan, "*Traité de Chimie minérale*," Paris, 1904, 1, 817.

[7] Fonzes-Diaçon, *Compt. rend.*, 1900, 130, 1315.

[8] Sérullas, *J. Physique*, 1820, 98, 136; *Edin. Phil. J.*, 1821, 4, 389.

[9] Janowsky, *loc. cit.*

[10] Fleitmann, *Annalen*, 1851, 77, 127; Hager, *Jahresber.*, 1872, p. 901; Reichardt, *Arch. Pharm.*, 1883, [3], 21, 592.

[11] Gatehouse, *Chem. News*, 1873, 27, 189; Johnson, *ibid.*, 1878, 38, 301.

[12] Davy, *ibid.*, 1876, 33, 58.

[13] Himmelmann, *Jahresber.*, 1868, p. 881.

[14] Vournazos, *Ber.*, 1910, 43, 2264; *Compt. rend.*, 1910, 150, 464.

on arsenic,[1] and in small quantities, with other reduction products, by the action of hydrogen under pressure on heated arsenites and arsenates.[2]

Electrolytic methods for the production of arsine have been investigated by a number of workers,[3] and in the reduction of arsenites and arsenates the mercury electrode has been recommended. The efficiency of such processes, however, is low. Thus, using solutions of arsenic acid in 2N-sulphuric acid containing up to 180 milligrams of elementary arsenic in 10 c.c., the efficiency under the best conditions, calculated as the percentage of the hydrogen produced at the cathode which was converted to arsine, was found by Lloyd [4] to vary between 1·71 and 14·1 per cent. In these experiments the arsenic acid was admitted to the cathode during periods varying from 20 to 60 minutes and, when measured by a commutator method, the overvoltage of the mercury cathode fell during this addition to a value representing the overvoltage of arsenic. Some arsenic therefore appears to be deposited on the mercury, but the amount is extremely small and if the cathode is put into pure sulphuric acid solution the normal cathodic overpotential of mercury is quickly re-established. With uninterrupted current, the decrease in overvoltage is less and varies directly with increasing concentration of arsenic acid. By using a zinc amalgam cathode, or by adding zinc sulphate, the decrease in overvoltage is diminished and the yield of arsine is greater. The reduction is also facilitated by increasing the current density, the concentration of the acid electrolyte and the time of the electrolysis. Lloyd [5] obtained the high yield of 60 per cent. of arsine from 4N-hydrochloric acid solution by employing alternating current electrolysis with an arsenic cathode, using a source of continuous current and a revolving three-point commutator. The optimum anodic and cathodic current densities were 44 and 525 milliamps. per sq. cm., respectively.

Arsine is formed also during the electrolysis of concentrated aqueous solutions of sodium acetate made acid with acetic acid and using an arsenic cathode.[6] At constant potential difference the yield rises with increasing current density, but never attains a high value, and the electrolytic method is greatly inferior as a mode of preparation of arsine to the usual method of acting upon metallic arsenides with dilute acids.

When fused borosilicate glass is drawn out so as to expose a fresh surface, a garlic-like odour may be observed; [7] this has been ascribed to the formation of arsine by reduction of arsenic present in the glass.

Preparation of Pure Arsine.—The gas was obtained in a very pure state by Lebeau [8] and Moissan [9] by the action of water or dilute acid on calcium arsenide. The moisture was completely removed from the gas by cooling to −20° C. and then passing through a series of tubes

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[1] Paneth, Matthies and Schmidt-Hebbel, *Ber.*, 1922, [B], 55, 775.

[2] Ipatiev and co-workers, *Ber.*, 1926, [B], 59, 1412.

[3] Thorpe, *J. Chem. Soc.*, 1903, 83, 974; Sand and Hackford, *ibid.*, 1904, 85, 1018; Thomson, *Chem. News*, 1909, 99, 157; Harkins, *J. Amer. Chem. Soc.*, 1910, 32, 518; Ramberg, *Lunds. Univ. Arrskr. N.F.*, 1918, [2], 21, 1; Aumonier, *J. Soc. Chem. Ind.*, 1927, 46, 341.

[4] Lloyd, *Trans. Faraday Soc.*, 1931, 27, 89.

[5] Lloyd, *Trans. Faraday Soc.*, 1930, 26, 15; Sand and Lloyd, *J. Chem. Soc.*, 1926, p. 2971.

[6] Hlasko and Maslowski, *Rocz. Chem.*, 1930, 10, 240 (in French).

[7] Elsey, *Science*, 1927, 66, 300.

[8] Lebeau, *Ann. Chim. Phys.*, 1902, [7], 25, 470.

[9] Moissan, "*Traité de Chimie minérale*," Paris, 1904, 1, 817.

containing metaphosphoric acid; the gas was then liquefied by means of a mixture of acetone and solid carbon dioxide. Natta and Gasazza[1] used pure zinc and arsenious oxide with aqueous hydrochloric acid, dried the gas with calcium chloride and obtained solidified arsine by surrounding with liquid air. The use of drying agents is liable to cause slight decomposition of the gas;[2] this is true of alkali hydroxides, calcium oxide, concentrated sulphuric acid, calcium chloride, and also of phosphorus pentoxide. The action is least with the last two agents, and when any quantity of the gas is to be prepared, hydrated and weathered calcium chloride and phosphorus pentoxide may be employed.

Robertson and his co-workers[3] prepared the pure liquid by the action of aqueous sulphuric acid on an alloy of zinc and arsenic. The apparatus used is illustrated in fig. 7, the procedure being as follows. By means of a pump attached at N the apparatus to the right of the tap D was evacuated. The tubes E and O contained phosphorus pentoxide, and the U-tube F calcium chloride. Hydrogen was introduced through C, passing by way of the trap G, containing mercury and aqueous copper sulphate, to the copper sulphate bubbler H, whence it escaped to the flue through S until the generating flask A was deemed to be free from oxygen. The alloy, of approximate composition 53 per cent. Zn, 47 per cent. As,[4] was introduced into A, a 200-ml. flask, which was then sealed with wax and hydrogen again passed for several minutes. Aqueous sulphuric acid (30 per cent.) was run in from B and the flask warmed. After the gas had been evolved for a short time, the tap D was opened and the receiver L was immersed in a mixture of solid carbon dioxide and chloroform contained in a Dewar flask M. When the evolution of gas in A ceased, D was closed and all the uncondensed gas was pumped off at N. The liquid arsine in L was then allowed to evaporate, the gas passing through the mercury and copper sulphate trap K to escape through H until samples taken from N showed complete absorption in copper sulphate solution. A little more gas was sent to waste and the middle fraction from L collected in the gas reservoir P, control samples being taken at R and tested for complete absorption in copper sulphate solution.

Robinson and his co-workers[5] prepared pure arsine in pure hydrogen by slowly dropping (during 2 hours) a solution of arsenious oxide (20 g.) in freshly boiled hydrochloric acid (250 c.c. acid : 50 c.c. water) on pure magnesium turnings (50 g.) in a 750-c.c. round-bottomed flask cooled in water. The reaction products passed through aqueous potash into successive tubes containing potash pellets, fused calcium chloride and phosphorus pentoxide, and thence to a vessel immersed in liquid air. The pure arsine was finally obtained by careful fractionation.

Physical Properties.—Pure arsine at ordinary temperatures is a colourless gas, with an obnoxious odour. It is extremely poisonous, its physiological effects being discussed on p. 290.

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[1] Natta and Gasazza, *Gazzetta*, 1930, 60, 851.

[2] Reckleben and Lockemann, *Zeitsch. anal. Chem.*, 1908, 47, 105; Guttich, "*Ueber Bestimmung für Arsen- und Antimon-wasserstoff*," Leipzig, 1909.

[3] Robertson, Fox and Hiscocks, *Proc. Roy. Soc.*, 1928, A 120, 160.

[4] Prepared as described by Cohen, *Zeitsch. physikal. Chem.*, 1898, 25, 483.

[5] Durrant, Pearson and Robinson, *J. Chem. Soc.*, 1934, p. 730. For the preparation of arsine by the action of ammonium bromide on sodium arsenides in liquid ammonia, see Johnson and Pechukas, *J. Amer. Chem. Soc.*, 1937, 59, 2065.

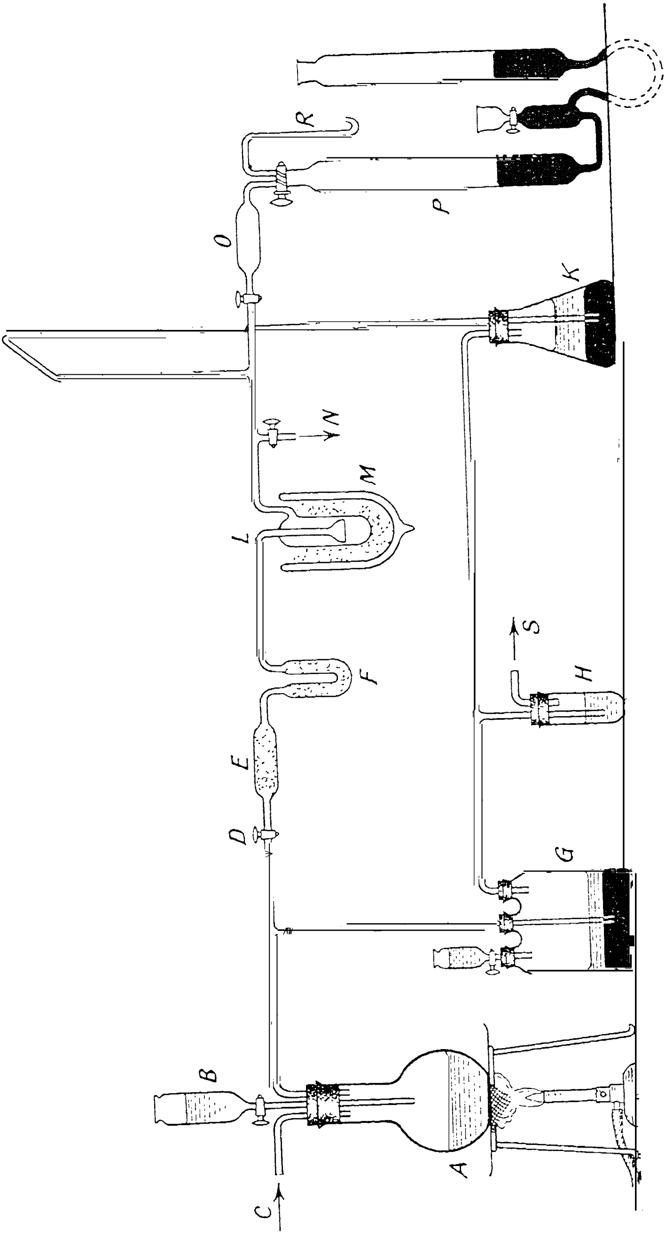

Fig. 7.—Robertson's Apparatus for the Preparation of Pure Arsine.

The *vapour density* was determined by Dumas,[1] who found the value 2·695 (air = 1; theory $AsH_3 = 2·692$).

The *viscosity* of the gas has been determined [2] to be 0·0001470 at 0° C.; 0·0001552 at 15° C.; and 0·0001997 at 100° C. Rankine has used these values to calculate the "mean collision area," that is the average area presented by the molecule in all possible orientations, which determines the frequency of molecular collisions; the value obtained was $0·985 \times 10^{-15}$ sq. cm.

The gas is somewhat soluble in water, 100 volumes of the latter dissolving 20 volumes of arsine.[3] It is not absorbed by aqueous alkalies, or by alcohol or ether; but it is rapidly absorbed by turpentine, and slightly by fixed oils.[4]

The trihydride is slowly decomposed by *ultraviolet light,* hydrogen and a brownish-black deposit, which is probably arsenic but may contain hydrogen,[5] being formed. The ultraviolet absorption spectrum is a continuous one,[5] showing no diffuse bands such as are observed with phosphine. The limit of the absorption depends on the conditions of the experiment—light intensity, pressure, and length of tube. There appears to be a regular gradation in the nature of the absorption spectra of the gaseous hydrides of the Group V B elements, that of ammonia showing [6] a series of predissociation bands between λ2100 and 1700 A., phosphine showing two [7] or three [8] more diffuse bands between 2320 and 2200 A., while stibine resembles arsine in giving only continuous absorption.

The *infra-red spectrum* between λ 15,800 and 16,600 A. has been investigated; [9] there is a very weak band at 16,300 A.

The *heat of formation* of arsine from crystalline arsenic is −36,700 calories.[10]

The *magnetic rotatory power* of the gas has been examined [11] and the Verdet constant at 0° C. and 760 mm. found to be 68×10^{-6} minute of arc. The molecular rotation is 44×10^{-5} radian ($\lambda = 578\ \mu\mu$).

The *dielectric constants* of arsine have been determined [12] at three temperatures and at three frequencies, the following being the mean absolute values at 1 atm. pressure:

t, °C. . . .	−47	16	100
ϵ	1·00251	1·001916	1·00146

From these figures the value of B in Debye's equation, $\epsilon - 1 = N(A + B/T)$, may be calculated and is found to be substantially zero,

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[1] Dumas, *Ann. Chim. Phys.*, 1826, [2], 33, 357; 1830, 44, 289.

[2] Rankine, *Trans. Faraday Soc.*, 1922, 17, 719; Rankine and Smith, *Proc. Phys. Soc.*, 1922, 34, 181.

[3] Berzelius, "*Traité de Chimie*," édit. franç., 1846, 2, 249; Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 407.

[4] Gmelin, "*Handbook of Chemistry*," 1850, 4, 268.

[5] Cheesman and Emeléus, *J. Chem. Soc.*, 1932, p. 2847; Simmons and Beckman, *J. Amer. Chem. Soc.*, 1936, 58, 454.

[6] Liefson, *Astrophys. J.*, 1926, 63, 73.

[7] Cheesman and Emeléus, *loc. cit.*

[8] Melville, *Nature*, 1932, 129, 546.

[9] Robertson and Fox, *Proc. Roy. Soc.*, 1928, A 120, 161, 189; Norris and Unger, *Phys. Review*, 1934, [2], 45, 68.

[10] Ogier, *Ann. Chim. Phys.*, 1880, [5], 20, 17.

[11] de Mallemann and Gabriano, *Compt. rend.*, 1934, 199, 600.

[12] Watson, *Proc. Roy. Soc.*, 1927, A 117, 43. See also Schlundt and Schaefer, *J. Physical Chem.*, 1912, 16, 253.

so that as far as its dielectric constant is concerned, arsine resembles the permanent gases. The variation of the dielectric constant with pressure justifies the assumption that $\epsilon - 1$ is proportional to the density, at least to a first approximation; thus at −47° C., using arbitrary units, the calculated values being derived on the above assumption, Watson gives the following figures:

p (mm.).	$(\epsilon - 1)$ calc.	$(\epsilon - 1)$ obs.
669·5	701	701
606	633	633
405	420	420
205·5	212	212
103·5	106	106
81	84	82
62	64	61
42	43	40
23	24	21

The gas may readily be liquefied (see p. 84), the colourless liquid having the following physical properties as determined by Robinson and his co-workers.[1]

Physical Properties of Liquid Arsine.

B.pt.	− 58·5° C.
M.pt.	−111·2° C.
Density at b.pt.	1·621
Mol. heat of vaporisation	4340 calories
Coefficient of expansion at b.pt.	195×10^{-5}
Mol. vol. at b.pt.	48·11
Mol. diameter	$8{\cdot}69 \times 10^{-9}$
Surface tension, σ, at b.pt.	21·98
$d\sigma/dt$	0·18
Ramsay-Shields constant, K	2·10
Trouton's constant	20·26
Mean mol. parachor	104·2

Olszewsky[2] found the boiling point to be −54·8° C., and by cooling the liquid to −118·9° C. he obtained a white crystalline mass which melted at −113·5° C.[3] The solid arsine is quite stable in air at −170° C.[4]

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[1] Durrant, Pearson and Robinson, *J. Chem. Soc.*, 1934, p. 735.

[2] Olszewsky, *Monatsh.*, 1884, 5, 127; *Phil. Mag.*, 1895, [5], 39, 118. See also Stromeyer, *Comment. Soc. Gott.*, 1808, 16, 141.

[3] Johnson and Pechukas (*J. Amer. Chem. Soc.*, 1937, 59, 2065) give the following values: B.pt. −62·4° C., m.pt. −116·3° C., latent heats of vaporisation and fusion 4165 and 675 calories per mol., respectively; also the vapour pressure of the solid and liquid has been measured at −138° to −63° C., and the density of the liquid at

The *density of the liquid* at various temperatures is as follows :[1]

t, ° C. . .	0	–20	–40	–60
d, g./c.c. . .	1·445	1·501	1·562	1·625

The *vapour pressures* are given in the following table :

Temperature, ° C.	Vapour Pressure, mm.	Observers.	Temperature, ° C.	Vapour Pressure, atm.	Observers.
–92·5	116·3	D., P. & R.[1]	–46·6	1·73	F.[3]
–74·8	335·5	,,	–30·6	3·33	,,
–60·6	697·9	,,	–17·8	5·21	,,
–58·5	767·0	,,	–12·2	6·24	,,
–54·8	*ca.* 760	O.[2]	0	8·95	,,
–59·0	760	F.[3]	10	11·56	,,
–59·4	714·4	,,	15·1	13·19	,,

The Ramsay-Shields and Trouton constants indicate that arsine is a normal liquid and differs from phosphine and to a greater extent from ammonia in not being associated.

The *surface tension* varies with temperature as follows :[4]

t, ° C. . .	–60	–50	–40	–30	–20
σ, dynes/cm. .	22·20	20·40	18·60	16·81	15·08

The liquid is a very poor conductor of electricity.

The *structure* of solid arsine has been investigated[5] by X-ray methods at –170° C. It crystallises in the cubic system and is isomorphous with phosphine. Its elementary cell contains four molecules, with a dimension of 6·40 ± 0·02 A., a volume of $2·62 \times 10^{-26}$ c.c. and density (calculated) of 1·96. The position of the As atom corresponds to a face-centred cube.

The dielectric constants and molecular rotations of solid and liquid arsine have been determined[6] from the temperature of liquid hydrogen to the boiling point over the frequency range 0·5 to 50 kilocycles. The molecule rotates freely down to 30·1° Abs.

Chemical Properties.—Arsine in the pure state is fairly stable, but in accordance with its endothermic nature it undergoes gradual decomposition into arsenic and hydrogen even when kept in a sealed tube in the dark. Under the latter conditions black particles of arsenic

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[1] Durrant, Pearson and Robinson, *loc. cit.*
[2] Olszewsky, *loc. cit.*
[3] Faraday, *Phil. Trans.*, 1845, 135, 155.
[4] Durrant, Pearson and Robinson, *loc. cit.*
[5] Natta and Gasazza, *loc. cit.*
[6] Smyth and McNeight, *J. Amer. Chem. Soc.*, 1936, 58, 1723.

become visible after about 8 days.[1] The decomposition is accelerated by exposure to light, by passing the gas through glass wool or cotton wool,[2] by the presence of alcohol,[2] and especially by gently warming; a sublimate of arsenic is rapidly obtainable at 230° C.,[3] the formation of this sublimate being made use of in Marsh's test (p. 317). At 300° C. the amount of decomposition reaches 95 per cent. after 3 days and is practically complete (99·93 per cent.) after 7 days.[4] The decomposition is catalysed by the film of arsenic which forms on the walls of the containing vessel, and until the walls are uniformly covered a velocity constant for the reaction is unobtainable.[5] In the presence of a gas which may react with the arsenic film, such as hydrogen sulphide or oxygen, the decomposition is sensibly retarded. The gas may be decomposed explosively by detonation with mercury fulminate.[6] The partial decomposition of arsine to form the solid hydride has been described on p. 80.

In contact with air or oxygen the gas may be ignited either by a flame or by the electric spark. It burns with a bluish-white flame and is oxidised according to the equation

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O$$

This quantitative relationship was observed by Dumas [7] and Soubeiran.[8] With excess of oxygen the hydride explodes violently, but if the supply of oxygen is insufficient the hydrogen is first oxidised and the arsenic liberated, and this takes place also in the spontaneous oxidation of arsine by oxygen at ordinary temperatures. Exposure of the mixed gases to β- or γ-rays results in the formation of arsenious acid: [9]

$$2AsH_3 + 3O_2 = 2H_3AsO_3$$

The aqueous solution in contact with air gradually deposits the solid hydride (see p. 80), but if the water is free from dissolved oxygen the solution appears to be stable.[10] Arsine may be completely oxidised by prolonged shaking with hydrogen peroxide solution; [11] arsenic is first deposited and is then gradually oxidised to arsenious or arsenic acid.

The gas reacts vigorously with the halogens. When mixed with chlorine a flame is produced and arsenic and hydrogen chloride are formed; [12] with excess of chlorine arsenic trichloride is produced, and in the presence of water arsenious and arsenic acids result. Bromine [13] reacts similarly, the oxidation in the presence of water to arsenic acid being quantitative.[14] With liquid chlorine, arsine reacts at temperatures as low as – 140° C., forming reddish products, apparently containing

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[1] Vogel, *J. prakt. Chem.*, 1835, [1], 6, 345.

[2] Lockemann, *Zeitsch. angew. Chem.*, 1905, 18, 491; *Zeitsch. anal. Chem.*, 1934, 99, 178.

[3] Brunn, *Ber.*, 1888, 21, 2546; 1889, 22, 3205.

[4] Echeandia, "*Ueber den Gang des Arsen- und Antimon-wasserstoff-zerfalles*," Berlin, 1909.

[5] Cohen, *Zeitsch. physikal. Chem.*, 1896, 20, 303.

[6] Berthelot, *Compt. rend.*, 1881, 93, 613; *Ann. Chim. Phys.*, 1882, [5], 27, 191.

[7] Dumas, *Ann. Chim. Phys.*, 1826, [2], 33, 355; 1830, [2], 44, 289.

[8] Soubeiran, *ibid.*, 1830, [2], 43, 407.

[9] Reckleben and Lockemann, *Zeitsch. anorg. Chem.*, 1915, 92, 145.

[10] Brunn, *loc. cit.*

[11] Reckleben and Lockemann, *Zeitsch. anal. Chem.*, 1908, 47, 105.

[12] Berzelius, *Ann. Chim. Phys.*, 1817, [2], 5, 179; 1819, [2], 11, 225; Soubeiran, *ibid.*, 1830, [2], 43, 407; Vogel, *J. prakt. Chem.*, 1835, [1], 6, 345.

[13] Simon, *Pogg. Annalen*, 1837, 41, 563.

[14] Reckleben and Lockemann, *loc. cit.*

the unstable hydrochlorides AsH_2Cl and $AsHCl_2$.[1] With iodine, arsine reacts slowly in the cold but more rapidly on heating to yield arsenic iodide and hydrogen iodide ;[2] with iodine and water the oxidation appears to proceed in two stages—[3]

$$AsH_3 + 3I_2 + 3H_2O = H_3AsO_3 + 6HI$$

and then if the solution is rendered alkaline with potassium hydrogen carbonate the oxidation to arsenate follows :

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI$$

An alcoholic solution of iodine is decolorised by arsine, some arsenious acid being formed in solution, and after passing the gas for some time a black precipitate appears.[4] Admixture of arsine with hydrogen chloride results in the formation of a brown cloud of arsenic ;[5] aqueous hydrochloric acid and arsine yield arsenic trichloride.[6] Arsine reacts quantitatively with iodine monochloride in aqueous solution with liberation of iodine, thus :

$$AsH_3 + 8ICl + 4H_2O = H_3AsO_4 + 4I_2 + 8HCl$$

The reaction may be applied to the volumetric determination of arsine.[7]

The oxidation of arsine may be accomplished by means of the halogen oxyacids and their salts,[8] although not so readily as with the halogens themselves. Hypochlorites and hypobromites cause complete oxidation to arsenic acid, but side reactions are liable to occur, especially if the gas is present in excess. Chloric acid slowly oxidises arsine to arsenious acid ; a trace of silver nitrate catalyses the reaction. Chlorates are quite inactive. More complete oxidation results with solutions of bromic acid and bromates, iodic acid and iodates, especially in the presence of catalysts. The reactions are of the type represented by the equation [8]

$$5AsH_3 + 8HBrO_3 = 5H_3AsO_4 + 4Br_2 + 4H_2O$$

Perchlorates even in the presence of a catalyst have only slight action. Periodates act like iodates, but much more slowly, the reaction being

$$AsH_3 + 4HIO_4 = H_3AsO_4 + 4HIO_3$$

When sulphur is heated with arsine, hydrogen sulphide is formed and a sublimate first of arsenic and then of arsenic sulphide is produced.[9] The reaction proceeds slowly at 100° C. and at lower temperatures in direct sunlight. Hydrogen sulphide does not react with arsine in the absence of air at the ordinary temperature even in direct sunlight, but on admission of air a deposit of arsenious sulphide is rapidly formed [10] whether the reactants are in the gaseous condition or in aqueous

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[1] Stock, *Ber.*, 1920, 53, 837.

[2] Soubeiran, *loc. cit.*; Jacobsen, *Ber.*, 1887, 20, 1999.

[3] Thoms and Hess, *Ber. deut. Pharm. Ges.*, 1920, 30, 483.

[4] Simon, *loc. cit.*

[5] Janowsky, *Ber.*, 1873, 6, 216.

[6] Napoli, *Amer. J. Sci.*, 1854, [2], 18, 190.

[7] Kubina, *Zeitsch. anal. Chem.*, 1929, 76, 39.

[8] Reckleben and Lockemann, *loc. cit.*; Parsons, *Chem. News*, 1877, 35, 235.

[9] Gay-Lussac and Thénard, *Ann. Chim. Phys.*, 1810, [1], 73, 229; "*Recherches physico-chimiques*," 1811, 1, 232; Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 407; Jones, *Chem. News*, 1878, 37, 36.

[10] Brunn, *Ber.*, 1888, 21, 2548; 1889, 22, 3205; Myers, *Annalen*, 1871, 159, 127.

solution. If the mixture of gases is heated, separation of arsenious sulphide commences at about 230° C., but the reaction is incomplete even at higher temperatures.[1] It has already been stated (p. 80) that arsine is itself acted upon by air or oxygen with formation of the solid hydride or arsenic, according to conditions, and also that the gas itself commences to decompose at 230° C. In the above reactions, therefore, the formation of arsenious sulphide appears to be a secondary reaction following the liberation of arsenic. Arsine may be entirely removed from hydrogen sulphide by passing the impure gas over "liver of sulphur" (potassium polysulphides) heated at 350° to 360° C. The absorption of the arsine may be represented thus: [1]

$$2AsH_3+3K_2S_3=2K_3AsS_3+3H_2S$$

Concentrated sulphuric acid is coloured brown when arsine is passed into it, brown flakes of arsenic, which may contain the solid hydride, separate,[2] and the liquid is found to contain hydrogen sulphide and arsenious sulphide. If the sulphuric acid is heated to 160° to 180° C., the passing in of arsine may result in the formation of an arsenical mirror. In spite of this reaction, according to Lyttkens and Lenz [3] hydrogen containing arsine as an impurity may be dried by concentrated sulphuric acid without any loss of arsenic. Dilute sulphuric acid, even when hot, has little action on the gas. Sulphur trioxide[4] reacts with formation of sulphur dioxide, arsenic and arsenious oxide; while sulphur dioxide [5] also reacts, forming arsenic and arsenious sulphide.

Nitric acid,[6] nitrous acid [7] and nitrogen peroxide[6] decompose the gas with liberation of arsenic, which then undergoes oxidation, as also does the hydrogen. Fuming nitric acid produces explosion and flame. Potassium nitrite in alkaline solution,[8] aqueous ammonium nitrate [9] and concentrated aqueous ammonia in the presence of air [10] also decompose the gas. Phosphorus, when vaporised in arsine, reacts to form arsenic phosphide and phosphine.[11] Phosphorus trichloride also produces arsenic phosphide together with hydrogen chloride,[12] while phosphorus pentachloride first yields the trichloride and the solid hydride (see p. 80). Phosphorus pentoxide has little action and may be used for drying the gas (p. 84). Hypophosphorous acid [13] is without action on arsine. Arsenic trichloride causes deposition of arsenic with liberation of hydrogen chloride.[14] If arsine is passed into a solution of arsenious oxide in hydrochloric or sulphuric acid, arsenic and water are produced.[15]

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[1] von der Pfordten, *Ber.*, 1884, 17, 2897.

[2] Soubeiran, *loc. cit.*; Humpert, *J. prakt. Chem.*, 1865, [1], 94, 392; Forbes, *Chem. News*, 1891, 64, 235; *Ber.*, 1891, 24, 2451.

[3] Lyttkens, *Zeitsch. anal. Chem.*, 1883, 22, 147; Lenz, *ibid.*, p. 148.

[4] Aimé, *J. Pharm. Chim.*, 1852, [3], 21, 84.

[5] Parsons, *Chem. News*, 1877, 35, 235; *Ber.*, 1877, 10, 233.

[6] Stromeyer, *Comment. Soc. Göttingen*, 1808, 16, 141.

[7] Parsons, *loc. cit.*

[8] Bozenhardt, *Apoth. Ztg.*, 1906, 21, 580.

[9] Bergstrom, *J. Physical Chem.*, 1925, 29, 168.

[10] Reckleben, Lockemann and Eckardt, *Zeitsch. anal. Chem.*, 1907, 46, 671.

[11] Soubeiran *loc. cit.*

[12] Janowsky, *Ber.*, 1875, 8, 1636.

[13] Parsons, *loc. cit.*

[14] Janowsky, *Ber.*, 1873, 6, 216.

[15] Tivoli, *Chem. Zentr.*, 1887, p. 1097; *Chem. Zeit. Rep.*, 1887, 11, 217; *Gazzetta*, 1884, 14, 487; 1889, 19, 630.

On mixing liquid boron chloride with liquid arsine in an atmosphere of hydrogen at −80° C. white prismatic crystals of the additive compound, boron arsenotrichloride, $BCl_3.AsH_3$, are obtained.[1] The hydrogen may be passed first through the arsine and then through the boron chloride, the entrained arsine being sufficient for the reaction. The product dissociates at −40° C., or if it is kept in a sealed tube at room temperature it decomposes into boron chloride, arsenic and hydrogen. With water it forms boric and hydrochloric acids, with liberation of arsine. A similar product, boron arsenotribromide, $BBr_3.AsH_3$, is obtained [2] as a white amorphous substance when boron bromide is slowly dropped into liquid arsine at −80° to −100° C., a stream of dry hydrogen being passed through the apparatus, from which all oxygen and moisture has previously been removed. The arsenobromide decomposes on heating, but by careful sublimation in a sealed tube it may be obtained in a crystalline form. At 0° C. slow decomposition into boron bromide and arsine is apparent, and if the latter is removed as it is formed by passing an indifferent gas through the apparatus, the decomposition is accelerated and some arsenic is deposited. It is completely decomposed into boron bromide, hydrogen and arsenic if kept in the dark for some weeks in a sealed vessel at ordinary temperature. It is readily oxidised in air or oxygen, and under certain conditions it is spontaneously inflammable. There is no action in oxygen below −40° C., but above this temperature, in a limited supply of oxygen, the products are boric oxide, hydrogen bromide, arsenic tribromide and arsenic. It decomposes in contact with water, boric acid, hydrobromic acid, arsine and some free arsenic being formed. Concentrated nitric acid causes oxidation with almost explosive violence; concentrated sulphuric acid does not appear to react. Ammonia reacts at 10° C. to form the compound $2BBr_3.9NH_3$. The arsenobromide is insoluble in carbon disulphide, but dissolves in boron tribromide.

When arsine is passed over a heated metal, such as the alkali and alkaline earth metals, zinc or tin, the decomposition of the gas is accelerated and the arsenide of the metal is formed. If platinum is used, the removal of arsenic from the gas is complete.[3] The action of sodium or potassium on arsine in liquid ammonia yields [4] the dihydrogen arsenide (MH_2As). Heated alkali hydroxides in the solid form quickly decompose the gas, forming arsenites, and at higher temperatures arsenates and arsenides of the metals.[5] The aqueous and alcoholic solutions have no appreciable action.[6] When the gas is passed over heated calcium oxide the amount of decomposition is not more than that due to the action of heat alone. Heated barium oxide, however, is converted into a dark brown mixture of barium arsenite and arsenate, hydrogen being liberated.[7] The gas is absorbed by soda-lime.[8]

The common salts of the alkali and alkaline earth metals have little,

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[1] Stieber, *Compt. rend.*, 1932, 195, 610.

[2] Stock, *Ber.*, 1920, 53, 837.

[3] Draper, *Amer. Chemist*, 1872, 2, 456.

[4] Johnson and Pechukas, *J. Amer. Chem. Soc.*, 1937, 59, 2068.

[5] Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 407.

[6] Schenkel and Ricker, *Jahrb. prakt. Pharm.*, 1849, 19, 257; Dragendorff, *Jahresber.*, 1866, p. 215.

[7] Soubeiran, *loc. cit.*

[8] Guareschi, *Atti Accad. Torino*, 1916, 51, 4, 59, 263.

if any, action on arsine, but aqueous solutions of alkali persulphates, chromates, dichromates and neutral ferricyanides absorb the gas to a slight extent. Potassium permanganate[1] in neutral or acid solution, and ferricyanides in alkaline solution, oxidise the gas slowly and incompletely. The main reaction with potassium permanganate may be represented thus:[2]

$$2KMnO_4 + AsH_3 = Mn_2O_3 + K_2HAsO_4 + H_2O$$

Salts of the heavy metals, both in the solid condition and in aqueous solution, generally react with formation of the metallic arsenide. Thus, dry copper chloride or sulphate[3] yields the arsenide, Cu_3As_2, and the mineral acid. In aqueous solutions of these salts, and in a solution of cuprous chloride in hydrochloric acid, absorption of arsine is only partial.[4] No precipitation occurs with ferric salts;[5] stannous and stannic salts are decomposed, a yellowish-brown precipitate being formed with stannic chloride. Zinc salts are only slowly decomposed. A concentrated neutral solution (80 per cent.) of cadmium acetate is able to absorb 40 times its own volume of the gas;[6] the absorption is rather slow. Salts of gold, platinum and rhodium give precipitates of the metals. By heating pure tungsten hexachloride in a current of arsine, the temperature being maintained at 150° to 200° C. for a time and then gradually raised to 350° C., a black crystalline mass of tungsten diarsenide is obtained;[7] by heating the hexachloride with liquid arsine in a sealed tube at 60° to 75° C. bluish-black hygroscopic crystals of tungsten chlorarsenide, W_2AsCl_9, are formed.[8]

The action of arsine on silver and mercury salts has attracted much attention owing to the important application to analytical methods for arsenic (p. 319). The action of arsine on a dilute aqueous solution of silver nitrate has long been known to yield metallic silver, arsenious acid and nitric acid.[9] With more concentrated solutions the introduction of a few bubbles of arsine produces a deep lemon-yellow coloration, the liquid also acquiring an acid reaction. The coloration disappears after one or two days, silver is precipitated and the colourless solution contains arsenious and arsenic acids.[10] If a rapid stream of arsine be passed into a concentrated solution of silver nitrate at 0° C. the whole liquid solidifies to a yellow crystalline mass which rapidly blackens with separation of silver. Lassaigne represented the reaction with the dilute solution by the equation

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 6HNO_3$$

but although the absorption of arsine is complete, the theoretical

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[1] Reckleben and Lockemann, *Zeitsch. anal. Chem.*, 1908, 47, 105, 126; Parsons, *Chem. News*, 1877, 35, 235; Schobig, *J. prakt. Chem.*, 1876, [2], 14, 289.

[2] Jones, *Chem. News*, 1878, 37, 36.

[3] Dumas, *Ann. Chim. Phys.*, 1826, [2], 33, 355; 1830, [2], 44, 289; Simon, *Pogg. Annalen*, 1837, 41, 463; Kane, *Proc. Irish Acad.*, 1840, 1, 182.

[4] Riban, *Compt. rend.*, 1879, 88, 581; Dowzard, *J. Chem. Soc.*, 1901, 79, 715.

[5] Soubeiran, *loc. cit.*

[6] Wilmet, *Compt. rend.*, 1927, 185, 1136.

[7] Defacqz, *Compt. rend.*, 1901, 132, 138.

[8] Defacqz, *loc. cit.*; *Ann. Chim. Phys.*, 1901, [7], 22, 238.

[9] Soubeiran, *Ann. Chim. Phys.*, 1830, [2], 43, 418; Lassaigne, *J. Chim. Méd.*, 1839, 16, 685; 1840, 17, 440.

[10] Reichardt, *Arch. Pharm.*, 1880, [3], 17, 1; Poleck and Thummel, *ibid.*, 1884, [3], 22, 1; *Ber.*, 1883, 16, 2435.

amount of silver is not at first precipitated unless the solution is alkaline.[1] In neutral solution the reaction

$$AsH_3 + 3AgNO_3 = Ag_3As + 3HNO_3$$

also occurs,[2] followed by:

$$Ag_3As + 3AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 3HNO_3$$

The yellow substance produced with more concentrated solutions is silver nitrato-arsenide,[3] $Ag_3As.3AgNO_3$, which is formed thus:

$$AsH_3 + 6AgNO_3 = Ag_3As.3AgNO_3 + 3HNO_3$$

This compound does not separate from dilute solutions because it is decomposed by water:

$$Ag_3As.3AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 3HNO_3$$

In alkaline or ammoniacal solutions,[4] salts of arsenic acid are also formed, probably owing to both of the following reactions:

$$H_3AsO_3 + 2AgNO_3 + H_2O = 2Ag + H_3AsO_4 + 2HNO_3$$

and

$$AsH_3 + 8AgNO_3 + 4H_2O = 8Ag + H_3AsO_4 + 8HNO_3$$

Fused silver nitrate is coloured first yellow and then black by arsine, the reaction being similar to that in solution.

When arsine is passed into an aqueous solution of mercuric chloride, a yellow to brown precipitate results. This was described by Rose [5] as a chlorarsenide of mercury, $AsHg_3Cl_3$. A similar precipitate is obtained from an alcoholic solution, and this was investigated by Partheil and Amort,[6] who passed in arsine largely diluted with hydrogen. The first product was shown to be yellow monochloromercurarsine, $AsH_2.HgCl$, followed by an orange di- and a brown tri-chloromercurarsine, $AsH(HgCl)_2$ and $As(HgCl)_3$; finally black mercury arsenide, Hg_3As_2, was formed. The first two, in the presence of excess of mercuric chloride solution, yield arsenious acid, hydrochloric acid and mercurous chloride, while the third yields arsenic and mercurous chloride. With water, the trichloromercurarsine decomposed to form arsenious and hydrochloric acids and mercury. Franceschi [7] also obtained the dichloromercurarsine by the action of arsine on an ether solution of mercuric chloride. The dry salts, mercurous and mercuric chlorides, are both attacked by arsine and coloured yellow to brown; mercuric bromide reacts similarly.

When arsine is passed into a solution of potassium mercuric iodide containing excess of potassium iodide, a brown crystalline precipitate of triiodomercurarsine, $As(HgI)_3$, is obtained.[8] The gas also precipitates

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[1] Reckleben and Lockemann, *Zeitsch. angew. Chem.*, 1906, 19, 275; Křepelka and Fanta, *Coll. Czech. Chem. Comm.*, 1937, 9, 47.

[2] Reckleben, Lockemann and Eckardt, *Zeitsch. anal. Chem.*, 1907, 46, 697; Pozzi, *Ind. Chim.*, 1914, 6, 144.

[3] Poleck and Thümmel, *loc. cit.*

[4] Reckleben and Lockemann, *Zeitsch. anal. Chem.*, 1908, 47, 126; and with Eckhardt, *loc. cit.*: Preis and Rayman, *Listy's Chemické*, 1887, 11, 34.

[5] Rose, *Pogg. Annalen*, 1837, 41, 463; also Mayençon and Bergeret, *Compt. rend.*, 1874, 79, 118; Vitali, *L'Orosi*, 1893, 16, 397; *Boll. Chim. Farm.*, 1905, 44, 49.

[6] Partheil and Amort, *Ber.*, 1898, 31, 594; *Arch. Pharm.*, 1899, [3], 37, 121.

[7] Franceschi, *Boll. Chim. Farm.*, 1890, 29, 317; *L'Orosi*, 1890, 13, 289.

[8] Lemoult, *Compt. rend.*, 1904, 139, 478.

from aqueous or alcoholic solutions of mercuric cyanide unstable reddish-brown substances which gradually undergo decomposition, especially in daylight, with liberation of mercury.[1]

According to Lebeau,[2] arsine does not enter into the composition of compounds analogous to the metal-ammines, and the latter in ammoniacal solution react with arsine to produce arsenides of the metals.

The activity of palladium as a catalyst in the determination of hydrogen by combustion is unaffected by the presence of traces of arsine.[3]

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[1] Hodgkinson, *Chem. News*, 1876, 34, 167.

[2] Lebeau, *Bull. Soc. chim.*, 1900, [3], 23, 251, 340.

[3] Vallery, *Compt. rend.*, 1927, 185, 538.

CHAPTER VI.

ARSENIC AND THE HALOGENS.

ARSENIC AND FLUORINE.

ARSENIC forms two fluorides, AsF_3 and AsF_5, both being produced by direct combination of the elements at ordinary temperature.[1] The reaction renders the mass incandescent. The trifluoride is a colourless liquid, and the pentafluoride a colourless gas, both of which fume in contact with air.

Arsenic Trifluoride, AsF_3, is formed when fluorine reacts with arsenic trichloride [1] or with the arsenides of the alkali or alkaline earth metals; [2] by the action of anhydrous hydrofluoric acid or of acid fluorides on arsenious oxide; [3] by the action of certain metallic fluorides, for example silver or lead fluoride on arsenic trichloride,[4] or of ammonium fluoride on arsenic tribromide; [5] and by the action of iodine pentafluoride on arsenic.[6]

The usual method of preparation is that employed by Dumas, who first discovered the compound in 1826, namely, by the addition of concentrated sulphuric acid (2 parts) to a mixture (1 part) containing equal weights of calcium fluoride and arsenious oxide.[7] The trifluoride is collected in a lead receiver immersed in ice water and rectified by distillation on a water-bath at 65° C. It is best kept in a platinum bottle.

Arsenic trifluoride is a colourless mobile liquid with an odour resembling that of silicon tetrafluoride. It fumes in air owing to its rapid reaction with water vapour (see below). A drop on the skin evaporates rapidly, leaving a painful burn similar to that produced by hydrofluoric acid. According to Thorpe,[8] the density at 0° to 4° C. is 2·6659 and at the boiling point 2·4497, the latter temperature being 60·4° C. Earlier workers [9] gave b.pt. 63° to 64° C. The liquid solidifies to a crystalline mass [10] at $-8{\cdot}5°$ C. The volume change on heating is expressed by the equation [11]

$$v_\theta = v_0(1 + 0{\cdot}001443\,\theta + 0{\cdot}000000297\,\theta^2)$$

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[1] Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 224; "*Le fluor et ses composés*" (Paris, 1900).

[2] Lebeau, *Bull. Soc. chim.*, 1900, [3], 23, 250; *Compt. rend.*, 1900, 130, 502.

[3] Dumas, *Ann. Chim. Phys.*, 1826, [2], 31, 433; *Quart. J. Sci.*, 1827, 22, 211.

[4] Moissan, *loc. cit.*

[5] MacIvor, *Chem. News*, 1874, 30, 169; 1875, 32, 258.

[6] Moissan, *Compt. rend.*, 1903, 136, 786; 1902, 135, 564.

[7] Dumas, *loc. cit.* See also Unverdorben, *Pogg. Annalen*, 1826, 7, 316. MacIvor, *loc. cit.*; Thorpe, *Proc. Roy. Soc.*, 1877, 25, 122, Moissan, *loc. cit.*

[8] Thorpe, *J. Chem. Soc.*, 1880, 37, 141, 327.

[9] Unverdorben, *loc. cit.*; MacIvor, *loc. cit.*

[10] Moissan, *Compt. rend.*, 1884, 99, 874.

[11] Thorpe, *loc. cit.*

The heat of formation of liquid arsenic trifluoride has been obtained[1] indirectly by determining the heats of dissolution of the trifluoride and of a mixture of arsenious oxide and sodium fluoride in about one litre of normal sodium hydroxide solution. The value obtained was 198,300 calories. Assuming Trouton's constant to be 21, the heat of vaporisation is about −7000 calories, so that the heat of formation of gaseous arsenic trifluoride is 191,300 calories.

The molecular volume in the liquid and gaseous states has been measured[2] and from the results the radii of the atoms constituting the molecule have been calculated.

The liquid is a poor conductor of electricity, but some decomposition due to electrolysis occurs, a gas which attacks platinum being liberated and arsenic deposited on the cathode.[3]

The Raman spectrum of arsenic trifluoride consists of four lines with the following frequencies: w_1 (1) 707, w_2 (1) 341, w_3 (2) 644, and w_4 (2) 274 cm.^{-1}; a pyramidal molecule is indicated.[4]

The trifluoride readily reacts with water, and a trace of the latter is sufficient to cause the liquid to show an acid reaction. If more water be added there is a slight heating effect and, according to Dumas, hydrofluoric and arsenious acids are formed. Berzelius concluded[5] that hydrofluoarsenic acid was the product. The solution reacts with tin and zinc and also attacks glass. The liquid trifluoride itself when heated in a glass vessel readily attacks the latter, thus:[6]

$$4AsF_3 + 3SiO_2 = 2As_2O_3 + 3SiF_4$$

Admixture of the trifluoride with alcohol or ether, or with fixed or volatile oils, causes some decomposition.[7] Ammonia readily combines to form a white powder, arsenic triamminotrifluoride,[8] $As(NH_3)_3F_3$; this compound is decomposed by water.[7] Phosphine reacts differently, yielding hydrogen fluoride:[8]

$$AsF_3 + PH_3 = AsP + 3HF$$

With the chlorides of phosphorus there is an interchange of halogens, thus—

$$AsF_3 + PCl_3 = AsCl_3 + PF_3 \text{ }^{9}$$
$$5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5 \text{ }^{10}$$

and this is also the case with silicon tetrachloride,[11] thionyl chloride[12] and thiophosphoryl chloride,[13] thus:

$$4AsF_3 + 3SiCl_4 = 4AsCl_3 + 3SiF_4$$
$$2AsF_3 + 3SOCl_2 = 2AsCl_3 + 3SOF_2$$
$$AsF_3 + PSCl_3 = AsCl_3 + PSF_3$$

Sulphur chloride and carbon tetrachloride do not react in the cold.[11]

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[1] Yost and Sherborne, *J. Amer. Chem. Soc.*, 1935, 57, 700; Yost and Anderson, *J. Chem. Phys.*, 1934, 2, 624; Yost and Sherborne, *ibid.*, 1934, 2, 125.

[2] Ruff and co-workers, *Zeitsch. anorg. Chem.*, 1932, 207, 46.

[3] Moissan, *loc. cit.*

[4] Yost and Sherborne, *loc. cit.*

[5] Berzelius, "*Lehrbuch der Chemie*" (Dresden, 1826), 2, i, 45.

[6] Moissan, *loc. cit.*

[7] *Cf.* Unverdorben, *loc. cit.*

[8] Besson, *Compt. rend.*, 1890, 110, 1258.

[9] Moissan, *Compt. rend.*, 1885, 100, 272.

[10] Thorpe, *J. Chem. Soc.*, 1880, 37, 385.

[11] Moissan, "*Le fluor et ses composés*" (Paris, 1900).

[12] Moissan and Lebeau, *Compt. rend.*, 1900, 130, 1436.

[13] Thorpe and Rodger, *J. Chem. Soc.*, 1888, 53, 766; 1889, 55, 306.

Silico-chloroform at ordinary temperature reacts vigorously, two simultaneous reactions apparently taking place :[1]

$$\text{(i)}\quad AsF_3 + SiHCl_3 = AsCl_3 + SiHF_3$$
$$\text{(ii)}\quad 4AsF_3 + 3SiHCl_3 = 2AsCl_3 + 3SiF_4 + 3HCl + 2As$$

Arsenic trifluoride reacts with bromine to form a crystalline substance ; iodine dissolves in the liquid yielding a purple-red solution ; the nature of these products has not been elucidated.

Arsenic Pentafluoride, AsF_5, may be prepared by the interaction of arsenic and fluorine in a platinum vessel,[2] or by the action of bromine and antimony pentafluoride on arsenic trifluoride.[3] The reagents should be dry, and if the reaction in the second case is carried out in a glass vessel, the apparatus should be in one piece and well dried. The bromine is added to the mixture of fluorides at $-20°$ C. and, after cooling in liquid air, the arsenic pentafluoride is obtained by heating on a water-bath at 55° C., the gas passing through a reflux condenser to a receiver surrounded by liquid air. The product contains bromine, which is removed by passing the gas over molten sulphur.

Arsenic pentafluoride is a colourless gas at ordinary temperature. It condenses to a pale yellow liquid of boiling point $-52\cdot8°$ C. and freezes to a white solid of melting point $-79\cdot8°$ C. The vapour density corresponds with a mol. wt. 169·5 ($AsF_5 = 169\cdot9$). The density curve of the liquid is represented by

$$D = 3\cdot505 - 0\cdot00534(273 + t)$$

The density of the solid is 3·02 at $-91°$ C. Vapour pressure determinations for the solid and liquid have been made,[4] the results being as follows :

Solid AsF_5 :						
t (° C.) . .	−116·7	−106·1	−98·4	−91·7	−87·3	−82·7
V.p. (mm.) .	1·3	6·5	18·3	42·2	69·8	114·7
Liquid AsF_5 :						
t (° C.) . .	−77·2	−71·2	−65·1	−61·1	−56·8	−53
V.p. (mm.) .	180·2	266·4	386·0	487·9	604·7	747·9

In contact with moist air the gas gives dense white fumes. It dissolves in water with evolution of heat. It also dissolves in alcohol, ether and benzene ; and in aqueous alkali and arsenic trifluoride, some heat being developed. In contact with paraffin oil or wax, charring gradually occurs ; sugar and paper, if moist, are also blackened. Turpentine vapour gives a black cloud on contact with the gas. When heated in contact with silicon, silicon tetrafluoride and arsenic are formed. The gas attacks dry glass when heated, silicon tetrafluoride and probably arsenic pentoxide being produced. With phosphorus, some phosphorus trifluoride is formed. The gas reacts with iodine in

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[1] Ruff and Albert, *Ber.*, 1905, 38, 54.
[2] Ruff and others, *Zeitsch. anorg. Chem.*, 1932, 206, 59.
[3] Ruff, Graf and Heller, *Ber.*, 1906, 39, 67.
[4] Ruff and others, *loc. cit.*

the cold. The metals mercury, zinc, lead, bismuth and iron are converted to fluorides ; copper is attacked only on heating. Tungsten is not affected by the gas.

Arsenic Nitrosyl Hexafluoride, $AsF_5.NOF$, was obtained by Ruff[1] by passing nitrosyl fluoride through arsenic trichloride, the mixture being kept cool. When absorption was complete, any nitrosyl chloride was removed by storage over fused sodium hydroxide in a vacuum. The product consists of white crystals, stable in dry air even at high temperature. It is decomposed by water and consequently is unstable in moist air ; it is also decomposed by caustic alkali and by concentrated hydrochloric acid. On warming with antimony pentafluoride, arsenic pentafluoride is produced thus :

$$AsF_5.NOF + SbF_5 = AsF_5 + SbF_5.NOF$$

The following **fluoarsenates** have been described by de Marignac.[2] *Potassium hexafluoarsenate*, $2KF.2AsF_5.H_2O$, obtained by addition of hydrofluoric acid to a solution of potassium arsenate, yields small rhombic crystals, stable when dry but decomposed by water. The crystals have axial ratios $a : b : c = 0{\cdot}8401 : 1 : 2{\cdot}5172$. When heated, the crystals melt and decompose, giving off water and hydrogen fluoride. The aqueous solution of the salt on crystallisation deposits rhombic plates of *potassium oxytetrafluoarsenate*, $KF.AsOF_3.H_2O$. A solution of potassium hexafluoarsenate containing excess of potassium fluoride and hydrofluoric acid, on crystallisation deposits rhombic crystals of *potassium heptafluoarsenate*, $2KF.AsF_5.H_2O$. The axial ratios of these crystals are $a : b : c = 0{\cdot}8847 : 1 : 0{\cdot}6453$. The arsenate is stable in dry air. By repeatedly crystallising this salt from its aqueous solution, or by crystallising a solution of the oxytetrafluoarsenate in dilute hydrofluoric acid, a crystalline mass is obtained to which the formula $4KF.AsF_5.AsOF_3.3H_2O$ has been ascribed.

A crystalline ammonium hexafluoarsenate has not been obtained. A mixture of ammonium arsenate and hydrofluoric acid on evaporation yields a gum-like mass. Arsenious oxide dissolves in a boiling solution of ammonium fluoride, but on cooling the arsenious oxide separates from the solution.[3]

ARSENIC AND CHLORINE.

One compound only of these two elements has been isolated, namely, arsenic trichloride, which at ordinary temperatures is a colourless oily liquid. Although a substance reported to be arsenic pentachloride has been described in the literature (see p. 110), evidence of the existence of such a compound is not forthcoming.

Arsenic Trichloride, $AsCl_3$, was discovered in 1648 by Glauber,[4] who obtained it by heating in a retort a mixture of white arsenic, common salt and sulphuric acid ; a thick oil, which he designated *butter of arsenic*, collected in the receiver.[5] The compound is produced in many reactions and is usually formed when arsenic and its compounds are

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[1] Ruff, *Zeitsch. anorg. Chem.*, 1908, 58, 325.

[2] de Marignac, *Bull. Soc. chim.*, 1867, [2], 8, 327; *Arch. Sci. Genève*, 1867, [2], 28, 5.

[3] von Helmholt, *Zeitsch. anorg. Chem.*, 1893, 3, 150.

[4] Glauber, "*Furni novi philosophici*," Amstelædami, 1648, p. 74.

[5] For a review of early literature on the distillation of arsenic trichloride, see Terényi

chlorinated. The more important methods of formation and preparation are as follows.

(1) By direct action of chlorine on arsenic. When powdered arsenic is sprinkled into chlorine gas,[1] or into liquid chlorine near its boiling point,[2] union occurs with incandescence and a white cloud of the trichloride is formed. If the gas is passed over arsenic in a tube connected with a receiver immersed in a freezing mixture, the powder which condenses is yellow, owing to excess of chlorine; the latter may be removed by distillation from powdered arsenic. The reaction is accelerated by the addition of a trace of bromine or of alkali halide.[3] When chlorine is passed into a solution of yellow arsenic in carbon disulphide, brown arsenic is first precipitated, which is then converted to arsenic trichloride.[4]

In order to obtain specimens of arsenic trichloride sufficiently pure for atomic weight determinations, Krěpelka fractionally distilled three times in nitrogen the product from the reaction of pure metallic arsenic and dry chlorine. The distillate was then fractioned *in vacuo*, the middle fraction being filled into bulbs.[5]

(2) By the action of chlorine compounds on arsenic. The trichloride is produced by the action on arsenic of boiling hydrochloric acid in the presence of oxygen,[6] or by gently heating arsenic with the chloride of ammonium,[7] magnesium,[8] aluminium[9] or mercury.[10] A convenient method of preparation is to heat a mixture containing arsenic (1 part) and mercuric chloride (6 parts). Other compounds which may be used are sulphur monochloride,[11] sulphuryl chloride,[12] chlorosulphonic acid,[12] phosphorus pentachloride and phosphorus oxychloride.[13]

(3) By the action of chlorine and chlorine compounds on arsenious oxide. Chlorine reacts with the heated oxide to form arsenic trichloride and arsenic pentoxide.[14] The gas also reacts with the aqueous solution or suspension. When chlorine is passed into a well-agitated 70 to 80 per cent. suspension of arsenious oxide at 60° to 70° C., about 30 per cent. of the latter is converted to the trichloride and the remainder to the pentoxide.[15] A saturated solution of arsenious oxide in concentrated hydrochloric acid when heated with concentrated sulphuric acid yields

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[1] Davy, *Phil. Trans.*, 1812, 102, 169; Dumas, *Ann. Chim. Phys.*, 1826, [2], 33, 351.

[2] Thomas and Dupuis, *Compt. rend.*, 1906, 143, 282.

[3] Jacobson, *British Patents*, 181385, 190688 (1922).

[4] Thiele, "*Ueber die allotropen Modifikationen des Arsens*," Berlin, 1910.

[5] Krěpelka, *Collection Czechoslov. Chem. Communications*, 1930, 2, 255. See also Baxter and co-workers (*J. Amer. Chem. Soc.*, 1933, 55, 1054), who distilled the product 29 times.

[6] Napoli, *Amer. J. Sci.*, 1854, [2], 18, 190; *Chem. Zentr.*, 1854, p. 842; Ditte and Metzner, *Compt. rend.*, 1892, 115, 936.

[7] Selmi, *Ber.*, 1880, 13, 579; *Jahresber.*, 1884, p. 1699.

[8] l'Hote, *J. Pharm. Chim.*, 1884, [5], 10, 254; *Compt. rend.*, 1884, 98, 1491.

[9] Ruff and Staib, *Zeitsch. anorg. Chem.*, 1921, 117, 191.

[10] Capitaine, *J. Pharm. Chim.*, 1839, [2], 25, 523; Ludwig, *Arch. Pharm.*, 1859, [2], 97, 23; Selmi, *loc. cit.*

[11] Wohler, *Annalen*, 1850, 73, 384; Chevrier, *Compt. rend.*, 1865, 63, 1003; Oddo and Serra, *Gazzetta*, 1899, 29, ii, 355.

[12] Heumann and Köchlin, *Ber.*, 1882, 15, 418, 1736.

[13] Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 11; Reinitzer and Goldschmidt, *Monatsh.*, 1881, 1, 427.

[14] Weber, *Pogg. Annalen*, 1861, 112, 624; Bloxam, *J. Chem. Soc.*, 1865, 18, 62.

[15] Cambi, *Giorn. Chim. Ind. Appl.*, 1924, 6, 527.

the trichloride,[1] and the latter is also produced when a mixture of arsenious oxide and sodium chloride [2] or lead chloride [3] is heated with concentrated sulphuric acid. An optimum yield (85 per cent. of theoretical) is obtained when the reactants in the proportions As_2O_3 99 g., NaCl 261 g. and conc. H_2SO_4 213 c.c. are slowly heated (3 to 4 hours) to 180° C.[4] Dry hydrogen chloride itself heated with arsenious oxide yields arsenic trichloride.[5] The following may also be used as chlorinating agents: ammonium chloride,[6] silicon tetrachloride,[7] phosphorus trichloride,[8] phosphorus pentachloride [9] and phosphorus oxychloride.[10] If chlorine is passed over a heated mixture of arsenious oxide and sulphur,[11] or into a suspension of these two substances in arsenic trichloride at the boiling point of the latter,[12] chlorination occurs and these are suitable methods of preparation. Sulphur monochloride itself may be used,[13] but sulphur is deposited, and to avoid this Partington recommends [14] passing chlorine into a mixture of arsenious oxide and sulphur monochloride, the reaction being

$$4As_2O_3+3S_2Cl_2+9Cl_2=8AsCl_3+6SO_2$$

Two-thirds of the requisite amount of arsenious oxide are first added and the remainder after the reaction has progressed for a time, the gas being passed continuously. The arsenic trichloride may be distilled off and does not require purification. The reaction is somewhat violent, however. Arsenic trichloride may also be prepared conveniently by passing carbonyl chloride over a mixture containing 80 per cent. of arsenious oxide and 20 per cent. of carbon heated at 200° to 260° C.; the yield is almost quantitative.[15]

(4) By the action of chlorine and chlorine compounds on arsenic pentoxide. Arsenic trichloride is formed when chlorine is passed over the heated oxide.[16] Hydrogen chloride reacts at ordinary temperatures, but not at $-20°$ C.[17] Aqueous hydrochloric acid, or sulphuric acid and a metallic chloride, also reacts with the oxide or with alkali arsenates to produce arsenic trichloride. The reaction with hydrochloric acid is greatly influenced by catalysts such as ferrous sulphate [18] or chloride,[19] potassium bromide [20] or iodide,[21] hydrobromic acid,[22] methyl alcohol [23]

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[1] Davy, *Phil. Trans.*, 1812, 102, 169.

[2] Dumas, *Ann. Chim. Phys.*, 1828, [2], 38, 337.

[3] Selmi, *Ber.*, 1880, 13, 579; *Riv. Chim. Med. Farm.*, 1884, 2, 444.

[4] Tseng, Hu and Hsu, *Sci. Quart. Nat. Univ. Peking*, 1935, 5, 317.

[5] Wallace and Penny, *Phil. Mag.*, 1852, [4], 4, 361; Wallace, *ibid.*, 1858, [4], 16, 358.

[6] de Luynes, *Compt. rend.*, 1857, 44, 1354.

[7] Rauter, *Annalen*, 1892, 270, 250.

[8] Michaelis, *Jahresber.*, 1870, p. 280; *Jena. Zeit.*, 1870, [1], 6, 239.

[9] Hurtzig and Geuther, *Annalen*, 1859, 111, 172.

[10] Reinitzer and Goldschmidt, *Monatsh.*, 1881, 1, 427.

[11] Oddo and Giachery, *Gazzetta*, 1923, 53, i, 56.

[12] Miller and Witherspoon, *U.S. Patent*, 1852183 (1932).

[13] Prinz, *Annalen*, 1884, 223, 357; Oddo and Serra, *Gazzetta*, 1899, 29, ii, 355.

[14] Partington, *J. Chem. Soc.*, 1929, p. 2577.

[15] Milligan, Baude and Boyd, *J. Ind. Eng. Chem.*, 1920, 12, 221.

[16] Weber, *Pogg. Annalen*, 1861, 112, 624.

[17] Rose, *Pogg. Annalen*, 1841, 52, 64; Liebig and Wohler, *ibid.*, 1827, 11, 149.

[18] Classen and Ludwig, *Ber.*, 1885, 18, 1110.

[19] Fischer, *Annalen*, 1881, 208, 182.

[20] Gooch and Phelps, *Amer. J. Sci.*, 1894, [3], 48, 216; *Zeitsch. anorg. Chem.*, 1894, 7, 123.

[21] Gooch and Danner, *Amer. J. Sci.*, 1892, [3], 42, 308; *Zeitsch. anorg. Chem.*, 1894, 6, 268.

[22] Bottger, *Oestern. Chem. Ztg.*, 1924, 27, 24.

[23] Friedheim and Michaelis, *Ber.*, 1895, 28, 1414; Duparc and Ramadier, *Helv. Chim. Acta*, 1922, 8, 552.

or pyrogallol,[1] and by this means arsenic may be completely removed from solution as the volatile chloride. Arsenic acid and arsenates heated with phosphorus pentachloride [2] or ammonium chloride [3] also yield arsenic trichloride. When an arsenate is reduced by the action of a hydrazine salt in the presence of aqueous hydrochloric acid and potassium bromide, arsenic trichloride and elementary arsenic are formed. The latter may be reduced to a minimum by increasing the concentration of the acid to 5·5N, when the trichloride is practically the sole product.[4]

(5) By the action of chlorine and chlorine compounds on the sulphides of arsenic. By passing chlorine over the dry sulphides, realgar or orpiment, at 130° to 140° C., theoretical yields of arsenic trichloride and of sulphur dichloride are obtained.[5] The trisulphide reacts with hydrogen chloride in the cold,[6] but chlorination by means of hydrochloric acid is difficult, only a small quantity of the chloride being volatilised.[7] The reaction is facilitated by the presence of ferric chloride,[8] cuprous chloride or potassium antimonyl tartrate.[9] Other chlorinating agents, effective with the sulphides, are sulphur monochloride,[10] a mixture of ammonium chloride and nitrate,[11] and mercuric chloride.[12]

Physical Properties.—Arsenic trichloride is a colourless, transparent oily liquid at ordinary temperatures. The following values for the density,[13] specific cohesion, surface tension [14] and molecular surface energy were determined by Jäger: [15]

Temperature, ° C.	−21·0°	0·0°	20·8°	50·2°	75·7°	110·0°
Density	2·245	2·205	2·165	2·105	2·051	1·968
Spec. Cohesion (sq. mm.) .	3·98	3·83	3·71	3·54	3·40	3·21
Surf. Tension (dynes per cm.). .	43·8	41·4	39·4	36·6	34·2	31·0
Mol. Surf. Energy (ergs per sq. cm.)	818·4	782·0	754·3	713·9	678·8	632·4

The parachor is 212·0.[16]

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[1] Bottger, *loc. cit.*

[2] Hurtzig and Geuther, *Annalen*, 1859, **111**, 172.

[3] Rose, *Pogg. Annalen*, 1862, **116**, 453.

[4] Kubina, *Zeitsch. anal. Chem.*, 1929, **78**, 1; Kubina and Plichta, *ibid.*, 1928, **74**, 235.

[5] Ionescu and Soare, *Bul. Chim. Soc. Romana Stiinte*, 1932, **35**, 25.

[6] Kelley and Smith, *Amer. Chem. J.*, 1896, **18**, 1096.

[7] Gmelin, "*Handbook of Chemistry*," London, 1850, **4**, 274; Schmidt, *Arch. Pharm.*, 1917, **255**, 45; Fyfe, *J. prakt. Chem.*, 1852, **55**, 103; Beckurts, *Arch. Pharm.*, 1884, [3], **22**, 654.

[8] Schneider, *Pogg. Annalen*, 1852, **85**, 433; Fyfe, *loc. cit.*; Riekher, *N. Jahrbuch Pharm.*, 1871, **36**, 9; Clark, *Ber.*, 1891, **24**, 921.

[9] Rammelsberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1881. p. 79.

[10] Baudrimont, *Compt. rend.*, 1867, **64**, 369.

[11] Fresenius, *Zeitsch. anal. Chem.*, 1886, **25**, 200.

[12] Ludwig, *Arch. Pharm* , 1859, [2], **97**, 33.

[13] For earlier determinations of density, see Pierre, *Ann. Chim. Phys.*, 1845, [3], **15**, 325; Wallace and Penny, *Phil. Mag.*, 1852, [4], **4**, 361; Haagen, *Pogg. Annalen*, 1867, **131**, 117; 1868, **133**, 295.

[14] See Lorenz and Herz, *Zeitsch. anorg. Chem.*, 1921, **120**, 320.

[15] Jager, *ibid.*, 1917, **101**, 174.

[16] Henley and Sugden, *J. Chem. Soc.*, 1929, p. 1058.

At the boiling point, 129·6° C. at 760 mm.,[1] the density is 1·91813. The density at different temperatures referred to water at 4° C. may be represented by the equation [2]

$$D = 2{\cdot}20511 - 0{\cdot}001856\theta - 0{\cdot}0000027\theta^2$$

The liquid may be used as a solvent for the ebullioscopic or cryoscopic determination of molecular weights, the ebullioscopic constant being 6·5 to 7·25.[3] Beckmann used it in this way for determining the molecular weight of sulphur,[4] but when this method is applied to solutions of the halides of phosphorus, antimony, titanium or tin in arsenic trichloride, or to solutions of any of these halides in one another, the molecular weights obtained are abnormally small, presumably owing to the halogen atoms being readily interchangeable so that, on mixing, reciprocal conversions occur with formation of mixed halides; the latter, however, cannot be isolated in solid or gaseous form.[5] Alcohol and ether mix readily with arsenic trichloride, the liquid becoming warm; turpentine, olive oil and certain resins also dissolve in the liquid,[6] as do many organic substances, often with formation of compounds (see p. 105).

The molecular volume of the liquid [7] at the ordinary temperature is 92·4 c.c., and the ratio of this value to the sum of the atomic volumes of the constituent elements [8] is 1·33. From measurements of density and coefficient of expansion at low temperature (−194° C.) the molecular volume at 0° Abs. has been calculated [9] to be 67·7 c.c.

Vapour pressure determinations at various temperatures have been made, but the results obtained by different investigators are not in agreement.[10] The following are probably the most reliable values: [11]

Temperature, ° C.	0	25	35	50	100	129·6
Vap. press., mm.	2·44	11·65	19·53	40·90	301	760

The specific heat of the liquid is [12] 0·17604. The thermal expansion with rise in temperature may be represented by the equation: [13]

$$v = 1 + 0{\cdot}000991338\theta + 0{\cdot}0_6 84914\theta^2 + 0{\cdot}0_8 27551\theta^3$$

v being unity at 0° C. The heat of vaporisation according to Regnault is 69·741 calories, but Beckmann gave the value 44·51 calories. The

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[1] Thorpe, *Annalen*, 1876, 182, 201; *Proc. Roy. Soc.*, 1877, 25, 122; *J. Chem. Soc.*, 1880, 37, 141, 327. For other determinations of b.pt., see Jager, *loc. cit.*; Pierre, *loc. cit.*; Haagen, *loc. cit.*; Biltz and Meinecke, *Zeitsch. anorg. Chem.*, 1923, 131, 1; Baxter, Bezzenberger and Wilson, *J. Amer. Chem. Soc.*, 1920, 42, 1386; Walden, *Zeitsch. physikal. Chem.*, 1903, 43, 420.

[2] Jäger, *loc. cit.*

[3] de Kolossowsky, *J. Chim. phys.*, 1926, 23, 353. See also Raeder, *Kgl. Norske Videnskab. Selskabs Skrifter*, 1929, No. 3, 1; *Zeitsch. anorg. Chem.*, 1933, 210, 145.

[4] Beckmann, *ibid.*, 1906, 51, 96.

[5] Beckmann, *loc. cit.*; Walden, *ibid.*, 1902, 29, 371; Garelli and Bassani, *Atti R. Accad. Lincei*, 1901, [5], 10, 255; Raeder, *loc. cit.*

[6] Davy, *Phil. Trans.*, 1812, 102, 169.

[7] Rabinowitsch, *Ber.*, 1925, 58, B, 2790.

[8] Saslavsky, *Zeitsch. anorg. Chem.*, 1925, 146, 315.

[9] Biltz and co-workers, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

[10] See Maier, "*Vapor Pressures of the Common Metallic Chlorides*." Washington, 1925. p. 42.

[11] Baxter and co-workers, *J. Amer. Chem. Soc.*, 1920, 42, 1386.

[12] Regnault, *Mém. Paris Acad.*, 1862, 26, 200; *Phil. Mag.*, 1853, [4], 5, 473.

[13] Beckmann, *loc. cit.*

molecular heat of vaporisation has been calculated[1] to be 7420 cals. at 0° C., 7290 cals. at 50° C. and 6680 cals. at 100° C. The specific heat of the vapour[2] is 0·11224. The critical temperature has been estimated[3] to be 356° C. The heat of formation of the liquid is 71,390 calories.[4]

The vapour density of arsenic trichloride was found by Dumas[5] to be 6·301 (air = 1), which value agrees with that required by the formula $AsCl_3$ (= 6·27).

Arsenic trichloride may be solidified by cooling. It forms white, nacreous, acicular crystals of melting point −16° C.[6] The solidification is accompanied by an appreciable decrease in volume.

The refractive index of the liquid for light of various wavelengths has been determined as follows :[7]

λ, A. .	2740	2980	3940	4800	5890	7680
n . .	1·781	1·73023	1·64540	1·61949	1·60395	1·59262

The specific refraction[8] is 0·2732 and the refraction equivalent 49·50. The absorption of light by a 0·01N-solution of arsenic trichloride in N-hydrochloric acid has been examined,[9] and it has been observed that the molecular extinction coefficient varies from 5 to 30 as the wavelength of the incident light decreases from 3570 to 2270 A.

The Raman spectra of arsenic trichloride and of its solutions in various organic solvents have been investigated;[10] on admixture, the Raman frequencies of the solvent, for example benzene, carbon tetrachloride, methyl or ethyl alcohol, remain unchanged, but those of the arsenic trichloride are altered. The deviations are attributed to the polar character of the molecule and it is suggested that, for the frequencies of one component of a binary mixture to be altered by the other, the latter must have a considerable dipole moment, and in the former the linking between the parts of the molecule participating in active vibrations, in this case As Cl, must be weak. The constants of the $AsCl_3$ molecule calculated from the results agree with those derived from electron diffraction data. The free energies of formation of liquid and gaseous arsenic trichloride, at 25° C., are respectively −65,190 and −62,718 calories ± 500 to 1400 calories.[11] The value for the electron polarisation, $P_E = 30{\cdot}24$, has been derived from measurements of the refractive index, and it has been shown mathematically, both

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[1] Baxter and co-workers, *loc. cit.* See also Maier, *loc. cit.*

[2] Regnault, *loc. cit.*

[3] Guldberg, *Christiana Vid. Selsk.*, 1882, p. 20.

[4] Thomsen, *Ber.*, 1883, 16, 39. See also Berthelot, *Ann. Chim. Phys.*, 1877, [5], 15, 209; Berthelot and Louguinine, *Compt. rend.*, 1875, 81, 1011, 1017, 1072.

[5] Dumas, *Ann. Chim. Phys.*, 1828, [2], 38, 337.

[6] Haase, *Ber.*, 1893, 26, 1052; Biltz and Meinecke, *Zeitsch. anorg. Chem.*, 1923, 131, 1; Smith and Hora, *J. Amer. Chem. Soc.*, 1904, 26, 632; Besson, *Compt. rend.*, 1889, 109, 940; 1890, 110, 1258.

[7] Stiefelhagen, *Dissertation*, Berlin, 1905.

[8] Haagen, *Pogg. Annalen*, 1867, 131, 117; 1868, 133, 295.

[9] Macbeth and Maxwell, *J. Chem. Soc.*, 1923, 123, 370.

[10] Brodskii and Sack, *J. Chem. Physics*, 1935, 3, 449; Brodsku, Sack and Besugli,

from energy considerations[1] and the Raman and X-ray spectra,[2] that the stable form for the molecule is a three-sided pyramid with the arsenic atom at the apex, the distance between the arsenic and chlorine atoms being 2·20 A. The atomic radius of the arsenic is 1·21 A.

Liquid arsenic trichloride when anhydrous is a very poor conductor of electricity, the specific conductivity[3] at 0° C. being 11×10^{-7} mho. The solution of the chloride in liquid hydrogen sulphide conducts electricity[4] (see p. 108), as also do solutions in certain organic solvents. Thus, in ethyl ether[5] the conductivity is very small up to 40 per cent. of trichloride, but then increases to a maximum at 94 per cent. concentration: the temperature coefficient of the conductivity is negative at all concentrations. The decomposition potential of a 68·81 per cent. solution of arsenic trichloride in ether at 18° C. is 1·22 volts. On electrolysis, arsenic is quantitatively deposited at the cathode. From a systematic study[6] of the viscosity and conductivity of the solutions of concentrations from 25 to 100 per cent. $AsCl_3$ and over the temperature range 0° to 50° C., it has been shown that the compound $AsCl_3.(C_2H_5)_2O$ is formed and acts as the electrolyte. Similar investigations of solutions in monochloromethyl ether,[7] benzene,[8] nitrobenzene and pyridine[9] indicate the formation of the following compounds: $AsCl_3.CH_2Cl.O.CH_3$; $2AsCl_3.C_6H_6$; $AsCl_3.2C_6H_5NO_2$; $AsCl_3.C_5H_5N$ (see p. 108). The decomposition potential of the solution in nitrobenzene is 0·78 volt.[10] Viscosity measurements of solutions in anisole[11] indicate the formation of the compound $AsCl_3.C_6H_5OCH_3$, but the solutions are non-conducting.

Arsenic trichloride appears to be a good ionising solvent for binary salts, although cobalt iodide is an exception.[12] The dielectric constant[12] is 12·8. From measurements of the dielectric constants and densities of solutions in benzene, the dipole moment[13] of arsenic trichloride has been calculated to be $2·15 \times 10^{-18}$ e.s.u.; the value previously obtained by Bergmann and Engel[14] was $1·97 \times 10^{-18}$ e.s.u.

The dangerous physiological effects of arsenic trichloride are described in Chapter XI. The vapour is readily adsorbed by fibres such as hair and wool, and also by rubber.

Chemical Properties.—Arsenic trichloride vapour reacts with hydrogen when the mixture is subjected to an electric discharge, a brown deposit, thought to be a mixture of arsenic and a subchloride, being formed on the walls of the containing vessel.[15] The vapour also reacts with oxygen when a mixture of the two is passed through a tube

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[1] Bergmann and Engel, *Zeitsch. physikal. Chem.*, 1931, Abt. B, 13, 232, 247.

[2] Coster and Klamer, *Physica*, 1934, 1, 889.

[3] Walden, *Zeitsch. physikal. Chem.*, 1903, 43, 437; 1904, 46, 103; *Zeitsch. anorg. Chem.*, 1900, 25, 209. See also Biltz and Klemm, *ibid.*, 1926, 152, 276.

[4] Quam and Wilkinson, *Proc. Iowa Acad. Sci.*, 1925, 32, 324.

[5] Ussanovitsch, *Zeitsch. physikal. Chem.*, 1929, 140, 429; *J. Gen. Chem.* (*U.S.S.R.*), 1935, 5, 996.

[6] Terpugov, *J. Gen. Chem.* (*U.S.S.R.*), 1932, 2, 868.

[7] Terpugov, *ibid.*, 1934, 4, 235.

[8] Schulgina, *ibid.*, 1934, 4, 225.

[9] Kondratenko, *ibid.*, 1934, 4, 244, 246.

[10] Finkelstein, *Zeitsch. physikal. Chem.*, 1925, 115, 303.

[11] Terpugov, *J. Gen. Chem.* (*U.S.S.R.*), 1934, 4, 222. See also Ussanovitsch, *ibid.*, 1932, 2, 443.

[12] Walden, *loc. cit.*

[13] Smith, *Proc. Roy. Soc.*, 1932, A 136, 251, 256.

[14] Bergmann and Engel, *Zeitsch. physikal. Chem.*, 1931, Abt. B, 13, 232.

[15] Besson and Fournier, *Compt. rend.*, 1910, 150, 872.

heated to redness, an oxychloride and chlorine being produced.[1] Water in small quantity also produces the oxychloride; with more water arsenious oxide is precipitated, while with an excess of water arsenious and hydrochloric acids are formed, the heat of the reaction being as follows:[2]

$$\mathrm{AsCl_3 + Aq. = H_3AsO_3\ aq. + 3HCl\ aq. + 17{,}600\ calories}$$

The solution is similar to that obtained by dissolving arsenious oxide in aqueous hydrochloric acid. When the liquid is distilled, all the arsenic passes over into the distillate[3] and by this means the element may be separated from antimony and tin.

The trichloride reacts violently with fluorine to form the trifluoride.[4] Chlorine dissolves readily at low temperatures without reaction (see p. 110), the gas being expelled on warming.[5] Iodine also dissolves without reaction,[6] the solubility increasing with temperature, thus:

Temperature, ° C.	0	15	90
Grams Iodine per 100 grams $AsCl_3$.	8·42	11·88	36·89

Concentrated hydrochloric acid also dissolves the trichloride, about 100 g. of the latter dissolving in 1 litre of acid at 100° C.[7] Dissolution in hydriodic acid is accompanied by evolution of heat and the triiodide is formed.[8] Ethyl iodide reacts similarly.[9] Double decomposition reactions occur when arsenic trichloride is heated with phosphorus triiodide, stannic iodide or germanium iodide, the reactions being complete.[10] Similarly, potassium iodide heated with arsenic trichloride in a sealed tube at 240° C., and potassium bromide at 180° to 200° C., form respectively arsenic triiodide and tribromide.[11] Stannous chloride, added to the solution in hydrochloric acid, causes reduction to arsenic (see p. 29). Arsenic trichloride may be completely separated from germanium chloride by extraction with concentrated hydrochloric acid.[12] Ammonium, sodium and cobaltic chlorides react with arsenic trichloride to form additive compounds; with magnesium, zinc and chromic chlorides there is no reaction.[13]

Ammonia is rapidly absorbed by liquid arsenic trichloride to yield a pale yellow solid which is usually described[14] as arsenic tetrammino-trichloride, $AsCl_3.4NH_3$, but which Hugot[15] stated to be a mixture of

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[1] Berthelot, *Compt. rend.*, 1878, 86, 863.

[2] Thomsen, *Zeitsch. anorg. Chem.*, 1883, 16, 39.

[3] Dupasquier, *J. Pharm. Chim.*, 1841, [3], 27, 717.

[4] Moissan, "*Le fluor et ses composés*" (Paris, 1900), p. 190.

[5] Janowsky, *Ber.*, 1873, 6, 219; 1875, 8, 1636; Mayrhofer, *Annalen*, 1871, 158, 326.

[6] Sloan, *Chem. News*, 1881, 44, 203; 1882, 46, 194. *Cf.* Gramp, *Ber.*, 1874, 7, 1723.

[7] Treadwell and Mussler, *Helv. Chim. Acta*, 1922, 5, 818; Wallace and Penny, *Phil. Mag.*, 1852, [4], 4, 361.

[8] Hautefeuille, *Compt. rend.*, 1867, 64, 704.

[9] Köhnlein, *Annalen*, 1884, 225, 176.

[10] Karantassis, *Ann. Chim.*, 1927, 8, 71; *Compt. rend.*, 1933, 196, 1894.

[11] Snape, *Chem. News*, 1896, 74, 27; Bamberger and Philipp, *Ber.*, 1881, 14, 2643.

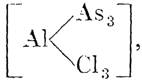
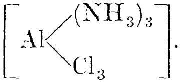
[12] Allison and Muller, *J. Amer. Chem. Soc.*, 1932, 54, 2833.

[13] Montignie, *Bull. Soc. chim.*, 1935, [5], 2, 1365.

[14] Persoz, *Ann. Chim. Phys.*, 1830, [2], 44, 320; Rose, *Pogg. Annalen*, 1841, 52, 62; Besson, *Compt. rend.*, 1889, 109, 940; 1890, 110, 1258.

[15] Hugot, *Compt. rend.*, 1895, 121, 206; 1904, 139, 54.

ammonium chloride and arsenic triamide. The product is readily decomposed; on heating, the substance completely volatilises, ammonia being first evolved;[1] on heating with water, ammonia, ammonium chloride and arsenious oxide are formed. Heating with concentrated sulphuric acid also causes decomposition. The addition of chloroplatinic acid to the aqueous solution does not cause precipitation of all the ammonia present.[2] Liquid ammonia also reacts with arsenic trichloride.[3] Hydroxylamine forms an addition compound.[4] A boiling alcoholic solution of the trichloride dissolves hydrazine hydrochloride, apparently forming a complex salt.[5] Nitrogen peroxide reacts to form nitrogen oxychloride and arsenic pentoxide.[6] There is no reaction with nitrogen sulphide.[7]

Phosphorus dissolves in arsenic trichloride on warming without reaction and is deposited on cooling.[8] If the mixture is heated in the presence of aluminium chloride at 130° to 150° C. for 40 minutes, a brownish-red compound of composition $AlAs_3Cl_3$ results,[9] from which, however, aluminium chloride can readily be removed by water or ammonia, leaving a residue of finely divided black arsenic. If the compound is heated to 190° C. in the absence of air, it turns black as arsenic trichloride and aluminium chloride distil off and a bright grey mixture of arsenic and arsenide remains. It has been suggested that the arsenic is co-ordinatively bound, and that the compound may be formulated  $\left[\mathrm{Al}\genfrac{}{}{0pt}{}{\diagup \mathrm{As}_3}{\diagdown \mathrm{Cl}_3}\right]$, analogous to the ammoniated compound  $\left[\mathrm{Al}\genfrac{}{}{0pt}{}{\diagup (\mathrm{NH}_3)_3}{\diagdown \mathrm{Cl}_3}\right]$. Phosphine reacts to produce a brown substance of indefinite character, possibly arsenic phosphide, AsP, but more probably a mixture containing the free elements.[10] Phosphorus trichloride, unlike the triiodide (see p. 106), causes reduction to arsenic,[11] as also do hypophosphorous and phosphorous acids,[12] while phosphorus pentachloride combines to form unstable double compounds[13] of composition $PCl_5.AsCl_3$ and $PCl_5.AsCl_5$. A solution of arsenic trichloride in nitrobenzene is reduced to arsenic by the action of yellow phosphorus, antimony or bismuth.[14]

Arsine reacts to yield arsenic, thus:[15]

$$AsH_3 + AsCl_3 = 2As + 3HCl$$

Arsenious oxide dissolves in the boiling trichloride to form arsenic oxychloride, AsOCl (see p. 109). Arsenic trisulphide yields thiochlorides.[16]

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[1] Pasteur, *J. Pharm. Chim.*, 1848, [4], 13, 395.

[2] Rose, *loc. cit.*

[3] Gore, *Proc. Roy. Soc.*, 1872, 20, 441; 1873, 21, 140; Hugot, *loc. cit.*

[4] Montignie, *Bull. Soc. chim.*, 1935, [5], 2, 1365.

[5] Ferratini, *Gazzetta*, 1912, 42, i, 138.

[6] Geuther, *J. prakt. Chem.*, 1873, [2], 8, 854.

[7] Davis, *J. Chem. Soc.*, 1906, 89, 1575.

[8] Davy, *Phil. Trans.*, 1812, 102, 169.

[9] Ruff and Staib, *Zeitsch. anorg. Chem.*, 1921, 117, 191; *cf.* Ruff, *Ber.*, 1901, 34, 1753.

[10] Besson, *Compt. rend.*, 1889, 109, 940; 1890, 110, 1258.

[11] Geuther, *loc. cit.*

[12] Janowsky, *Ber.*, 1873, 6, 219; 1875, 8, 1636; Engel, *Compt. rend.*, 1873, 77, 1543; Thiele, *Annalen*, 1891, 265, 55.

[13] Cronander, *Bull. Soc. chim.*, 1873, [2], 19, 499; *Ber.*, 1873, 6, 1466.

[14] Finkelstein, *Zeitsch. physikal. Chem.*, 1925, 115, 303.

[15] Janowsky, *loc. cit.*

[16] Ouvrard, *Compt. rend.*, 1893, 116, 1516.

Sulphur is unattacked at room temperature,[1] dissolves readily in hot arsenic trichloride and is deposited unchanged on cooling.[2] The reaction with liquid hydrogen sulphide has been investigated[3] at temperatures from -77° C. up to room temperature. Thiohydrolysis occurs and arsenious sulphide is precipitated immediately at all temperatures. The reaction differs from that with water, where the soluble acid is formed, the thio-acid not being produced. The specific conductivity of the saturated solution of arsenic trichloride in liquid hydrogen sulphide, after standing until equilibrium is attained, is $11{\cdot}51 \times 10^{-7}$ mho.[4] Gaseous hydrogen sulphide reacts with arsenic trichloride to give a yellow precipitate of a thiochloride, $As_4S_5Cl_2$, if the reactants are quite dry, but if water is present arsenious sulphide is precipitated.[5]

Selenium and tellurium are attacked at room temperature, arsenic being liberated and selenium monochloride or tellurium tetrachloride formed.[6]

Many carbon compounds, *e.g.* hydrocarbons, ketones, organic acids, bases and esters, dissolve in arsenic trichloride with formation of additive or complex compounds. The organic derivatives of arsenic are described in Volume XI, Part II, of this Series. Trialkyl arsines are formed by the addition of alkali to the double salts obtained by the interaction of zinc dialkyls and arsenic trichloride—

$$3ZnR_2 + 2AsCl_3 = 2R_3As + 3ZnCl_2$$

or by treating Grignard reagents with the trichloride :[7]

$$3RMgCl + AsCl_3 = R_3As + 3MgCl_2$$

Free arsenic is also produced owing to the reducing action of the arsine. If the tertiary arsine is heated with arsenic trichloride under pressure at a high temperature, the following reaction takes place—

$$R_3As + 2AsCl_3 = 3RAsCl_2$$

and similar products may be obtained by heating arsenic trichloride with mercury diaryls or with aryl mercuric chlorides :

$$R_2Hg + 2AsCl_3 = 2RAsCl_2 + HgCl_2$$
$$RHgCl + AsCl_3 = RAsCl_2 + HgCl_2$$

Additive compounds are formed with aniline, piperazine, hexamethylenetetramine and quinoline ;[8] with pyridine, the two compounds, $AsCl_3.C_5H_5N$ (m.pt. 138–9° C.) and $AsCl_3.2C_5H_5N$ (m.pt. 64° C.), have been isolated.[9] Addition of arsenic trichloride to dry 1 : 4-dioxan gives an oxonium compound, $(C_4H_8O_2)_3.2AsCl_3$ (m.pt. 62° C.).[10]

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[1] Montignie, *Bull. Soc. chim.*, 1936, [5], 3, 190.

[2] Davy, *loc. cit.*

[3] Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, 50, 258; Biltz and Keunecke, *Zeitsch. anorg. Chem.*, 1925, 147, 171; Ruff, *loc. cit.*

[4] Quam and Wilkinson, *Proc. Iowa Acad. Sci.*, 1925, 32, 324; *J. Amer. Chem. Soc.*, 1925, 47, 989; Ralston and Wilkinson, *loc. cit.*

[5] Ouvrard, *Compt. rend.*, 1893, 116, 1516; 117, 107.

[6] Montignie, *loc. cit.*

[7] See Dyke and Jones, *J. Chem. Soc.*, 1930, p. 2426. Also see Petzold, *Zeitsch. anorg. Chem.*, 1933, 214, 355, 365.

[8] Montignie, *Bull. Soc. chim.*, 1935, [5], 2, 1365. See also Schiff, *Compt. rend.*, 1863, 56, 1095; *Annalen*, 1864, 131, 116; Grossmann, *Zeitsch. physikal. Chem.*, 1907, 57, 545.

[9] Shirey, *J. Amer. Chem. Soc.*, 1930, 52, 1720; Gibson and others, *J. Chem. Soc*, 1930, p. 1710; Montignie, *loc. cit.*

[10] Doak, *J. Amer. Pharm. Assoc.*, 1934, 23, 541.

The trichloride dissolves in liquid cyanogen.[1] It combines with cyanogen bromide when a mixture of the two is slowly heated in an autoclave to 180° C., followed by cooling and keeping at 120° C. for one hour: [2] the product, of composition $AsCl_3.2BrCN$, decomposes on heating above 190° C. Arsenic trichloride reacts with potassium thiocyanate solution,[3] the latter being decomposed with liberation of ammonia, but no precipitate is produced, whereas both tin and antimony are precipitated as hydroxides under similar conditions; the reaction with excess of potassium thiocyanate may be used to effect a quantitative separation of these two metals from arsenic.

Boron bromide reacts with the trichloride thus: [4]

$$AsCl_3 + BBr_3 = BCl_3 + AsBr_3 + 25 \text{ calories}$$

Many metals when immersed in arsenic trichloride precipitate arsenic. With sodium, magnesium, zinc, aluminium, tin and lead, at the ordinary temperature, a coating of arsenic immediately forms on the metal and slows down the reaction;[5] at 100° C. the reaction is vigorous. With copper, plating occurs very slowly but the reaction takes place more rapidly on heating. With iron, cobalt, nickel, antimony, bismuth, cadmium, mercury, silver and gold, the action is only slight at temperatures up to 100° C. Platinum and molybdenum are not acted upon. In acid solution magnesium precipitates arsenic and liberates arsine; [6] cobalt [7] and nickel [8] yield arsenides. Aluminium in the presence of a little aluminium chloride behaves like phosphorus (see p. 107) and when heated with the trichloride at 130° to 150° C. produces the brownish-red arsenochloride, $AlAs_3Cl_3$, which with water yields arsenic and aluminium chloride.[9] Finely divided reduced silver heated with the trichloride in a sealed tube yields a product[10] of composition $7Ag.2AsCl_3$, which however is probably not a chemical entity; copper yields a similar product. A boiling solution of the trichloride in toluene is reduced by potassium with separation of arsenic.[11]

Rubidium and cæsium salts of composition $3RbCl.2AsCl_3$ and $3CsCl.2AsCl_3$ have been obtained in the form of trigonal crystals by mixing saturated solutions of the alkali chloride and of arsenious oxide in 20 per cent. hydrochloric acid and then adding concentrated hydrochloric acid.[12]

Arsenic Oxychloride (*Arsenyl Chloride*), $AsOCl$, may be obtained[13]

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[1] Centnerszwer, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 545.

[2] Oberhauser, *Ber.*, 1927, 60, B, 1434.

[3] Miquel, *Ann. Chim. Phys.*, 1877, [5], 11, 352; Dalietos, *Praktika* (*Akad. Athenon*), 1931, 6, 92; *Chem. Zentr.*, 1931, ii, 1687; *Zeitsch. anorg. Chem.*, 1934, 217, 381.

[4] Tarible, *Thesis*, Paris, 1899; *Compt. rend.*, 1901, 132, 206.

[5] Fischer, *Pogg. Annalen*, 1826, 9, 261; Kahlenberg and Steinle, *Trans. Amer. Electrochem. Soc.*, 1923, 44, 493; *cf.* Montignie, *loc. cit.*

[6] Seubert and Schmidt, *Annalen*, 1892, 267, 237.

[7] Ducelliez, *Compt. rend.*, 1908, 147, 424.

[8] Granger and Didier, *Bull. Soc. chim.*, 1900, [3], 23, 506; Vigouroux, *Compt. rend.*, 1908, 147, 426; Arrivaut, *ibid.*, 1931, 192, 1238.

[9] Ruff and Staib, *Zeitsch. anorg. Chem.*, 1921, 117, 191.

[10] Hilpert and Herrmann, *Ber.*, 1913, 46, 2218. Montignie (*loc. cit.*) states that a compound $3Ag.AsCl_3$ is formed at ordinary temperatures.

[11] Vournazos, *Zeitsch. anorg. Chem.*, 1913, 81, 264; 1927, 164, 263.

[12] Wheeler, *ibid.*, 1893, 4, 455; *Amer. J. Sci.*, 1893, [3], 46, 88; Ducloux, *Anal. Assoc. Quim. Argentina*, 1921, 9, 215.

[13] Wallace and Penny, *Phil. Mag.*, 1852, [4], 4, 361; Wallace, *ibid.*, 1858, [4], 16, 358; Hurtzig and Geuther, *Annalen*, 1859, 111, 172.

in solution by passing hydrogen chloride into an aqueous suspension of arsenious oxide, or by boiling together molecular proportions of arsenic trichloride and arsenious oxide, the process being continued in each case until the oxide is dissolved. On gently distilling the solution until it begins to foam, the oxychloride separates as a brown viscous mass; if the distillation is carried out at a higher temperature the deposit has the composition $AsOCl.As_2O_3$. The monohydrate, $AsOCl.H_2O$, may be obtained by allowing a solution of the trichloride in water to crystallise slowly. It separates in stellate aggregates. With ammonium chloride the oxychloride reacts to form the double compound $AsOCl.2NH_4Cl$.

Arsenic Pentachloride (?), $AsCl_5$.—By the action of chlorine on arsenic trichloride at a low temperature Baskerville and Bennett [1] obtained a greenish-yellow liquid which they believed to be arsenic pentachloride. Pure solid arsenic trichloride was placed in a vessel surrounded by carbon dioxide snow and saturated with chlorine, the temperature being −33° C. The liquid approximated in composition to $AsCl_5$. It was soluble in carbon disulphide and in ether, and the ether solution, on evaporation at −30° C., left yellow crystals which readily decomposed with slight rise in temperature. The formation of this compound has not been confirmed, however, and its existence is doubtful.

At −23° C. almost sufficient chlorine is absorbed by arsenic trichloride to produce the pentachloride,[2] but there is no evidence of compound formation and the chlorine may be expelled by warming or by passing a current of air through the liquid. If arsenic trichloride is saturated with chlorine at 0° C. the mixture, on cooling, solidifies at about −30° C. with considerable diminution in volume.[3] If more chlorine is passed into the liquid before solidification occurs, there is further absorption and the resulting yellow liquid may be cooled below −60° C. without freezing. If this liquid is brought into contact with water, the excess of chlorine is rapidly evolved and the aqueous solution contains tervalent arsenic only, so that again there is no evidence of the formation of the pentachloride. Solid arsenic trichloride at −35° C. is not acted upon by liquid chlorine, and if the mixture is gently heated until the former melts, the two liquids mix without reaction.

The freezing point curve of mixtures of chlorine and arsenic trichloride is smooth and shows no indication of combination.[4]

ARSENIC AND BROMINE.

Only one bromide of arsenic has been isolated; this is the tribromide, $AsBr_3$, and an investigation of the system $AsBr_3$–Br_2 gives no indication of the formation of a higher bromide. The freezing point curve shows a eutectic point at −34° C. and 81 atomic per cent. of bromine.[5]

Arsenic Tribromide, $AsBr_3$, was first obtained in 1828 by Sérullas,[6] who added dry powdered arsenic in small quantities to

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[1] Baskerville and Bennett, *J. Amer. Chem. Soc.*, 1902, 24, 1070. See also Dumas, *Ann. Chim. Phys.*, 1828, [2], 38, 337; Capitaine, *J. Pharm. Chim.*, 1839, [3], 25, 524.

[2] Sloan, *Chem. News*, 1881, 44, 203; 1882, 46, 194.

[3] Besson, *Compt. rend.*, 1889, 109, 940; 1890, 110, 1258.

[4] Biltz and Meinecke, *Zeitsch. anorg. Chem.*, 1923, 131, 1; Smith and Hora, *J. Amer. Chem. Soc.*, 1904, 26, 632. See also Biltz and Jeep, *Zeitsch. anorg. Chem.*, 1927, 162, 32.

[5] Biltz and Jeep, *Zeitsch. anorg. Chem.*, 1927, 162, 32.

[6] Sérullas, *Ann. Chim. Phys.*, 1828, [2], 38, 318.

bromine contained in a glass retort until no further action occurred. On contact with the bromine the arsenic inflamed brilliantly, and on distillation of the product, arsenic tribromide condensed in the receiver in the form of prismatic crystals. A more convenient method [1] is to pass bromine vapour over an excess of arsenic contained in a hard glass tube. By repeated distillation of the product, very pure arsenic tribromide may be obtained.[2]

The bromide may also be prepared (1) by adding arsenic powder to a mixture of carbon disulphide and bromine (2 : 1 by weight) and agitating the liquid until decolorised; [3] on evaporation, crystals of the bromide remain; (2) by heating a mixture of arsenious oxide, potassium bromide and acetic acid at 100° C.; [4] (3) by heating a mixture of arsenious oxide and sulphur in a current of bromine vapour.[5]

Physical Properties.—Arsenic tribromide is a solid at ordinary temperatures, crystallising in beautiful colourless rhombic prisms [6] which possess a feebly aromatic odour [7] and are stable in dry air. In the presence of moisture slight fuming occurs. The crystals melt sharply at 31° C.[8] The density [9] at 15° C. is 3·66; after fusion and resolidification, the product has density 3·54 at 25° C.[10] The density of the liquid at various temperatures may be obtained from the expression [11]

$$D_4^\theta = 3{\cdot}3972 - 0{\cdot}002822(\theta - 25) + 0{\cdot}00000248(\theta - 25)^2$$

The surface tension, σ, and molecular surface energy, μ, of the liquid at various temperatures have been found [12] to be:

t, ° C.	49·6	74·5	90·0	121·0	149·6	165·0	179·7
σ, dynes per cm.	49·6	46·6	44·8	41·0	38·2	37·0	36·1
μ, ergs per sq. cm.	1029·5	980·5	947·8	884·1	835·6	815·6	801·6

The parachor is 253·5.

The molecular volume at the ordinary temperature [13] is 111 c.c., and the ratio of this value to the sum of the atomic volumes of the constituent elements [14] is 1·21. From measurements of density and coefficient of expansion at −194° C. the molecular volume at 0° Abs. has been calculated [15] to be 76·1. The molecular weight determined by

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[1] Jory, *J. Pharm. Chim.*, 1900, [6], 12, 312.

[2] Baxter and co-workers, *J. Amer. Chem. Soc.*, 1933, 55, 1054.

[3] Nicklès, *J. Pharm. Chim.*, 1862, [3], 41, 143.

[4] Vournazos, *Compt. rend.*, 1918, 166, 526.

[5] Oddo and Giachery, *Gazzetta*, 1923, 53, i, 56.

[6] The crystal structure has been investigated, see Gregg and others, *Trans. Faraday Soc.*, 1937, 33, 852; Braekken, *Chem. Zentr.*, 1936, i, 961.

[7] Walden, *Zeitsch. anorg. Chem.*, 1902, 29, 373; *Zeitsch. physikal. Chem.*, 1903, 43, 335; 1904, 46, 104.

[8] Tolloczko, *Chem. Zentr.*, 1901, I, 989; *Bull. Acad. Cracovie*, 1901, p. 1; Tolloczko and Meyer, *Kosmos*, 1910, 35, 64; Jager, *Zeitsch. anorg. Chem.*, 1917, 101, 174; Pushin and Löwy, *ibid.*, 1926, 150, 167.

[9] Bodecker, *Thesis*, Leipzig, 1860.

[10] Retgers, *Zeitsch. physikal. Chem.*, 1893, 11, 342.

[11] Jager, *loc. cit.*

[12] Henley and Sugden, *J. Chem. Soc.*, 1929, p. 1058.

[13] Rabinowitsch, *Ber.*, 1925, 58, 2790.

[14] Saslavsky, *Zeitsch. anorg. Chem.*, 1925, 146, 315.

[15] Biltz and co-workers, *ibid.*, 1932, 203, 277.

ebullioscopic and cryoscopic methods[1] with bromine as solvent agrees with the formula $AsBr_3$. The solution in bromine is a non-conductor of electricity; on the other hand, the solution in liquid sulphur dioxide is a conductor,[2] the equivalent conductivity of 1 mole of $AsBr_3$ in 101·4 and 925·3 litres of the solvent being respectively 0·249 and 2·347. The solution in liquid hydrogen sulphide also conducts electricity.[3] Arsenic tribromide itself may be used as a solvent in molecular weight determinations; the cryoscopic constant has been given values[4] ranging from 189 to 206. It behaves similarly to arsenic trichloride in forming mixed halides with halides of the elements of Groups IV and V[5] (see p. 103). The ionising power of arsenic tribromide is somewhat less than that of the trichloride. The liquid boils at 221° C. (760 mm.);[6] at lower pressures the following temperatures have been observed: 109° C. (20 mm.),[7] 92° C. (14 mm.).[8]

The heat of fusion is 8·93 calories per gram.[9] The heat of formation is:[10]

$$\text{As(cryst.)} + 3\text{Br(liq.)} = \text{AsBr}_3\text{(cryst.)} + 45{,}500 \text{ calories}$$

The following values for the refractive index for sodium, lithium and thallium light, respectively, have been obtained:[11]

Temperature, ° C.	n_{Na}	n_{Li}	n_{Tl}
24	1·7849	1·7716	1·7983
30	1·7815	1·7678	1·7939

The value for the electron polarisation,[12] P_E, is 41·97, and the stable form of the molecule is a three-sided pyramid (*cf.* p. 105). The dipole moment[13] is $1·66 \times 10^{-18}$ e.s.u. The dielectric constant[14] at 20° C. is 3·4, and at 35° C. 9·3.

Arsenic tribromide dissolves in many organic liquids,[15] such as carbon disulphide, methylene iodide[16] and benzene; in the last named the decomposition voltage is 0·50 volt.[17] In solutions in diethyl ether[18] the electrical conductance at 18° C. rapidly increases with increase in the bromide concentration up to 95 per cent., after which it quickly falls to

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[1] Finkelstein, *Zeitsch. physikal. Chem.*, 1923, 105, 10.

[2] Walden, *Zeitsch. physikal. Chem.*, 1903, 43, 335; 1904, 46, 103; *Zeitsch. anorg. Chem.*, 1902, 29, 373.

[3] Quam and Wilkinson, *Proc. Iowa Acad. Sci.*, 1925, 32, 324.

[4] Walden, *loc. cit.*; Garelli and Bassani, *Atti R. Accad. Lincei*, 1901, [5], 10, i, 255; Tolloczko, *Bull. Acad. Cracovie*, 1901, p. 1; Raeder, *Zeitsch. anorg. Chem.*, 1933, 210, 145.

[5] Raeder, *loc. cit.*

[6] Walden, *loc. cit.*

[7] Jager, *loc. cit.*

[8] Walden, *loc. cit.*

[9] Tolloczko and Meyer, *Kosmos*, 1910, 35, 64; "*Radiszewsky's Festband*," 1910, p. 641.

[10] Berthelot, *Compt. rend.*, 1878, 86, 859.

[11] Borgstrom, *Bull. comm. géol. Finlande*, 1929, 87, 58.

[12] Bergmann and Engel, *Zeitsch. physikal. Chem.*, 1931, Abt. B, 13, 232, 247.

[13] Bergmann and Engel, *loc. cit.* See also Malone and Ferguson, *J. Chem. Physics*, 1934, 2, 99.

[14] Walden, *loc. cit.*

[15] See Pushin, *Bull. Soc. chim. Yougoslav.*, 1936, 7, 73.

[16] Retgers, *Zeitsch. physikal. Chem.*, 1893, 11, 342.

[17] Finkelstein, *loc. cit.*

[18] Ussanovitsch, *Zeitsch. physikal. Chem.*, 1926, 124, 427; 1929, 140, 429. See also Nicklès, *Compt. rend.*, 1859, 48, 837.

the value for the pure bromide. For high concentrations the temperature coefficient is positive, but decreases with falling concentration and for concentrations below 75 per cent. is negative. This effect does not appear to be due to interaction between solvent and solute; if the molecular conductivity is calculated with reference to the bromide as electrolyte, the conductivity-concentration curve shows two maxima, but if the ether is taken as the electrolyte a normal curve results. For solutions in methylethyl ether[1] the specific conductivity and its temperature coefficient are at a maximum for solutions containing the two components in equimolecular proportions, indicating the formation of the compound $AsBr_3.CH_3OC_2H_5$. The solution of arsenic tribromide in anisole is non-conducting.[2] The tribromide also dissolves in boron bromide [3] and in phosphoryl chloride.[4]

Arsenic tribromide is itself a good solvent for certain halides.[5] The following freezing points and densities at 15° C. of saturated solutions have been determined:

Solute.	Freezing Point, ° C.	Density.
$SbBr_3$	47	3·685
SbI_3	40	3·720
ZnI_2	15	3·73

Arsenic triiodide also dissolves, the saturated solution at 15° C. having density 3·661. Other soluble halides are potassium bromide, anhydrous ferric and aluminium chlorides [6] and tetramethyl ammonium iodide; but the iodides of rubidium, cadmium, manganese and cobalt, also mercuric and stannic iodides, and cobalt and stannic bromides, are insoluble or only very slightly soluble in arsenic tribromide. The liquid also dissolves phosphoryl bromide and, very slightly, ammonium thiocyanate. In the mixed solutions of halides, the components may react chemically (*cf.* p. 106), but such is not always the case; for example, with antimony tribromide a continuous series of solid solutions is formed.[7]

Chemical Properties.—Arsenic tribromide reacts with water in small quantity to form the oxybromide, AsOBr; in larger quantity arsenious and hydrobromic acids are formed.[8] One part of the tribromide dissolves in three parts of boiling water,[9] and on cooling the solution deposits crystals of arsenious oxide. The tribromide is less soluble in aqueous hydrobromic acid. It dissolves in bromine, but does not combine

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[1] Ussanovitsch and Rozentreter, *J. Gen. Chem.* (*U.S.S.R.*), 1932, 2, 864; Ussanovitsch and Terpugov, *Zeitsch. physikal. Chem.*, 1933, 165, A, 49.

[2] Ussanovitsch, *J. Gen. Chem.* (*U.S.S.R.*), 1932, 2, 443.

[3] Tarible, *Compt. rend.*, 1901, 132, 206.

[4] Cady and Taft, *J. Physical Chem.*, 1925, 29, 1057.

[5] Walden, *loc. cit.*

[6] The following ternary systems have been investigated electrochemically: $AsBr_3$–$AlBr_3$–C_6H_6 and $AsBr_3$–$AlBr_3$–C_2H_5Br. Compound formation is doubtful. See Plotnikov and Jakubson, *Mem. Inst. Chem. Ukrain. Acad. Sci.*, 1935, 2, 99; 1936, 3, 131.

[7] Pushin and Lowy, *Zeitsch. anorg. Chem.*, 1926, 150, 167.

[8] Sérullas, *Ann. Chim. Phys.*, 1828, [2], 38, 318; Wallace, *J. prakt. Chem.*, 1859, [1], 78, 119.

[9] Wallace and Penny, *Phil. Mag.*, 1852, [4], 4, 361.

with it (see p. 110). Oxygen reacts with arsenic tribromide vapour at red heat to form arsenious oxide, arsenic oxybromide, AsOBr, and free bromine.[1] Hydrogen sulphide passed over the tribromide at 150° C. yields the bromosulphide, AsSBr (m.pt. 118° C.).[2] Ammonia gas is absorbed by arsenic tribromide to yield a pale yellow solid of composition [3] $AsBr_3.3NH_3$; if the bromide is in benzene solution the product, according to Landau,[4] is a white precipitate of composition $2AsBr_3.7NH_3$. The latter can be crystallised from hot absolute alcohol; it is soluble in cold water, but the solution decomposes on warming, as also does the dry ammine, losing ammonia. The pale yellow triammino-compound also decomposes on heating yielding, at 300° C., nitrogen, ammonium bromide and arsenic. Organic amines react similarly with arsenic tribromide. Phosphine [5] yields hydrogen bromide and arsenic phosphide, AsP.

Carbon tetrachloride is partially transformed into the bromide [6] by prolonged heating with arsenic tribromide at 150° to 200° C. Acetylene, in the presence of aluminium chloride or bromide as catalyst, forms the bromovinylarsines [7] $(CHBr : CH)AsBr_2$ and $(CHBr : CH)_2AsBr$, and with an increased quantity of the catalyst [8] $(CHBr : CH)_3As$. When a mixture of arsenic tribromide and cyanogen bromide is slowly heated in an autoclave to 180° C. and then cooled and kept for an hour at 120° C., the additive compound $AsBr_3.2BrCN$ is formed. It is decomposed when heated above 190° C.

Certain compounds with metals and metallic salts have been described. Thus, by heating finely divided silver or copper with arsenic tribromide in a sealed tube, substances of composition $3Ag.AsBr_3$ and $7Cu.2AsBr_3$ have been isolated,[9] the latter probably containing uncombined copper in solid solution. Similar products are obtained by the action of arsenic vapour on silver bromide or cuprous bromide at 500° C. Double decomposition reactions occur when arsenic tribromide is heated with stannic iodide [10] or germanium iodide,[11] the reactions being complete. Sodium azide [12] reacts with the tribromide in acetone or methyl alcohol solution to form a white compound of composition $Na_8[AsBr_3(N_3)_8]$. Rubidium and cæsium salts of composition $3RbBr.2AsBr_3$ and $3CsBr.2AsBr_3$ have been obtained [13] in the form of trigonal crystals by a method analogous to that used for the corresponding chlorides (see p. 109).

Arsenic Oxybromide (*Arsenyl Bromide*), AsOBr, may be prepared[14] by dissolving arsenious oxide in molten arsenic tribromide and distilling off excess of the latter; the remaining liquid separates into two layers, the upper one consisting of the oxybromide and the lower one a mixture

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[1] Berthelot, *Compt. rend.*, 1878, 86, 859.
[2] van Valkenburgh and Davis, *J. Colo.-Wyo. Acad. Sci.*, 1929, 1, No. 1, 51.
[3] Besson, *Compt. rend.*, 1890, 110, 1258.
[4] Landau, *Thesis*, Berlin, 1888.
[5] Besson, *loc. cit.*
[6] Gustavson, *Ann. Chim. Phys.*, 1874, [5], 2, 200.
[7] See this Series, Vol. XI, Part II, p. 56.
[8] Schmidt, *Bull. Soc. chim.*, 1927, [4], 41, 49.
[9] Hilpert and Herrmann, *Ber.*, 1913, 46, 2218.
[10] Karantassis, *Ann. Chim.*, 1927, 8, 71.
[11] Karantassis, *Compt. rend.*, 1933, 196, 1894.
[12] Vournazos, *Zeitsch. anorg. Chem.*, 1927, 164, 263.
[13] Wheeler, *ibid.*, 1893, 4, 451; *Amer. J. Sci.*, 1893, [3], 46, 88.
[14] Wallace and Penny, *loc. cit.* See also Sérullas, *loc. cit.*; Berthelot, *loc. cit.*

of the oxybromide and excess of arsenious oxide. The oxybromide sets to a brown buttery mass on cooling. The hydrated form, $2AsOBr.3H_2O$, may be obtained by evaporation over sulphuric acid of a solution of the tribromide in aqueous hydrobromic acid, or by the action of bromine on aqueous phenylarsinic acid.[1] It is decomposed on heating, yielding arsenious oxide and the tribromide. If the solution in dilute aqueous hydrobromic acid is cooled, a compound of composition $2AsOBr.3As_2O_3.12H_2O$ is obtained.[2]

Arsenic and Iodine.

The existence of two iodides has been established: arsenic diiodide, AsI_2 or As_2I_4, analogous to the corresponding phosphorus compound, and arsenic triiodide, AsI_3, which is the more important. In addition, a moniodide, AsI, and a pentiodide, AsI_5, have been described. The binary system As–I has been investigated,[3] but the freezing point curve gives no indication of the formation of either of the two latter iodides. The oxyiodide of arsenic, AsOI, has not been isolated.[4]

Arsenic Moniodide (?), AsI, was described [5] as a chocolate-brown substance resulting from the action of an excess of arsine on an alcoholic solution of iodine, and Schiff [6] claimed to have obtained it by the addition of boiling alcohol to arsenic trianilino-triiodide. The identity of these products has not been confirmed.

Arsenic Diiodide, AsI_2 or As_2I_4, may be prepared [7] by heating a mixture of arsenic (1 part) and iodine (2 parts) in a sealed tube at 250° C. for about 8 hours. After cooling, the tube is placed vertically and the dark red product again heated to 150° C., when the diiodide sublimes into the upper part of the tube; or the diiodide may be extracted from the product by means of carbon disulphide and crystallised from the latter in an atmosphere of carbon dioxide. A modification of this method was employed by Karantassis,[8] who heated a finely powdered mixture of the elements in a sealed retort from which the air had been displaced by pure dry hydrogen; the mixture was kept at the boiling point for two hours and pure arsenic diiodide was obtained from the product by careful distillation. The diiodide is also formed by heating in a sealed tube at 150° to 190° C. a mixture of arsenic and arsenic triiodide in carbon disulphide solution; [9] the reaction is not complete, however, some triiodide remaining undecomposed.

Arsenic diiodide crystallises in thin prisms of a deep cherry-red colour. In air they are rapidly oxidised [9] and become opaque and brick-red. The crystals, when purified by careful distillation, melt at 130° C., but the undistilled product, as generally prepared, melts at about 120° C. owing to the presence of dissolved arsenic.[10] The boiling point[10] in an atmosphere of hydrogen or carbon dioxide is 375° to 380° C.

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[1] Michaelis, *Ber.*, 1877, 10, 625.

[2] Wallace, *Phil. Mag.*, 1858, [4], 16, 358.

[3] Jager and Doornbosch, *Zeitsch. anorg. Chem.*, 1912, 75, 261.

[4] Plisson, *Ann. Chim. Phys.*, 1828, [2], 39, 265; Zinno, *Repert. Pharm.*, 1873, [3], 22, 385; Wegner, *Annalen*, 1874, 174, 129. Also see p. 119.

[5] Gopel, *Arch. Pharm.*, 1849, [2], 60, 129, 141; Meurer, *ibid.*, 1847, [2], 52, 1.

[6] Schiff, *Compt. rend.*, 1863, 56, 1096.

[7] Bamberger and Philipp, *Ber.*, 1881, 14, 2644.

[8] Karantassis, *Bull. Soc. chim.*, 1925, [4], 37, 853.

[9] Bamberger and Philipp, *loc. cit.*

[10] Karantassis, *loc. cit.* *Cf.* Frank, *Thesis*, Berne, 1912, p. 19.

The crystals dissolve in carbon disulphide and ebullioscopic measurements indicate[1] that the molecular formula is As_2I_4; they also dissolve in ether, alcohol and chloroform. When exposed to air, these solutions darken in colour owing to the formation of the triiodide, and the diiodide cannot be recovered by evaporation owing to complete decomposition. Boiling acetic anhydride also dissolves the crystals but, on cooling, a yellow substance which appears to contain a derivative of the triiodide separates. The diiodide is also decomposed by pyridine with separation of arsenic, the triiodide being found in solution.

The addition of water or alkali to the crystals, or to the alcoholic solution, causes blackening, the triiodide and arsenic being formed; the decomposition is accelerated by warming. Concentrated sulphuric acid and fuming nitric acid have little action in the cold but, on heating, iodine vapour is expelled, and with the latter acid, iodic and arsenic acids are formed.

Arsenic Triiodide, AsI_3, may be prepared by gently heating a mixture of the elements.[2] The combination is accompanied by evolution of heat and, on cooling, the triiodide can be obtained by crystallisation from carbon disulphide or xylol. The elements may be heated under a reflux condenser in the presence of a solvent such as carbon disulphide, ether or chloroform, until the colour due to free iodine has disappeared[3] (the removal of the latter is accelerated by having a small excess of arsenic present);[4] the solution is then decanted and cooled, and the triiodide which separates is recrystallised. The product, which is a pharmaceutical preparation, should contain not less than 99 per cent. AsI_3.

Many other methods of preparation have been employed. For example, the triiodide is formed when arsenious oxide,[5] or a mixture of this oxide with sulphur,[6] is heated in iodine vapour; or when arsenious oxide is heated with iodine,[7] hydriodic acid,[8] a mixture of potassium iodide and acetic acid,[9] or a mixture of potassium iodide and potassium hydrogen sulphate.[10] When arsenic disulphide and iodine, in the proportions $1As_2S_2 : 3I_2$, are heated together, arsenic triiodide is formed.[11] When arsenic trisulphide is fused with an excess of iodine, the product is soluble in carbon disulphide and the solution on evaporation deposits arsenic triiodide, then a sulphiodide and finally sulphur; with excess of sulphide the product is the sulphiodide, AsS_2I. If a solution of iodine in carbon disulphide is added to arsenic di- or tri-sulphide, the triiodide and sulphur are formed. The triiodide is also produced when a mixture of the trisulphide and mercuric iodide is heated;[12] when hydriodic

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[1] Hewitt and Winmill, *J. Chem. Soc.*, 1907, 91, 962.

[2] Sérullas and Hottot, *J. Pharm. Chim.*, 1828, [2], 14, 49, 164, 598; Plisson, *ibid.*, 1828, [2], 14, 46, 592; Thomson, *Lancet*, 1838, p. 176; *Repert. Pharm.*, 1839, [2], 17, 360; Bette, *Annalen*, 1840, 33, 349; Gopel, *Arch. Pharm.*, 1849, [2], 60, 129, 141.

[3] Nicklès, *J. Pharm. Chim.*, 1862, [3], 41, 147; Bamberger and Philipp, *Ber*, 1881, 14, 2644.

[4] Fisk, *Amer. Mineral.*, 1930, 15, 263.

[5] Brame, *Compt. rend.*, 1851, 33, 579.

[6] Oddo and Giachery, *Gazzetta*, 1923, 53, i, 56.

[7] Richter, *Apoth. Ztg.*, 1911, 26, 728, 742.

[8] Babcock, *Arch. Pharm.*, 1877, [3], 9, 455.

[9] Vournazos, *Zeitsch. anorg. Chem.*, 1927, 164, 263.

[10] Gopel, *loc. cit.*

[11] Schneider, *J. prakt. Chem.*, 1886, [2], 34, 505; 1887, [2], 36, 498.

[12] Duflos, *Pharmakol. Chem.*, Breslau, 1842, p. 153.

acid reacts with arsenic trichloride;[1] and when arsine acts upon iodine, either dry[2] or in alcoholic solution.[3]

Commercial arsenic triiodide frequently contains considerable impurity, and samples prepared from arsenic and ether solutions of iodine have been found to contain up to 30 per cent. of free arsenic owing to the premature stopping of the reaction.[4] This may be avoided by preparing the iodide by the action of potassium iodide on arsenious oxide in hydrochloric acid solution. Free iodine may also be present as an impurity.[5] The following procedure, recommended by Paternosto,[6] yields a product of 99·8 per cent. purity: 2 g. of arsenious oxide are treated with 30 c.c. of hydrochloric acid (dens. 1·19) and to the product is added a solution made by heating together 10 g. of potassium iodide and 10 c.c. of water. The mixture is allowed to react for about 5 minutes and the resulting precipitate is collected on asbestos and dried in a vacuum. The arsenic triiodide is extracted by repeated washing with carbon disulphide; when the latter is removed by evaporation in a vacuum, fine hexagonal plates of the pure triiodide remain. The pure product may also be obtained[7] by refluxing a mixture containing 26·5 g. of arsenious oxide, 5·27 g. of sulphur and 102 g. of iodine at 200° C. for 14 hours, subsequently extracting at 90° C. with mustard oil and recrystallising rapidly from carbon disulphide by cooling in liquid air.

Physical Properties.—Arsenic triiodide crystallises in orange-red hexagonal plates. The structure[8] is a layer lattice and there are six molecules per unit cell. The iodine atoms are in hexagonal close packing, each arsenic atom being surrounded by six iodine atoms. The distances of closest approach of iodine atoms are 4·28 and 4·13 A., and of arsenic and iodine about 2·97 A. The dimensions of *a* and *c* are, respectively, 7·187 and 21·394 A. When fused or sublimed, the colour is brick-red.[9] The crystals are odourless and of density[10] 4·374. The melting point,[11] according to Madson and Krauskopf,[12] is 138·6° C.; the boiling point[13] is 394° to 414° C.

There are indications that the triiodide exists in two polymeric forms. The ordinary red form, when sublimed in a vacuum, gives a yellow sublimate which slowly changes to orange-red at ordinary temperatures; the yellow form is also obtained by cooling to a low temperature by means of solid carbon dioxide and alcohol, the product changing to the

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[1] Hautefeuille, *Compt. rend.*, 1867, 64, 704; *Bull. Soc. chim.*, 1867, [2], 7, 189. See also Bamberger and Philipp, *loc. cit.*

[2] Husson, *Compt. rend.*, 1868, 67, 56. See also Jacobsen, *Ber.*, 1887, 20, 1999; 1888, 21, 2546.

[3] Meurer, *Arch. Pharm.*, 1847, [2], 52, 1.

[4] Bryant, *Pharm. J.*, 1933, 130, 175.

[5] Husa, *J. Amer. Pharm. Assoc.*, 1931, 20, 1024.

[6] Paternosto, *Rev. fac. cien. quim. La Plata*, 1930, 7, 43.

[7] Madson and Krauskopf, *Rec. Trav. chim.*, 1931, 50, 1005.

[8] Brackken, *Zeitsch. Krist.*, 1930, 74, 67; 75, 574; Heyworth, *ibid.*, 1930, 75, 574; *Phys. Review*, 1931, [2], 38, 351, 1792; Gregg and others, *Trans. Faraday Soc.*, 1937, 33, 852; *cf.* Friedlander, *Zeitsch. Kryst. Min.*, 1879, 3, 214.

[9] Bette, *Annalen*, 1840, 33, 349.

[10] Schroder, "*Dichtigkeitsmessungen*," Heidelberg, 1873.

[11] See also Sloan, *Chem. News*, 1882, 46, 194; Carnelley, *J. Chem. Soc.*, 1884, 45, 409; Horiba and Inouye, *Report Osaka Celebration*, Kyōtō, 1927, p. 279; Jager and Doornbosch found the f.pt. to be 140·7° C., see p. 120.

[12] Madson and Krauskopf, *loc. cit.*

[13] Carnelley and Williams, *J. Chem. Soc.*, 1880, 37, 125.

orange form as the temperature rises. The two forms possess different vapour pressures, and for this reason the results obtained in determinations of the vapour pressure of the solid are irregular and discordant. The following values for the vapour pressure of the orange form have been obtained :[1]

Temp., ° C. .	11·35	34·73	85·60	130·98	145·79	160·39	182·41
Vap. press., mm.	0·000	0·015	0·203	0·706	1·158	2·777	7·891

The $T/\log p$ curve shows the melting point of this variety to be about 144° C. The molecular heat of vaporisation is 19,200 calories.

The vapour density[2] is 16·1 (air = 1) corresponding to the molecular formula AsI_3 (15·8), but the vapour, which is yellow, generally contains the products of thermal decomposition (see below). The heat of formation, according to Berthelot,[3] is $(As, 3I_{gas})$ 28,800 calories and $(As, 3I_{solid})$ 12,600 calories. From measurements of density and coefficient of expansion at low temperatures the molecular volume at 0° Abs. has been calculated[4] to be 93·2, a value which corresponds with that similarly derived for the molecular volume of phosphorus triiodide.

Arsenic triiodide is soluble in carbon disulphide, alcohol, ether, chloroform, benzene, toluene and the xylenes.[5] The solution in carbon disulphide gradually darkens owing to absorption of oxygen and liberation of iodine.[6] With alcohol at 150° C. ethyl iodide is formed. In methylene iodide[5] the triiodide dissolves to the extent of 17·4 parts of AsI_3 in 100 parts of solvent at 12° C. The dipole moment in various solvents has been determined.[7]

The triiodide dissolves freely in water to give a yellow solution with an acid taste and reaction.[8] The concentrated solution is fairly stable and the triiodide may be recovered by distilling off the solvent.[9]

In the solid and liquid forms, arsenic triiodide is a non-conductor of electricity, but some of its solutions are weak conductors;[10] thus, a saturated solution in allyl isothiocyanate at 60° C. has a conductivity of $1{\cdot}4 \times 10^{-4}$ mho.

Chemical Properties.—When heated above 100° C. arsenic triiodide dissociates slowly into its elements; above its melting point this decomposition becomes more rapid.[11] In air, the products are arsenic, arsenious oxide and iodine, and the action proceeds slowly even below 100° C. and is rapid at 200° C.; at higher temperatures the triiodide burns with a pale blue flame.[12] Heated in an atmosphere of nitrogen in

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[1] Horiba and Inouye, *Report Osaka Celebration*, Kyōtō, 1927, p. 279.

[2] Wurtz, "*Dictionnaire de Chimie*," Paris, 1868, I, 463.

[3] Berthelot, *Compt. rend.*, 1878, 86, 862.

[4] Biltz, Sapper and Wunnenberg, *Zeitsch. anorg. Chem.*, 1932, 203, 277.

[5] Retgers, *ibid.*, 1893, 3, 344.

[6] Schneider, *J. prakt. Chem.*, 1886, [2], 34, 505, 1887, [2], 36, 498.

[7] Malone and Ferguson, *J. Chem. Physics*, 1934, 2, 99.

[8] Plisson, *Ann. Chim. Phys.*, 1828, [2], 39, 265; *J. Pharm. Chim.*, 1828, [2], 14, 46, 592.

[9] Bamberger and Philipp, *Ber.*, 1881, 14, 2644; Richter, *Apoth. Ztg.*, 1911, 26, 728, 742.

[10] Mathews, *J. Physical Chem.*, 1906, 9, 641.

[11] Madson and Krauskopf, *Rec. Trav. chim.*, 1931, 50, 1005.

[12] Berthelot, *loc. cit.*

a sealed tube, it dissociates appreciably at 165° C. Although the aqueous solution appears to be stable and does not darken on exposure to air, if allowed to evaporate slowly in an open vessel crystals of an oxyiodide, $2AsOI.3As_2O_3.12H_2O$,[1] remain. It has been shown,[2] however, that a very dilute aqueous solution of arsenic triiodide is almost completely hydrolysed and is essentially a solution of arsenious acid and hydriodic acid in equilibrium with a small quantity of the triiodide. In freshly prepared solutions this equilibrium is reached within a few minutes, and for an approximately 0·1N-solution the *p*H value is 1·1, which is the same as that of a 0·1N-solution of hydriodic acid. In the presence of an excess of hydriodic acid spontaneous evaporation leaves only the triiodide.[1] Solutions in many organic solvents, for example acetone, benzene, glacial acetic acid, are unstable,[3] decomposing with liberation of iodine, as in the case of carbon disulphide solutions mentioned above ; the decomposition is accelerated by the presence of water or oxygen, but is apparently unaffected by light. When sulphur is added to a solution of arsenic triiodide in carbon disulphide, orange-coloured crystals of a sulphiodide of melting point 104° C. and of composition $AsI_3.3S_8$ separate ; [4] this compound crystallises in the trigonal system, the dimensions of the unit cell,[5] which contains one molecule, being $a = 14·2$, $b = 24·6$ and $c = 4·48$ A.

Dry hydrogen sulphide in the cold does not react with arsenic triiodide. At 200° C. some of the latter volatilises and is carried away by the gas stream, while the remainder is converted [6] to a crystalline iodosulphide, As_2S_5I. The aqueous solution with hydrogen sulphide yields a precipitate of arsenic trisulphide.[7]

Ammonia is slowly absorbed by the triiodide and a voluminous yellow substance is produced [8] which, if kept over sulphuric acid, loses ammonia until the composition corresponds with the tetrammino-triiodide, $AsI_3.4NH_3$. At 0° C. more ammonia can be absorbed to yield the dodecammino-compound, $AsI_3.12NH_3$. If ammonia is passed into a solution of the triiodide in benzene or ether, a voluminous white precipitate, of composition $2AsI_3.9NH_3$, is formed.[9] The existence of these ammines as definite compounds has not been established.[10] With phosphine, arsenic phosphide is produced :

$$AsI_3 + PH_3 = AsP + 3HI$$

Cryoscopic and ebullioscopic measurements indicate that the halides of phosphorus, arsenic, antimony, titanium and tin readily undergo reciprocal interaction with interchange of halogen atoms and that mixed halides can be formed [11] (see p. 103). Melting and freezing point curves are, however, generally of the eutectic or mixed crystal types, without

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[1] Wallace and Penny, *Phil. Mag.*, 1852, [4], 4, 361.

[2] Cocking, *Quart. J. Pharm. Pharmacol.*, 1929, 2, 409; Husa, *J. Amer. Pharm. Assoc.*, 1930, 19, 1287.

[3] Madson and Krauskopf, *loc. cit.*

[4] Auger, *Compt. rend.*, 1908, 146, 477.

[5] Hertel, *Zeitsch. physikal. Chem.*, 1931, 15, B, 51.

maxima corresponding with compound formation, and the mixed halides have not been isolated. The molecular weight of the triiodide calculated from the lowering of the freezing point of arsenic tribromide[1] agrees with the formula AsI_3, but in antimony trichloride the result is abnormal, the molecular weight being about half the normal value. This has been attributed[2] to the reaction

$$3SbCl_3 + AsI_3 = AsCl_3 + 3SbCl_2I$$

resulting in an increased number of solute molecules. The system AsI_3–PI_3 has been investigated;[3] an isodimorphous series of crystals is formed with a transition point at 73·5° C. According to Karantassis,[4] double decomposition occurs between arsenic triiodide and stannic chloride, but there is no reaction between the triiodide and phosphorus trichloride. With stannic iodide,[5] arsenic triiodide forms a eutectic at 106·2° C. the composition of which is $1SnI_4 : 0{\cdot}6936AsI_3$. By mixing together a saturated solution of lead iodide and a boiling saturated solution of arsenic triiodide in hydriodic acid, the compound $3PbI_2.AsI_3.12H_2O$ has been obtained.[6] This is decomposed by water, alcohol or ether. The anhydrous salt may be obtained by heating at 45° C.

Donovan's solution, *Liquor Arseni et Hydrargyri Iodidi,* a well-known pharmaceutical preparation, is an aqueous solution containing about 1 per cent. each of mercuric iodide and arsenic triiodide. Owing to hydrolysis of the latter (see p. 119) the solution, which is colourless or very pale yellow, consists essentially of arsenious acid, mercuric hydrogen iodide, $HHgI_3$, and hydriodic acid, the pH of the freshly prepared solution being[7] 1·2 to 1·3. On keeping, the solution deteriorates owing to oxidation to arsenic acid, both by the air in contact with the solution and by the oxidising action of iodine and water; free iodine appears in the solution only after a long time. The oxidation is accelerated by light, that of wavelengths between 3200 and 4600 A. being most active.[8] Therefore, in dispensing, the solution should be freshly prepared or, if not used immediately, kept in a well-filled amber bottle, preferably in a refrigerator. The stability of the solution may be increased[9] by replacement of the air in the bottle by an inert gas, replacement of 25 per cent. of the water by honey or syrup, the addition of calcium carbonate or of sodium bicarbonate to ensure the most favourable pH (6·5 to 7·5), or by the addition of 0·4 per cent. of terpin hydrate or of an excess of potassium iodide.

Arsenic triiodide forms unstable complexes with the alkali halides.[10] The rubidium and caesium compounds,[11] $3RbI.2AsI_3$ (pseudo-hexagonal, $a : c = 1 : 2{\cdot}486$) and $3CsI.2AsI_3$ (hexagonal bipyramids, $a : c = 1 : 2{\cdot}488$), are formed in an analogous manner to the corresponding chlorides

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[1] Walden, *Zeitsch. anorg. Chem.*, 1902, 29, 376.

[2] Tolloczko, *Bull. Acad. Cracovie*, 1901, p. 1.

[3] Jäger and Doornbosch, *Zeitsch. anorg. Chem.*, 1912, 75, 261.

[4] Karantassis, *Ann. Chim.*, 1927, 8, 71.

[5] Wasiléeff, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1076; 1917, 49, 88.

[6] Mosnier, *Ann. Chim. Phys.*, 1897, [7], 12, 374.

[7] Husa, *J. Amer. Pharm. Assoc.*, 1931, 19, 1287.

[8] Husa and Enz, *ibid.*, 1930, 19, 328.

[9] Schulze, *ibid.*, 1926, 15, 464; Husa and Enz, *loc. cit.*; *ibid.*, 1930, 19, 1228; Husa, *loc. cit.*; *ibid.*, 1932, 21, 211; Cocking, *Quart. J. Pharm. Pharmacol.*, 1929, 2, 409; Morton and Bateson, *ibid.*, 1934, 7, 447; Acton, *Amer. J. Pharm.*, 1930, 102, 132.

[10] Nicklès, *J. Pharm. Chim.*, 1862, [3], 41, 147.

[11] Wheeler, *Zeitsch. anorg. Chem.*, 1893, 4, 455.

(see p. 109). Sodium azide reacts with arsenic triiodide in methyl alcohol or acetone solution [1] to form the compound $Na_8[AsI_3(N_3)_8]$.

Boron tribromide dissolves in arsenic triiodide.[2]

Arsenic Pentiodide (?), AsI_5.—When a mixture of arsenic and iodine in the requisite proportions is heated in an atmosphere of carbon dioxide in a sealed tube at 150° C., a brown crystalline product is obtained.[3] The crystals, which melt at 70° C. and have density 3·93, are soluble in water, carbon disulphide, alcohol, ether and chloroform. The solution in carbon disulphide yields, when allowed to crystallise, a mixture of arsenic triiodide and iodine. The latter is readily lost from the pentiodide, and heating at 100° C. in nitrogen in a sealed tube brings about the decomposition. Like the triiodide, the pentiodide dissolves boron tribromide.[4]

The fusion curve of mixtures of arsenic and iodine shows no evidence of the formation of a pentiodide, but there is a eutectic, of freezing point 71·5° C., which has the approximate composition of this substance.[5] The absorption spectrum of the solution in carbon disulphide is similar to that of a mixture of the triiodide and iodine.[3]

A series of **double compounds** of arsenious oxide and the iodides of bivalent light and heavy metals has been described.[6] The compounds are obtained in crystalline form by saturating hot moderately concentrated solutions of the iodides with arsenious oxide and allowing to cool. The following have been prepared :

$BeI_2.3As_2O_3.8H_2O$
$Mg(\text{or Ca or Sr})I_2.3As_2O_3.12H_2O$
$BaI_2.3As_2O_3.9H_2O$
$ZnI_2.3As_2O_3.10H_2O$
$Mn(\text{or Fe or Co})I_2.4As_2O_3.12H_2O$
$NiI_2.4As_2O_3.10H_2O$
Also $AlI_3.6As_2O_3.18(?)H_2O$

These compounds resemble in properties the arsenites of the metals, the characters of the iodides being suppressed. They are moderately stable in dry air but tend to become oxidised on keeping. With the exception of the magnesium compound they are slightly soluble in water, the solution apparently containing a complex salt with a simple metallic cation. When heated with water they undergo partial decomposition into the iodide and arsenious oxide.

Similar compounds of the alkali metals are also known, but except in the case of the *lithium* salt,[7] $LiI.2As_2O_3.3H_2O$, prepared as above, the crystals are anhydrous. Thus a solution containing ammonium dihydrogen arsenite, ammonium iodide and arsenious oxide yields [8] hexagonal prisms of composition $NH_4I.2As_2O_3$, stable up to 180° C. The *sodium* salt, $NaI.2As_2O_3$, crystallises from a hot solution containing sodium iodide and arsenious oxide or sodium arsenite; it is decom-

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[1] Vournazos, *Zeitsch. anorg. Chem.*, 1927, 164, 263.
[2] Tarible, *Thesis*, Paris, 1899; *Compt. rend.*, 1901, 132, 206.
[3] Sloan, *Chem. News*, 1882, 46, 194.
[4] Tarible, *loc. cit.*
[5] Quercigh, *Atti Accad. Ist Veneto*, 1912, 70, ii, 667.
[6] Weinland and Gruhl, *Arch. Pharm.*, 1917, 255, 467.
[7] Weinland and Gruhl, *loc. cit.*
[8] Rüdorff, *Ber.*, 1886, 19, 2668; 1888, 21, 3051.

posed by water. Two *potassium* salts are known: $KI.As_2O_3$, which separates in yellow plates from a hot solution containing potassium iodide and arsenic triiodide in dilute hydriodic acid,[1] and also $KI.2As_2O_3$, prepared analogously to the sodium salt.[2] The *rubidium* salt, $RbI.As_2O_3$, and the *cæsium* salt, $CsI.As_2O_3$, have been obtained by the method used for the corresponding potassium salt.[1]

A complex *bromiodide* of mercury and arsenic, $AsHg_6Br_{12}I_3$, presumably the arsenic salt of the acid $HI(HgBr_2)_2$, prepared by addition of hydriodic acid to a benzene solution of mercuric bromide, has been obtained.[3]

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[1] Wheeler, *Amer. J. Sci.*, 1893, [3], 46, 88; *Zeitsch. anorg. Chem.*, 1893, 4, 457.

[2] Rudorff, *loc. cit.*; Schiff and Sestini, *Annalen*, 1885, 228, 72.

[3] Vournazos, *J. prakt. Chem.*, 1933, 136, 41.

CHAPTER VII.

THE LOWER OXIDES OF ARSENIC AND THE METALLIC ARSENITES.

Two well-defined oxides are known: arsenious oxide, As_2O_3, and arsenic pentoxide, As_2O_5. The former is the most important compound of arsenic, being the form in which the element is most used. A suboxide, As_2O, and a tetroxide, As_2O_4, have been described, but the existence of neither as a pure compound has been established.

Arsenic Suboxide (?), As_2O, was considered by Berzelius [1] to constitute the superficial dark brown film which forms on arsenic owing to oxidation. Retgers [2] stated that the brown deposit which accompanies the mirror formed by sublimation of commercial arsenic was the suboxide. It was looked upon [3] as an intermediate product in the oxidation of arsenic, but the material so described was undoubtedly a mixture of arsenic and arsenious oxide [4] or, in some cases, merely the amorphous variety of arsenic.

Arsenious Oxide (*Arsenic Trioxide*), As_2O_3 or As_4O_6, also known as *white arsenic, arsenic, flowers of arsenic* and *arsenious acid*, was known to the Arabian alchemists of the twelfth century. Roger Bacon described it [5] as a white, transparent substance resulting from the sublimation of a mixture of orpiment and iron filings. It is obtained commercially in large quantities by the roasting of arseniferous minerals, a method of production known from early times, the product being called *Huttenrauch* (furnace smoke) by Basil Valentine. When arsenopyrite (mispickel), FeAsS, is heated in air below red heat, arsenic sulphide vapour is liberated, but at a higher temperature arsenious oxide and sulphur dioxide are evolved, leaving a residue of ferric oxide, sulphide and arsenate. Likewise, löllingite produces arsenious oxide at a bright red heat. But although some arsenic ores are thus treated for arsenic alone, almost the whole of the world's supply is produced as a by-product in the treatment of ores for gold, copper, lead and tin, etc.

In 1914 the annual world production of white arsenic was about 10,000 tons. Germany was the foremost producer, but the production of the United States and Canada was of increasing importance; England, which in the prosperous days of Cornish tin mining had produced even more than Germany, was still an important producer. In recent years the annual production has expanded until, since 1933, it has reached more than

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[1] Berzelius, *Ann. Chim. Phys.*, 1811, [1], 80, 9; 1817, [2], 5, 179; 1819, [2], 11, 237.

[2] Retgers, *Zeitsch. anorg. Chem.*, 1893, 4, 403; see also von Bonsdorff, *L'Inst.*, 1835, 3, 99.

[3] Mitchell, *Amer. J. Sci.*, 1831, [1], 19, 122.

[4] Geuther, *Annalen*, 1887, 240, 217. See also Thomson, *Ann. Chim. Phys.*, 1815, [1], 93, 289; Buchner, *Rep. fur Pharm.*, 1825, 21, 28.

70,000 tons,[1] the lead being taken by Sweden and the United States. The outputs for 1933 and 1934 of the principal countries concerned are shown in the following table.[1] The available figures do not distinguish between crude and refined white arsenic, such division being practically impossible, for what is designated "crude arsenic" in some countries contains as much as 98 per cent. As_2O_3 and compares favourably with the refined product exported from other sources.

WORLD PRODUCTION OF WHITE ARSENIC, 1933–34, IN METRIC TONS.

Country.	1933.	1934.
Australia	1,804	2,289
Belgium-Luxemburg Economic Union .	2,579	3,554
Brazil	322	322
Canada	666	747
France	6,886	7,508
Germany	2,662	2,752
Japan	2,375	2,734
Mexico	4,697	7,860
Sweden	38,446 *	28,618 *
Turkey	762 *	6,596 *
United Kingdom	123 †	188 †
United States	10,702	14,173

* Expressed as arsenic content of ore.
† White arsenic and arsenic soot.

Sweden, which produced virtually no arsenic prior to 1926, has rapidly become the dominant producer, and the smelting works and electrolytic refineries recently erected at Boliden on the Gulf of Bothnia[2] are able to deal with 400,000 tons of ore per annum; they produce refined copper, gold, silver and white arsenic. The ore used is a mixture of chalcopyrite, arsenopyrite and iron pyrites containing only 2 per cent. of copper, small quantities of gold and silver, and some lead, zinc and antimony. The arsenic content averages nearly 11 per cent. and the annual production is now more than 40,000 tons—more than world requirements. This production on such an unprecedented and, at present, unmarketable scale of so toxic a substance presented an interesting problem both from the economic and metallurgical points of view. At first the crude arsenical fume was rendered innocuous by mixing with cement and water and allowing the mixture to harden before dumping,[3] or the condensed product was placed in large concrete cylinders and sunk in deep water in the Gulf of Bothnia. This method of disposal, however, proved too expensive and the product is therefore stored in huge concrete structures.

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[1] See van Sielen and Gerry, "*Minerals Yearbook,*" *U.S. Bureau of Mines*, 1936, p. 500.

[2] Palén, *Eng. and Min. J.*, 1932, 133, No. 6, 339; Tyler and Gerry, "*Minerals Yearbook,*" *U.S. Bureau of Mines*, 1932–33, p. 323; Sielen and Gerry, *loc. cit.*

[3] Lindblad, *American Patents*, 1822103 (1931), 1729351 (1929); *Swedish Patent*, 74722 (1932).

In the preliminary roast the arsenic is almost completely removed from the ore, less than 1 per cent. remaining in the calcines. The gases are cooled below 150° C., first in large chambers of sheet iron equipped with air-cooled jackets, where about one-third of the arsenious oxide condenses, the rest being caught in Cottrell "treaters" of the plate type.[1] These are chambers packed with vertical collecting plates of corrugated iron; the gas flow is horizontal across the face of the plates and the latter are cleaned by tapping with "knockers," whereupon the condensed dust falls into hoppers. From these, the dust passes in closed cars or by screw-conveyors to a belt-conveyor which runs in an underground tunnel to an elevator which carries the powder to the top of the arsenic storage into which it is discharged through slots in the roof.

In the United States[2] about 90 per cent. of the white arsenic produced is recovered as a by-product in the smelting of copper ores, the remainder being obtained from lead, gold and iron concentrates. No ores are now mined directly for arsenic, the above sources being sufficient to satisfy existing demands. The chief producing states are Montana, where arsenic occurs chiefly as *enargite*, and Utah, where the deposits contain *arsenopyrite* and *scorodite*. The roaster plants yield flue dusts containing about 20 per cent. of As_2O_3. Lead "bag-house dust" carries from 30 to 40 per cent. As_2O_3. The dust is smelted in a reverberatory furnace, producing a matte, and the gases are passed through a hot Cottrell "treater" maintained at a temperature which precipitates the dust but allows the arsenical fume to pass on to a cold Cottrell "treater" where it is condensed, yielding a product containing 70 per cent. As_2O_3. This crude product is resublimed until the desired colour and purity are obtained, and in the final stages reverberatory type furnaces with iron hearths, heated both below and above, are employed and smokeless fuel is used in order to prevent contamination of the product with soot. The fumes are condensed in "kitchens," which are long chambers divided into compartments, and the white arsenic finally obtained contains 99·9 per cent. As_2O_3.[3] This constitutes *refined white arsenic*, but crude white arsenic, "black dust" and "treater dust" are also marketable products. Part of the latter is made directly into sodium arsenate or "weed-killer" (see p. 159).

In Cornwall and Devon the ores used contain arsenopyrite mixed with iron and copper pyrites, tin ore, zinc blende, galena, etc. Before roasting, the ores are separated as far as possible by hand, and tinstone is removed by washing the finely powdered material. The roasting is conducted in a reverberatory furnace having a revolving floor over which a number of scrapers are fixed. The ore, which contains 10 to 30 per cent. As, is introduced through a hopper on to the floor, which revolves once every 12 minutes or so. It is heated to dull redness for

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[1] See Hayward, "*Outline of Metallurgical Practice*," van Nostrand, 1929, p. 58, for description and sectional diagrams of Cottrell "treaters."

[2] Tyler and Petar, *Electrochem. Soc.* (Preprint), 1932, 61, 431; Gerry and Meyer, *Bur. Min.*, "*Mineral Resources of U.S.*," 1931, i, 9; Tyler and Gerry, "*Minerals Yearbook*," 1932–33; Hayward, "*Outline of Metallurgical Practice*," van Nostrand, 1929, p. 319.

[3] For methods of roasting arsenical ores to form arsenates, see Lindblad, *American Patents*, 1729351 (1929), 1763435 (1930); Coolbaugh and Read, *American Patent*, 1597018 (1926). For further methods of procedure, see Doremus, *Trans. Amer. Electrochem. Soc.*, 1919, 35, 187; Williams, *Eng. Min. J.*, 1920, 110, 671; Young, *ibid.*, 1924, 117, 757; Bassett and Sadtler, *American Patent*, 1528004 (1925); Tafel and Lampe, *Metall u. Erz*, 1935, 32, 183.

about 10 hours and the arsenious oxide, with some sulphur and carbon, collects in the flues and condensing chambers as dark grey *arsenic soot*. This is refined by recalcination with smokeless fuel and condensed in zigzag chambers (of which there are several types), the product of the first chamber being reground and recalcined. In the other chambers crystalline white arsenic collects and this is ground and passed through leather pipes into casks under conditions which prevent escape. About 60 per cent. of the arsenic in the ores is thus recovered, the remainder being lost in the slimes formed during the early treatment.

Special methods of treatment are frequently necessary in order to purify the crude oxide or flue dust from the less volatile antimony oxide and also from metallic and other constituents. A flue dust containing up to 6 per cent. of antimony, if volatilised in a tube furnace in a slow current of air and condensed in baffled flues maintained at about 350° C., gives in the zone nearest the furnace a vitreous deposit containing a small amount of arsenious oxide and most of the antimonious oxide, and beyond a crystalline deposit of arsenious oxide of high purity.[1] Purification may also be accomplished [2] by heating the dust under pressure at 150° C. with water, dilute sulphuric acid or dilute alkali solutions; on cooling, after concentration, the pure arsenious oxide crystallises, and the deposition may be assisted by stirring the solution in the presence of a large amount of powdered arsenious oxide. Another method [3] for removing antimony oxide consists in converting the arsenic to the trichloride, which is then repeatedly shaken with concentrated hydrochloric acid, in which antimony trichloride is more soluble than the arsenic compound. The latter may then be hydrolysed to the oxide by slowly adding to a considerable quantity of boiling water. Lead and cadmium may be removed by heating with alkali solution to about 200° C. under pressure.[4] The arsenic and lead pass into solution and the latter is precipitated by passing in carbon dioxide. The arsenious oxide is then crystallised from the alkali and any alkali hydroxide removed by hydrolysis.

Arsenious oxide may be precipitated from acid solutions containing arsenic acid by treatment with reducing agents,[5] for example, by passing sulphur dioxide under pressure into the agitated liquid. Precipitation may be assisted by concentration or cooling, or by addition of finely divided arsenious oxide to the well-stirred solution.

The removal of small quantities of arsenic from metals and ores is a commercial problem which may be mentioned at this point. The Harris process of softening lead,[6] used in several refineries, is based on the principle that such impurities as arsenic, antimony and tin may easily be oxidised and in the presence of certain alkali salts can be converted into arsenates, antimonates and stannates. Certain fluxes, such as sodium nitrate, sodium hydroxide, sodium chloride or lead oxide, are added to the molten lead, the presence of an oxidising agent and an alkali salt being essential. The alkaline slag obtained is fused [7] and

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[1] Read, *Ind. Eng. Chem.*, 1928, 20, 97; *American Patent*, 1681496 (1928).

[2] Norddeutsche Affinerie, *British Patent*, 368316 (1930). See also Schopper, *American Patent*, 1921706 (1933), and Gardner, *American Patent*, 1755985 (1930).

[3] Foulk and Horton, *J. Amer. Chem. Soc.*, 1929, 51, 2416.

[4] Kubel, *German Patent*, 510750 (1928).

[5] Norddeutsche Affinerie, *British Patent*, 372189 (1932), addition to 368316 (1930).

[6] Winter, *Eng. Min. J.*, 1928, 125, 725, 809, 893.

[7] Hall, *American Patent*, 1747709 (1930).

poured in a thin stream into a saturated solution of sodium chloride containing sufficient sodium hydroxide to give a liquid of density 1·4. The mixture is agitated at 90° C. and the hot alkali arsenate solution separated by decantation from the insoluble residue of sodium stannate and antimonate. On cooling, the solution deposits trisodium orthoarsenate. Another method[1] of extracting the sodium arsenate from the alkaline slag is to digest the crushed slag with cold water, which dissolves out most of the stannate; the residue is then leached with hot water, which dissolves all the arsenate and the remaining stannate, and this solution, when concentrated and cooled, deposits the arsenate. Arsenical tin may be treated in a similar manner;[2] the molten metal is mixed with sodium hydroxide and chloride and small quantities of sodium nitrate added from time to time. The slag, containing sodium arsenate, is skimmed off and the latter recovered by boiling with water and evaporation of the clear solution.

From iron and manganese ores traces of arsenic may be eliminated[3] by heating at a temperature above 500° C. in an atmosphere containing carbon dioxide mixed with certain reducing gases, such as hydrogen, carbon monoxide or hydrocarbons, of such composition that the ores are reduced to lower oxides, but not allowing the formation of the metals or carbides; the arsenic is expelled as arsenious oxide. To eliminate arsenic from tungsten ore the latter may be roasted, or free sulphur may be added and the mixture heated to above the boiling point of sulphur and sufficiently high to volatilise the major portion of the arsenic present.

Arsenic-bearing ores or materials may be mixed with carbonaceous material and ignited in a current of air under low pressure in order to volatilise the arsenious oxide.[4] Other methods of de-arsenising depend on converting the element into volatile sulphide[5] or, in the case of metals, into some compound, such as calcium arsenide, insoluble in the molten metal;[6] or again, finely ground ores may be agitated with carbon disulphide until the arsenic compounds are dissolved.[7]

Sulphur may be freed from arsenic by treating it in the molten state with compounds, such as lime or sodium sulphide, which react to form compounds insoluble in the sulphur and which may be separated by settling and filtration;[8] or the sulphur may be treated in the vapour or liquid state with chlorine or sulphur dichloride in excess, to form arsenic chloride, which may be removed by distillation and by scrubbing with air or an inert gas under reduced pressure.[8] Other methods consist in

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[1] Heberlein, *American Patent*, 1779272 (1930). Perkins, Hanson and O'Harra (*American Patent*, 1756007 (1930)) give a method for extracting as calcium arsenate.

[2] Harris, *English Patents*, 257023 (1925), 273440 (1926). See also Little, *American Patent*, 1670307 (1928); Fitzpatrick and Elford, *Proc. Australasian Inst. Mining Met.*, 1930, 78, 81.

[3] Vereinigte Stahlwerke A.-G., *French Patent*, 730749 (1932); Selivanov and others, *Chemical Abstracts* (*Amer.*), 1932, 26, 5044.

[4] Hills, *American Patent*, 1713127 (1929); Kirmse and Schopper, *American Patent*, 1718825 (1929).

[5] Grondal, *Swedish Patent*, 68506 (1929); Palén, *Swedish Patent*, 68610 (1929); Cheluishev, *Tzvetnuie Metal.*, 1931, 6, 1225; *Chimie et Industrie*, 1932, 27, 1081.

[6] Skorchelletti and Shultin, *Soobshcheniya Vsesoyuznogo Inst. Metal.*, 1931, Nos. 3 and 4, 67. For elimination from copper, see Eddy, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, p. 104.

[7] Sanders, *American Patent*, 1581475 (1926).

[8] Levy, *British Patents*, 350573–4 (1930); *French Patents*, 712945–6 (1931); *German Patent*, 576251 (1933).

treating sulphur vapour with a molten alkali sulphide or polysulphide, or with alkali or alkali carbonate which, with sulphur, forms sulphides; or again, the sulphur may be digested with a solution of ammonia, ammonium sulphide or ammonium carbonate, preferably under pressure at 120° to 130° C.[1]

The principle of flotation has been applied to the extraction of arsenic concentrates from residual sands obtained in the treatment of gold ores.[2] The sands contained about 5·8 per cent. of arsenic in the form of small grains of arsenopyrite, associated with pyrites and some quartz and felspars. The best results, whereby 90 per cent. of the arsenic was recovered, were obtained with the following flotation agents in acidulated medium: (1) thiocarbanilide (in solution in *o*-toluidine) with turpentine, (2) the same reagent containing xanthate, (3) the same reagent with xanthate and pine oil.[3]

Polymorphism and Physical Properties of Arsenious Oxide.

Two distinct crystalline varieties of white arsenic are well known, namely, the octahedral (α-) form and the prismatic (β-) form.[4] The existence of a third crystalline (γ-) form has been suggested by Smits and Beljaars (*vide infra*). An amorphous form of the oxide also occurs as vitreous white arsenic. The conditions of formation of the α-, β- and amorphous varieties may be demonstrated[5] by heating either the octahedral or the vitreous form in a sealed tube fixed vertically, the temperature being maintained at about 400° C. at the lower end and at about 200° C. near the top. The oxide sublimes and condenses in the cooler upper part of the tube as the octahedral form, in the hot lower part as the vitreous form, and in the middle region as the prismatic form. When the octahedral crystals are heated, some volatilisation occurs at about 100° to 125° C. and, as the temperature rises, they sublime without melting; under the pressure of its own vapour, however, fusion occurs at about 272° C. (26·1 mm.),[6] and if the temperature is maintained at a somewhat higher level, starlike masses of the prismatic form gradually appear.[7] This change of the octahedral to the prismatic variety is extremely slow, several days being required for completion; in the presence of moisture, however, which acts as an accelerator, the change has been observed after heating for a few hours at 100° C. The melting point of the prismatic crystals is approximately 315° C.

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[1] I.C.I., *French Patent*, 737664 (1932).

[2] Truslevich, *Tzvetnuie Metal.*, 1932, p. 492; *Brit. Chemical Abs.*, B, 1933, p. 1062; *Chemical Abs.* (*Amer.*), 1933, 27, 4503.

[3] For methods of removing arsenic from sulphide roasting gases, see Klencke, *German Patent*, 533232 (1929); Ikebe and Otani, *Japanese Patent*, 90844 (1931); Pouthier, *Génie civil*, 1931, 99, 263; from sulphuric acid, see Lang and Muller, *German Patent*, 542781 (1929), Weinstock, *German Patent*, 578034 (1933). Also see *British Patents*, 349472 (1929), 349715 (1930); *Belgian Patent*, 374288 (1930).

[4] Smits and Beljaars, in their original papers, designate the prismatic as the α-form and the octahedral as the β-form.

[5] Debray, *Bull. Soc. chim.*, 1864, [2], 2, 9.

[6] Smits and Beljaars, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, 34, 1141. This temperature was obtained from the intersection of vapour pressure curves of solid and liquid. See also Rushton and Daniels, *J. Amer. Chem. Soc.*, 1926, 48, 384. For temperature-pressure fusion curves for the octahedral and vitreous modifications, see Tammann and Batz, *Zeitsch. anorg. Chem.*, 1926, 156, 94.

[7] Welch and Duschak, "*The Vapour Pressure of Arsenic Trioxide*," Washington, 1915. These authors gave 251° C. for the m.pt. of octahedral arsenious oxide.

The relation between the octahedral and prismatic modifications has not yet been satisfactorily elucidated. The former is the stable form at ordinary temperatures and the latter at higher temperatures; the transition point according to Rushton and Daniels is 250° C. and according to Smits and Beljaars 200° C., but the prismatic form is persistent at much lower temperatures and the change from octahedral to prismatic may be monotropic. Interesting information has been obtained from measurements of the vapour pressure of the oxide. The following values have been obtained:

Temp., ° C. . .	60–61	81–86	101–105	117–124	119–126	149–152
Vap. Press.[1] (mm.) .	$2{\cdot}4 \times 10^{-7}$	$2{\cdot}5 \times 10^{-5}$	$4{\cdot}6 \times 10^{-4}$	$1{\cdot}9 \times 10^{-3}$	$2{\cdot}2 \times 10^{-3}$	$2{\cdot}6 \times 10^{-2}$

Temp., ° C. . . .	129	153·5	165
Vap. Press.[2] (mm.). .	0·00	0·01	0·027

Temp., ° C. . . .	240·8	253·1	268·6	290·9	306·8
Vap. Press.[3] (mm.). .	6·3	12·2	24·4	65·4	100·6

According to Welch and Duschak,[4] the last set of results refers to the vitreous modification, the following being the values for the octahedral form, which is unstable at the given temperatures:

Temp., ° C.. .	100	120	140	160	180	200	240
Vap. Press. (mm.)	0·000266	0·00180	0·01035	0·0473	0·186	0·653	5·96

and for the vitreous form:

Temp., ° C. . .	260	280	300
Vap. Press. (mm.) .	15·7	38·5	89·1

Rushton and Daniels,[5] from vapour pressure determinations of both solid and liquid over the range 220° to 520° C., derived the following equations:

$$\text{For the octahedral form,} \quad \log p = -(6670/T) + 13{\cdot}728$$
$$\text{For the liquid form,} \quad \log p = -(2722/T) + 6{\cdot}513$$

The latter equation holds for any sample above 315° C.

Smits and Beljaars [6] investigated the vapour pressure between 240° and 380° C. and found the following values. The oxide was prepared by repeated sublimation at 320° C. under reduced pressure, followed by heating at 200° C. for 6 to 8 hours. Each sample was maintained at the temperature indicated for 20 minutes.

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[1] Smellie, *J. Soc. Chem. Ind.*, 1923, 42, 466T.
[2] Niederschulte, "*Ueber den Dampfdruck fester Korper*," Erlangen, 1903.
[3] Stelzner, "*Ueber den Dampfdruck fester Körper*," Braunschweig, 1901.
[4] Welch and Duschak, *loc. cit.*
[5] Rushton and Daniels, *loc. cit.*
[6] Smits and Beljaars, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, 34, 1141, 1318.

Phase:	Octahedral Crystals (α).			
Temp., ° C.	239·8	253·2	264·8	270·0
Vap. Press. (mm.)	4·5	9·8	18·3	23·4

Phase:	Liquid.					
Temp., ° C.	273·4	293·7	307·4	318·9	333·2	368·1
Vap. Press. (mm.)	24·9	43·0	59·9	77·1	102·5	188·6

Phase:	Supercooled Liquid.	
Temp., ° C.	265·9	243·5
Vap. Press. (mm.)	22·9	12·7

From the vapour pressure-temperature curves, fig. 8, the melting point of octahedral arsenious oxide is found to be 272·1° C. By not heating the samples too long, the following points on the metastable vapour pressure curve, M, were obtained :

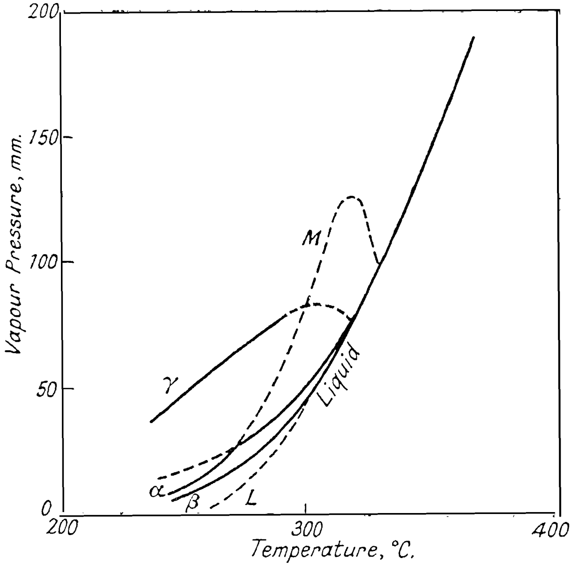

Fig. 8.—Vapour Pressure Curves of Arsenious Oxide.

Temp., ° C.	278·3	293·4	309·0	318·9	326·7
Vap. Press. (mm.)	37·5	68·0	111·2	122·9	94·1

As seen in the figure, this curve passes through a maximum and decreases to cut the liquid-vapour line. On prolonged keeping of the octahedral form at a temperature above 258° C. a product was obtained which melted at 289·6° C. and was considered to be a new γ-form; this yielded abnormally high vapour pressure values:

Phase:	γ-form.								
Temp., ° C.	243·1	263·8	274·2	279·3	284·6	289·8	295·1	310·0	315·7
Vap. Press. (mm.)	39·4	57·0	65·7	69·2	74·2	77·7	80·4	77·7	75·9

The following values for the prismatic variety were obtained:

Phase:	Prismatic Crystals (β).							
Temp., ° C.	243·1	253·4	263·8	274·2	279·3	284·6	289·8	295·1
Vap. Press. (mm.)	4·9	7·6	11·7	17·2	21·4	24·8	31·1	37·2

After partial distillation of the prismatic crystals, a residue was obtained which on heating gave abnormally low vapour pressures (curve L), thus:

Temp., ° C.	263·8	274·2	279·3	284·6	289·8	295·1
Vap. Press. (mm.)	2·3	9·61	15·9	22·4	29·5	37·2

but, on cooling, the β curve was followed. The above product, if partly sublimed in a closed vessel, yielded a sublimate having the high vapour pressures of the γ-form. It is therefore concluded that the prismatic form behaves as a mixed crystal phase in internal equilibrium which is disturbed by partial distillation.

The following stable triple points were determined: α-β-vapour, about 200° C. (0·26 mm.); β-liquid-vapour, 312·3° C. (66·1 mm.); and the metastable points, α-liquid-vapour, 272·1° C. (26·1 mm.); α-γ-vapour, 258·4° C. (13·9 mm.); γ-liquid-vapour, 289·6° C. (40·7 mm.).

The following thermal values were also obtained:—Molar heats of sublimation: α-As_2O_3, 29,833; β, 23,676; γ, 21,130 calories. Molar heats of fusion: α, 15,099; β, 8942; γ, 6396 calories. Molar heat of vaporisation: β, 14,734 calories.[1]

The *octahedral* form of arsenious oxide crystallises in the cubic system. It is produced whenever the vapour is condensed on a cold surface under conditions of rapid cooling; it also results by the slow transformation of the vitreous modification.[2] It may be obtained by crystallisation from a hot saturated aqueous solution of the latter; the crystallisation may be attended by the emission of flashes of light, easily seen in a darkened room.[3] This is the case when crystallisation takes place from solutions containing hydrochloric acid, or a mixture

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[1] For thermal values obtained by calculation using the Clausius-Clapeyron equation, see Rushton and Daniels, *J. Amer. Chem. Soc.*, 1926, 48, 384.

[2] Hausmann, *Annalen*, 1850, 74, 188; von Fuchs, *Schweigger's J.*, 1833, 67, 429.

[3] Rose, *Pogg. Annalen*, 1835, 35, 481.

of hydrochloric and nitric acids, even when the latter is in sufficient quantity to cause complete oxidation of the arsenious oxide. The phenomenon persists after recrystallisation [1] and has been attributed to triboluminescence, since light is also emitted when the crystals are crushed [2] or well stirred with a metal rod. The emitted rays exhibit no electrical properties and the spectrum is continuous. The phenomenon has been investigated by Bhatnagar and his co-workers,[3] who suggest that during crystallisation a small quantity of the solution forms a dispersed phase in the crystal and, according to the physical conditions existing, microcrystallisation takes place more or less rapidly with the emission of light.

When exposed to filtered ultraviolet light, the pure oxide does not exhibit any characteristic fluorescence suitable for its identification.[4]

This cubic modification is the stable form of the oxide at ordinary temperatures and occurs in Nature as *arsenite* or *arsenolite* (see p. 8), usually accompanying ores of lead, iron, cobalt, nickel, silver, etc. It is a product of the decomposition of arsenical ores. It is frequently found also as a greyish crust on native arsenic, its presence being due to superficial oxidation. The crystals are isomorphous with senarmontite, a cubic variety of antimony trioxide, and a study of the crystal structure, based on powder photographs, shows that the space-lattice in both cases is of the diamond form. The molecules preserve their identity in the crystal and possess the 24-fold symmetry of the regular tetrahedron; the four arsenic atoms are associated with the four corners of the tetrahedron and the oxygen atoms with the six edges.[5] This is in accordance with the experimental evidence (see p. 136) which suggests that the molecule of the oxide agrees with the formula As_4O_6. The unit cube contains [6] eight molecules and the side $a = 11{\cdot}0457 \pm 0{\cdot}0002$ A.; the shortest distance between the arsenic and oxygen atoms is 2·01 A., and the calculated density is 3·877. The As–As separation is [7] 3·20 ± 0·05 A.

When either arsenolite or senarmontite is sublimed on to mica, it is deposited in octahedra, respectively isotropic and birefringent, oriented so that similar dimensions of the crystal meshes coincide,[8] for example: As_4O_6 13·54, Sb_4O_6 13·64, mica 13·66 A. Such orientation appears only to occur with minerals of ionic structure [9] and when both substances concerned have heteropolar linkings,[10] so that the phenomenon is said to provide evidence of this type of linking.

The actual density of the cubic crystals, according to Baxter and Hawkins,[11] is 3·874 at 0° C., 3·865 at 25° C. and 3·851 at 50° C., but lower values have usually been obtained; [12] the density of the natural product

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[1] Baudrowsky, *Zeitsch. physikal. Chem.*, 1895, 17, 234.

[2] Guinchant, *Compt. rend.*, 1905, 140, 1101, 1170; Gernez, *ibid.*, 1905, 140, 1134. See also Trautz, *Zeitsch. physikal. Chem.*, 1905, 53, 1.

[3] Bhatnagar, Mathur and Budhiraja, *ibid.*, 1932, A, 163, 8.

[4] Kutzelnigg, *Zeitsch. anorg. Chem.*, 1932, 208, 29. This is contrary to reports by Lenz, *Zeitsch. anal. Chem.*, 1915, 54, 27; and Eibner, *Chem. Ztg.*, 1931, 55, 593, 614, 635, 655.

[5] Bozorth, *J. Amer. Chem. Soc.*, 1923, 45, 1621.

[6] Lihl, *Zeitsch. Krist.*, 1932, 81, 142; Passerini, *Gazzetta*, 1928, 58, 775.

[7] Maxwell and others, *J. Chem. Physics*, 1937, 5, 626.

[8] Hocart, *Compt. rend.*, 1933, 196, 1234.

[9] Royer, *ibid.*, 1933, 196, 282.

[10] Friedel, *ibid.*, 1933, 196, 284.

[11] Baxter and Hawkins, *J. Amer. Chem. Soc.*, 1916, 38, 266.

[12] Taylor (3·529), *Phil. Mag.*, 1801, 9, 482; Guibourt (3·695), *J. Chim. méd.*, 1826, 1, 2, 55, 106; Karsten (3·720), *Schweigger's J.*, 1832, 65, 394; Winkler (3·628), *J. prakt. Chem.*, 1885, [2], 31, 247.

usually varies between 3·70 and 3·72. The hardness is 1·5. The compressibility, β, under pressures up to 9000 atm. has been determined[1] with the following results:

$$\text{At } 30^\circ\text{ C. } \beta \ (i.e.\ -\Delta V/V_0) = 92{\cdot}49 \times 10^{-7}p - 272{\cdot}4 \times 10^{-12}p^2$$
$$\text{At } 75^\circ\text{ C. } \beta = 92{\cdot}88 \times 10^{-7}p - 250{\cdot}5 \times 10^{-12}p^2$$

This very high compressibility is to be expected from the structure of the crystal which, as seen above, is molecular rather than ionic and moreover contains large open spaces between the atoms. The refractive indices at 17° C. are 1·755 for sodium light and 1·748 for lithium light.[2] Klocke observed[3] that for yellow light the sublimed crystals exhibit double refraction, but this could not be confirmed by Brauns.[4]

The crystals on heating volatilise without melting, but when heated under pressure liquefy with initial formation of the vitreous form. The specific heat is[5] 0·1279, and the molar heat[6] over the range 3° to 41° C. is 28·83. The coefficient of cubical expansion[7] is 0·00011 from 0° to 25° C., and 0·00012 from 25° to 50° C.

The heat of formation is as follows:[8]

$$2\text{As(cryst.)} + 3\text{O} = \text{As}_2\text{O}_3\text{(octahedral)} + 154{,}670 \text{ cal.}$$

From E.M.F. measurements at 25° and 45° C. of the cell

$$\text{As(metallic)} \mid \text{As}_2\text{O}_3\text{(octahedral)} + \text{HClO}_4(0{\cdot}22 - 0{\cdot}94\text{M}) \mid \text{H}_2$$

Schuhmann[9] derived the free energy and heat content of arsenious oxide. The electrode, which consisted of arsenic deposited on platinum, was immersed in a mixture of perchloric acid and arsenious oxide and the E.M.F. was found to be, at 25° C., −0·2340 volt[10] and, at 45° C., −0·2250 volt. The free energy of formation at 25° C. of As_2O_3 (octahedral) from metallic arsenic and oxygen was computed to be −137,300 calories, and the heat content, derived from the measurements at the two temperatures, was found to be −153,800 calories, in fair agreement with Thomsen's value,[11] −154,700 calories, obtained by an indirect method. Experiments with an adiabatic calorimeter, in which heat changes as small as $1 - 5 \times 10^{-5}$ calories per gram-hour could be registered, revealed no continuous heat evolution from arsenious oxide.[12]

The heat capacity of the oxide has been investigated[13] at temperatures from about 57° to 296° Abs., and the entropy at 25° C., in gram-calories per degree, is calculated to be 25·6.

The crystals dissolve slowly in cold water, more readily in boiling water, and the solution is feebly acidic (see p. 138).

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[1] Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1932, 67, 345.

[2] Des Cloiseaux, *Mém. Paris Acad.*, 1868, 18, 511; "*Manuel de Minéralogie*," Paris, 1893, 13, 16.

[3] Klocke, *Neues Jahrb. Min.*, 1880, i, 82.

[4] Brauns, "*Die optischen Anomalien der Krystalle*," Leipzig, 1891, p. 191.

[5] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129.

[6] Russell, *Phys. Zeit.*, 1912, 13, 60.

[7] Baxter and Hawkins, *loc. cit.*: Fizeau, *Compt. rend.*, 1865, 60, 1161.

[8] Thomsen, "*Thermochemistry*" (Longmans, Green and Co.), 1908, p. 227; de Passillé, *Ann. Chim.*, 1936, [11], 5, 83; Berthelot ("*Thermochimie*," Paris, 1897, 2, 117) gave 148,900 calories.

[9] Schuhmann, *J. Amer. Chem. Soc.*, 1924, 46, 1444.

[10] *Cf.* Neumann, *Zeitsch. physikal. Chem.*, 1894, 14, 193.

[11] Thomsen, *loc. cit.* See also Berthelot, *loc. cit.*

[12] Swientoslawski and Bartoszewicz, *Bull. Acad. Polonaise*, 1934, A, p. 69.

[13] Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2296.

The *prismatic* crystals, which belong to the monoclinic system,[1] occur naturally as *claudetite*, *rhombarsenite* or *arsenophyllite* (p. 8). They sometimes occur in thin plates, and there may be penetration twins. The artificially produced crystals were first observed by Wöhler,[2] who discovered them in the arsenical sublimate of a furnace in which cobalt ores were roasted for the manufacture of cobalt blue. The prismatic oxide is frequently formed in this way during the roasting of arseniferous minerals [3] if the condensation takes place at temperatures above 250° C., and it has been found to occur in mines in which arsenopyrite has been decomposed by combustion.[4] The oxide may also be obtained in this form from solution if crystallisation takes place at a high temperature or if a hot solution is cooled rapidly; thus it may be obtained from a boiling saturated solution of the oxide in aqueous alkali,[5] or from a hot solution in arsenic acid; [6] also by the addition of ammonia to a boiling saturated ammoniacal solution of the oxide and rapidly cooling.[7] Prismatic crystals have also been separated from the solution resulting from the action of nitric acid on silver arsenite.[8]

The crystallographic elements are given as [9] $a:b:c=0{\cdot}4040:1:0{\cdot}3445$ and $\beta=86^\circ\ 3'$. The cleavage on the (010) face is perfect. The optical axial angle $2H=66^\circ\ 14'$ for red light and $65^\circ\ 21'$ for yellow light. The crystals exhibit strong double refraction.[10] The optical character is negative. The density of claudetite is 3·85 to 4·15 and the hardness 2·5.

The *vitreous* or amorphous form of arsenious oxide, "white arsenic glass," may be prepared by heating ordinary white arsenic, preferably under slight pressure but not at a temperature sufficiently high to volatilise too large an amount, and condensing the fume at a temperature just above the point of fusion, say 350° to 400° C. It is sometimes formed even below 315° C., the melting point of the monoclinic crystals.[11] The operation is generally performed in a cast-iron bell-covered pan; the vitreous arsenic collects as a layer in the bell and by continually adding arsenious oxide to the pan the process is continued until the layer is about one inch in thickness.[12] When freshly formed, it is transparent, but it gradually becomes opaque owing to transformation to the octahedral form [13] and in this state it resembles porcelain. The

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[1] Des Cloiseaux, *Compt. rend.*, 1887, **105**, 96; Schmidt, *Zeitsch. Kryst. Min.*, 1888, **14**, 575; 1890, **17**, 515.

[2] Wöhler, *Ann. Chim. Phys.*, 1832, [2], **51**, 201.

[3] Ulrich, *Jahresber.*, 1858, p. 173; Scheurer-Kestner, *Bull. Soc. chim.*, 1868, [2], **10**, 344; Groth, *Pogg. Annalen*, 1869, **137**, 414.

[4] Claudet, *J. Chem. Soc.*, 1868, [2], 6, 179; *Bull. Soc. chim.*, 1868, [2], **10**, 230; Zenzen and others, *Arkiv Kemi Min. Geol.*, 1922, 8, 20; Hintze, "*Handb. der Mineralogie*," Leipzig, 1904, **1**, 1230.

[5] Pasteur, *J. Pharm. Chim.*, 1848, [3], **14**, 399; Hirzel, *Zeitsch. Pharm.*, 1852, **4**, 81; Wöhler, *Annalen*, 1857, **101**, 365; Nordenskjold, *Pogg. Annalen*, 1861, **114**, 612.

[6] Scheurer-Kestner, *loc. cit.*

[7] Hirzel, *loc. cit.*

[8] Kühn, *Arch. Pharm.*, 1852, [2], **69**, 267.

[9] Schmidt, *Zeitsch. Kryst. Min.*, 1888, **14**, 579; 1890, **17**, 515.

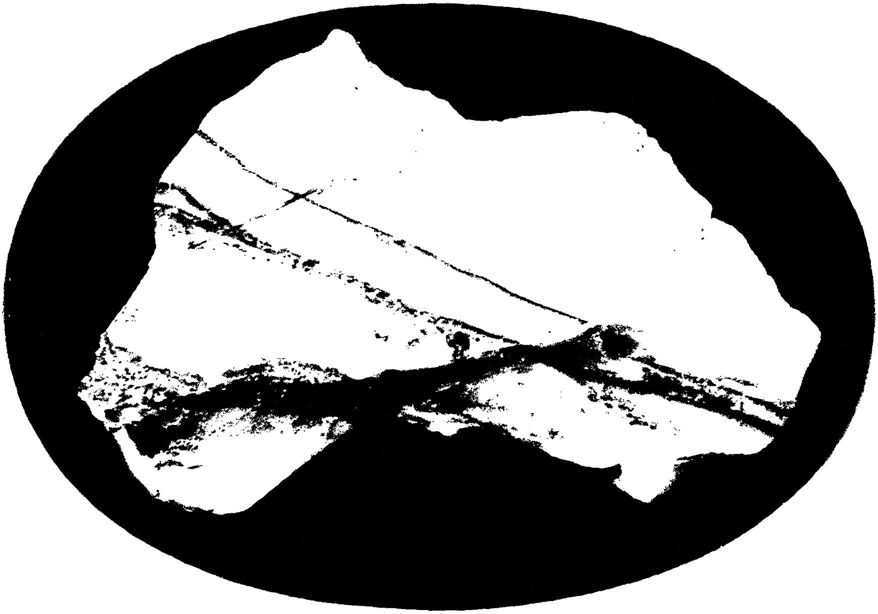
[10] Des Cloiseaux, "*Manuel de Minéralogie*," Paris, 1893, **2**, 364.

[11] Rushton and Daniels, *J. Amer. Chem. Soc.*, 1926, **48**, 384.

[12] Sims and Terrill, *British Patent*, 9076 (1896); Souheur, *German Patent*, 159541 (1903); Thorpe, "*Dictionary of Applied Chemistry*," 1912, **1**, 298. For methods of purification, see also Chapin, *J. Ind. Eng. Chem.*, 1918, **10**, 522; Vié, *Chem. Trade J.*, 1921, 68, 35; Linville, *U.S. Patent*, 1372332 (1921); Suchy and Michel, *U.S. Patent*, 1532454 (1925); Collins and others, *J. Ind. Eng. Chem.*, 1927, **19**, 1370.

[13] von Fuchs, *Schweigger's J.*, 1833, **67**, 429; Hausmann, *Annalen*, 1850, **74**, 188.

A Text-Book of Inorganic Chemistry, Vol. VI, Part IV.] [To face page [illegible]



Vitreous Arsenious Oxide from the Furnaces at Wiluna (Australia).

arsenic glass may be kept in the transparent condition by excluding air, or by confining it in thoroughly dried air, hydrogen or carbon dioxide.[1] When placed in boiling water octahedral crystals rapidly form at the surface of the arsenic glass.[2] The latter often appears to retain its transparency under cold water, in which it is more soluble than the octahedral form; according to Winkler,[3] however, transformation to the octahedral takes place thus—on being immersed in water the vitreous arsenic is dissolved at the surface and the layer of solution so formed deposits crystals of the less soluble variety; dissolution of the vitreous and deposition of the octahedral is repeated towards the interior until the transformation is complete. The change is retarded by the presence of alcohol.[4] If a trace of iodine is added to a piece of vitreous arsenic while undergoing transformation, the latter is coloured more intensely than the octahedral form and the progress of the change may thus be observed.[5] The heat of transformation of vitreous arsenic to the octahedral form is 2400 calories,[6] and the heat of transformation of the monoclinic to the vitreous is 1200 calories.[7]

Unlike the octahedral form, vitreous white arsenic on heating melts before volatilisation begins.[8] The density of the glass has been variously given [9] as 3·70 to 3·88; Winkler found the density under water to be 3·7165 at 12·5° C. but under petroleum 4·6815. The glass is brittle and its hardness is comparable with that of Iceland spar.[10]

Colloidal arsenious oxide may be obtained in a highly dispersed condition by the vaporisation of arsenic in the electric arc and oxidation of the fume in a current of air.[11] The size of the particles thus obtainable corresponds with the upper limit of the colloidal state (100 $\mu\mu$).

In smoke prepared by volatilisation of arsenious oxide, the particles, which consist almost entirely of octahedral crystals, show only a slight degree of aggregation.[12] In aerosols prepared by rapidly cooling the vapour of the oxide the number of particles per unit volume decreases rapidly during the first hour, especially in concentrated sols containing 150 to 500 mg. per cubic metre. After a preliminary ageing period the variation of mean particle weight with concentration is linear.[13]

Dispersed in aqueous medium, arsenious oxide forms a negatively charged colloid; [14] the magnitude of the charge decreases on increasing the concentration of hydrogen ion, but there is no reversal. The coagulating effect of positive ions increases in the order Li, Na, K, Mg, Ca, Ba, Al. If an alkali chloride is first added to the negative sol, the

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[1] Winkler, *J. prakt. Chem.*, 1885, [2], 31, 247. See also Krüger, *Kastner's Arch.*, 1824, 2, 473.

[2] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 144.

[3] Winkler, *loc. cit.* See Bussy, *J. Pharm. Chim.*, 1847, [3], 12, 321.

[4] Christison, *Pogg. Annalen*, 1835, 36, 494; Rose, *ibid.*, 1841, 52, 454.

[5] Brame, *Ann. Chim. Phys.*, 1853, [3], 37, 221.

[6] Berthelot, "*Thermochimie*," 1897; Favre (*J. Pharm. Chim.*, 1853, [3], 24, 241, 311, 412) gave 2700 calories.

[7] Troost and Hautefeuille (*Compt. rend.*, 1869, 69, 48) gave 1300 calories.

[8] Wöhler, *Annalen*, 1842, 41, 155.

[9] Taylor, *Phil. Mag.*, 1801, 9, 482; Herapath, *ibid.*, 1824, 64, 321; Guibourt, *J. Chem. Med.*, 1826, 1, 2, 55, 106; Karsten, *Schweigger's J.*, 1832, 65, 394; Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415.

[10] Hausmann, *Annalen*, 1850, 74, 188.

[11] Kohlschutter and Tuscher, *Zeitsch. Elektrochem.*, 1921, 27, 225.

[12] Patterson, Whytlaw-Gray and Cawood, *Proc. Roy. Soc.*, 1929, A 124, 523.

[13] Winkel and Jander, *Kolloid-Zeitsch.*, 1933, 65, 290.

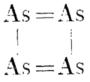
ionic antagonism increases with the series Ca, Ba, Al.[1] If a salt of the metal of higher valency is first added, then a slight ionic antagonism is shown with the alkali salt, but it disappears with time.

Arsenious oxide is not appreciably volatile at ordinary temperatures,[2] but vapour is emitted at 100° C.[3] Vapour density determinations[4] indicate that at lower temperatures the molecules are mainly As_4O_6 but, as the temperature rises, dissociation occurs, which is appreciable at 850° C. and practically complete at 1800° C., simple As_2O_3 molecules being formed. The following values for the vapour density (Theory : $As_4O_6 = 13{\cdot}76$) were obtained by Biltz:[5]

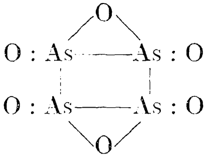
Temp., ° C. .	518	769	851	1059	1256	1450	1584	1732	1800
Vap. Density	13·92	13·62	13·15	12·76	12·36	9·41	8·81	7·32	6·93

The vapour is odourless.

The molecular weight, determined ebullioscopically by dissolution of the octahedral crystals in nitrobenzene, agrees according to Biltz[5] with the formula As_4O_6. Determinations in water, which yields a slightly acidic solution, indicate that the solute molecules contain only one atom of arsenic,[6] apparently existing as the very weak acid H_3AsO_3 or $HAsO_2$ (*vide infra*). When arsenious oxide is reduced with zinc dust in the presence of carbon disulphide, the product consists in part of the yellow modification of arsenic; Erdmann[7] therefore suggested the following related formulæ (*cf.* p. 132):



and



The X-ray spectrum has been investigated by Robinson,[8] who also examined the secondary and tertiary radiations emitted by the oxide under the influence of molybdenum K rays as primary X-radiation.[9] Whiddington[10] estimated the frequencies of high-speed electrons ejected from the oxide by impinging X-rays.

Arsenious oxide is not a very polar substance chemically, and it would be expected to have a rather small molecular moment. That this is so was shown by Clark,[11] who found the electrostatic moment to be $1{\cdot}3 \times 10^{-19}$ electrostatic units. This value was not affected by varying

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[1] Freundlich and Tamchyna, *Kolloid-Zeitsch.*, 1930, 53, 288.

[2] Faraday, *Pogg. Annalen*, 1830, 19, 551.

[3] Selmi, *Jahresber.*, 1878, p. 1049; *cf.* Mitchell, *Amer. J. Sci.*, 1831, 19, 122.

[4] Mitscherlich, *Annalen*, 1834, 12, 165; V. and C. Meyer, *Ber.*, 1879, 12, 1116; 1880, 13, 609, 1112, 1195, 1282; *Bull. Soc. chim.*, 1880, [2], 33, 114.

[5] Biltz, *Zeitsch. physikal. Chem.*, 1896, 19, 385; *Chem. Zentr.*, 1895, i, 770.

[6] von Zawidzki, *Ber.*, 1903, 36, 1427; *Bull. Soc. chim.*, 1903, [3], 30, 1162; Biltz, *loc. cit.*

[7] Erdmann, *Zeitsch. anorg. Chem.*, 1902, 32, 453.

[8] Robinson, *Phil. Mag.*, 1925, [6], 50, 241.

[9] Robinson and Cassie, *Proc. Roy. Soc.*, 1926, A 113, 282.

[10] Whiddington, *Phil. Mag.*, 1922, [6], 43, 1116.

[11] Clark, *Proc. Roy. Soc.*, 1929, A 124, 689.

the strength of the electric field, so that it appears to be a permanent characteristic of the molecule. The moment is of the right order to conform with Debye's theory of permanent dipoles. There was no evidence of any definite orientation of the molecules save parallel or antiparallel to the field.

In the solid state arsenious oxide is a very poor conductor of electricity.[1]

The rate of dissolution of arsenious oxide in water is extremely slow and solubility data have been very discordant,[2] probably due in part to insufficient time having been given for saturation, but also owing to the difference in solubility of the crystalline and amorphous varieties and to the tendency of the latter to pass into the octahedral form. The following figures are reliable, however, having been obtained by constantly agitating mixtures of the pure octahedral oxide and water in a thermostat, saturation being approached from above; periods of 10 to 14 days were necessary for the attainment of equilibrium and the arsenic was determined iodometrically.[3]

SOLUBILITY OF As_2O_3 IN WATER.

Temperature, ° C.	Grams As_2O_3 per 100 grams H_2O.	Temperature, ° C.	Grams As_2O_3 per 100 grams H_2O.
0	1·21	48·2	3·43
15	1·66	62	4·45
25	2·05	75	5·62
39·8	2·93	98·5	8·18

From these results Anderson and Story deduced the following equation for the solubility at θ° C.:

$$S = 1{\cdot}21 + 0{\cdot}021\theta + 0{\cdot}000505\theta^2$$

Schnellbach and Rosin,[4] after 131 days' agitation of the oxide with water, the tube being revolved end over end, found the solubility at 25° C. to be 2·03 g. in 100 g. H_2O. For the more soluble vitreous form Winkler[5] determined the solubility in 100 c.c. of water to be 3·7 g. at the ordinary temperature and 11·86 g. at the boiling point. Small octahedral crystals were deposited in the former case within 12 hours (*cf.* p. 131) and the solubility gradually diminished until, after 3 or 4 weeks, it approximated to that of the octahedral form. For the monoclinic crystals Claudet[6] found the solubility in 100 parts of water to be

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[1] Bleekrode, *Jahresber.*, 1878, p. 148; Beijerinck, *Neues Jahrb. Min.*, 1897, 11, 442.

[2] See, for example, Rose, *Pogg. Annalen*, 1835, 36, 494; Taylor, *Phil. Mag.*, 1837, [3], 14, 482; Buchner, *Bull. Soc. chim.*, 1873, [2], 20, 10; Clayton, *Chem. News*, 1891, 64, 27; Chodounsky, *Chem. Listy*, 1888, 13, 114; *Chem. Zentr.*, 1889, p. 569; Winkler, *J. prakt. Chem.*, 1885, [2], 31, 247; Wood, *J. Chem. Soc.*, 1908, 93, 412; Schreinemakers and de Baat, *Proc. Akad. Amsterdam*, 1916, 17, 1111.

[3] Anderson and Story, *J. Amer. Chem. Soc.*, 1923, 45, 1104. The data closely agree with results of Bruner and Tolloczko, *Zeitsch. anorg. Chem.*, 1903, 37, 456.

[4] Schnellbach and Rosin, *J. Amer. Pharm. Assoc.*, 1929, 18, 1230.

[5] Winkler, *loc. cit.* See also Buchner, *N. Repert. Pharm.*, 1873, 22, 265; *Bull. Soc.*

1·75 parts at the ordinary temperature and 2·75 parts at 100° C. The rate of dissolution of arsenious oxide is accelerated by the presence of acid or alkali.[1]

The density and refractive index of aqueous solutions increase linearly with concentration.[2] The following values have been determined : [3]

Concentration, g. per l.	1·796	3·212	5·060	7·184	10·13	12·85	14·368
D (25° C.) . .	1·0014	1·0025	1·0039	1·0057	1·0080	1·0102	1·0113
n (22° C.) . . .	1·33309	1·33326	1·33340	1·33376	1·33417	1·33450	1·33469

Increase in temperature causes a slight decrease in refractive index. The heat of dissolution[4] of the octahedral form is -7550 calories at 18° C. The velocity of crystallisation from supersaturated solutions corresponds with[5] $-dc/dt = kc^4$, where c is the concentration ; the temperature coefficient for the interval 0 to 25° C. is zero.

Arsenious oxide is soluble in a number of organic liquids. Thus, 100 parts of absolute alcohol dissolve at 15° C. 0·025 part, and at boiling point 3·402 parts of the octahedral form. The solubility is increased by the addition of water.[6] The vitreous modification dissolves to the extent of 1·060 parts per 100 at 15° C. and addition of water decreases the solubility. Esters of arsenious acid may be obtained by heating, with stirring, a mixture of the oxide and an alcohol in the presence of a hydrocarbon such as benzene, toluene or xylene.[7]

At 25° C. 100 grams of glycerol very slowly dissolve 20·8 grams of the oxide.[8] In ethyl malonate the solubility in 100 g. is 0·058 g. at 15° C. and 0·061 g. at 100° C.[9] Arsenious oxide is volatile in ethyl malonate vapour, 0·09 g. having been observed to be carried over during the distillation of 100 g. of the ester. The oxide dissolves in warm ethylene glycol, but no definite chemical compound is obtainable from the solution.[10] The vitreous form dissolves slightly in ether, carbon disulphide, fatty oils and turpentine.

The absorption spectrum of 0·1N aqueous solutions of arsenious oxide differs from that of aqueous solutions of alkali arsenites.[11] This is characteristic of weak acids, the un-ionised molecules of which appear to be capable of absorbing more light than ionised molecules ; there is little or no difference in the absorption spectrum of a strong acid and its salts.

The aqueous solution of arsenious oxide is colourless and sufficiently acidic to cause a slight reddening of litmus,[12] the *p*H of the saturated

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[1] Drucker, *Zeitsch. physikal. Chem.*, 1901, 36, 173, 693.

[2] Birstein and Kronman, *Rocz. Chem.*, 1934, 14, 975.

[3] Anderson and Story, *loc. cit.*

[4] Thomsen, *Ber.*, 1874, 7, 935, 1002; "*Thermochemische Untersuchungen*," Leipzig, 1882, 2, 236.

[5] Birstein and Kronman, *loc. cit.*

[6] Girardin, *J. Pharm. Chim.*, 1864, [3], 46, 269; *Bull. Soc. chim.*, 1865, [1], 3, 458.

[7] Pascal and Dupire, *Compt. rend.*, 1932, 195, 14.

[8] Schnellbach and Rosin, *loc. cit.*

[9] Zappi and Manini, *Anal. Asoc. Quim. Argentina*, 1929, 17, 90.

[10] Englund, *Svensk Kem. Tidskr.*, 1928, 40, 278.

[11] Wright, *J. Chem. Soc.*, 1914, 105, 669. The extinction coefficient of the aqueous solution has been measured by Ghosh and Bisvas, *Zeitsch. Elektrochem.*, 1924, 30, 97.

[12] Bussy, *Phil. Mag.*, 1847, [3], 31, 151.

solution being[1] approximately 5. The solution is a poor conductor of electricity, there being only slight ionisation, and the purity of the oxide may conveniently be determined by measuring the conductivity of a saturated solution. The most common impurity is arsenic pentoxide, which is indicated by the reaction of the solution to methyl orange or methyl red.[2] The oxide, even in the most dilute solutions which can be examined cryoscopically, is believed[3] to contain some associated molecules and in addition to be converted almost completely into the weak acid $HAsO_2$ or H_3AsO_3. The following values for the molecular weight in aqueous solution have been obtained :[4] by the boiling point method 92·5, and by the freezing point method 99·17. This supports the view that at 0° C. the trioxide is in the hydrated form, probably as metarsenious acid, $HAsO_2$. With increasing concentration, however, association increases to a limiting value corresponding with As_2O_3,[5] and evaporation of the aqueous solution yields only crystals of the oxide itself. Titration with standard alkali appears to indicate that the solute behaves as a monobasic acid, the salt produced being NaH_2AsO_3, and although the electrical conductivity increases on dilution, the increase is accounted for by hydrolysis and is not due to further ionisation of the acid.

Orthoarsenious acid, H_3AsO_3, corresponding to phosphorous acid, has not been isolated, although alkali salts of the type M_3AsO_3 are known (see p. 172) ; even these in solution appear to behave as salts of a monobasic acid.[6] Walden suggested that the acid in solution was dimetarsenious acid, $H_2As_2O_4$ or HO.OAs : AsO.OH, but as already mentioned (p. 136), the solute molecule appears to contain only one arsenic atom.

The solution obtained by neutralisation of an aqueous solution of arsenious oxide with sodium hydroxide exhibits the same electrical conductivity and freezing point depression as an aqueous solution of sodium metarsenite, $NaAsO_2$, of the same concentration.[7] Conductivity measurements also suggest that the potassium salt produced by neutralisation must be of composition $KAsO_2$, since the difference between the limiting equivalent conductivity, corrected for hydrolysis, of a neutral aqueous mixture of 1 mol. of KOH with 0·5 mol. of As_2O_3, and that of a similar mixture of sodium hydroxide with arsenious oxide, is equal to the difference in the ionic mobilities of K^+ and Na^+. From a mixture of equivalent amounts of potassium hydroxide and arsenious oxide a salt may be crystallised which, according to cryoscopic measurements, appears to exist in aqueous solution as $K_2As_2O_4$. The conductivity of an aqueous solution of tripotassium arsenite, K_3AsO_3, is not the same as that of a mixture of aqueous arsenious oxide and potassium hydroxide in the molecular ratio $1As_2O_3 : 6KOH$ and of corresponding concentration.

Assuming the formula H_3AsO_3 for the acid, Goldfinger and

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[1] The reaction with various indicators is mentioned by Flückiger, *Arch. Pharm.*, 1884, [3], **22**, 605; Thomson, *Chem. News*, 1884, **49**, 119; 1885, **52**, 18, 29; Favrel, *J. Pharm. Chim.*, 1893, [5], 28, 301; *Bull. Soc. chim.*, 1893, [3], **9**, 448; Cohn, "*Indicators and Test-papers*," New York, 1899.

[2] Kolthoff, *Pharm. Weekblad*, 1919, **56**, 621.

[3] Roth and Schwartz, *Ber.*, 1926, **59**, [B], 338.

[4] Anderson and Story, *J. Amer. Chem. Soc.*, 1923, **45**, 1102.

[5] Birstein and Kronman, *Rocz. Chem.*, 1934, **14**, 975.

[6] Walden, *Zeitsch. physikal. Chem.*, 1888, **2**, 56.

[7] Cernatescu and Mayer, *ibid.*, 1932, **160**, 305.

von Schweinitz[1] calculated the first dissociation constant, k_1, from the neutralisation curve to be 2×10^{-10} to 8×10^{-10}, whereas spectroscopic determination of the ionic concentrations in the presence of varying amounts of alkali gave 1×10^{-14} to 6×10^{-14} for the second dissociation constant. The long wave limit of continuous absorption in molecular solution is 2680 A. for $H_2AsO_3^-$ and 2800 A. for $HAsO_3^{=}$. Cernatescu and Mayer[2] deduced the dissociation constant of arsenious acid from the hydrolysis constants of the sodium and potassium salts to be 9×10^{-10}. Wood[3] obtained the value $6{\cdot}3 \times 10^{-10}$ from the velocity of saponification of methyl acetate in the presence of sodium metarsenite, but by the electrical conductivity method the mean value found was[4] $26{\cdot}5 \times 10^{-10}$, a discrepancy attributed to the presence of slight impurity and the fact that air was not excluded from the conductivity cell. The following values for the molecular conductivity, μ, and for the ionisation constant, k, were obtained (c = concentration of the solution of metarsenious acid):

c . . .	0·195N	0·086N	0·0542N	0·0385N
μ . . .	0·0553	0·0654	0·0756	0·0824
$k \times 10^{10}$ . .	38·6	23·9	20·1	16·9

The view that aqueous arsenious oxide behaves as a weak monobasic acid is supported by the observation of Thomsen[5] that the heat of neutralisation of 1 mole of As_2O_3 with 2 moles of NaOH was 13,780 calories and that the addition of a further 4 moles of NaOH liberated only 1800 calories. The neutralisation curve, whether determined conductometrically[6] or potentiometrically,[7] indicates the replacement of one equivalent of hydrogen only, as also does the curve obtained by plotting the depressions of the freezing point against the composition of the mixtures during neutralisation.[8] These methods, however, are not able to decide between the formulæ $HAsO_2$ and H_3AsO_3.

The acidity of arsenious acid in aqueous solution is increased by the addition of mannitol, sorbitol or *α*-mannitan, probably owing to the formation and superior ionisation of an acid of the type $HAsD_2$ (D representing the diol residue).[9] When sublimed arsenious oxide is heated with water on a water-bath for 5 hours, the dissolved acid has less than the normal acidity, but by boiling the solution for 7 hours under a reflux condenser it attains its original acidity.

Arsenious oxide in solution exhibits a slightly amphoteric character, but its basic nature is extremely feeble. By determining the solubility

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[1] Goldfinger and von Schweinitz, *Zeitsch. physikal. Chem.*, 1932, B 19, 219.

[2] Cernatescu and Mayer, *loc. cit.*

[3] Wood, *J. Chem. Soc.*, 1908, 93, 411. This value agrees with that of Hughes (*ibid.*, 1928, p. 491), who obtained $k_1 = 6 \times 10^{-10}$ from *p*H measurements of half-neutralised buffer mixtures.

[4] *Cf.* von Zawidzki (*Ber.*, 1903, 36, 1427), who gave 210×10^{-10}. The electrical conductivity of aqueous solutions of arsenious oxide was also investigated by Bleekrode, *Proc. Roy. Soc.*, 1877, 25, 322; *Phil. Mag.*, 1878, [5], 5, 375, 439; Bouty, *Ann. Chim. Phys.*, 1884, [6], 3, 478.

[5] Thomsen, *Ber.*, 1874, 7, 935; "*Thermochemische Untersuchungen*," Leipzig, 1882, 1, 200.

[6] Miolati and Mascetti, *Gazzetta*, 1901, 31, i, 93.

[7] Böttger, *Zeitsch. physikal. Chem.*, 1897, 24, 293.

[8] Cornec, *Ann. Chim. Phys.*, 1913, [8], 29, 490.

in various concentrations of hydrochloric acid at 15° C. (approx.) Wood [1] obtained the curve shown in fig. 9. From the fact that the first effect of the addition of hydrochloric acid is to cause a steady fall in the solubility, it is evident that the acidic dissociation constant of arsenious hydroxide is much greater than the basic constant. It is only when the hydrogen ions have reached such a concentration to make the acidic ionisation of the hydroxide impossible that it becomes possible to see the effect which a further increase in the concentration of hydrochloric acid has on the solubility of arsenious oxide by virtue of the basic character of its hydroxide. Beyond the minimum of the curve the increase in solubility can only be accounted for by the assumption that the hydroxide possesses feeble basic properties. The basic dissociation constant was calculated to be of the order of 1×10^{-14}. The ionisation was considered to be

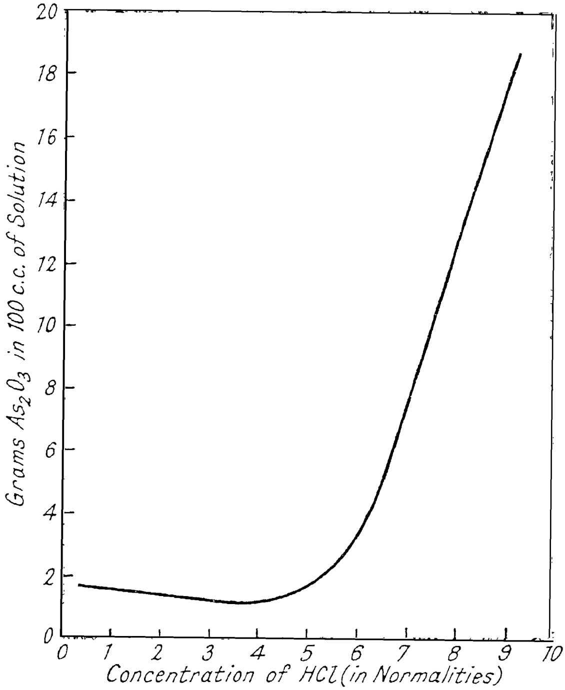

FIG. 9.—Solubility of Arsenious Oxide in Aqueous Hydrochloric Acid of Varying Concentration (Temperature 15° C., approx.).

$$\text{(i) } As(OH)_3 \rightleftharpoons AsO(OH)_2^- + H^+$$

$$\text{(ii) } As(OH)_3 \rightleftharpoons As(OH)_2^+ + OH^-$$

The basic ionisation constant [2] at 25° C. in a solution having an ion concentration of 0·1 equivalent per litre is given as

$$[AsO^+][OH^-]/H_3AsO_3 = 0{\cdot}15 \times 10^{-14}$$

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[1] Wood, *J. Chem. Soc.*, 1908, 93, 414.

[2] Washburn and Strachan, *J. Amer. Chem. Soc.*, 1913, 35, 681.

Chemical Properties of Arsenious Oxide.

When pure hydrogen is passed over heated arsenious oxide reduction to arsenic occurs with consequent loss in weight and formation of water;[1] the reduction becomes appreciable at 185° C. In aqueous solution, and in the presence of acid or alkali, nascent hydrogen causes reduction to arsine (see p. 81), and a similar reduction may be brought about electrolytically, but the amount of arsine liberated depends upon the nature of the cathode,[2] the following being given in order of efficiency: Pb, Zn, Cd, Sn, Ag, C (graphite), Fe, Pt, Al, Au, Co, Ni and Pd; in the case of the first five metals, the reduction proceeds as a unimolecular reaction. A polarographic investigation of the electro-reduction in acid solutions of arsenious oxide, using the dropping mercury cathode, has been made.[3] In 0·1N or N hydrochloric acid, the current-voltage curve exhibits four sudden increases of current and two maxima. The first rise is due to the electro-reduction of arsenious acid to arsenic, probably by the primarily deposited hydrogen. The second rise is very steep and is due to the formation of arsine; it occurs at the more negative potentials, the greater the concentration of arsenious oxide. The third increase, which is followed by a prominent maximum, is probably caused by absorption of positively charged dissociation products of arsenious acid; it is suppressed by the addition of small quantities of dyes, the maximum practically disappearing on addition of 0·001M solutions of methylene blue and fuchsin hydrochloride. The fourth increase is attributed to the evolution of hydrogen from the hydrogen ions of the strong acid. Similar results were obtained with sulphuric and nitric acids at various concentrations, and the form of the curve was unchanged by addition of potassium chloride or calcium chloride. Under the influence of occluded hydrogen from palladium or platinum, the reduction in aqueous solution produces arsenic only.[4]

Fluorine reacts vigorously with arsenious oxide to yield a colourless liquid consisting of arsenic trifluoride and oxyfluoride.[5] The oxide becomes incandescent in hydrogen fluoride and if heated with acid fluorides, or with calcium fluoride and sulphuric acid, the trifluoride may be distilled from the mixture.[6] The action of chlorine and hydrogen chloride has previously been mentioned (p. 100). When chlorine is passed into an aqueous suspension containing 70 to 80 per cent. of the oxide at a temperature of 60° to 70° C., the absorption of chlorine is rapid and exothermic, about 70 per cent. of the arsenious oxide being converted to the pentoxide and the remainder to the trichloride.[7] When solutions of arsenious oxide in hydrochloric acid are boiled, the arsenic volatilises, the amount escaping depending on the concentration of the acid.[8] With solutions containing less than 180 g. HCl per litre the

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[1] St John, *J. Physical Chem.*, 1929, 33, 1438.

[2] Thomson, *Proc. Roy. Soc. Edin.*, 1909, 29, 84.

[3] Kačirková, *Coll. Czech. Chem. Comm.*, 1929, 1, 477.

[4] Gladstone and Tribe, *J. Chem. Soc.*, 1878, 33, 306.

[5] Moissan, "*Le fluor et ses composés,*" Paris, 1900, p. 136.

[6] Dumas, *Ann. Chim. Phys.*, 1826, [2], 31, 433; *Quart. J. Sci.*, 1827, 22, 211.

[7] Cambi, *Giorn. Chim. Ind. Appl.*, 1924, 6, 527. See also Weber, *Pogg. Annalen*, 1861, 112, 619; Bloxam, *J. Chem. Soc.*, 1865, 18, 3.

[8] Hinds, *Report 8th Internat. Cong. Appl. Chem.*, 1912, 1, 277.

concentration of the arsenic remaining in the undistilled liquid rises, although some arsenic passes over; the ratio, arsenic : acid, becomes practically constant when the solution contains 185 g. HCl per litre (*i.e.* $HCl.10H_2O$), but with more than this the concentration of arsenic remaining rapidly falls.[1] When such solutions are exposed to the air, slight oxidation occurs.[2]

Oxidation is readily brought about by hypochlorites[3] and by chlorates. In the latter case, in the presence of hydrochloric acid, the reaction is independent of the concentration of the arsenious acid and, according to Kubina,[4] reduction of the chlorate first to a hypothetical intermediate product occurs, probably as follows:

$$ClO_3^- + Cl^- + 2H^+ \longrightarrow H_2ClO_3 + Cl$$

This reaction, which proceeds at a measurable rate, is succeeded by the following rapid reactions:

$$H_2ClO_3 + 4Cl^- + 4H^+ \longrightarrow 5Cl + 3H_2O$$

and

$$3Cl_2 + 3As_3^{\equiv}O + 3H_2O \longrightarrow 3AsO_4^{\equiv} + 6Cl^- + 6H^+$$

The chlorine ion produced does not accelerate the oxidation, as might be expected, owing to the high initial concentration of this ion.

Arsenious oxide and arsenites may be oxidised similarly by bromine or bromic acid. In hydrochloric acid solution the reaction with bromine may be represented by the equation

$$As_2O_3 + 2Br_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HBr$$

and if the concentration of the hydrochloric acid is less than 24 per cent. the reaction proceeds entirely from left to right.[5] Under such conditions arsenites may be titrated accurately with bromine, the end-point of the titration being unaffected by the actual concentration of hydrochloric acid. If the latter exceeds 24 per cent., however, the reverse reaction may take place, the equilibrium conditions depending on the concentrations of arsenate, bromide and hydrochloric acid.[6] The oxidation by means of bromic acid is extremely slow at ordinary temperatures, but is accelerated by the addition of sulphurous or sulphuric acid.[7] At 40° C., in the presence of an excess of H^+ ions, and at lower temperatures in the presence of sulphuric acid, the reaction proceeds at a measurable rate.[8] It is autocatalytic and of the second order, according to the equation $dx/dt = kax(1-x)$; in the presence of 0·1 mol. of sulphuric acid the velocity constant is 9·7 at 30·7° C. The initial production of hydrobromic acid must be due to the interaction of bromic acid with arsenious acid; the latter, however, does not appear to influence the reaction other than by acting as an inductor of the reaction between hydrobromic and bromic acids. The action of the sulphuric acid is proportional to the square of the concentration of H^+ ion

[1] Smart and Philpot, *J. Soc. Chem. Ind.*, 1914, 33, 900.
[2] Kessler, *Pogg. Annalen*, 1863, 118, 17.
[3] Orton and Blackmann, *J. Chem. Soc.*, 1900, 77, 830.
[4] Kubina, *Monatsh.*, 1923, 43, 439.
[5] Manchot and Oberhauser, *Zeitsch. anorg. Chem.*, 1924, 138, 357.
[6] See also Francis, *J. Amer. Chem. Soc.*, 1926, 48, 655.
[7] Schiloff, *Zeitsch. physikal. Chem.*, 1903, 42, 461.
[8] Chodkowski, *Rocz. Chem.*, 1923, 2, 183.

and the addition of neutral sulphates, which reduce this concentration, retards the reaction. On the addition of hydrogen bromide, the reaction proceeds in accordance with the formula $dx/dt = ka(b+x)(1-x)$, where b is the concentration of hydrobromic acid and x the initial concentration of bromic acid; the velocity constant, k, remains as before. Hydriodic acid has a similar but much greater effect. Arsenic acid, which is the final product of the reaction, also acts as a positive catalyst, although its effect is about nine times weaker than that of an equivalent quantity of sulphuric acid. The addition of neutral halides also accelerates the reaction, the relative effects of potassium chloride, bromide and iodide being as 1 : 15 : 3000.

Vitreous arsenious oxide is coloured brown by iodine vapour, but the octahedral form appears to be unaffected.[1]

In hydrochloric acid solution arsenious acid is oxidised by iodine, but the reaction is reversible owing to the reducing action of hydriodic acid. The kinetics of the reaction were first investigated by Roebuck,[2] who concluded that the balanced reaction could be represented thus—

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 3I^- \quad . \quad . \quad \text{(i)}$$

and assumed that the reverse reaction proceeded in two stages:

$$H_3AsO_4 + H^+ + I^- = H_3AsO_4.HI \quad . \quad . \quad . \quad \text{(ii)}$$
$$H_3AsO_4.HI = H_3AsO_3 + HIO \quad . \quad . \quad \text{(iii)}$$

From the reaction velocities in the neighbourhood of equilibrium he determined the equilibrium constant $[AsO_3^{\equiv}][I_3^-]/[AsO_4^{\equiv}][I^-]^3[H^+]^2$ to be $1{\cdot}5 \times 10^5$ and the temperature coefficient between 10° and 0° C. to be 1·41. The equilibrium adheres to the requirements of the law of mass action over a considerable range of concentration,[3] and Roebuck's views are confirmed by recent work. Liebhafsky [4] considers that, over a sufficient concentration range, the equilibrium constant, k_1, expressed as $[H_3AsO_4][H^+]^2[I^-]^3/[I_3^-][H_3AsO_3]$ is equal to k_2/k_3 derived from the velocity equations (a) $-dI_3^-/dt = k_2[I_3^-][H_3AsO_3]/[H^+][I^-]^2$ and (b) $+dI_3^-/dt = k_3[H_3AsO_4][H^+][I^-]$. Both the forward and the reverse reactions are concerned with the rate-determining step

$$HIO + H_3AsO_3 = H_3AsO_4 + H^+ + I^- \quad . \quad . \quad \text{(iv)}$$

which can be interpreted by assuming that the concentration of hypoiodous acid is governed by the relatively rapid equilibrium

$$I_3^- + H_2O \rightleftharpoons H^+ + 2I^- + HIO \quad . \quad . \quad . \quad \text{(v)}$$

which is the sum of the equilibria

$$I_3^- \rightleftharpoons I_2 + I^- \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

and

$$I_2 + H_2O \rightleftharpoons H^+ + I^- + HIO \quad . \quad . \quad . \quad \text{(vii)}$$

since I_3^- is not hydrolysed directly, while I_2 and H_2O react with moderate speed. Thus the rate of the latter hydrolysis is the limiting rate realised

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[1] Brame, *Ann. Chim. Phys.*, 1853, [3], 37, 221; *Compt. rend.*, 1844, 19, 1107.

[2] Roebuck, *J. Physical Chem.*, 1902, 6, 365.

[3] Washburn and Strachan, *J. Amer. Chem. Soc.*, 1913, 35, 681.

[4] Liebhafsky, *J. Physical Chem.*, 1931, 35, 1648.

as the concentrations of H^+ and I^- ions decrease. At 0° C. $k_2 = 9{\cdot}4 \times 10^{-4}$ and $k_3 = 6{\cdot}3 \times 10^{-3}$, so that the equilibrium constant $k_1 = 1{\cdot}5 \times 10^{-1}$.

The addition of neutral salts, such as chlorides and bromides of the alkali and alkaline earth metals, at concentrations from 0·5 to 3N, also nitrates of sodium and potassium, causes the reversal of reaction (vii),[1] and consequently considerably reduces the rate of oxidation of arsenious acid, whilst augmenting slightly that of the reduction of arsenic acid, thus shifting the equilibrium point in the direction of arsenious acid formation. The effect of sulphates is much less than that of corresponding chlorides. The maximum effect is obtained with lithium chloride, that of the other alkali chlorides being in the order K, Na, NH_4.[2] Józefowicz studied the reaction at 25° C. in the presence of excess of hydriodic acid and found the heat of reaction (i) under these conditions to be -1640 calories, while the heats of reactions (vi) and (vii) from left to right were respectively -4300 and $-23{,}200$ calories. Washburn and Strachan [3] found the heat of the reaction between arsenious acid and iodine to be 1360 calories, the effect of temperature being represented by $\log_{10} K = -1{\cdot}3495 + 0{\cdot}00372t$, and the free energy of the reaction $RT \log_e K = 5690 + 5{\cdot}42T$ joules for ionic concentrations of about 0·1 equivalent per litre.

Under appropriate conditions either the direct or the reverse reaction represented in equation (i) may proceed to completion, and the reactions are therefore applied to the volumetric estimation of arsenites and arsenates respectively. Thus an arsenite is oxidised quantitatively to arsenate if the hydriodic acid is removed as quickly as it is formed and the solution kept approximately neutral. This is best accomplished by adding sodium bicarbonate to the arsenite solution; sodium hydroxide and carbonate could not be used owing to their reaction with iodine. On the other hand, the reduction of arsenate to arsenite by means of hydriodic acid proceeds to completion in strongly acid solution.[4] The action of the acid is not catalytic, but appears to be similar to that of a neutral electrolyte [5] as mentioned above, causing reversal of reaction (vii). The reducing action of the hydriodic acid is augmented by the presence of potassium iodide. In a solution containing 25 per cent. of the latter salt and 3·6 per cent. of hydrochloric acid the reaction is complete in 5 minutes if the reacting mixture is heated to 100° C.[6] In employing this reaction for the determination of arsenic acid, the liberation of iodine from hydriodic acid by means of atmospheric oxygen should be prevented by the addition of a small quantity of sodium bicarbonate previous to the addition of the potassium iodide.[7] Pure arsenious oxide may be used as a trustworthy standard for iodometric estimations.[8]

Solubility data at 25° C. for solutions of arsenious oxide in aqueous alkali halides have been obtained.[9]

Aqueous arsenious acid is readily oxidised by hypoiodites,[10] iodates [11]

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[1] Józefowicz, *Rocz. Chem.*, 1932, 12, 441, 787.

[2] Bobtelski and Rosovskaja-Rossienskaja, *Zeitsch. anorg. Chem.*, 1930, 190, 346.

[3] Washburn and Strachan, *loc. cit.*

[4] Kolthoff, *Pharm. Weekblad*, 1919, 56, 621.

[5] Bobtelski and Rosovskaja-Rossienskaja, *loc. cit.*

[6] Fleury, *J. Pharm. Chim.*, 1920, [7], 21, 385; *Bull. Soc. chim.*, 1920, [4], 27, 490.

and periodates. The oxidation by iodic acid or iodates is an induced reaction which proceeds with rapid initial acceleration owing to the catalytic effect of the I^- ion produced. The reaction appears to proceed according to the following scheme,[1] the first reaction only occurring at a measurable rate :

$$\text{(i)}\ IO_3^- + 2I^- + H^+ \longrightarrow HIO + 2IO^-$$
$$\text{(ii)}\ 2IO^- + 2AsO_3^{\equiv} \longrightarrow 2AsO_4^{\equiv} + 2I^-$$

and

$$HIO + AsO_3^{\equiv} \longrightarrow AsO_4^{\equiv} + H^+ + I^-$$

The induction period of the reaction may be curtailed[2] by (1) the presence of an excess of iodic acid, (2) an increase in the concentrations of the reactants, (3) the addition of a trace of arsenic acid, (4) the addition of a mineral acid and (5) exposure to sunlight. On the other hand, the period may be prolonged by the addition of mercuric chloride or by violent shaking. The proportion of the iodine liberated increases with the arsenious acid concentration and passes through a maximum. The iodine appears on the surface of the solution even though the latter may be covered with benzene (or occasionally it appears at a nucleus on the glass). The reduction of periodate to iodate by means of arsenite is a bimolecular reaction and is of the first order with respect to both components.[3] At 25° C. it proceeds according to the velocity equation

$$d[IO_4^-]/dt = 5{\cdot}5[IO_4^-][AsO_2^-]$$

the units being minutes and gram-molecules. The reaction velocity is independent of the concentration of H^+ ion over the range $[H^+] = 1{\cdot}3 \times 10^{-3}$ to $3{\cdot}4 \times 10^{-7}$.

Arsenious oxide in the solid state is not affected by oxygen under ordinary conditions,[4] but if subjected at high temperature to oxygen under pressure oxidation to the pentoxide results. Thus, if heated at 400° to 480° C. with oxygen at pressures of 130 to 180 atm., oxidation occurs, but is incomplete ; the amount oxidised increases with the temperature.[5] According to Razuvaev and Malinovskiĭ,[6] at 200° to 300° C. the optimum pressure for oxidation by air is 60 to 80 atm., and under these conditions the reaction is complete in about 20 minutes ; finely divided iron has a weak and copper a strong catalytic effect. In the presence of potassium iodide or activated carbon, a suspension of the oxide in water is oxidised by air or oxygen at 130° to 140° C. and 4 to 5 atm. pressure.[7] The usually accepted reaction is

$$As_2O_3 + O_2 = As_2O_5$$

but Reissaus,[8] from a study of the effects of heat on the oxide and metallic arsenites both in the absence and presence of air or oxygen, concluded that direct oxidation was not involved, but that the change was invariably based on the reaction :

$$5As_2O_3 \longrightarrow 3As_2O_5 + 4As$$

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[1] Kubina, *Monatsh.*, 1923, 43, 439.

[2] Sanyal and Dhar, *Zeitsch. anorg. Chem.*, 1924, 139, 161.

[3] Abel and Furth, *Zeitsch. physikal. Chem.*, 1923, 107, 305.

[4] Berthelot, *Compt. rend.*, 1877, 84, 408.

[5] Matignon and Lecanu, *ibid.*, 1920, 170, 941.

[6] Razuvaiev and Malinovski, *J. Appl. Chem.* (*U.S.S.R.*), 1932, 5, 25.

[7] Boller, *British Patent*, 445468 (1934); *American Patent*, 1999053 (1935).

[8] Reissaus, *Zeitsch. angew. Chem.*, 1931, 44, 959.

Arsenious oxide is formed subsequently from the arsenic liberated and then undergoes further decomposition; the arsenic thus acts as an oxygen carrier. By thus heating arsenious oxide under pressure pure arsenic may be prepared.

In neutral, weakly acid or weakly alkaline solutions, arsenious oxide and arsenites are very stable towards gaseous oxygen and such solutions may be kept indefinitely without undergoing change, but in the presence of an excess of alkali, oxidation readily takes place.[1] For this reason standard arsenious solutions containing alkali gradually diminish in titre. Thus a 0·1N solution of arsenious oxide in N sodium hydroxide suffers a daily loss[2] equal to about 0·176 per cent. of As_2O_3. The oxidation rate is directly proportional to the alkalinity of the solution. Weakly alkaline solutions (*p*H 7 to 9) have been found to be unchanged after 18 months. Stable solutions are best prepared by dissolving pure arsenious oxide in carbonate-free sodium hydrogen carbonate solution; in such solutions micro-organisms do not develop nor is arsine produced.

An arsenical solution containing the equivalent of 1 per cent. of arsenious oxide appears as an official preparation in the British Pharmacopœia, 1932, under the name *liquor arsenicalis* or *Fowler's solution.* It is prepared by dissolving 10 g. of the oxide in 100 c.c. of a 5 per cent. potassium hydroxide solution, warming as may be necessary, and adding 500 c.c. of distilled water; this solution is neutralised with dilute hydrochloric acid and made up to 1 litre. This preparation is extremely stable both to light and air, and is compatible with both acids and alkalies. Fungoid growths, however, frequently develop,[3] the causes apparently being contamination either of the water used or of the air with which the solution has been in contact, and also a suitable *p*H value which allows the mould to develop. The addition of preventive agents, *e.g.* 0·25 per cent. of chloroform, has been recommended.[4] Conductivity and potential measurements suggest that the arsenic is present in solution as As_2O_3 and not as potassium arsenite;[5] dissolution in the potassium hydroxide results in the formation of some potassium metarsenite, but this regenerates the oxide on neutralisation with hydrochloric acid.[6] This official solution replaces the "Fowler's solution" of previous editions of the Pharmacopœia, the composition of which was similar to that introduced by Fowler about 1778 under the name of *Compound Spirit of Lavender.* In this the arsenious oxide was dissolved in aqueous potassium carbonate and compound tincture of lavender added; the liquid was thus reddish in colour and alkaline in reaction. Its disadvantage was its frequent incompatibility in modern dispensing; it also undergoes oxidation on keeping.[7] It was therefore supplemented by a 1 per cent. solution containing hydrochloric acid, *liquor arsenici hydrochloricus*, and also by a simple 1 per cent. solution,

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[1] Kolthoff, *Pharm. Weekblad*, 1919, 56, 621.

[2] Tananaev, *Ukraine Chem. J.*, 1930, 5, [Sci.], 217.

[3] Dyer, *Pharm. J.*, 1932, 129, 559; 1933, 130, 5, 176, 215; Rae, *ibid.*, 130, 339; Milne and Rattray, *ibid.*, 130, 246; *Chemist and Druggist*, 1933, 118, 418.

[4] Lum, *Pharm. J.*, 1933, 130, 412.

[5] Morton, *Quart. J. Pharm.*, 1933, 6, 1.

[6] *Cf.* Millar, *Pharm. J.*, 1928, 120, 214, 224; *Chemist and Druggist*, 1928, 108, 352.

[7] Lyons, *Proc. Amer. Pharm. Assoc.*, 1909, p. 901; Reinthaler, *Chem. Ztg.*, 1912, 36, 713; Delany, *Austral. J. Pharm.*, 1923, 4, 27; Danckwortt, *Arch. Pharm.*, 1924, 262, 563; Remders and Vles, *Rec. Trav. chim.*, 1925, 44, 29; Trease, *Pharm. J.*, 1928, 120, 602.

liquor acidi arseniosi (B.P. Codex); the latter, however, deposits octahedral crystals on keeping 2 to 3 weeks.[1]

Matignon and Lecanu[2] observed that a concentrated solution of arsenious oxide in sodium hydroxide under an oxygen pressure of 50 atmospheres at 80° C. was oxidised to the extent of 10·9 per cent. after 5 hours. Under ordinary atmospheric conditions the absorption of oxygen by the arsenite occurs more readily in the presence of a second easily oxidisable substance such as sodium sulphite[3] or ferrous sulphate. In the latter case the amount of oxygen absorbed depends upon the quantity of sodium hydroxide present.[4] Manchot[5] considered that the oxidation of Fe^{++} to Fe^{+++} involved the activation of 1 equivalent of oxygen which was used in the conversion of arsenite to arsenate, but Wieland and Franks[6] found that in the most concentrated solution of arsenite obtainable, of which the *p*H was 6, the activation of only 0·88 equivalent occurred; for solutions of *p*H 10, corresponding with the metarsenite, $NaAsO_2$, activation corresponded with 0·6 equivalent, and for more strongly alkaline solutions corresponding with Na_2HAsO_3 it corresponded with not more than 1 equivalent.[7] When alkalinity corresponded with Na_3AsO_3 activation exceeded 1 equivalent owing to spontaneous oxidation of the arsenite independent of the influence of the ferric salt. This catalytic action of readily oxidisable substances, from which it would appear that one chemical change is able to promote another of the same type, is probably due to the formation of intermediate compounds. The addition of a cerous salt dissolved in concentrated potassium carbonate solution to an excess of aqueous potassium arsenite results in the induced oxidation of the latter, which acts as oxygen acceptor.[8] The cerous solution passes to the quadrivalent ceric state and, according to Baur,[9] 2 molecules of oxygen are fixed on the arsenite for 1 molecule on the cerium. In the presence of glucose, however, the cerous salt exerts purely a catalytic action and under suitable conditions a very small quantity can effect the atmospheric oxidation of an unlimited quantity of the arsenite;[10] this is due to the more profound reducing action of the glucose, which continually converts the ceric salt to the cerous state, in which the cerium is again capable of fixing atmospheric oxygen. These reactions have been investigated from the standpoint of the relative oxidation potentials of the reacting substances.[11]

Another interesting example of induced oxidation is the reaction between chromic acid and a manganous salt in the presence of arsenious acid.[12] The chromic acid is reduced to a chromic salt, while the manganous salt is oxidised to the manganic state and the arsenious acid to

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[1] Franklin, *Pharm. J.*, 1930, 124, 50. *Cf.* Knight, *ibid.*, 1928, 121, 396.

[2] Matignon and Lecanu, *Compt. rend.*, 1920, 170, 941.

[3] Mohr, *Annalen*, 1855, 93, 384; Jorissen, *Rec. Trav. chim.*, 1923, 42, 855; Jorissen and Belmfante, *ibid.*, 1929, 48, 711; Mittra and Dhar, *Zeitsch. anorg. Chem.*, 1922, 122, 146; Palit and Dhar, *J. Phys. Chem.*, 1926, 30, 939.

[4] Gire, *Compt. rend.*, 1920, 171, 174.

[5] Manchot, *Zeitsch. anorg. Chem.*, 1901, 27, 420.

[6] Wieland and Franks, *Annalen*, 1928, 464, 101.

[7] *Cf.* Gire, *loc. cit.*

[8] Goard and Rideal, *Proc. Roy. Soc.*, 1924, A 105, 135.

[9] Baur, *Zeitsch. anorg. Chem.*, 1902, 30, 25; *Ber.*, 1903, 36, 3038. *Cf.* Engler and Wild, *ibid.*, 1903, 36, 2642.

[10] Job, *Ann. Chim. Phys.*, 1900, [7], 20, 205; *Compt. rend.*, 1902, 134, 1052.

[11] Goard and Rideal, *loc. cit.*

[12] Zwerina, *Zeitsch. anorg. Chem.*, 1928, 170, 389.

arsenic acid, probably in accordance with the equations:

$$(1)\ \mathrm{Cr^{VI} + As^{III} = Cr^{IV} + As^{V}}$$
$$(2)\ \mathrm{Cr^{IV} + Mn^{II} = Cr^{III} + Mn^{III}}$$

The relation of $\mathrm{Mn^{II}}$ oxidised to $\mathrm{As^{III}}$ oxidised is known as the "induction factor," and is found to be about 0·5 at the beginning of the reaction, whatever amount of manganous salt may be present; but the value diminishes as the action proceeds, for as the chromate concentration falls, the tervalent manganese is reduced by the tervalent arsenic to an increasing extent. The presence of a trace of potassium iodate produces great irregularity in the induction factor and lowers its initial value to about 0·25.

A further example of an induced reaction consists in the atmospheric oxidation of an ammoniacal solution of arsenite, which is brought about by the addition of cobaltous sulphate, the latter also being oxidised.[1]

The oxidation of arsenites by oxygen in the presence of sodium hydroxide is affected by the presence of other types of catalysts (see p. 175). Thus in the presence of copper sulphate and with less alkali than corresponds with $\mathrm{Na_3AsO_3}$, the velocity of oxidation is very small, but with an increased amount of sodium hydroxide present, copper hydroxide or oxide is formed and the action is accelerated, and indeed copper oxide itself may be used as catalyst.[2] With an excess of sodium hydroxide and a suitable quantity of copper oxide, normal sodium arsenite may be completely oxidised to arsenate in a few hours. Similarly the presence of an excess of sodium carbonate facilitates oxidation.[3]

On the other hand, an aqueous solution containing an alkali dihydrogen arsenite and sodium hydrogen carbonate is extremely stable towards oxygen and at ordinary temperature no oxidation can be observed after 4 months, although slight oxidation occurs on heating.[4] Shilov and Pevzner,[5] in studying the atmospheric oxidation of potassium dihydrogen arsenite, found that salts of copper, iron and manganese, free iodine and titanic acid were ineffective as catalysts, whilst chromates, molybdates and cerium salts were only slightly effective. Complete oxidation was possible, however, in the combined presence of oxides of nitrogen and hydriodic acid. Into a column filled with glass beads, aqueous solutions of the arsenite and potassium iodide were introduced dropwise. Into the same column were introduced air, hydrogen chloride and nitrous acid. The addition of these components could be regulated and by proper adjustment of the ratio of the ingredients and the velocity of the gases through the column, complete oxidation to arsenate was attained. In view of the ready oxidation of arsenious acid by iodine (p. 144), the following series of reactions appears possible:

$$\mathrm{2HNO_2 + 2HI = 2H_2O + I_2 + 2NO} \quad . \quad . \quad \text{(i)}$$
$$\mathrm{I_2 + KH_2AsO_3 + H_2O = KH_2AsO_4 + 2HI} \quad . \quad . \quad \text{(ii)}$$
$$\mathrm{2NO + O_2 + H_2O = HNO_3 + HNO_2} \quad . \quad . \quad \text{(iii)}$$

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[1] Pavlinova, *Ukraine Chem. J.*, 1929, 4, 475.

[2] Kato and Murakami, *J. Soc. Chem. Ind. Japan*, 1930, 33, 226.

[3] Crofts, *Canadian J. Ind.*, 1858, 3, 126; *Chem. Gaz.*, 1858, 16, 121; McDonnell, *ibid.*, 1859, 17, 414; *J. prakt. Chem.*, 1860, [1], 79, 502; Ludwig, *Arch. Pharm.*, 1859, [2], 97, 27; Vogel, *Repert. Pharm.*, 1873, 22, 577.

[4] Reinthaler, *Chem. Ztg.*, 1912, 36, 713; *cf.* Mohr, *Annalen*, 1855, 93, 384.

[5] Shilov and Pevzner, *J. Chem. Ind. (U.S.S.R.)*, 1930, 7, 759.

We have already seen, however, that equation (ii) becomes reversed in acid medium, and the prevention of this reversal here appears to be due to the removal of the hydriodic acid according to equation (i).

Tingle[1] observed that a solution of arsenious oxide in aqueous alcohol, after boiling for 26 hours, was oxidised to arsenic acid, but this was denied by Edgerton.[2] Kessler[3] observed that when sodium arsenite was undergoing oxidation by chromic acid, oxidation by atmospheric oxygen occurred simultaneously.

Arsenious oxide is oxidised to the pentoxide by hydrogen peroxide and by ozone;[4] in alkaline solution the oxidation by ozone is incomplete.[5]

By exposing an aqueous solution of arsenious acid to X-rays oxidation to arsenic acid occurs accompanied by the liberation of an equivalent amount of hydrogen.[6]

When heated with sulphur, arsenious oxide yields the disulphide or trisulphide according to the proportion of sulphur employed (see pp. 240, 244); sulphur dioxide is also produced.[7] An aqueous solution of arsenious oxide or of an arsenite is coloured yellow on passing hydrogen sulphide and in the presence of an acid a precipitate of arsenic trisulphide is produced[8] (see p. 244). The addition of arsenious oxide in small quantity (0·2 per cent.) to aqueous sodium carbonate increases the amount of hydrogen sulphide that can be absorbed by the solution,[9] but on regenerating with air the whole of the hydrogen sulphide is not evolved. Arsenious oxide is soluble in aqueous sulphuric acid, the solubility varying somewhat irregularly with the acid concentration and the temperature;[10] the oxide may be recovered either by crystallisation or by distillation of the acid. It also dissolves readily in fuming sulphuric acid[11] and from the solution sulphato-compounds of the type $As_2O_3.nSO_3$ may be obtained (see p. 284), thus indicating a base-like tendency in arsenious oxide; but the products have not the properties of metallic sulphates. The presence of arsenious oxide retards the oxidation of sodium sulphite.[12]

When dry arsenious oxide is fused with sodium thiosulphate a mixture of the di- and tri-sulphides results.[13] In aqueous solution and in acidified solutions of arsenites the addition of aqueous sodium thiosulphate causes the precipitation of arsenious sulphide after a sharply defined induction period, the duration of which is in inverse proportion to the thiosulphate concentration and practically independent

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[1] Tingle, *J. Amer. Chem. Soc.*, 1911, 33, 1762.

[2] Edgerton, *J. Amer. Chem. Soc.*, 1913, 35, 1769.

[3] Kessler, *Pogg. Annalen*, 1861, 113, 145.

[4] Schonbein, *ibid.*, 1848, 75, 361.

[5] Schonbein, *loc. cit.*; Soret, *Compt. rend.*, 1854, 38, 445; Thénard, *ibid.*, 1872, 75, 174, 458; Ladenburg, *Ber.*, 1903, 36, 115.

[6] Fricke and Hart, *J. Chem. Physics*, 1935, 3, 596.

[7] Berzelius, *Schweigger's J.*, 1822, 34, 46; *Pogg. Annalen*, 1826, 7, 1, 137; Nilson, *Akad. Handl. Stockholm*, 1871, 10, 2; *Oefvers. Akad. Stockholm*, 1871, 28, 303; *J. prakt. Chem.*, 1876, [2], 14, 159; Marckwald and Foisik, *Ber.*, 1910, 43, 1710.

[8] Brandes, *Brandes' Arch.*, 1828, 25, 269; Reinsch, *J. prakt. Chem.*, 1838, [1], 13, 133; Lassaigne, *J. Chim. Méd.*, 1842, [2], 8, 584; Becker, *Arch. Pharm.*, 1847, 156, 287; Lefort and Thibault, *Pharm. J.*, 1882, [3], 13, 301.

[9] Pieters and Smeets, *Chem. Weekblad*, 1932, 29, 73.

[10] Chodounsky, *Chem. Listy*, 1888, 13, 114.

[11] Schultze-Sellac, *Ber.*, 1871, 4, 109.

[12] Moureu and others, *Compt. rend.*, 1928, 187, 917.

[13] Faktor, *Pharm. Post*, 1905, 38, 527.

of the concentration of the acid.[1] The nature of the acid, however, influences the time, a longer period being observed with hydrochloric acid than with acetic acid. This reaction may be employed for the experimental demonstration of induction periods and of the relation between concentration and reaction velocity. There is evidence of the formation of intermediate unstable thio-compounds. Thus, from a solution containing arsenious oxide in hydrochloric acid, potassium chloride and sodium thiosulphate, a white compound,[2] potassium arsenothiosulphate, $K_3As(S_2O_3)_3$, may be precipitated by means of alcohol. This compound in aqueous solution[3] deposits arsenious sulphide "after a shorter or longer time according to concentration and temperature," *i.e.* after an induction period. It is stable when dry but on heating decomposes thus:

$$2K_3As(S_2O_3)_3 = As_2S_3 + 3K_2SO_4 + 3SO_2 + 3S$$

In alkaline solutions of arsenites, thioarsenates are formed, which may be crystallised out, while sulphite or bisulphite remains in solution, thus:[4]

$$Na_3AsO_3 + Na_2S_2O_3 = Na_3AsO_3S + Na_2SO_3$$

and

$$Na_2HAsO_3 + Na_2S_2O_3 = Na_3AsO_3S + NaHSO_3$$

A small quantity of arsenic is precipitated in each case. Sodium dihydrogen arsenite yields a considerable precipitate of arsenic and also of the red disulphide. The polythionates react similarly to thiosulphates, yielding sulphite, thioarsenate and arsenate.[5] The persulphates also cause oxidation to arsenate.[6] Sodium hydrosulphite added to an aqueous solution of arsenious oxide precipitates brown arsenic; if the solution is strongly acid the precipitate also contains arsenious sulphide and sulphur.[7] Arsenious oxide heated at 120° C. in a sealed tube with sulphur monochloride yields arsenic trichloride, thus:[8]

$$2As_2O_3 + 6S_2Cl_2 = 4AsCl_3 + 3SO_2 + 9S$$

Arsenious oxide appears to undergo no change when heated in gaseous ammonia;[9] it is insoluble in liquid ammonia,[10] but dissolves readily in hot aqueous ammonia. Heated with solid ammonium chloride, arsenious chloride and ammonia are produced.[11] With nitrogen iodide the following reaction occurs:[12]

$$3As_2O_3 + 2N_2H_3I_3 + 6H_2O = 3As_2O_5 + 4NH_3 + 6HI$$

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[1] Vortmann, *Ber.*, 1889, 22, 2308; Forbes, Estill and Walker, *J. Amer. Chem. Soc.*, 1922, 44, 97.

[2] von Szilàgyi, *Zeitsch. anorg. Chem.*, 1920, 113, 75.

[3] See also Foerster and Stuhmer (*ibid.*, 1930, 206, 1) and Kurtenacker and Czernotzky (*ibid.*, 1928, 175, 367) on the catalytic influence of arsenious acid on the decomposition of thiosulphates to polythionates.

[4] Weinland and Gutmann, *ibid.*, 1898, 17, 409.

[5] Gutmann, *Ber.*, 1905, 38, 1728, 3277; 1907, 40, 2818; 1908, 41, 1650.

[6] Grutzner, *Arch. Pharm.*, 1899, 237, 507; Newbery, *J. Chem. Soc.*, 1925, 127, 1751.

[7] Brunck, *Annalen*, 1904, 336, 281.

[8] Oddo and Serra, *Gazzetta*, 1899, 29, ii, 355.

[9] Bachmann, *Amer. Chem. J.*, 1888, 10, 42.

[10] Gore, *Proc. Roy. Soc.*, 1872, 20, 441; 1873, 21, 140; Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 820.

In alkaline solution, oxidation may be brought about by hydroxylamine or nitric oxide; thus with the former the following reactions occur concurrently:[1]

$$Na_3AsO_3 + NH_2OH = Na_3AsO_4 + NH_3$$
$$3NH_2OH = NH_3 + N_2 + 3H_2O$$

With nitric oxide the reaction appears to be termolecular—[2]

$$Na_3AsO_3 + 2NO = Na_3AsO_4 + N_2O$$

the velocity increasing with increasing concentration of alkali hydroxide. A similar change occurs when an excess of sodium arsenite is added to a fresh solution of nitric oxide in a strongly alkaline solution of sodium sulphite.[3] Nitrous acid acts extremely slowly on a solution of the oxide in aqueous sulphuric acid; the reaction speed is at a maximum[4] when the sulphuric acid is of density 1·39 to 1·47.

In the finely divided state, arsenious oxide can be oxidised with oxygen under pressure in the presence of nitric acid, which acts as oxygen carrier.[5] The oxidising action of the nitric acid usually ceases when reduction to nitric oxide has occurred, but nitric acid is regenerated by oxygen under pressure, thus:

$$4NO + 3O_2 + 2H_2O = 4HNO_3$$

The oxidation of the arsenious oxide is practically quantitative at 90° C. with nitric acid of 40 to 60 per cent. concentration and the oxygen under 20 atm. pressure; the rate of the oxidation and of re-formation of nitric acid increases with rise in temperature and with increase in oxygen pressure. Increase of acid concentration accelerates oxidation, but retards regeneration. Nitric acid alone also brings about oxidation, oxides of nitrogen and nitrous acid being formed as intermediate products.[6] It is suggested[7] that the nitrous acid produces nitrogen trioxide, which determines the rate of oxidation:

$$2HNO_2 = N_2O_3 + H_2O$$
$$N_2O_3 + H_3AsO_3 = H_3AsO_4 + 2NO$$

The speed of the reaction is thus proportional to the concentration of arsenious acid and to the square of the concentration of nitrous acid present. The effect of the presence of mercuric salts on the velocity of this oxidation is peculiar;[8] at a concentration of $7 \cdot 7 \times 10^{-6}$ mol. per litre the reaction is completely inhibited, but with diminishing concentration the inhibiting effect becomes less marked until, at $7 \cdot 7 \times 10^{-9}$ mol. per litre, there is a definite positive catalytic effect which becomes more marked at the extremely low concentration of $7 \cdot 7 \times 10^{-11}$ mol. per litre. The retarding effect of the mercuric salt may be overcome by the addition of a small amount of halogen acid to the nitric acid.[9] The

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[1] Gutmann, *Ber.*, 1922, 55, [B], 3007.

[2] Klemenc, *ibid.*, 1925, 58, [B], 492.

[3] Gutmann, *loc. cit.*

[4] Bailey, *62nd Ann. Rept. on Alkali, etc. Works*, 1926, p. 12.

[5] Askenasy, Elöd and Zieler, *Zeitsch. anorg. Chem.*, 1927, 162, 161.

[6] Lunge, *Ber.*, 1878, 11, 1229; Geuther, *Annalen*, 1888, 245, 96.

[7] Abel, Schmid and Weiss, *Zeitsch. physikal. Chem.*, 1930, 147, A, 69.

[8] Klemenc and Pollak, *Zeitsch. anorg. Chem.*, 1921, 115, 131. See also Klemenc and Schöller, *ibid.*, 1924, 141, 231.

[9] Smith and Miller, *Ind. Eng. Chem.*, 1924, 16, 1168.

oxidation by nitric acid may be facilitated by the addition of a small quantity of iodine or potassium iodide.[1]

Phosphorus converts arsenious oxide to phosphide[2] (see p. 286). When an aqueous solution is heated with phosphorus to 200° C., a precipitate of arsenic and arsenic phosphide is formed.[3] A mixture of the dry oxide with phosphorus trichloride heated to 120° C. in a sealed tube reacts as follows:[4]

$$6PCl_3 + 5As_2O_3 = 3P_2O_5 + 6AsCl_3 + 4As$$

The addition of phosphorus trichloride to an aqueous solution precipitates brown amorphous arsenic; the reaction does not occur if the trichloride is first dissolved in water, nor when phosphorous acid is used.[5] The reaction, which accords with the equation

$$3PCl_3 + As_2O_3 + 9H_2O = 2As + 3H_3PO_4 + 9HCl$$

is very delicate and is able to detect the presence of 0·000075 g. As per c.c. Phosphorus tribromide and triiodide react similarly, but more slowly; in the latter case the precipitate is contaminated with red phosphorus. The reaction proceeds also when an aqueous solution of the tribromide or triiodide is used. Phosphorus oxychloride yields arsenic trichloride[6] at 250° C., thus:

$$As_2O_3 + 2POCl_3 = 2AsCl_3 + P_2O_5$$

Phosphorus pentachloride also reacts to yield arsenic trichloride.[7] Arsenious oxide in aqueous solution is reduced by hypophosphorous acid, especially on boiling, when phosphine is liberated and brown arsenic precipitated.[8] The reduction is readily brought about by calcium hypophosphite dissolved in 10 parts of hydrochloric acid (dens. 1·126), this salt being preferable in use to the sodium salt and providing an extremely sensitive reagent, although in the presence of slight traces of arsenic the brown colour may appear only after the lapse of 20 to 30 minutes.[9] Arsenious oxide dissolves in arsenic trichloride to form an oxychloride.[10]

Carbon brings about reduction of arsenious oxide at a temperature below red heat,[11] while in carbon monoxide reduction begins at 60° C.[12] The numerous reactions of arsenious oxide with organic compounds are described in Vol. XI, Part II, of this Series. Silicon tetrachloride heated for 30 hours at 270° to 280° C. with the oxide yields arsenic trichloride,[13] whilst silicochloroform when heated with the oxide in the presence of aqueous sodium hydroxide or sodium hydrogen carbonate

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[1] Latimer, *American Patent*, 1974747 (1934).

[2] Berzelius, *Ann. Chim. Phys.*, 1817, [2], 5, 179; 1819, [2], 11, 225.

[3] Oppenheim, *Bull. Soc. chim.*, 1864, [2], 1, 165.

[4] Michaelis, *Jenaische Zeitsch.*, 1870, [1], 6, 239.

[5] Sen, *J. Proc. Asiatic Soc. Bengal*, 1919, 15, 263.

[6] Reinitzer and Goldschmidt, *Monatsh.*, 1881, 1, 427. *Cf.* Michaelis, *loc. cit.*

[7] Hurtzig and Geuther, *Annalen*, 1859, 111, 172.

[8] Fischer, *Pogg. Annalen*, 1827, 9, 260; Janowsky, *Ber.*, 1875, 8, 1636; Engel, *Compt. rend.*, 1883, 96, 498; Thiele, *Apoth. Ztg.*, 1890, 5, 86; Rupp and Muschiol, *Ber. deut. pharm. Ges.*, 1923, 33, 62; Deussen, *Arch. Pharm.*, 1926, 264, 355.

[9] Rupp and Muschiol, *loc. cit.*

[10] Wallace and Penny, *Phil. Mag.*, 1852, [4], 4, 361; Hurtzig and Geuther, *loc. cit.*

[11] Berzelius, *Ann. Chim. Phys.*, 1817, [2], 5, 179; 1819, [2], 11, 225; Vogel, *Dingl. poly. J.*, 1857, 144, 159; Pereira, *Riv. Chim. Appl.*, 1919, 4, 174.

[12] Fay and co-workers, *Polyt. Eng.*, 1910, 10, 72.

[13] Rauter, *Annalen*, 1892, 270, 236; *Jahresber.*, 1892, p. 646.

causes reduction to arsenic, thus :[1]

$$As_2O_3 + 3SiHCl_3 + 9NaOH = 3Si(OH)_4 + 9NaCl + 2As$$

Reduction to arsenic also results on heating with boron nitride.[2]

When heated to redness with an alkali metal or with zinc or aluminium, reduction of the oxide readily occurs.[3] The production of hydrides by the action of metals on the dissolved oxide has been described (see pp. 80, 81). Reaction with various metallic oxides, hydroxides and carbonates results in the formation of arsenites and arsenates. Certain hydroxides, however, particularly those of iron, aluminium, chromium, magnesium, manganese and zinc, have the power of removing arsenious oxide from solution, although no chemical combination appears to take place. The action was first observed by Bunsen and Berthold in connection with ferric hydroxide; they suggested the use of the latter as an antidote for arsenical poisoning (see p. 298), the removal of arsenic being attributed to the formation of a hydrolysed ferric arsenite.[4] The formation of such a compound could not be demonstrated, however,[5] and Biltz showed [6] that the phenomenon was one of reversible adsorption. He observed that the amount of arsenious oxide adsorbed from solution diminished with the ageing of the ferric hydroxide, and suggested that at equilibrium the distribution of the oxide between the hydroxide and water could be represented by the usual adsorption isotherm, $C_1 = kC_2^{1/n}$, where C_1 is the concentration of arsenious oxide in the ferric hydroxide, C_2 the concentration of arsenious oxide in solution, and k and n are constants. Later workers have shown that this relation is not quite true,[7] and that for samples of the adsorbent prepared under different conditions and of different ages, whilst there is little variation in the value of n, k varies between wide limits. Thus in an investigation by Boswell and Dickson it was found that $1/n$ varied only from 0·183 to 0·284, but that k varied from 33·3 to 200. Sen [8] observed that the adsorptive power of a sample of ferric hydroxide after ageing four months was diminished by 50 per cent. If the hydroxide is prepared by the addition of ammonium hydroxide to a solution of a ferric salt the adsorptive capacity is greater than if prepared by addition of a ferric salt to ammonium hydroxide.[9] Also the adsorptive power decreases the higher the temperature at which the hydroxide is produced,[10] and with specimens prepared at 75° and 100° C. the amount of adsorption deviates greatly from the relation expressed above.

Both arsenious acid and sodium arsenite are strongly adsorbed by ferric hydroxide. The amount adsorbed from a given volume of solution

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[1] Ruff and Albert, *Ber.*, 1905, 38, 2234.

[2] Möser and Eidmann, *Ber.*, 1902, 35, 535.

[3] Gay-Lussac and Thénard, "*Recherches physico-chimiques*," Paris, 1811, 1, 516; Gehlen, *Schweigger's J.*, 1815, 15, 501; 1817, 20, 353; Frémy, *Compt. rend.*, 1870, 70, 66; Berger, *ibid.*, 1920, 170, 1492.

[4] Bunsen, *Pogg. Annalen*, 1834, 32, 124; Guibourt, *J. Chim. Méd.*, 1839, 15, 306; Reychler, *J. Chim. phys.*, 1909, 7, 362; 1910, 8, 10; Oryng, *Kolloid-Zeitsch.*, 1918, 22, 149.

[5] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[6] Biltz, *Ber.*, 1904, 37, 1766, 3138; *J. Chim. phys.*, 1909, 7, 370.

[7] Mecklenberg, *Zeitsch. physikal. Chem.*, 1913, 83, 609; Boswell and Dickson, *J. Amer. Chem. Soc.*, 1918, 40, 1793.

[8] Sen, *J. Physical Chem.*, 1927, 31, 419.

[9] Clavera, *Anal. Fis. Quim.*, 1926, 24, 168.

[10] Yoe, *J. Amer. Chem. Soc.*, 1930, 52, 2785.

increases with the initial concentration, and for a given concentration the adsorption increases with the volume.[1] The amount of adsorption depends also on the quantity of ferric hydroxide employed, but in a decreasing ratio.[2] The curvature of the adsorption isotherms depends therefore on these factors. Adsorption takes place very rapidly, but the time taken for the limiting value to be reached appears to vary with conditions, from one to twelve hours being recorded. Temperature has little influence.

Sodium hydroxide is adsorbed appreciably by ferric hydroxide and the presence of the alkali in solution diminishes the amount of arsenic adsorbed. On the other hand, salts such as potassium or ammonium chloride have no effect on the adsorption. The ferric hydroxide, especially when fresh, is liable to become peptised by arsenious acid in certain dilutions. Apparently peptisation results when a definite quantity of arsenious acid has been adsorbed by each particle.[3] Excess of arsenious acid, however, causes flocculation.

Colloidal saccharated iron is sometimes used in place of ferric hydroxide as an antidote in arsenical poisoning, but its adsorptive capacity depends on the alkalinity of the medium.[4] Thus a commercial preparation containing 0·75 per cent. of sodium hydroxide was found to adsorb 12·57 per cent. of arsenious oxide (reckoned on the amount of iron present); addition of alkali increased the adsorption until, with 1·28 per cent. of sodium hydroxide present, there was a maximum adsorption of 27 per cent. The addition of acid correspondingly diminished the adsorption. A gel of ferric magnesium hydroxide, if prepared without boiling, also adsorbs arsenic from sodium arsenite solutions.[5]

Ferric hydroxide is far from being the best adsorbent for arsenious oxide. According to Boutaric and Perreau,[6] the most active hydroxides are those of zinc and manganese, while the following are in order of decreasing adsorptive activity: cadmium, chromium, iron, aluminium and magnesium. The last two adsorb arsenic from Fowler's arsenite solution (see p. 147) but not from sodium cacodylate.[7] Aluminium hydroxide behaves similarly to ferric hydroxide; the presence of potassium chloride has no effect upon the equilibrium, which is reversible, nor does sucrose or alcohol affect the adsorption. If the aluminium hydroxide gel is boiled with water for 15 minutes, the adsorptive power at the ordinary temperature is greatly reduced.[8] Adsorption of arsenious oxide by chromium hydroxide is much greater than by ferric or aluminium hydroxide and the action differs from that of the two latter gels in that the equilibrium is not reversible and, in fact, no true equilibrium can be attained.[9] Moreover, arsenious acid is adsorbed to a greater extent than is sodium arsenite, whereas in the

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[1] Sen, *loc. cit.*; Boutaric and Perreau, *J. Pharm. Chim.*, 1928, [8], 8, 211.

[2] Lockemann, *Verh. Ges. deut. Naturforsch. Aerzte*, 1911, **II**, 25; Boutaric and Perreau, *loc. cit.*

[3] Boutaric and Perreau, *Rev. gén. Colloid.*, 1928, 6, 1.

[4] Herboth, *Arch. Pharm.*, 1926, **264**, 181. *Cf.* Mannich and Rojahn, *ibid.*, 1924, **262**,

case of aluminium hydroxide no difference is observed. Zirconium hydroxide exhibits considerable adsorptive power,[1] as also does suitably prepared wood charcoal.[2]

After an extensive study of the adsorption of arsenious oxide by metallic hydroxides,[3] Sen concluded that this type of adsorption resembles that of cations by manganese dioxide, and that the chemical affinity between the adsorbent and the substance adsorbed plays an important part, thus differing from adsorption by charcoal. It has been observed that soils having a high absorption capacity for bases also absorb the arsenite ion from solutions of 0·001 to 0·01N concentration.[4] The absorption increases with time, without reaching an end-point, and the process follows the normal adsorption equation $C_1 = kC_2^{1/n}$. The addition of ferric oxide or calcium carbonate to the soil considerably increases the capacity for absorption, but such salts as calcium sulphate or copper sulphate have no effect.

The reducing power of arsenious oxide has been the subject of much investigation, especially in regard to its reaction with the more important oxidising agents. Arsenious acid and arsenites undergo oxidation in the presence of chromic acid or dichromates.[5] With a mixture of potassium dichromate and sulphuric acid, the oxidation of arsenious acid proceeds at a rate nearly proportional to the first power of the concentration of the dichromate,[6] to the first power of the concentration of the arsenious acid and to the 1·4th power of that of the sulphuric acid; the inexactness of the proportionality is probably due to incomplete ionic dissociation of the dichromate and to the influence of the hydrogen ion concentration on the dissociation of the arsenious acid. Between 0° and 10° C. the temperature coefficient is low, the increase in the rate of oxidation over this interval being only 26 per cent. If potassium iodide is added to the mixture of arsenious acid, dichromate and sulphuric acid, an induced reaction occurs in which the arsenious acid acts as the inductor and the iodide as the acceptor of the oxidation.[7] Under these conditions the rate at which the chromic acid is reduced equals the sum of the rates at which it is reduced in solutions of arsenious acid and potassium iodide separately, the former reaction being retarded as much as the latter is accelerated. The temperature coefficients of the single actions and the joint action are equal.

The oxidation of arsenious oxide or arsenites by means of potassium permanganate has attracted considerable attention owing to its analytical applications. It was early recognised that the course and speed of the reaction and the nature of the products depended on conditions of temperature, acid concentration and the nature of the ions present.[8] In neutral or alkaline solution the oxidation proceeds slowly,

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[1] Sen, *Zeitsch. anorg. Chem.*, 1928, 174, 75.

[2] Dubinin, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 1187.

[3] Sen, *loc. cit.*; *J. Physical Chem.*, 1927, 31, 419, 686, 922, 1840.

[4] Dratschev, *Zeitsch. Pflanz. Dung.*, 1933, 30 A, 156.

[5] Kessler, *Pogg. Annalen*, 1853, 95, 204; 1863, 118, 17; de St Gilles, *Compt. rend.*, 1858, 46, 424; Feigl and Weiner, *Zeitsch. anal. Chem.*, 1924, 64, 302.

[6] de Lury, *J. Phys. Chem.*, 1907, 11, 47.

[7] de Lury, *ibid.*, 1907, 11, 54.

[8] Bussy, *Compt. rend.*, 1847, 24, 774; Kessler, *Pogg. Annalen*, 1853, 95, 204; 1863, 118, 17; de St Gilles, *Compt. rend.*, 1858, 46, 424; *Ann. Chim. Phys.*, 1859, [3], 55, 385; Lenssen, *J. prakt. Chem.*, 1859, [1], 78, 197; Waitz, *Zeitsch. anal. Chem.*, 1871, 10, 174; Vanino, *ibid.*, 1895, 34, 426; Kuhling, *Ber.*, 1901, 34, 404; Deiss, *Chem. Zeit.*, 1910, 34, 237; Trautmann, *Zeitsch. anal. Chem.*, 1911, 50, 371; Moser and Perjatel, *Monatsh.*, 1912, 33, 751.

but it is more rapid in acid solution. In alkaline solution the reduction of the permanganate results in the precipitation of manganese dioxide according to the equation [1]

$$3As_2O_3 + 4KMnO_4 = 3As_2O_5 + 2K_2O + 4MnO_2$$

but an excess of permanganate is necessary for the complete oxidation of the arsenious oxide. Some manganese remains in colloidal solution as manganic hydroxide, and this is precipitated if an electrolyte such as potassium sulphate be present.[2] If the arsenite is in excess, reduction proceeds further, the precipitate consisting of an indefinite mixture of manganous oxide and manganese dioxide; in complete absence of air the product is manganous hydroxide.[3] These precipitates adsorb a considerable quantity of arsenic from the solution. In slightly acid medium a green colloidal solution of manganese dioxide may be obtained; [4] this on keeping deposits as a black precipitate containing arsenic.

In the presence of a mineral acid the complete oxidation of arsenic to the quinquevalent state by means of permanganate is difficult, probably owing to the fact that whereas the permanganate is rapidly reduced to the manganic condition, the complete reduction to the manganous state usually occurs slowly.[5] With sulphuric [6] or nitric acid this is the case even at 100° C., but with hydrochloric acid the reaction proceeds more rapidly to completion.[7] Under the influence of certain catalysts, however, the reaction may be accelerated so that it takes place practically instantaneously in the cold, and accurate estimation of arsenious acid may thus be made by titration with permanganate. Suitable catalysts are potassium iodide, potassium iodate, silver chloride,[8] iodine chloride [9] and osmium tetroxide.[10] In the presence of hydrochloric acid, the concentration of which should be from 0·5 to 2N, the addition of one drop of 0·0025N solution of potassium iodide or iodate to the portion to be titrated is sufficient.[11] In the presence of sulphuric acid, the latter should be at least 0·5N and should contain about 1 g. of sodium chloride per 100 c.c., the same amount of iodide being added. The effect of the catalyst is presumably due to the primary formation of hypoiodous acid by the action of the tervalent manganese on the iodide, the hypoiodous acid immediately oxidising the arsenious acid. The favourable effect of the iodide is hindered by the presence of such compounds as mercuric salts or hydrofluoric, metaphosphoric and tungstic acids, which allow the formation of undissociated or slightly ionised complexes. The end-point of the

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[1] Feigl and Weiner, *Zeitsch. anal. Chem.*, 1924, 64, 302.

[2] Brauner, *ibid.*, 1916, 55, 225.

[3] Feigl and Weiner, *loc. cit.*

[4] Geloso, *Bull. Soc. chim.*, 1925, [4], 37, 641; *Compt. rend.*, 1920, 171, 1145.

[5] Lang, *Zeitsch. anal. Chem.*, 1931, 85, 176; Travers, *Bull. Soc. chim.*, 1925, [4], 37, 456.

[6] The mechanism of the reaction between arsenites and potassium permanganate in dilute sulphuric acid solution is discussed by Oryng, *Roczniki Chem.*, 1927, 7, 334; *Zeitsch. anorg. Chem.*, 1927, 163, 195; Holluta, *ibid.*, 1928, 168, 361.

[7] Kolthoff, *Pharm. Weekblad*, 1924, 61, 738.

[8] Lang, *Zeitsch. anorg. Chem.*, 1926, 152, 197; *Zeitsch. anal. Chem.*, 1931, 85, 176; Cantoni, *Annali Chim. Appl.*, 1926, 16, 153.

[9] Swift and Gregory, *J. Amer. Chem. Soc.*, 1930, 52, 901.

[10] Gleu, *Zeitsch. anal. Chem.*, 1933, 95, 305.

[11] Lang, *loc. cit.*

titration may be determined potentiometrically.[1] If osmium tetroxide is used as catalyst, a few drops of a 0·01M aqueous solution should be added to each portion to be titrated.

Quadrivalent cerium salts may be volumetrically determined by arsenious acid in aqueous sulphuric acid solution using a manganese salt as catalyst, with potassium iodate present as a promoter.[2] Excess of arsenious acid is used and back-titrated with permanganate. If nitric acid is present in place of sulphuric acid, an alkali chloride and a trace of iodine are used to promote the action of the manganese salt. Direct potentiometric titration with arsenious acid may also be employed.

If arsenious oxide is heated in a sealed tube with ferric chloride in aqueous hydrochloric acid (1·5 to 4N), reaction proceeds according to the equation [3]

$$2FeCl_3 + H_3AsO_3 + H_2O \rightleftharpoons 2FeCl_2 + H_3AsO_4 + 2HCl$$

The equilibrium constant K as given by $[H_3AsO_3][FeCl_3]^2/[H_3AsO_4][FeCl_2]^2[HCl]^2$ is 0·0354 at 107° C. and 0·117 at 127° C. The forward and reverse reactions are both termolecular and are accelerated by hydrochloric acid. The thermal value of the reaction from left to right is 18,000 calories. Sarma [4] studied the reaction in aqueous solution at 50° C. in the presence of potassium iodide as catalyst. Equilibrium was attained in 10 hours. The reaction is bimolecular in respect of the ferric salt and unimolecular in respect of the arsenious acid. There appear to be two consecutive reactions—

$$\text{(i)} \quad 2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$$
$$\text{(ii)} \quad I_2 + H_3AsO_3 + H_2O = 2HI + H_3AsO_4$$

the latter being relatively slow, but increasing with the concentration of the catalyst. The heat evolved in the oxidation of 1 gram-molecule of arsenious acid was found to be 13,600 calories.

Silver nitrate in ammoniacal solution may be completely reduced to silver by aqueous arsenious oxide. The reduction is hindered by the presence of ammonium sulphate, owing to the decrease in concentration of the hydroxyl ions ; [5] neutral salts such as sodium sulphate or sodium nitrate have no effect. Similarly, auric chloride may be reduced to gold.[6] At 20° C. an aqueous solution of vitreous arsenious oxide reacts 4 to 5 times as rapidly as an aqueous solution of the octahedral form ; [7] the greater rate of dissolution in water of the former variety has been mentioned (p. 137), but from supersaturated solutions of the two forms there is no appreciable difference in the rates of deposition. The explanation of the inferior reducing power of the crystalline variety may be that there exist "anisotropic molecules" which only slowly lose their anisotropic properties. An ammoniacal solution of arsenious oxide heated with cupric sulphate in a sealed tube at 100° C. causes reduction

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[1] For suitable cell combinations for the electrometric titration of arsenites with permanganate, see Lang, *Zeitsch. Elektrochem.*, 1926, 32, 454; also Hall and Carlson, *J. Amer. Chem. Soc.*, 1923, 45, 1615.

[2] Lang and Zweřina, *Zeitsch. anal. Chem.*, 1932, 91, 5.

[3] Jellinek and Winogradoff, *Zeitsch. Elektrochem.*, 1924, 30, 477.

[4] Sarma, *J. Indian Chem. Soc.*, 1930, 7, 31.

[5] Kohn, *Monatsh.*, 1923, 43, 367.

[6] Rose, *Pogg. Annalen*, 1849, 76, 734.

[7] Jenckel, *Zeitsch. anorg. Chem.*, 1929, 182, 314.

to the cuprous salt. The reduction is retarded by the presence of ammonium salts, but is not affected by the presence of neutral salts such as potassium chloride or nitrate.[1]

The reduction of arsenious acid by means of stannous chloride has already been described (p. 28), the well-known "Bettendorff's test" depending upon the reaction.[2] In the presence of concentrated hydrochloric acid, a voluminous brown precipitate, consisting mainly of yellow arsenic with small amounts of tin, is formed. Velocity measurements lead to the view [3] that the reaction takes place between arsenious and chloride ions and the complex H_2SnCl_4. Dilution with water decreases the velocity and ultimately prevents precipitation. The reaction is endothermic.[4]

Arsenious oxide exhibits considerable catalytic activity, which may act either positively or negatively. The effect on many oxidation and reduction reactions has been mentioned above. Other examples are the increase in the rate of dissolution of zinc by dilute acids and the retardation of the dissolution of marble. In the latter case a concentration of 0·005N As_2O_3 reduces the velocity constant for the dissolution of marble in 0·1N HCl by 12 per cent.[5]

Uses of Arsenious Oxide.

The most important application of arsenious oxide is in the manufacture of arsenates, which are used extensively, in the form of poison sprays or dusts, as insecticides to control the various pests which attack fruit and vegetable crops. The most important arsenates in this respect are those of calcium and lead. The former is effective in destroying the boll weevil of the cotton fields, while the latter controls the codling moth, plum curculio, cabbage worm, potato beetle, tobacco hornworm and other pests (see Chapter XII, p. 301). Emerald green (copper acetoarsenite), magnesium arsenate and manganese arsenate are also used as insecticides. The refined white arsenic is usually employed in the manufacture of the above products, but the crude arsenical flue dust or "treater" dust (see p. 125) is used for the production of weed killers, fungicides and wood preservatives, while some is converted into sodium arsenite for sheep dipping purposes. Railroads may be kept free from grass and weeds by the judicious use of arsenical preparations. Wood preservatives may contain aqueous arsenious oxide,[6] copper arsenite or acetoarsenite, or zinc metarsenite, such being useful for telegraph poles, fences, mine props, etc. In India and in Germany arsenious oxide is used with chromates and chromic acid, which fix the arsenic in the wood. Emerald green is used in preservative paints for such purposes as the painting of the bottoms of ships to prevent weed and barnacle growth. It is also used to a limited extent in the arts for giving vivid green tints.

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[1] Kohn, *loc. cit.*

[2] Bettendorff, *Sitzungsber. Niederrhein. Ges. Bonn*, 1869, p. 128.

[3] Durrant, *J. Chem. Soc.*, 1919, 115, 134.

[4] Zwicknagl, *Zeitsch. anorg. Chem.*, 1926, 151, 41.

[5] Jabłczyński and Maczkowska, *Zeitsch. anorg. Chem.*, 1931, 197, 292; *Rocz. Chem.*, 1931, 11, 139, and (in German) 152. See also Moureu and others, *Compt. rend.*, 1928, 187, 917; Hahn, *Zeitsch. anal. Chem.*, 1928, 73, 412; Adadurov and Dziskko, *J. Phys. Chem.* (*U.S.S.R.*), 1932, 3, 489.

[6] Kamesam, *Current Sci.*, 1935, 4, 409.

In the form of arsenical soap arsenic is used in taxidermy to prevent insect damage. It has been stated, however, that skins treated with arsenates do not dry-out well, and tend to heat when piled.[1]

Arsenious oxide is used in the glass industry as a decoloriser, opacifier and refining agent.[2] When the oxide is added to either soda-lime-silica or potash-lead oxide-silica glasses, the arsenic is either wholly or mainly retained on melting. Thus Turner[3] found that with the former type of glass and with 10 parts of arsenious oxide to 1000 parts of sand, practically the whole of the arsenic remains in the glass when melted in closed pots at 1400° C., while with 250 parts of the oxide to 1000 of sand the amount retained at 1350° C. was 78 per cent. and at 1400° C. 53 per cent. of the total added, the amounts varying somewhat with charging conditions. During melting, 40 to 70 per cent. of the arsenious oxide, even in the absence of oxidising agents, is converted to arsenic pentoxide or arsenates,[4] the solutions of which in glass at high temperatures are remarkably stable. The arsenic exerts no beneficial effect on the process of melting, the temperature of which is raised by large amounts, and the time of melting is prolonged. The rate of melting may be accelerated by the addition of nitre. In batches rich in silica, addition of more than 2 parts of arsenic to 1000 parts of sand tends to cause a surface scum. The green tint due to iron is definitely reduced by the arsenic, the improvement being continuous with increasing proportions of the oxide. When the latter is added to the extent of 150 to 250 parts per 1000 of sand, an opalescent glass is produced, the degree of opacity depending on the amount of arsenious oxide added. The latter is similarly employed as an opacifying agent in the production of opalescent glazes.

A soda-lime glass rendered colourless by means of arsenic may turn yellow under the influence of sunlight owing to conversion of ferrous to ferric iron.[5] Also a glass containing arsenic tends to darken in colour if reworked ;[6] the presence of the element facilitates clarifying in lead glasses, but is objectionable where these must be subjected to subsequent heating. The presence of arsenic in chemical glass is undesirable because of its ready extraction by strong acids and alkalis. Foodstuffs, however, may be safely contained in suitable arsenic-bearing glass without contamination.[7] In 6-hour boiling tests[8] with vinegar and a concentrated sugar solution, a good soda-lime glass containing 0·27 per cent. of arsenious oxide showed no loss of the latter by extraction, and the amount extracted under similar conditions by a 2N-sodium carbonate solution corresponded to only 0·2 per cent. of the total loss of weight.

The temperature of devitrification of glass is lowered by the presence of arsenic.[9] With a series of glasses made from soda-lime batches containing from 0 to 250 parts of arsenious oxide per 1000 parts of

[1] Huc, "*Halle aux Cuirs*," 1926, pp. 97, 129.

[2] Turner and co-workers, *J. Soc. Glass Tech.*, 1926, 10, 3; 1927, 11, 65, 190, 205; Bloch and Sharp, *Glass Ind.*, 1930, 11, 153; Silverman, *Trans. Electrochem. Soc.*, 1932, 61, 12.

[3] Turner and co-workers, *loc. cit.*; Turner, *J. Soc. Chem. Ind.*, 1929, 48, 65T.

[4] See also Heinrichs and Salaquarda, *Glastech. Ber.*, 1926, 4, 130.

[5] Silverman, *loc. cit.*; Eckert and Schmidt, *Glastech. Ber.*, 1932, 10, 80.

[6] Bloch and Sharp, *loc. cit.*

[7] Bloch and Sharp, *loc. cit.*

[8] Turner and co-workers, *J. Soc. Glass Tech.*, 1927, 11, 190.

[9] Parkin and Turner, *ibid.*, 1926, 10, 20.

sand a minimum devitrification temperature (575° to 600° C.) occurred with a glass made from the batch in which 100 parts of the oxide had been employed. Devitrification of glasses with higher arsenic content is probably hindered by the increased hardness of the glass.

In weak solution, arsenious oxide is used in medicine (see p. 147).

In recent years use of the oxide as a constituent of cement has been advocated,[1] especially in Sweden. Thus, a mixture of Portland cement (60 to 70 per cent.) and white arsenic (40 to 30 per cent.) heated to 200° to 250° C. affords a hydraulic cement of normal setting time and of less solubility than ordinary cement, so that lime liberation is inhibited and the resistance to water improved. Wooden structures exposed to the action of sea water may be protected by spraying with a concrete composed of white arsenic, cement and sand in the proportions 1 : 3 : 12. The arsenic makes the mixture elastic and helps the cement to adhere to the wood. There is, however, danger in the too widespread application of arsenic in the directions described above.

THE ARSENITES.

Aluminium Arsenite, $AlAsO_3$, has been obtained by the addition of barium arsenite[2] or potassium tetrarsenite,[3] $K_2As_4O_7.2H_2O$, to an aqueous solution of aluminium sulphate. In the former case, after filtration and concentration over sulphuric acid, rhombic pyramids were obtained. The second method yielded a gelatinous precipitate which after drying left a white powder. The arsenite decomposes on heating, alumina and arsenious oxide being the sole products;[4] it is slightly soluble in boiling water, readily soluble in acids and in aqueous sodium hydroxide.

Ammonium Arsenites.—The solubility of arsenious oxide in aqueous ammonia at 30° C. has been studied,[5] *ammonium metarsenite*, NH_4AsO_2, has been separated, and evidence of the existence of *ammonium dihydrogen arsenite*, $(NH_4)H_2AsO_3$, obtained. The metarsenite has been prepared in the form of acicular crystals by allowing ammonia to react with an aqueous solution of arsenious oxide at 70° to 80° C.,[6] and as rhombic prisms by the action of concentrated aqueous ammonia on powdered arsenious oxide, warming the mixture until a clear solution is obtained and allowing to crystallise.[7] The product loses ammonia on exposure to air. It is readily soluble in water, but on evaporation of the solution arsenious oxide is deposited. Precipitation of the oxide may be brought about by adding a little alcohol to the solution; excess of alcohol leaves the solution clear. The metarsenite is only slightly soluble in aqueous ammonia. When concentrated aqueous ammonia is poured on to arsenious oxide, the crystalline mass first formed was

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[1] Werner and Giertz-Hedström, *Tek. Tids.*, 1930, 60, 41; Shann, *Zement*, 1931, 20, 816; Stalhane, Werner and Giertz-Hedstrom, *American Patent*, 1875897 (1932); Stalhane, *American Patent*, 1900670 (1933): Assarsson, *Zement*, 1932, 21, 64.

[2] Thorey, *Russ. J. Pharm.*, 1871, 10, 331.

[3] Reichard, *Ber.*, 1894, 27, 1019.

[4] Rushton, *J. Physical Chem.*, 1932, 36, 1772.

[5] Schreinemakers and de Baat, *Proc. Acad. Amsterdam*, 1915, 17, 111. See also Stamm, "*Ueber die Loslichkeit von Ammonsalzen und Alkalisalzen in wässerigem Ammoniak,*" Halle, 1926.

[6] de Luynes, *J. prakt. Chem.*, 1857, [1], 72, 80; *Compt. rend.*, 1857, 44, 1354.

[7] Fischer, *Kastner's Arch.*, 1827, 11, 236.

described by Pasteur[1] as *ammonium pyroarsenite*, $(NH_4)_4As_2O_5$. The crystals, oblique rectangular prisms, were obtained pure by Stein[2] after washing with alcohol and ether and drying between absorbent paper. They are stable only in contact with the ammoniacal solution; in air, or when dissolved in water, decomposition occurs with loss of ammonia. Stavenhagen,[3] who endeavoured to prepare the above arsenites, could obtain only products of uncertain composition.

The variation of the specific conductivity[4] and of the freezing point[5] of a solution of arsenious oxide progressively neutralised by aqueous ammonia has been investigated, but evidence of compound formation is not obtained.

Antimony Arsenite.—When powdered antimony is digested with a concentrated aqueous solution of arsenic acid, and the solution then diluted with water, a precipitate forms, which was described by Berzelius[6] as antimony arsenite. He obtained a similar product by heating a mixture of arsenic and antimony pentoxide; it remained as a transparent vitreous mass. The exact composition of these products does not appear to have been investigated.

Barium Arsenites.—In an investigation[7] of the ternary system $BaO–As_2O_3–H_2O$ in which the two oxides in varying proportions were shaken with water at the temperatures 25° and 50° C., the solution and solid phase subsequently being analysed, evidence of the formation of only two arsenites was obtained: a basic metarsenite, $Ba(OH)AsO_2.2H_2O$, and an arsenite of composition $2BaO.3As_2O_3.4H_2O$.

Barium Orthoarsenite, $Ba_3(AsO_3)_2$, has been prepared[8] by the addition of potassium orthoarsenite to an aqueous solution of barium chloride and drying the precipitate at 100° C. in a current of hydrogen. It is obtained as a white amorphous powder, readily soluble in hot water and in dilute acids. When heated rapidly to about 730° C. it is decomposed into arsenic and the arsenate;[9] the mechanism of the reaction is not understood. Slow heating below 300° C. causes loss of arsenious oxide.

Barium Dihydrogen Orthoarsenite, $Ba(H_2AsO_3)_2$.aq., is obtained, according to Perper,[10] by adding an excess of baryta water to aqueous arsenious acid, by treating an ammoniacal solution of arsenious oxide with excess of barium chloride, or by adding potassium pyroarsenite to barium chloride solution. According to Stavenhagen and others,[11] this salt is to be regarded as *barium pyroarsenite*, $Ba_2As_2O_5$.aq. If the precipitate is air-dried, it contains 8 molecules of water of crystallisation according to Stavenhagen, and 4 molecules according to Stein; if dried at 100° C. it retains 2 molecules. Perper formulated the dihydrogen

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[1] Pasteur, *J. Pharm. Chim.*, 1847, [3], 13, 395; *Compt. rend.*, 1847, 24, 774.

[2] Stein, *Annalen*, 1850, 74, 218.

[3] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[4] Miolati and Mascetti, *Gazzetta*, 1901, 31, i, 93.

[5] Cornec, *Compt. rend.*, 1909, 149, 676; *Ann. Chim. Phys.*, 1913, [8], 29, 490; 1913, [8], 30, 63.

[6] Berzelius, *Pogg. Annalen*, 1826, 7, 28; *Schweigger's J.*, 1821, 32, 162.

[7] Story and Anderson, *J. Amer. Chem. Soc.*, 1924, 46, 533.

[8] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 17.

[9] Rat, *Compt. rend.*, 1933, 197, 59; Rushton, *J. Physical Chem.*, 1932, 36, 1772.

[10] Perper, "*Beiträge zur Kenntnis der arsenigsauren Salze,*" Berlin, 1890; Bloxam, *J. Chem. Soc.*, 1862, 15, 281.

[11] Stavenhagen, *loc. cit.*; Stein, *Annalen*, 1850, 74, 218; Filhol, *ibid.*, 1848, 68, 310; *J. Pharm. Chim.*, 1848, [3], 14, 331, 401.

orthoarsenite with $34H_2O$, but stated that it lost water on exposure to air. When heated to a high temperature it yields arsenic and barium arsenate.[1] It is slightly soluble in cold water, more readily in hot water, the solution having a slightly alkaline reaction. Whether the products obtained by the various methods described above are identical, and what their exact constitution is, are problems which have not yet been clarified. Further, Story and Anderson's basic metarsenite may equally well be formulated as barium monohydrogen orthoarsenite, $BaHAsO_3.2H_2O$.

Barium Metarsenite, $Ba(AsO_2)_2$, may be obtained by warming barium chloride with a solution of ammonium arsenite to which acetic acid has been added until arsenious acid is on the point of precipitation. The precipitate is then dried at 100° C.[2] It is a white powder, easily soluble in water, but it can also be obtained as a gelatinous mass [3] when a mixture of barium chloride and potassium metarsenite in solution is left to stand for a few hours. On strongly heating it decomposes to form arsenate and free arsenic, but to a much less extent than is the case with the orthoarsenite.[4]

Beryllium Arsenite.—Attempts to prepare definite compounds of beryllium with arsenious acid have not been successful.[5] When beryllium hydroxide is precipitated from solutions containing arsenious oxide, much of the latter is adsorbed.

Bismuth Arsenite.—When arsenious acid acts upon a solution of sodium bismuth chloride, a white precipitate of approximate composition $BiAsO_3.5H_2O$ is formed.[6] The substance has not been obtained pure. It is not decomposed by boiling aqueous alkali ; [7] it is soluble in nitric acid.[8]

Cadmium Arsenites.—When a solution of cadmium chloride in 50 per cent. alcohol is treated with potassium orthoarsenite solution neutralised with acetic acid, a white precipitate of *cadmium orthoarsenite*, $Cd_3(AsO_3)_2$, is formed.[9] It is obtained anhydrous by heating at 100° C. in a stream of hydrogen. It is slightly soluble in water, easily soluble in aqueous ammonia or in dilute acids. *Cadmium pyroarsenite*, $Cd_2As_2O_5$, is obtained as a white precipitate by adding sodium metarsenite to a solution of cadmium sulphate.[10] It is soluble in acids, unattacked by alkalis, and on ignition decomposes, leaving a residue of cadmium oxide contaminated with arsenic. A basic pyroarsenate, of composition $Cd_2As_2O_5.3CdO.2H_2O$, is obtained as a gelatinous precipitate by the addition of sodium orthoarsenite to a solution of a cadmium salt. The water may be removed by gently heating. Strong heat causes decomposition. It resembles the pyroarsenite in being readily dissolved by acids but unattacked by alkalis.

Calcium Arsenites.—The ternary system $CaO–As_2O_3–H_2O$, investigated at 0°, 25° and 99° C. by the method indicated under barium arsenites [11] (p. 162), gives evidence of the formation of two arsenites,

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[1] Stein, *loc. cit.*; Rat, *loc. cit.*

[2] Stavenhagen, *loc. cit.* See Bloxam, *loc. cit.*; Perper, *loc. cit.*; Reichard, *Ber.*, 1894, 27, 1019.

[3] Filhol, *loc. cit.*

[4] Rat, *loc. cit.*

[5] Bleyer and Muller, *Arch. Pharm.*, 1913, 251, 304.

[6] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[7] Jassoy, *Arch. Pharm.*, 1883, [3], 21, 745.

[8] Schneider, *J. prakt. Chem.*, 1879, [2], 20, 419.

[9] Stavenhagen, *loc. cit.*

[10] Reichard, *Ber.*, 1898, 31, 2163; 1894, 27, 1019.

[11] Story and Anderson, *J. Amer. Chem. Soc.*, 1924, 46, 533.

$Ca(OH)AsO_2$ or $CaHAsO_3$, which may be considered to be either a basic metarsenite or calcium hydrogen orthoarsenite, and $Ca(AsO_2)_2$, calcium metarsenite. When mixtures of arsenious oxide and quicklime are heated, reaction commences at about 300° C. and at 465° C. considerable heat is evolved and *calcium orthoarsenite*, $Ca_3(AsO_3)_2$, is formed.[1] An industrial process for the manufacture of this compound[2] consists in treating a dry mixture of quicklime (3 moles) and arsenious oxide (1 mole) with dry steam. It may also be obtained by precipitation of dilute calcium chloride solution with potassium orthoarsenite,[3] or of lime-water with boiling aqueous arsenious acid.[4] It is a white amorphous powder, which may be dried at 100° C. It is only slightly soluble in water, but dissolves in acids. At red heat it decomposes with volatilisation of arsenic, leaving calcium arsenate. The latter is also formed when the arsenite is heated in oxygen.[5] *Calcium dihydrogen arsenite*, $Ca(H_2AsO_3)_2$.aq., is formed[6] when excess of lime-water is added to an ammoniacal solution of arsenious oxide, or when lime-water, or a solution of calcium chloride, is added to aqueous ammonium metarsenite, keeping the latter in excess. It is obtained as a white powder or as a gelatinous mass, and contains 5 to $11H_2O$. It is fairly soluble in water, the solution having an alkaline reaction. It is insoluble in absolute alcohol. *Calcium monohydrogen arsenite* is mentioned above.

Calcium Pyroarsenite, $Ca_2As_2O_5$, is a white powder obtained by slowly precipitating a solution of arsenious acid with excess of lime-water, or by adding calcium chloride or sulphate to aqueous ammonium arsenite, and heating the precipitate to 105° C.[7] If the product is dried in the air at the ordinary temperature, the monohydrate is obtained. At red heat calcium arsenate is formed. The pyroarsenite is only slightly soluble in water, 100 parts dissolving 0·025 to 0·030 part of the salt. It is more soluble in the presence of alkali chlorides and some ammonium salts, such as the nitrate, sulphate, acetate and succinate.[8] It also dissolves in dilute acids.

Calcium Metarsenite, $Ca(AsO_2)_2$, is an amorphous white powder, anhydrous at 100° C., obtained by precipitation of calcium chloride with ammonium arsenite in ammoniacal solution.[7] It is also produced as a commercial preparation[9] by the interaction of milk of lime and arsenious oxide with vigorous stirring at 100° C., or by heating together at 60° to 70° C. arsenious oxide and slaked lime.[10] This product is somewhat impure, containing calcium arsenate and a trace of free lime. Its solubility in water at 15° C. is about 0·04 to 0·05 per cent. When strongly heated in an inert gas it decomposes, forming calcium and arsenious oxides and a little arsenic.[11]

A salt of composition $Ca_3As_4O_9.3H_2O$, which may be regarded as

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[1] Tammann, *Zeitsch. anorg. Chem.*, 1925, **149**, 68.

[2] Altwegg and Dutel, *American Patent*, 1700756 (1929).

[3] Stavenhagen, *J. prakt. Chem.*, 1895, [2], **51**, 1.

[4] Kuhn, *Arch. Pharm.*, 1852, [2], **69**, 267.

[5] Altwegg, *American Patent*, 1545873 (1925).

[6] Perper, "*Beitrage zur Kenntnis der arsenigsauren Salze*," Berlin, 1890.

[7] Simon, *Pogg. Annalen*, 1837, **40**, 417; Stavenhagen, *J. prakt. Chem.*, 1895, [2], **51**, 1.

[8] Giesecke, *Schweigger's J.*, 1825, **43**, 359; Wach, *ibid.*, 1830, **59**, 272; Wittstein, *Repert. Pharm.*, 1848, [3], **1**, 41; *Zeitsch. anal. Chem.*, 1863, **2**, 19.

[9] Krestovnikov and Lutringsgauser, *Min. Ssyrje*, 1930, **5**, 870; *Chem. Zentr.*, 1931, i, 1257.

[10] Bonvech, *Anilinokrasochnaya Prom.*, 1931, Nos. 4–5, 37; *Chem. Zentr.*, 1932, i, 1408.

[11] Rushton, *J. Physical Chem.*, 1932, **36**, 1772.

consisting of 1 molecule of pyro- combined with 1 molecule of metarsenite, $Ca_2As_2O_5.Ca(AsO_2)_2$, or as a derivative of a hypothetical tetrarsenious acid derived thus—

$$2As_2O_3 + 3H_2O = H_6As_4O_9$$

has been prepared by adding a solution of the corresponding potassium salt to a concentrated solution of calcium chloride.[1] The white precipitate, after washing with alcohol, may be dried in the air. At 100° C. it loses 1 molecule of water. It is somewhat soluble in water.

Chromic Arsenite, $CrAsO_3$, was described by Neville[2] as a dark green powder which separated when a concentrated solution of pure chromic acid was boiled for some time with a saturated solution of arsenious acid. Stavenhagen[3] could not obtain it by this method. It may be obtained, however, by digesting a concentrated solution of chromic sulphate with potassium tetrarsenite;[4] a precipitate containing the arsenite and arsenious oxide slowly forms, and the former may be isolated by dissolving in hydrochloric acid and reprecipitating with aqueous ammonia. It is obtained as a dark green mass, soluble in potassium hydroxide solution and in dilute acids.

Cobalt Arsenites.—Several compounds have been prepared. *Cobalt orthoarsenite*, $Co_3(AsO_3)_2.4H_2O$, is obtained[3] as a pink precipitate when a solution of cobaltous chloride in 50 per cent. alcohol is treated with a solution of potassium orthoarsenite which has been just neutralised with acetic acid. The precipitate is soluble in dilute acids. On heating it turns black. A basic salt, of composition $7CoO.As_2O_3$, is obtained when a solution of cobalt nitrate is treated with sodium orthoarsenite,[5] the former being in excess; the amethyst-coloured precipitate first formed contains combined water, which may be completely removed at 150° C.

Cobalt Pyroarsenite, $Co_2As_2O_5$, is obtained when a dilute solution of cobaltous nitrate is precipitated with sodium metarsenite,[6]

$$2Co(NO_3)_2 + 2NaAsO_2 + H_2O = Co_2As_2O_5 + 2NaNO_3 + 2HNO_3$$

or with potassium pyroarsenite.[7] It forms as a violet-blue voluminous deposit, which decomposes at red heat, arsenious oxide subliming and leaving a dark blue residue. It dissolves in dilute acids and in aqueous ammonia.

Cobalt Tetrarsenite, $Co_3As_4O_9$, is obtained as an amethyst-coloured powder by the interaction of solutions of potassium hydrogen diarsenite and cobaltous nitrate.[8] It dissolves in dilute hydrochloric and nitric acids; also in caustic potash, in which it forms a blue solution which decomposes on heating. In aqueous ammonia it gives a brown solution, and in aqueous potassium cyanide a yellow one.

Copper Arsenites.—A natural arsenite known as *trippkeite*, of composition $nCuO.As_2O_3$, is found in the form of bluish-green tetragonal crystals[9] ($a : c = 1 : 0{\cdot}9160$) associated with cuprite in Chile. By

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[1] Reichard, *Ber.*, 1894, 27, 1019. See also Stein, *Annalen*, 1850, 74, 218.

[2] Neville, *Chem. News*, 1876, 34, 220.

[3] Stavenhagen, *loc. cit.*

[4] Reichard, *loc. cit.*

[5] Reichard, *Chem. Zeit.*, 1902, 26, 1145; *Zeitsch. anal. Chem.*, 1903, 42, 10.

[6] Reichard, *Ber.*, 1898, 31, 2163.

[7] Girard, *Compt. rend.*, 1852, 34, 918; Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[8] Girard, *loc. cit.*; Reichard, *Ber.*, 1894, 27, 1019.

[9] Damour and vom Rath, *Zeitsch. Kryst. Min.*, 1880, 5, 245; Krenner, *ibid.*, 1921, 56, 198; Larsen, *Bull. U.S. Geol. Survey*, 1921, p. 679.

treating solutions of copper salts with arsenious oxide under various conditions products are obtained which contain more or less pure arsenites.

Copper Orthoarsenite, $Cu_3(AsO_3)_2.2H_2O$, was obtained by Sharples[1] by boiling a solution of copper sulphate with arsenious oxide and sodium carbonate, and drying the precipitate at 100° C. At 150° C. it still retains water. It is soluble in dilute acids and alkalis and in ammonia, but is decomposed by concentrated alkali. The anhydrous salt was described by Stavenhagen[2] as resulting when alcoholic solutions of cupric chloride and potassium orthoarsenite were mixed, the precipitate being dried at 100° C. The product darkened in colour in contact with water and its purity and identity are doubtful.

The pigment first prepared by Scheele[3] in 1778, and known as *Scheele's green*, is essentially cupric orthoarsenite containing excess of cupric oxide, the composition varying with the mode of preparation. It is best obtained by a method similar to that used by the discoverer. Hot aqueous solutions of arsenious oxide and copper sulphate are mixed and to the mixture is added, in small successive portions, a solution of potassium carbonate, until the precipitate attains its maximum colour intensity. After filtration, the precipitate is washed with hot water and dried at a moderate temperature. Similar products are obtained by treating aqueous arsenious acid or potassium hydrogen di-arsenite with a hot aqueous or ammoniacal solution of a copper salt.[4] The use of this pigment, owing to its poisonous nature, is prohibited. It resembles Emerald green, but is in every way inferior to that pigment. Pigments prepared by slightly modified processes, but of essentially the same composition, are known under many designations, including *Swedish green*, *Vienna green*, *Mitis green* and *Veronese green*. Bloxam[5] stated that when the green precipitate was dried in the air, its composition corresponded with *copper pyroarsenite*, $Cu_2As_2O_5$ or $2CuO.As_2O_3$, with $2{\cdot}89H_2O$, and when dried at 100° C. to yield Scheele's green it was $CuHAsO_3$ (copper monohydrogen arsenite). Other investigators[6] maintain that the composition approximates more closely to the normal orthoarsenite; but it is undoubtedly variable and the amount of cupric oxide present increases with the amount of alkali used in its preparation. The compound decomposes on heating, giving off arsenious oxide and water and leaving a residue of copper arsenide and arsenate.[7]

Efforts to prepare an improved Scheele's green resulted in 1814 in the production of *Emerald green*, cupric aceto-arsenite, the colour of which is a nearly normal green, slightly verging upon bluish-green. It is brighter and more opaque than Scheele's green, and like it is extremely poisonous. It is generally prepared by adding a solution of verdigris in acetic acid to a boiling solution of white arsenic; on continued

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[1] Sharples, *Chem. News*, 1877, 35, 89, 108; *Proc. Amer. Acad.*, 1877, 12, 11.

[2] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 25.

[3] Scheele, *Svenska Akad. Handl.*, 1778, 40, 316.

[4] Proust, *Phil. Mag.*, 1808, 30, 337; Braconnot, *Ann. Chim. Phys.*, 1822, [2], 21, 53; Bloxam, *J. Chem. Soc.*, 1862, 15, 281; Sattler, *Zeitsch. angew. Chem.*, 1888, 1, 40; Reichard, *Ber.*, 1894, 27, 1020; 1897, 30, 1914.

[5] Bloxam, *loc. cit.*

[6] Sharples, *loc. cit.*; Stavenhagen, *loc. cit.*; Bornemann, *Zeitsch. anorg. Chem.*, 1922, 124, 36.

[7] Proust, *loc. cit.*; Simon, *Pogg. Annalen*, 1837, 40, 440; 41, 424.

ebullition the Emerald green is deposited. A mixture of copper sulphate, acetic acid and potassium arsenite may also be employed. The product must be washed free of soluble salts with boiling water. The pigment is known also under the names Schweinfurt green and Paris green. The composition[1] approximates very nearly to $3Cu(AsO_2)_2.Cu(C_2H_3O_2)_2$. The pigment dissolves in boiling dilute mineral acids. After boiling for some time with a large excess of arsenious oxide solution, the substance suddenly becomes paler in colour and is converted to anhydrous *copper metarsenite*,[2] $Cu(AsO_2)_2$, a grey crystalline powder. The *dihydrate*, $Cu(AsO_2)_2.2H_2O$, was obtained by Stavenhagen[3] as a pale green amorphous precipitate by adding a solution of arsenious oxide in 50 per cent. aqueous alcohol to a slightly acid solution of cupric chloride in alcohol. The precipitate was dried over sulphuric acid. At 100° C. it lost 1 molecule of water; above this temperature arsenious oxide was also liberated.

Gold Arsenites.—Solutions of auric salts are reduced to the metal by the addition of aqueous solutions of arsenious oxide. *Aurous orthoarsenite*, Au_3AsO_3, is obtained[4] by treatment of a solution of auric chloride with potassium tetrarsenite. It is a purple-red powder, which blackens when heated or exposed to light. By adding potassium orthoarsenite to a solution of auric chloride in 50 per cent. alcohol, *auric arsenite*, $AuAsO_3.2H_2O$, is obtained[5] as a pale brown powder, which is unstable in air at ordinary temperatures and on warming rapidly decomposes forming gold arsenide and gold. It is readily soluble in water, dilute acids and aqueous ammonia.

Iron Arsenites.—Both ferrous and ferric compounds are known, but the existence of *ferrous orthoarsenite* has not been established.[6] *Ferrous metarsenite*, $Fe(AsO_2)_2$, has been obtained[7] by the action of potassium tetrarsenite, $K_2As_4O_7.2H_2O$, upon a dilute solution of ferrous sulphate. It is greenish in colour, becoming brown on exposure to air. It decomposes when heated. When a hot, saturated solution of arsenious acid containing ferrous iodide is allowed to cool, crystals of the compound $FeI_2.4As_2O_3.12H_2O$ are obtained, which slowly oxidise in air, and *in vacuo* over concentrated sulphuric acid yield up all their combined water. The iodide character of the salt is suppressed, from which it may be inferred that the iodine has combined with the arsenious oxide to yield a complex negative radical.[8]

Ferric Orthoarsenite, $FeAsO_3$, was described by Reichard[9] as a rust-yellow powder obtained by adding potassium tetrarsenite to a dilute aqueous solution of ferric chloride. A substance of similar chemical composition has been found in a crystalline deposit formed during the Deacon process of making chlorine. The crystals of the pure salt are monoclinic, their crystallographic elements being:[10]

$$a : b : c = 0{\cdot}9405 : 1 : 0{\cdot}6234 \qquad \beta = 105^\circ\ 10{\cdot}5'$$

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[1] Ehrmann, *Annalen*, 1834, 12, 92; Avery, *J. Amer. Chem. Soc.*, 1906, 28, 1155. *Cf.* Schiff and Sestini, *Annalen*, 1885, 228, 91.

[2] Avery, *loc. cit.*

[3] Stavenhagen, *loc. cit.*

[4] Reichard, *Ber.*, 1894, 27, 1019.

[5] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[6] See Guibourt, *J. Chim. Méd.*, 1839, 15, 306; Wittstein, *Repert. Pharm.*, 1848, [3], 1, 41; *Zeitsch. anal. Chem.*, 1863, 2. 19; *Viertelj. Pharm.*, 1866, 15, 185.

[7] Reichard, *Ber.*, 1894, 27. 1019.

[8] Weinland and Gruhl, *Arch. Pharm.*, 1917, 255, 467.

[9] Reichard, *loc. cit.*

[10] Arzruni and Schütz, *Zeitsch. Kryst. Min.*, 1894, 23, 529.

The *pentahydrate*, $FeAsO_3.5H_2O$, found with the preceding salt, crystallises in the rhombic system.

Ferric arsenite is reduced to a slight extent when heated in an inert atmosphere;[1] if heated in hydrogen under pressure it decomposes, forming iron arsenide, iron oxide and arsenious oxide.[2]

On adding freshly precipitated ferric arsenite to potassium hydroxide solution until no more dissolves, and subsequently evaporating, the soluble potassium salt, $6K_2O.5Fe_2O_3.9As_2O_3.24H_2O$, is obtained as a reddish-brown amorphous substance, which dissolves in water, yielding an alkaline solution.[3]

Ferric orthoarsenite cannot be prepared directly from ferric hydroxide and arsenious oxide.[4] The brown product obtained by shaking freshly precipitated ferric hydroxide with an aqueous solution of arsenious oxide has been described[5] as a basic ferric arsenite of composition $4Fe_2O_3.As_2O_3.5H_2O$. A similar substance is obtained by adding aqueous arsenious oxide or sodium arsenite to ferric acetate solution. If ferric chloride, sulphate or nitrate is used, the ferric salt is not completely precipitated. The product is oxidised in moist air, and decomposes when heated. It is very doubtful whether this is a chemical individual, however, for it has been shown that the removal of arsenious oxide from the solution by the ferric hydroxide is due to adsorption, the amount removed depending upon the conditions and the age of the adsorbent. This subject is discussed more fully on p. 154.

When a mixture of ferric oxide and arsenious oxide is heated, a mixture of orthoarsenite and orthoarsenate is formed[6] above 225° C., and above 600° C. the latter is the sole product.

Ferric Pyroarsenite, $Fe_4(As_2O_5)_3.7H_2O$, has been described[7] as a yellow substance obtained by adding ferric hydroxide to a hot saturated solution of arsenious oxide in concentrated sodium hydroxide. On cooling, excess of arsenious oxide separates, and after keeping for 24 hours a yellow precipitate of the above composition is formed. The existence of the pyroarsenite has not been confirmed, however.

Lead Arsenites.—An investigation of the ternary system $PbO-As_2O_3-H_2O$ at 25° C. gives evidence of the formation of the metarsenite, $Pb(AsO_2)_2$, only.[8] Several other well-defined arsenites are known, however.

Lead Orthoarsenite, $Pb_3(AsO_3)_2$, is obtained as a white precipitate on adding a solution of basic lead acetate to a boiling aqueous solution of arsenious oxide,[9] or of potassium tetrarsenite,[10] or by the action of an alkali plumbite on an alkali arsenite.[11] When dried in a dark air oven the arsenite remains white, but when exposed to light some specimens turn brown, a change which has been attributed to reduction of the lead to suboxide,[12] but some arsenate and free arsenic are formed. All specimens

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[1] Rushton, *J. Physical Chem.*, 1932, 36, 1772.

[2] Ipatiev, *Ber.*, 1926, 59, B, 1412.

[3] Dobbin, *Pharm. J.*, 1904, [4], 18, 585.

[4] Stavenhagen, *loc. cit.*

[5] Bunsen and Berthold, *Thesis*, Gottingen, 1834; Simon, *Pogg. Annalen*, 1837, 40, 442; von Fehling, *Annalen*, 1850, 74, 87.

[6] Dubrovin, *J. Appl. Chem. (U.S.S.R.)*, 1936, 9, 1049.

[7] Guibourt, *loc. cit.*

[8] Story and Anderson, *J. Amer. Chem. Soc.*, 1924, 46, 533.

[9] Kühn, *Arch. Pharm.*, 1852, [2], 69, 267.

[10] Reichard, *Ber.*, 1894, 27, 1019; Filhol, *J. Pharm. Chim.*, 1848, [3], 14, 331, 401.

of the orthoarsenite are not photo-sensitive.[1] A dry mixture of litharge and arsenious oxide is remarkably sensitive, arsenic being liberated in the reaction which occurs; and when the arsenite is prepared from lead hydroxide by heating with arsenious oxide and dilute aqueous sodium hydroxide, the product is also light-sensitive. The commercial product and those obtained by the methods described above are not sensitive. It has been suggested that in the latter case the salt has the composition $3Pb(OH)_2.As_2O_3$. No other metallic arsenite has been observed to be photo-sensitive. Lead arsenite may be used as a light-sensitive agent in photographic, photometric and actinometric compositions, the exposed negative being developed by dry heating or wet reduction;[2] other light-sensitive substances may be admixed.

When a mixture of litharge and arsenious oxide is heated, formation of lead orthoarsenite begins at 250° C., but oxidation occurs,[3] and with rising temperature increasing amounts of the orthoarsenate are formed, the latter being the sole product above 450° C.

The Swedish mineral *finnemanite*[4] contains lead orthoarsenite in combination with lead chloride, the composition being $3Pb_3(AsO_3)_2.PbCl_2$ (see p. 15). It occurs in dark grey or black prismatic crystals belonging to the hexagonal system and of axial ratio $a : c = 1 : 0{\cdot}6880$.

Lead arsenite is readily obtained by an electrolytic process.[5] The catholyte may be a 15 per cent. solution of sodium hydroxide or of a sodium salt, or a 30 per cent. solution of potassium hydroxide, the cathode being of nickel. The anolyte is a solution of an alkali arsenite neutralised towards phenolphthalein by means of acetic acid, and the anode is of lead. The cathode space is separated by a diaphragm of vegetable parchment. Ormont obtained a current yield of 97 per cent., and the average energy yield amounted to 1 kg. per kilowatt-hour.

The *monohydrate*, $Pb_3(AsO_3)_2.H_2O$, was described by Stavenhagen,[6] who obtained it by drying in air the precipitate resulting from the addition of potassium orthoarsenite to a dilute aqueous solution of lead nitrate.

Lead Pyroarsenite, $Pb_2As_2O_5$, is a white powder formed by decomposing normal lead acetate with ammoniacal arsenious oxide solution,[7] or with potassium tetrarsenite[8] or pyroarsenite.[9] According to Simon,[10] it is also formed by the combination of arsenious oxide vapour with lead oxide; Stavenhagen,[11] however, found the product to be merely a mixture of oxides. When heated, lead pyroarsenite fuses to form a yellow glass. It liberates ammonia from ammonium salts even in the cold.

Lead Metarsenite, $Pb(AsO_2)_2$, is formed from a hot saturated solution of arsenious oxide in ammonia by addition of a neutral lead salt.[12] It

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[1] Reissaus, *Zeitsch. angew. Chem.*, 1931, 44, 959.

[2] Reissaus, *German Patent*, 540888 (1930).

[3] Dubrovin, *J. Appl. Chem. (U.S.S.R.)*, 1936, 9, 1049.

[4] Aminoff, *Geol. För. Förh. Stockholm*, 1923, 45, 160.

[5] Ormont, *Ukraine Chem. J.*, 1926, 2, 20.

[6] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[7] Bloxam, *J. Chem. Soc.*, 1862, 15, 281.

forms microscopic prisms of density[1] 5·85 at 23° C., very slightly soluble in water. When heated in an inert atmosphere it decomposes readily into lead oxide and arsenious oxide.[2]

A tetrarsenite, $Pb_3As_4O_9.3H_2O$, was described by Bloxam but could not be obtained by Stavenhagen.

A colloidal solution of lead arsenite has been obtained by the following method. A solution of lead acetate is treated with a 10 per cent. solution of sodium lysalbinate, and after washing the precipitate with hot water, it is dissolved in a dilute aqueous solution of sodium hydroxide containing sodium dihydrogen arsenite. The liquid, after keeping for some hours, is filtered and dialysed until the outside liquor is free from arsenic. The solution in the dialyser is concentrated, mixed with alcohol and ether, and dried over sulphuric acid in a vacuum. A pale yellow horny mass remains, which dissolves readily in water to form a sol.[3]

Lithium Arsenite.—A study of the ternary system Li_2O–As_2O_3–H_2O at 25° C. reveals the existence of lithium metarsenite, $LiAsO_2$, which is soluble in water without decomposition.[4]

Magnesium Arsenites.—An investigation of the ternary system MgO–As_2O_3–H_2O at 25° C. gave no evidence of chemical combination,[5] but considerable adsorption of arsenious oxide by the magnesium hydroxide occurred (see p. 155). Combination of the two oxides occurs on heating;[6] at the melting point of arsenious oxide some *metarsenite* is formed, and at a higher temperature a *basic arsenite* of composition $Mg_3(AsO_3)_2.3MgO$ is produced.

Magnesium Orthoarsenite, $Mg_3(AsO_3)_2$, is obtained as a white precipitate, easily soluble in water and in dilute acids, by adding to a solution of magnesium chloride in 50 per cent. alcohol a solution of potassium orthoarsenite made just neutral with acetic acid.[7] It is also formed when a solution of potassium tetrarsenite is added slowly to an aqueous solution of a magnesium salt.[8] When heated in an inert atmosphere the salt decomposes forming arsenious and magnesium oxides.[9]

Magnesium Pyroarsenite, $Mg_2As_2O_5.4H_2O$, is produced by double decomposition between barium pyroarsenite and magnesium sulphate.[10] It is a white, granular, hygroscopic, amorphous powder, soluble in water and dilute acids; on heating it undergoes decomposition and darkens in colour. Bloxam[11] obtained a product which he described as the pyroarsenite by precipitating magnesium sulphate with ammonium arsenite and heating the precipitate; but Stavenhagen[10] could not obtain the salt by this method.

Magnesium Tetrarsenite, $Mg_3As_4O_9.nH_2O$, is formed when a solution of magnesium sulphate or magnesia mixture is added to an aqueous solution of arsenious oxide.[12]

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[1] Shafarik, *loc. cit.*

[2] Rushton, *J. Physical Chem.*, 1932, 36, 1772.

[3] Dexheimer, *Thesis*, Erlangen, 1919, p. 56.

[4] Schreinemakers and de Baat, *Rec. Trav. chim.*, 1920, 39, 423.

[5] Story and Anderson, *J. Amer. Chem. Soc.*, 1924, 46, 533. See also Filhol, *loc. cit.*

[6] Tammann, *Zeitsch. anorg. Chem.*, 1925, 149, 68. See also Simon, *loc. cit.*

[7] Stavenhagen, *loc. cit.* See also Stein, *Annalen*, 1850, 74, 221.

[8] Reichard, *loc. cit.*

[9] Rushton, *J. Physical Chem.*, 1932, 36, 1772.

[10] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 20.

[11] Bloxam, *ibid.*, 1862, [1], 87, 118.

[12] Perper, *Thesis*, Berlin, 1890.

Manganese Arsenites.—The *orthoarsenite*, $Mn_3(AsO_3)_2$, occurs in Nature as the mineral *armangite*, and is associated with lead in *trigonite* (see p. 16). X-ray examination of Swedish armangite showed that it contains a hexagonal cell of 9 molecules, with $a = 13{\cdot}44$ and $c = 8{\cdot}72$ Å.[1] The arsenite has been obtained as the *trihydrate*, $Mn_3(AsO_3)_2.3H_2O$, by adding a solution of potassium orthoarsenite, made nearly neutral with acetic acid, to a solution of manganese acetate.[2] The pale rose-coloured precipitate is washed with aqueous alcohol and dried in hydrogen over sulphuric acid. In the air it rapidly darkens in colour. *Manganese tetrarsenite*, $Mn_3As_4O_9.5H_2O$, is precipitated when potassium tetrarsenite[3] or ammonium arsenite[4] is added to a solution of a manganese salt. The pure compound is white, but in contact with air it rapidly turns reddish-brown. It loses 1 molecule of water at 100° C. and the remainder at 130° C., while at a higher temperature it decomposes. By adding a slight excess of sodium metarsenite to manganese sulphate solution Reichard[3] obtained a precipitate of empirical composition $Mn_5As_2O_8$, which, if a chemical individual, may be considered a basic orthoarsenite, $Mn_3(AsO_3)_2.2MnO$. It is decomposed on heating.

Mercury Arsenites.—*Mercurous Orthoarsenite*, Hg_3AsO_3, may be obtained by treating a solution of mercurous nitrate with one of sodium orthoarsenite[5] or with a solution of arsenious oxide in 50 per cent. alcohol;[6] in the latter case the mercurous nitrate solution should be acidified with nitric acid and sufficient alcohol added to produce a slight turbidity. The precipitate is pale yellow, but rapidly turns brown on exposure to air. It is slightly soluble in water, being slowly decomposed with separation of mercury. It is also decomposed by hydroxides and carbonates of alkali metals and of barium, and by ammonia. It dissolves in acids, but when these are dilute, basic salts gradually separate.

Complex salts of composition $2Hg_3AsO_3.Hg_2SO_4$ and $2Hg_3AsO_3.HgNO_3$ have been obtained.[7]

Mercurous Metarsenite, $HgAsO_2$, separates as a yellowish precipitate when potassium tetrarsenite is gradually added to mercurous nitrate solution.[5] The salt is dried at 125° C. It is unstable and is decomposed by excess of the alkali arsenite, by alkali hydroxides and by aqueous ammonia.

Mercuric Orthoarsenite, $Hg_3(AsO_3)_2$, is precipitated in an impure state when an aqueous solution of mercuric chloride is treated with a solution of arsenious oxide in 50 per cent. alcohol.[8] The salt is unstable and loses arsenious oxide at 150° C. It is slowly reduced to mercury and mercurous hydroxide by water, in which it is sparingly soluble, and by aqueous alkalis and ammonia. It dissolves in acids, but with sulphuric acid a basic sulphate is formed.

Mercuric Pyroarsenite, $Hg_2As_2O_5$, was described[9] as a yellowish-white mass, decomposing in light, obtained by adding a solution of potassium tetrarsenite to one of mercuric chloride. According to Dessner,[10] however, the precipitate so obtained is a mixture of arsenite

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[1] Aminoff, *Kgl. Svenska Vetensk. Handl.*, 1933, 11, No. 4, 19.

[2] Stavenhagen, *loc. cit.*

[3] Reichard, *loc. cit.*

[4] Stein, *loc. cit.*

[5] Reichard, *loc. cit.*

[6] Stavenhagen, *loc. cit.*

[7] Dessner, *Thesis*, Proskoroff, 1897.

[8] Stavenhagen, *loc. cit.* See also Berzelius, 1826, 7, 28; *Ann. Chim. Phys.*, 1819, [2], 11, 233.

[9] Reichard, *Ber.*, 1894, 27, 1019.

[10] Dessner, *loc. cit.*

and arsenate. A *basic arsenite* of composition $Hg_5As_2O_8$ was described by Reichard[1] also as a white mass, turning yellow and decomposing in daylight; this was obtained when sodium metarsenite was added to an aqueous solution of mercuric chloride.

Molybdenum Arsenites have not been prepared, but complex molybdoarsenites similar to the tungstoarsenites are known.

Nickel Arsenites.—*Nickel Orthoarsenite*, $Ni_3(AsO_3)_2$, is formed when a mixture of nickel oxide and arsenious oxide is heated to about 465° C.[2] It is obtained as a bright green amorphous precipitate by the addition of a solution of sodium metarsenite to aqueous nickel nitrate.[3] If an alkali orthoarsenite or tetrarsenite is added to a solution of a nickel salt, the *tetrarsenite*, $Ni_3As_4O_9$, is obtained as a light-green precipitate.[4] Both salts are decomposed by heat with loss of arsenious oxide. A basic salt of composition $14NiO.As_2O_3$ has also been described.[5]

Palladium Pyroarsenite, $PdAs_2O_5$, has been prepared[6] by addition of potassium tetrarsenite to a solution containing an equivalent amount of palladium tetrachloride and drying the yellow precipitate at 100° C.

Platinum Arsenites.—*Platinic Orthoarsenite*, $Pt_3(AsO_3)_4$, was described by Stavenhagen[7] as a pale yellow precipitate formed on the addition of alcohol to a mixture of an aqueous solution of arsenious oxide and an alcoholic solution of platinic chloride. The precipitate is unstable, decomposing at ordinary temperatures into arsenic pentoxide and arsenical platinum. *Platinic pyroarsenite*, $PtAs_2O_5$, is obtained[6] in a manner similar to that employed for the corresponding palladium salt described above. It is not attacked by caustic alkali, but decomposes when heated. A complex *ammonium platinous arsenite* of composition $5(NH_4)_2O.As_2O_3.3(2PtO.As_2O_3).7H_2O$ has been described.[8]

Potassium Arsenites.—At 25° C. the ternary system $K_2O–As_2O_3–H_2O$ indicates the existence of two arsenites of potassium, soluble in water without decomposition;[9] these are potassium tetrarsenite, $K_2As_4O_7$, and potassium metatetrarsenite, $K_6As_4O_9.12H_2O$.

Potassium Orthoarsenite, K_3AsO_3, has been obtained[10] by the action of alcoholic potassium hydroxide on arsenious oxide; by the addition of potassium sulphate to a solution of barium orthoarsenite and evaporating the filtered solution to dryness over concentrated sulphuric acid in an atmosphere of hydrogen: and by the addition of potassium iodide to an aqueous solution of arsenious oxide and allowing the solution to evaporate in the air.[11] It crystallises in transparent needles, which become turbid on exposure to air. It is readily soluble in water, and by adding excess of arsenious oxide and alcohol, *potassium hydrogen diarsenite*, $KHAs_2O_4$, may be obtained by slow crystallisation.[12] The

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[1] Reichard, *Ber.*, 1898, 31, 2163.

[2] Tammann, *Zeitsch. anorg. Chem.*, 1925, 149, 68.

[3] Reichard, *loc. cit.* See also Proust, *Ann. Chim. Phys.*, 1806, [1], 60, 260; *Nicholson's J.*, 1807, 17, 46; *Phil. Mag.*, 1808, 30, 337; Berzelius, *loc. cit.*; Reynoso, *Compt. rend.*, 1850, 31, 68.

[4] Girard, *Compt. rend.*, 1852, 34, 918.

[5] Reichard, *Chem. Zeit.*, 1902, 26, 1141.

[6] Reichard, *Ber.*, 1894, 27, 1019; Simon, *Pogg. Annalen*, 1837, 40, 442.

[7] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[8] Gibbs, *Amer. Chem. J.*, 1886, 8, 290.

[9] Schreinemakers and de Baat, *Rec. Trav. chim.*, 1920, 39, 423.

[10] Stavenhagen, *loc. cit.* See also Vanzetti, *Gazzetta*, 1925, 55, 106, 110.

[11] Schulze, *J. prakt. Chem.*, 1885, [2], 21, 407.

[12] Pasteur, *Annalen*, 1848, 68, 309; *J. Pharm. Chim.*, 1848, 13, 397.

aqueous solution of the orthoarsenite reacts alkaline, and on exposure to air undergoes oxidation to arsenate.

Potassium Pyroarsenite, $K_4As_2O_5.6H_2O$, may be obtained[1] by addition of potassium sulphate to an aqueous solution of barium pyroarsenite; on evaporation of the filtered solution the potassium salt separates as white crystals.

Potassium Metarsenite, $KAsO_2$, is obtained in an impure form when potassium carbonate and the above diarsenite are boiled together in aqueous solution for several hours.[1] A syrupy mass is obtained. That the metarsenite should exist has been shown[2] by results obtained in measuring the effect of the progressive neutralisation of arsenious acid by potassium hydroxide on the freezing point of aqueous solutions.

Potassium Tetrarsenite, $K_2As_4O_7.2H_2O$, is formed[1] when an excess of arsenious oxide is treated with cold aqueous potassium hydroxide, and alcohol added; it forms a syrupy liquid which crystallises in prisms on long standing. It also separates after boiling a concentrated solution containing arsenious oxide and potassium carbonate.[3] If the crystals are dried over sulphuric acid, some water of crystallisation is lost. At 100° C. one molecule of water is lost, and at a slightly higher temperature the salt melts and undergoes partial decomposition; on cooling it sets to a glassy mass.

The effect of rapidly heating to 730° C. the various arsenites of potassium has been investigated.[4] The diarsenite was undecomposed after several hours at that temperature; the others were gradually decomposed to arsenate and arsenic, the decomposition proceeding until an approximately fixed proportion of arsenious oxide was so converted. This proportion was about 14 per cent. for the meta-, 74 per cent. for the pyro- and 100 per cent. for the ortho-arsenite.

Arsenites of the Rare Earth Metals.—When cerium dioxide is heated with arsenious oxide some oxidation of the latter occurs, but the product appears to be a mixture of oxides.[5] *Didymium hydrogen orthoarsenite*, $Di_2(HAsO_3)_3$, has been obtained[6] as a white, granular, insoluble powder by boiling didymium hydroxide with an aqueous solution of arsenious oxide. *Lanthanum hydrogen orthoarsenite*, $La_2(HAsO_3)_3$, has been prepared in a similar manner. The existence of these compounds needs confirmation, however.[7]

Rubidium Metarsenite, $RbAsO_2$, has been prepared[8] by the action of arsenious oxide on rubidium carbonate in aqueous solution. It is a white amorphous powder which is converted to arsenate in aqueous solution and by the action of heat. The solution is alkaline in reaction.

Silver Arsenites.—*Silver Orthoarsenite*, Ag_3AsO_3, is obtained as a yellow precipitate when an aqueous solution of silver nitrate is treated with an alkali orthoarsenite,[9] metarsenite[10] or tetrarsenite,[11] or when ammoniacal silver nitrate is added to an aqueous solution of arsenious

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[1] Stavenhagen, *loc. cit.*; Pasteur, *loc. cit.*

[2] Cornec, *Compt. rend.*, 1909, 149, 676; *Ann. Chim. Phys.*, 1913, [8], 29, 490.

[3] Bloxam, *J. Chem. Soc.*, 1862, 15, 281.

[4] Rat, *Compt. rend.*, 1933, 197, 59.

[5] Tammann, *Zeitsch. anorg. Chem.*, 1925, 149, 68.

[6] Frerichs and Smith, *Annalen*, 1878, 191, 331.

[7] See Cleve, *Ber.*, 1878, 11, 912.

[8] Bouchonnet, *Compt. rend.*, 1907, 144, 641.

[9] Santos, *Chem. News*, 1878, 38, 94.

[10] Bloxam, *J. Chem. Soc.*, 1862, 15, 281.

[11] Reichard, *Ber.*, 1894, 27, 1019.

oxide.[1] According to Santos,[2] by mixing silver nitrate and sodium arsenite in suitable molecular proportions, mono- and di-hydrogen arsenites may also be obtained. The normal arsenite is practically insoluble in water (solubility at 20° C. 0·0115 g. per litre of water)[3] but dissolves in the presence of acids or of alkali nitrates.[4] It is also soluble in an excess of alkali or ammonium arsenite, and if the solution is heated silver is deposited.[5] It dissolves also in aqueous ammonia if freshly precipitated, and in caustic alkali; if the former solution is boiled for some time with continual replenishing of ammonia, an arsenate is formed and silver deposited; in the caustic alkali solution decomposition occurs with deposition of silver and silver arsenide, alkali arsenite and arsenate remaining in the solution.[6] Silver orthoarsenite melts at about 150° C.[7] At red heat arsenious oxide sublimes, leaving a residue of silver and silver arsenate.[8]

Silver Pyroarsenite, $Ag_4As_2O_5$, is formed when an alkali pyroarsenite is added to an aqueous solution of silver nitrate,[9] but the salt could not be obtained in a pure state by Stavenhagen [10] or Bloxam.[11] An ammino-compound, $Ag_4As_2O_5.4NH_3$, in the form of prismatic crystals, was obtained by Reichard [12] by adding alcohol to an ammoniacal solution of silver orthoarsenite. The *tetrarsenite*, $Ag_6As_4O_9$, has been reported,[13] but could not be obtained by Stavenhagen.

Silver Arsenite Sol.—A colloidal solution of silver arsenite has been prepared by the following method.[14] A 10 per cent. solution of sodium lysalbinate was added to aqueous silver nitrate and the precipitate separated, washed, and dissolved in an alkaline solution of sodium dihydrogen arsenite. After dialysis, the solution yielded on evaporation to dryness a pale yellowish-brown mass which could be dispersed in water to form a sol.

Sodium Arsenites.—It is difficult to obtain arsenites of sodium in the crystalline state and there is some doubt as to the possibility of preparing them in a pure form. A study [15] of the ternary system Na_2O–As_2O_3–H_2O at 30° C. suggests the existence of solid arsenites of composition $NaAsO_2$, $Na_4As_2O_5$ and $Na_{10}As_4O_{11}.26H_2O$. As the proportion of alkali in the solution increases, the solubility of the arsenious oxide increases rapidly. By digesting the latter with excess of alcoholic sodium hydroxide and extracting with alcohol, a product approximating in composition to *sodium orthoarsenite*, Na_3AsO_3, has been obtained,[16] and Vanzetti,[17] in an attempt to obtain this compound in the absence of water, dissolved arsenious oxide in a methyl alcohol solution of sodium methoxide, using quantities in accordance with the reaction

$$As_2O_3 + 6NaOCH_3 = 2Na_3AsO_3 + 3(CH_3)_2O$$

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[1] Filhol, *J. Pharm. Chim.*, 1848, [3], 14, 331.

[2] Santos, *loc. cit.*

[3] Whitby, *Zeitsch. anorg. Chem.*, 1910, 67, 107.

[4] Santos, *loc. cit.*

[5] Kühn, *Arch. Pharm.*, 1852, [2], 69, 267.

[6] Wohler, *Annalen*, 1857, 101, 363; Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 26.

[7] Filhol, *loc. cit.*

[8] Simon, *Ann. Phys. Chem.*, 1837, 40, 442; Stavenhagen, *loc. cit.*

[9] Pasteur, *J. Pharm. Chim.*, 1848, [3], 14, 331; *Annalen*, 1848, 68, 309; Girard, *Compt. rend.*, 1852, 34, 918.

[10] Stavenhagen, *loc. cit.*

[11] Bloxam, *loc. cit.*

[12] Reichard, *Ber.*, 1894, 27, 1019.

[13] Girard, *loc. cit.*

[14] Dexheimer, *Thesis*, Erlangen, 1919, p. 53.

[15] Schreinemakers and de Baat, *Chem. Weekblad*, 1917, 14, 262, 288; *Rec. Trav. chim.*, 1920, 39, 423.

[16] Stavenhagen, *loc. cit.*

[17] Vanzetti, *Gazzetta*, 1925, 55, 110.

The excess of alcohol was evaporated off to give a syrup, which was then left to crystallise in a vacuum desiccator containing calcium chloride. The crystals formed were highly hygroscopic and varied in composition, the arsenic content diminishing from about 80 per cent. in the first fractions to about 20 per cent. in the last of that required by the formula Na_3AsO_3. Very little ether was apparently liberated during the reaction, which did not go to completion. The crystals were white, dissolved readily in water, and the solution with silver nitrate gave a precipitate of yellow silver orthoarsenite.

The equivalent electrical conductivity of the aqueous solution has been determined by several investigators. Walden,[1] using solutions containing one-third of a mole of Na_3AsO_3 in v litres, obtained the following values :

v . .	32	64	128	256	512	1024
Λ . .	158·3	160·1	161·1	160·6	156·7	154·3

Using the dihydrogen salt, NaH_2AsO_3, von Zawidzki [2] determined the equivalent conductivity in the presence of N/32 arsenious acid in order to diminish hydrolytic dissociation, and concluded that it resembled the salt of a monobasic acid. At extreme dilutions the equivalent conductivity increased, apparently owing to hydrolysis and oxidation. This view that arsenious acid is essentially a feeble monobasic acid is supported by Thomsen's thermochemical values for the heats of neutralisation of the acid (see p. 140).

The aqueous solution of sodium arsenite undergoes slow oxidation when exposed to the air; but according to Reinders and Vles,[3] this can only proceed in the presence of a catalyst. Suitable catalysts are finely divided copper and copper salts ; [4] the former dissolves in a cold solution of sodium arsenite in the presence of oxygen. Oxidation may readily be effected at the ordinary temperature by passing air through a solution of the arsenite containing in suspension copper powder, cuprous oxide, cuprous chloride, zinc dust or yellow phosphorus.[5] The oxidation is more readily effected in the presence of a second easily oxidisable substance, such as stannous chloride, manganous or cobaltous hydroxide, or sodium sulphite; with the last-named the oxidation of the arsenite is not induced if the solution is strongly alkaline. These induced oxidation reactions are discussed on p. 148. The oxidation of the added substance may be retarded by the presence of the sodium arsenite ; this is the case with stannous salts, sulphites, phosphorus, chloroform and certain aldehydes.[6] The arsenite is also oxidised in aqueous solution by nitric oxide,[7]

$$Na_3AsO_3 + 2NO = Na_3AsO_4 + N_2O$$

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[1] Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 51.

[2] von Zawidzki, *Ber.*, 1903, 36, 1427.

[3] Reinders and Vles, *Rec. Trav. chim.*, 1925, 44, 29; Vles, *ibid.*, 1927, 46, 743.

[4] Jenkins and Berger, *U.S. Patent*, 159662 (1926).

[5] Dey and Dhar, *Zeitsch. anorg. Chem.*, 1925, 144, 307; *Proc. Asiatic Soc. Bengal*, 1921, 8, 130.

[6] Jorissen, *Rec. Trav. chim.*, 1923, 42, 855; Jorissen and van den Pol, *ibid.*, 1924, 43, 582; 1925, 44, 805; Dhar, *Zeitsch. anorg. Chem.*, 1925, 144, 289; Mittra and Dhar, *J. Physical Chem.*, 1925, 29, 376; Palit and Dhar, *ibid.*, 1926, 30, 939.

[7] Gutmann, *Ber.*, 1922, 55, B, 3007.

and by hydroxylamine,

$$Na_3AsO_3 + NH_2OH = Na_3AsO_4 + NH_3$$

Nitrogen is also evolved due to simultaneous decomposition of hydroxylamine as follows:

$$3NH_2OH = NH_3 + N_2 + 3H_2O$$

With sodium thiosulphate the arsenite forms oxythioarsenates (see p. 282), as it also does with tri- and tetra-thionates; sodium dithionate does not react either in cold or boiling solution. Sodium tellurate causes oxidation to arsenate.[1] An ammoniacal solution of silver azide is reduced to silver by sodium arsenite; other metallic azides do not react.

Sodium orthoarsenite is converted largely to arsenate and free arsenic when heated in an inert atmosphere;[2] slow heating below 300° C. causes loss of arsenious oxide. Fusion with sodium hydroxide causes conversion to arsenate.[3]

Schreinemakers and de Baat's[4] study of the system $Na_2O-As_2O_3-H_2O$ afforded evidence of the formation of *sodium pyroarsenite*, $Na_4As_2O_5$, both in the anhydrous state and as the hydrated salt, $Na_4As_2O_5.9H_2O$, but the isolation of these compounds in a pure form is difficult.[5]

Sodium Metarsenite, $NaAsO_2$, may be prepared by boiling an aqueous solution of sodium carbonate with an excess of arsenious oxide and evaporating the solution to dryness.[6] It is a white powder which, when heated, yields arsenic and sodium arsenate.[7] It undergoes oxidation by atmospheric oxygen under pressure, and determinations of the velocity of the reaction at 100° to 250° C. show it to be a reaction of the first order.[8] The addition of sodium metarsenite to excess of a solution of a metallic salt generally causes precipitation, but the composition of the precipitate varies with the nature of the salt.[9] Thus the orthoarsenite is obtained with nickel and lead nitrates, zinc sulphate and stannous chloride. With stannic chloride a basic arsenite, $7SnO_2.As_2O_3$, is formed. Cobalt nitrate and cadmium sulphate yield the corresponding pyroarsenites; metarsenites do not appear to be precipitated by this means.

Strontium Arsenites.—An impure *strontium orthoarsenite*, containing more strontium than corresponds to the formula $Sr_3(AsO_3)_2$, has been obtained[10] as a white flocculent precipitate by treating strontium chloride solution with potassium orthoarsenite in the cold. If the precipitate is dissolved in a dilute solution of acetic acid, on evaporation strontium hydrogen orthoarsenite, $SrHAsO_3.H_2O$, is obtained.

Strontium Pyroarsenite, $Sr_2As_2O_5.2H_2O$, may be prepared[10] by adding an aqueous arsenious acid solution to strontium chloride dissolved in alcohol. The solution is filtered after standing for a time,

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[1] Stroup and Meloche, *J. Amer. Chem. Soc.*, 1931, 53, 3331.

[2] Rushton, *J. Physical Chem.*, 1932, 36, 1772; Rat, *Compt. rend.*, 1933, 197, 59.

[3] Boswell and Dickson, *J. Amer. Chem. Soc.*, 1918, 40, 1773.

[4] Schreinemakers and de Baat, *loc. cit.*

[5] Pasteur, *Annalen*, 1848, 68, 309; Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

[6] Bloxam, *J. Chem. Soc.*, 1862, 15, 281.

[7] Rushton, *loc. cit.*; Rat, *loc. cit.*

[8] Malinovski and Lopatina, *J. Appl. Chem.* (*U.S.S.R.*), 1935, 8, 425.

[9] Reichard, *Ber.*, 1898, 31, 2163.

[10] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 16.

and the white flocculent precipitate is dried at 100° C. It is easily soluble in water and in acids.

Strontium Metarsenite, $Sr(AsO_2)_2.4H_2O$, may be obtained by the action of ammonium arsenite on a solution of a strontium salt.[1] The precipitation is increased by the addition of alcohol, since the arsenite is fairly soluble in water. When dried at 100° C. it has the composition $Sr(AsO_2)_2.3H_2O$. At higher temperatures it decomposes to form strontium oxide, arsenious oxide and a little arsenic.[2] Stavenhagen was unable to obtain the metarsenite in a pure state.

Thallous Orthoarsenite, Tl_3AsO_3, is a yellowish-red crystalline solid obtained [3] by boiling a solution of thallous sulphate with potassium orthoarsenite and gradually adding potassium hydroxide solution; or the thallous salt may be boiled with alkali and then treated with aqueous arsenious oxide or potassium orthoarsenite. The crystals are sparingly soluble in water or alcohol, but readily dissolve in acids.

Tin Arsenites.—*Stannous Orthoarsenite*, $Sn_3(AsO_3)_2.H_2O$, was obtained by Stavenhagen [3] by adding a solution of arsenious oxide to a solution containing potassium chlorostannite and potassium chloride. It may also be obtained [4] by the action of sodium metarsenite or potassium tetrarsenite on a solution of stannous chloride. It is a white amorphous powder, sparingly soluble in water, but readily dissolved by dilute acids and alkalis with separation of metallic arsenic. It is also soluble in excess of arsenious acid.

Stannic Orthoarsenite, $Sn_3(AsO_3)_4.5\frac{1}{2}H_2O$, was obtained by Stavenhagen [5] by adding an aqueous solution of arsenious oxide to one containing stannic and sodium chlorides. Addition of potassium tetrarsenite to a solution of stannic chloride gives a yellowish-white precipitate of a basic salt, $2SnO_2.Sn_3(AsO_3)_4$; while with sodium metarsenite the composition of the precipitate corresponds with $Sn_7As_2O_{17}$.[4] These compounds decompose on heating.

Titanyl Tetrarsenite, $(TiO)_5As_4O_{11}$, is obtained by the action of potassium tetrarsenite in excess on an almost neutral solution of titanyl sulphate. The gelatinous precipitate first formed gradually crystallises. The arsenite dissolves in acids without decomposition, but is insoluble in aqueous potassium hydroxide or ammonia. It decomposes when heated.

Tungsto-arsenites.—By treating solutions of tungstates with arsenious acid the following crystalline compounds have been obtained: [6]

$$7(NH_4)_2O.2As_2O_3.18WO_3.18H_2O$$
$$4BaO.As_2O_3.9WO_3.21H_2O$$
$$9Na_2O.8As_2O_3.16WO_3.55H_2O$$

By addition of small quantities of arsenious oxide to a boiling solution of sodium paratungstate until tungstic acid is no longer precipitated on acidifying with hydrochloric acid, a syrup is obtained which, on treatment with potassium chloride, yields [7] gradually on cooling needle-shaped crystals of a very soluble salt of composition $7K_2O.As_2O_3.18WO_3.24H_2O$. If ammonium chloride is used, the salt formed has the

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[1] Stein, *Annalen*, 1850, 74, 218.
[2] Rushton, *J. Physical Chem.*, 1932, 36, 1772.
[3] Stavenhagen, *loc. cit.*
[4] Reichard, *Ber*, 1894, 27, 1024; 1898, 31, 2166.
[5] Stavenhagen, *loc. cit.*
[6] Gibbs, *Amer. Chem. J.*, 1885, 7, 317.
[7] Rosenheim and Wolff, *Zeitsch. anorg. Chem.*, 1930, 193, 64.

composition $3\frac{1}{2}(NH_4)_2O.As_2O_3.18WO_3.45H_2O$. These complex salts resemble metatungstates in their reactions.

Compounds of the following composition have also been described :[1]

$$10K_2O.As_2O_3.4As_2O_5.21WO_3.26H_2O$$
$$10K_2O.14As_2O_3.3P_2O_5.32WO_3.28H_2O$$
$$5K_2O.Na_2O.2As_2O_3.2P_2O_5.12WO_3.15H_2O$$
$$7K_2O.As_2O_3.4P_2O_5.60WO_3.55H_2O$$

Uranyl Metarsenite, $UO_2(AsO_2)_2$, is formed as a yellow precipitate when a solution of sodium metarsenite[2] or of potassium tetrarsenite[3] is added to one of uranyl nitrate. It is insoluble in ammonia, but dissolves readily in acids. On heating, it darkens in colour and decomposes.

Zinc Arsenites.—When a mixture of zinc oxide and arsenious oxide is heated, combination occurs ;[4] at about 250° C. the metarsenite is formed, and at about 420° C. the orthoarsenite is the product. At higher temperatures oxidation occurs[5] and at 500° C. As^{III} and As^{V} are present in approximately equal amounts, although the total arsenic content is reduced owing to volatilisation. At 600° C. the product contains only As^{V}, and with rising temperature the rate of combination rises to a maximum at 700° C., thereafter remaining constant.

The mineral *barthite* (p. 14), occurring in the Otavi valley,[6] contains zinc metarsenite associated with copper.

Zinc Orthoarsenite, $Zn_3(AsO_3)_2$, is obtained[7] as a white crystalline precipitate when aqueous arsenious acid is added to a solution of zinc sulphate containing ammonia and ammonium chloride; precipitation occurs in the cold, an aggregate of crystalline needles being rapidly formed. A similar precipitate is thrown down by potassium orthoarsenite from a solution of zinc chloride in 50 per cent. alcohol,[8] or from a solution of zinc sulphate by potassium tetrarsenite[9] or sodium metarsenite.[10] Zinc orthoarsenite dissolves readily in acids. It decomposes when heated.

Zinc Metarsenite, $Zn(AsO_2)_2$, is obtained as a granular white powder by dissolving arsenious acid in sodium hydroxide solution, making just acid to phenolphthalein with dilute sulphuric acid and adding hot zinc sulphate solution.[11] It is also formed when aqueous arsenious acid is mixed with a solution of zinc acetate in dilute acetic acid.

Zirconium Arsenite. A hydrogel of zirconium dioxide forms true adsorption complexes with arsenious oxide, but there is no evidence of the formation of an arsenite.[12]

Arsenic Tetroxide (?), As_2O_4. Attempts to isolate this oxide have proved unsuccessful, but a number of products have been described

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[1] Gibbs, *Amer. Chem. J.*, 1885, 7, 317.

[2] Rammelsberg, *Ber. K. Preuss. Akad.*, 1872, p. 447.

[3] Reichard, *Ber.*, 1894, 27, 1028.

[4] Tammann, *Zeitsch. anorg. Chem.*, 1925, 149, 68.

[5] Dubrovin, *J. Appl. Chem.* (*U.S.S.R.*), 1936, 9, 1049.

[6] Henglein and Meigen, *Centr. Min.*, 1914, p. 353.

[7] Bloxam, *J. Chem. Soc.*, 1862, 15, 281.

[8] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 21.

[9] Reichard, *Ber.*, 1894, 27, 1032.

[10] Reichard, *ibid.*, 1898, 31, 2167.

[11] Avery, *J. Amer. Chem. Soc.*, 1906, 28, 1163.

[12] Wedekind and Wilke, *Kolloid-Zeitsch.*, 1924, 34, 83.

which appear to contain arsenic in an intermediate stage of oxidation. Thus, by the action of chlorine on arsenious oxide at a moderate heat Bloxam[1] obtained a transparent glass of composition $2As_2O_3.As_2O_5$, and a similar product was formed by heating the pentoxide with an excess of the trioxide. More recently, products approximating in composition to As_2O_4 have been described [2] as resulting when arsenious oxide was heated in oxygen at 400° to 480° C. and under pressures of 127 to 180 atmospheres. If equimolecular proportions of the tri- and pent-oxides are heated together, no sublimation of the former occurs even at 350° C. and combination appears to take place.[3] According to Weidenbach,[4] the product at temperatures between 800° and 1200° C. has the composition $2As_2O_3.As_2O_5$, and on cooling yields a clear glass which gradually loses its transparency. The glass is slightly soluble in water, more readily soluble in aqueous alkali or in dilute hydrochloric acid. It may be precipitated from aqueous solution by the addition of alcohol.

Hydrated products have also been obtained. When arsenious oxide (100 g.) is gently warmed with concentrated nitric acid (25 to 30 c.c.), oxides of nitrogen are evolved and, after standing, a mass of microscopic needle-shaped crystals remains,[5] the composition of which is $3As_2O_3.2As_2O_5.3H_2O$. If excess of arsenic acid or of arsenious oxide is present, the products are respectively $As_2O_3.As_2O_5.xH_2O$ or $2As_2O_3.As_2O_5.xH_2O$. The addition of water causes separation of arsenious oxide.

Arsenious oxide dissolves in boiling aqueous arsenic acid, but as the solution cools it is reprecipitated and after three weeks only about 1·8 per cent. of that originally dissolved remains in solution. [6]

The solubility is greater in concentrated arsenious acid solution and there is evidence that the tetroxide exists in the form of arsenious arsenate,[7] $AsAsO_4$.

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[1] Bloxam, *J. Chem. Soc.*, 1865, 18, 62.
[2] Matignon and Lecanu, *Compt. rend.*, 1920, 170, 941.
[3] Herbst, "*Ueber Arsentetroxyd*," München, 1894; *Inaug. Dissert.*, Bern, 1894.
[4] Weidenbach, *Thesis*, Berlin, 1915.
[5] Joly, *Compt. rend.*, 1885, 100, 1223.
[6] Bacaloglo, *J. prakt. Chem.*, 1861, [1], 83, 111; *Jahresber.*, 1861, p. 263.
[7] Ghiron and Mangili, *Gazzetta*, 1935, 65, 1244.

CHAPTER VIII.

ARSENIC PENTOXIDE AND THE ARSENATES.

Arsenic Pentoxide and its Hydrates—Arsenic Acid.

Arsenic Pentoxide, As_2O_5, may be obtained in the dry way by the oxidation of arsenious oxide by heating with oxygen[1] under pressure (see p. 146) or with chlorine[2] (see p. 100). In the former case the oxidation is only partial. It is accelerated by pressure or by the presence of a catalyst. If arsenious oxide is introduced into a mass of ferric oxide or alumina at about 218° C. in a current of air or oxygen, arsenic pentoxide is formed;[3] activated charcoal containing cupric oxide also acts as an efficient catalyst.[4] The pentoxide is more readily obtained by digesting arsenious oxide with nitric acid, preferably in the presence of oxygen (*cf.* p. 152), and dehydrating at 180° to 200° C. the "arsenic acid" produced (the methods of obtaining the latter are described on p. 182).

Arsenic pentoxide is a white amorphous powder of density[5] 3·7 to 4·3. It is tasteless when first introduced into the mouth, but rapidly becomes sharp and bitter and exerts a toxic action[6] similar to that of arsenious oxide (see Chapter XI), probably owing to the formation of the latter by reduction. The heat of formation (2As, 5O) is 218,300 calories,[7] and (As_2O_3, O_2) 64,710 calories;[8] the heat of dissolution (As_2O_5, aq.) is 6000 calories.

From determinations of the heat capacity of the oxide at temperatures from about 57° to 296° Abs. the entropy at 25° C. has been calculated[9] to be 25·2 calories per degree, and the free energy of formation is computed to be $-185{,}400$ calories per mole.

The pentoxide is hygroscopic and dissolves slowly in cold water, more readily in hot, to form an acid solution, apparently containing orthoarsenic acid, H_3AsO_4 (see p. 185). The solubility at various temperatures is given on p. 184. It is soluble in alcohol, and in certain oils and other organic liquids; thus poppy oil[10] at boiling temperature dissolves 2·7 parts per 100, while castor oil dissolves more than that amount; 95 per cent. formic acid[11] dissolves 7·6 parts per 100 at 19° C.

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[1] Berthelot, *Bull. Soc. chim.*, 1877, [2], 28, 496.

[2] Weber, *Pogg. Annalen*, 1861, 112, 619.

[3] Ikebe and Otani, *Japanese Patent*, 94024 (1931).

[4] Adadurov and Dziskko, *J. Phys. Chem.* (*U.S.S.R.*), 1932, 3, 489.

[5] Karsten, *Schweigger's J.*, 1832, 65, 394; Herapath, *Phil. Mag.*, 1824, [1], 64, 321; Playfair and Joule, *Mem. Chem. Soc.*, 1848, 3, 83; Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415; Auger, *Compt. rend.*, 1902, 134, 1059.

[6] Joachimoglu, *Biochem. Zeitsch.*, 1915, 70, 144.

[7] de Passillé, *Ann. Chim.*, 1936, [11], 5, 83.

[8] Thomsen, "*Thermochemistry*" (Longmans), 1908, p. 227.

[9] Anderson, *J. Amer. Chem. Soc.*, 1930, 52, 2296.

[10] von Grundner, *Repert. Pharm.*, 1837, 61, 289.

When heated, arsenic pentoxide, unlike phosphorus pentoxide, loses oxygen :

$$As_2O_5 \rightleftharpoons As_2O_3 + O_2$$

The reaction commences at a temperature above 400° C., before the melting temperature is reached, and the fused product therefore always contains some arsenious oxide.[1] When heated in hydrogen, the pentoxide is reduced first to arsenious oxide and then to free arsenic. Similar reduction occurs when it is heated with carbon or phosphorus ; with sulphur, arsenious sulphide is formed. Arsenic and metallic arsenides result when the pentoxide is heated with alkali metals,[2] zinc, lead, iron or most other heavy metals ; mercury and silver react only at high temperature ; gold and platinum do not react.

Hydrogen chloride is absorbed by arsenic pentoxide with formation of arsenic trichloride (see p. 101) :

$$As_2O_5 + 10HCl = 2AsCl_3 + 2Cl_2 + 5H_2O$$

Phosphorus pentachloride reacts according to the equation [3]

$$As_2O_5 + 5PCl_5 = 2AsCl_3 + 5POCl_3 + 2Cl_2$$

Iodine is liberated when the pentoxide is heated with an alkali iodide, thus [4]

$$3As_2O_5 + 4KI = 4KAsO_3 + As_2O_3 + 2I_2$$

a similar reaction proceeding with alkali bromides but not with chlorides unless oxygen is present.[5]

Hydrogen sulphide is absorbed with formation of the pentasulphide : [6]

$$As_2O_5 + 5H_2S = As_2S_5 + 5H_2O$$

Fusion with sodium thiosulphate yields arsenic trisulphide.[7]

With liquid ammonia in a sealed tube at the ordinary temperature, combination occurs [8] to form the triammine, $As_2O_5.3NH_3$.

Arsenic pentoxide catalyses the reaction between sulphur dioxide and oxygen,[9] the amount of sulphur trioxide formed reaching 54 per cent. at 660° C. The reaction consists in the alternate reduction of the pentoxide to arsenious oxide by the sulphur dioxide and reoxidation to the pentoxide, so that arsenious oxide acts similarly. The catalytic activity is less than that of ferric oxide, but the latter is activated by addition of arsenic pentoxide ; the maximum amount of conversion increases from 69·5 to 78·5 per cent. and occurs at a temperature 63° lower than is required in the absence of the promoter. Arsenic pentoxide does not activate catalysts which act rapidly, such as vanadium pentoxide. Platinum and silver catalysts are poisoned by arsenic pentoxide.[10]

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[1] Auger, *loc. cit.*; Kopp, *Ann. Chim. Phys.*, 1856, [3], 48, 106; Szarvasy and Messinger, *Ber.*, 1897, 30, 1344.

[2] Gay-Lussac and Thénard, "*Recherches physico-chimiques*," Paris, 1811, 1, 232.

[3] Hurtzig and Geuther, *Annalen*, 1859, 111, 172.

[4] Schönbein, *Pogg. Annalen*, 1849, 78, 514.

[5] Schulze, *J. prakt. Chem.*, 1880, [2], 21, 437.

[6] von Vogel, *Kastner's Arch.*, 1826, 9, 319.

[7] Faktor, *Pharm. Post.*, 1905, 38, 527; *Chem. Zentr.*, 1905, ii, 1218.

[8] Rosenheim and Jacobsohn, *Zeitsch. anorg. Chem.*, 1906, 50, 297.

[9] Neumann and Juttner, *Zeitsch. Elektrochem.*, 1930, 36, 87.

[10] Concerning the influence of arsenic on the catalytic activity of platinum for the oxidation of sulphur dioxide, see Maxted and Dunsby, *J. Chem. Soc.*, 1928, p. 1600.

Hydrates of Arsenic Pentoxide.—The existence of hydrates of arsenic pentoxide corresponding to the ortho-, meta- and pyro-phosphoric acids has not been established. Many such products have been described in the literature, the formation of which could not be confirmed by subsequent workers.[1] It appears certain that a *tetrahydrate*, $As_2O_5.4H_2O$, and a *(3, 5)-hydrate*, $3As_2O_5.5H_2O$, exist; there is also evidence of the formation of a *heptahydrate*, $As_2O_5.7H_2O$, and of a *dihydrate* (pyroarsenic acid), $As_2O_5.2H_2O$.

The *tetrahydrate* separates on cooling concentrated aqueous solutions of arsenic acid and is the product obtained in the industrial preparation of "arsenic acid" (see p. 183). It may be obtained[2] by concentrating the aqueous solution until it boils at 150° C.; a small portion is then inoculated with a crystal of the isomorphous tetrahydrate of phosphorus pentoxide[3] and the crystals which separate used to inoculate the main solution. The crystals are rhombic prisms or plates which melt[4] at $36 \cdot 14 \pm 0 \cdot 05$° C.

If the tetrahydrate is kept for some time in a superfused state, the *(3, 5)-hydrate* is formed as a hard white crystalline scale,[5] and this hydrate may also be obtained[6] by evaporating a solution of arsenic acid in an open vessel at temperatures from 50° to 100° C. or under increased pressure at 150° C.

The tetrahydrate loses water[7] even at −10° C., and dehydration over sulphuric acid, phosphorus pentoxide or potassium hydroxide proceeds regularly at the ordinary temperature until the (3, 5)-hydrate remains; under these conditions there is no indication that pyroarsenic acid, $As_2O_5.2H_2O$, is formed as an intermediate product. Complete dehydration occurs when either of the above hydrates is heated to 180° to 200° C., and the isobaric decomposition curve[8] of the tetrahydrate gives no indication of the formation of any hydrate other than $3As_2O_5.5H_2O$; neither solid solutions nor mixed crystals appear to be formed.

A *heptahydrate*, $As_2O_5.7H_2O$, is stated[9] to be obtained by evaporating at 130° C. a solution of arsenic acid and then cooling to −20° to −30° C.

The *dihydrate*, $As_2O_5.2H_2O$, or pyroarsenic acid, $H_4As_2O_7$, was described by Kopp[10] as a hard mass formed when aqueous arsenic acid was evaporated at a temperature between 140° and 180° C., but the compound could not be obtained by Auger[11] and other workers.[12] Rosenheim and Antelmann,[13] however, maintain that pyroarsenic acid does exist and is obtained in the form of hard microscopic prismatic crystals by evaporating a concentrated aqueous solution of pure arsenic

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[1] Bucholz, *Schweigger's J.*, 1823, 39, 397; Kopp, *Ann. Chim. Phys.*, 1856, [3], 48, 106; Geuther, *Annalen*, 1859, 111, 159; Joly, *Compt. rend.*, 1885, 100, 1221; 101, 1262; 1886, 102, 316, 431; Auger, *ibid.*, 1902, 134, 1059, Balareff, *Zeitsch. anorg. Chem.*, 1911, 71, 73.

[2] Menzies and Potter, *J. Amer. Chem. Soc.*, 1912, 34, 1452; *Intern. Cong. Appl. Chem.*, 1912, 8, ii, 179.

[3] Joly, *loc. cit.*

[4] Menzies and Potter, *loc. cit.*; Kopp, *loc. cit.*

[5] Menzies and Potter, *loc. cit.*

[6] Balareff, *loc. cit.*

[7] Auger, *loc. cit.*; *Compt. rend.*, 1908, 146, 585.

acid in an open dish until a temperature of 170° to 180° C. is reached. The product remains at constant weight even when heated at 155° C. A number of pyroarsenates have been prepared (see pp. 190–235), and Rosenheim and Antelmann conclude that pyroarsenic acid exists in solution in equilibrium with the ortho-acid, but is hydrolysed to the latter much more rapidly than is the case with the corresponding pyrophosphoric acid.

Manufacture of Arsenic Acid.—The large-scale preparation of arsenic acid usually depends on the oxidation of arsenious oxide or sulphide with moderately concentrated nitric acid (sp. gr. not less than 1·35) or some other oxidising agent. The operation with nitric acid is conducted in chambers or steam-jacketed kettles made of acid-resisting material such as ferro-silicon alloy.[1] The mixture of oxide and nitric acid is violently agitated and at the same time allowed to pass gradually into a second chamber or kettle. Considerable foaming accompanies the reaction and may be excessive with low-grade ore; this is met by causing the bulk of the reaction to take place outside the main batch kettle and within the pump or agitator below, the nitrous gases being released from a fountain discharge above the surface in the main kettle. The nitrous fumes may be recovered by passing over moist coke. The reaction is facilitated catalytically by the presence of a little hydrochloric acid or other halogen hydracid.[2]

The oxidation is more satisfactorily carried out in the presence of air or oxygen. One method [3] consists in treating arsenious oxide with nitric acid at a raised temperature and under an oxygen pressure of about 20 atmospheres. The arsenious oxide (or arsenious sulphide) is introduced into a closed vessel having a stirrer, and an equal weight of 60 per cent. nitric acid is added, together with a small amount of arsenic pentoxide or other catalyst. Oxygen at 20 atmospheres is then forced in and the mixture stirred for 12 to 18 hours at 70° to 90° C. The nitric acid, which remains almost unchanged and thus acts as a catalyst, can be distilled off and the arsenic acid remains as a syrupy liquid which crystallises (as the tetrahydrate, see p. 182) on cooling. This may be converted into the pentoxide by dehydration at 180° to 200° C. or may be converted into an arsenate.

If arsenious sulphide is used instead of the oxide, arsenic acid and sulphuric acid are formed and may be separated by precipitation of the latter by addition of lime. In the absence of nitric acid, oxygen at 20 atmospheres, even at 200° C., produces only arsenious acid from arsenious oxide (*cf.* p. 146), and arsenious and sulphuric acids from arsenious sulphide.

By passing arsenious oxide vapour and air into a tower containing nitric acid and water vapour, arsenic acid is produced and the nitrogen oxides formed are reoxidised by the air present.[4]

An alkali chlorate is sometimes employed as the oxidising agent.[5]

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[1] Ambruster, *U.S. Patent*, 1603308 (1926); Suverkrop, *Chem. Met. Eng.*, 1927, 34, 96.

[2] Behse, *U.S. Patent*, 1493798 (1924). See also Smith and Miller, *Ind. Eng. Chem.*, 1924, 16, 1168; *J. Franklin Inst.*, 1925, 199, 556.

[3] Askenasy and Elod, *German Patent*, 550402 (1924); *English Patent*, 255522 (1925); *U.S. Patent*, 1650860 (1927); Askenasy, Elod and Zieler, *Zeitsch. anorg. Chem.*, 1927, 162, 161.

[4] Piver, *U.S. Patent*, 1615193 (1927).

[5] Ullman and Trewendt, *U.S. Patents*, 1677257 (1928), 1699823 (1929); Bálint,

Thus a solution containing arsenious oxide (10 parts), sodium chlorate (4 parts) or potassium chlorate (3·8 parts) and water (20 parts) is heated to the boiling point, a little hydrochloric acid being added as catalyst.

The oxidation may also be accomplished by means of chlorine,[1] bromine [2] or iodine,[3] hypochlorous acid,[4] aqua regia,[5] chromic acid [6] or permanganic acid,[6] and some metallic oxides [7] (see p. 180). Arsenic acid is also formed by decomposition of arsenic trichloride by the action of chlorine water [8] or chromic acid,[9] or by the action of bromine water on arsenious sulphide.[10]

Properties of Aqueous Solutions of Arsenic Acid.—The system As_2O_5–H_2O has been investigated [11] by determining the solubility curves of the (1, 4)- and the (3, 5)-hydrates, and also the curve for the depression of the freezing point of water. The data obtained are given in the following table and are graphically represented in fig. 10.

Temperature, ° C.	Solubility, g. H_3AsO_4 in 100 g. Solution.	Solid Phase.	Temperature, ° C.	Solubility, g. H_3AsO_4 in 100 g. Solution.	Solid Phase.
− 4·2	21·1	Ice	9·2	88·3	$3As_2O_5.5H_2O$
−18·8	46·2		19·3	89·2	
−30·8	54·4		25·3	89·5	
−46·0	63·4		26·8	89·75	
−37·3	73·7	$As_2O_5.4H_2O$	34·35	89·75	
−21·8	76·6		35·3	89·9	
0·0	81·1		45·2	90·5	
9·8	83·7		45·5	90·5	
15·5	85·6		64·15	91·9	
19·8	86·6		74·85	92·0	
24·6	87·9		79·15	93·2	
30·1	90·4		99·25	94·35	
34·8	92·6		141·0	96·9	
36·2	94·1				

The tetrahydrate readily forms supersaturated solutions and in the above investigation it was never observed to separate spontaneously

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[1] Bergman, "*De arsenico*," Upsala, 1777; Ellis and Stewart, *U.S. Patents*, 1415323 (1922), 1515079 (1924).

[2] Balard, *Ann. Chim. Phys.*, 1834, [2], 57, 265; Wagner, *Wagner's Jahresber.*, 1876, p. 569; Francis, *J. Amer. Chem. Soc.*, 1926, 48, 655.

[3] Simon, *Repert. Pharm.*, 1839, 65, 198.

[4] Balard, *loc. cit.*

[5] Scheele, *Svenska Vet. Akad. Handl.*, 1775, 36, 265; Bucholz, *Scherer's J.*, 1802, 9, 397; *Schweigger's J.*, 1813, 7, 387.

[6] Kessler, *Pogg. Annalen*, 1855, 95, 205.

[7] Vauquelin, *J. Pharm. Chim.*, 1823, [2], 9, 230; Ikebe and Otani, *Japanese Patent*, 94024 (1932).

[8] Kaiser, *Zeitsch. anal. Chem.*, 1875, 14, 255.

[9] Wallace, *Phil. Mag.*, 1859, [4], 18, 279; *B A. Reports*, 1859, 69, 88.

[10] de Koninck, *Zeitsch. anal. Chem.*, 1880, 19, 468.

from the solution, inoculation always being necessary. Above 29·5° C. the (3, 5)-hydrate is the more stable. The cryohydric point appears to lie close to −60° C. with about 69 per cent. of H_3AsO_4.

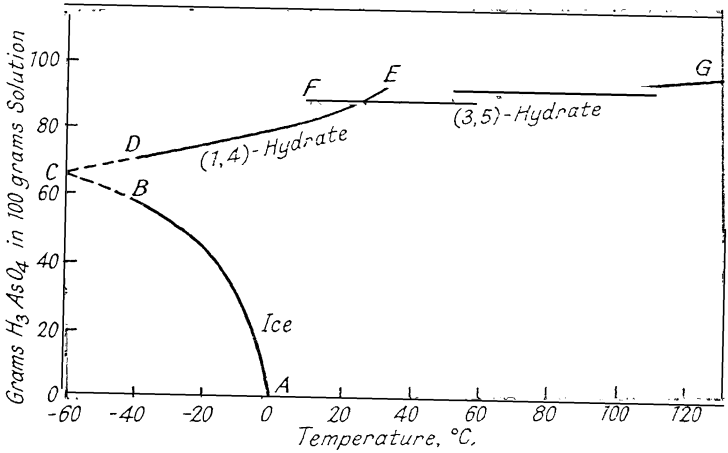

FIG. 10.—The Two-component System As_2O_5–H_2O.

The density of an aqueous solution containing p per cent. of H_3AsO_4 at 15° C. may be expressed[1] as

$$D_4^{15} = 0·9992 + 0·0060p + 0·0000576p^2$$

Gerlach[2] gave the following data for densities at 15° C., the concentrations being expressed in parts of As_2O_5 in 100 parts of solution :

Concentration.	Density.	Concentration.	Density.
2	1·016	30	1·298
6	1·048	40	1·441
10	1·083	50	1·620
16	1·140	60	1·850
20	1·180	70	2·150

The relative viscosities of the following aqueous solutions at 25° C. have been determined :[3] N-H_3AsO_4, 1·2707 ; N/2, 1·1291 ; N/4, 1·0595 ; N/8, 1·0309.

Although the acid itself has not been isolated (see p. 182), the solution behaves as though it contained a tribasic acid and reacts successively with three equivalents of sodium hydroxide.[4] The aqueous solution is strongly acid to litmus. During neutralisation in the presence of methyl orange or lacmoid, the colour change occurs when one equivalent

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[1] Mendeléeff, *Ber.*, 1886, 19, 379: "*Étude des Dissolutions aqueuses*," St Petersburg, 1887, p. 365.

[2] Gerlach, *Zeitsch. anal. Chem.*, 1888, 27, 316. See also von Vogel, *loc. cit.*; Schiff, *Annalen*, 1860, 113, 193.

[3] Reyher, *Zeitsch. physikal. Chem.*, 1888, 2, 744.

of alkali hydroxide has been added; with phenolphthalein the colour change occurs after two equivalents have been added.[1] The successive heats of neutralisation[2] with sodium hydroxide are: 1st mol. NaOH, 14,990 calories; 2nd mol., 12,590 calories; and 3rd mol., 8340 calories; total, 35,920 calories. The heat of dissolution is represented by Thomsen[2] as $(H_3AsO_4, aq.) = -400$ calories.

The electrical conductivities (molecular) at 25° C. of aqueous solutions containing 1 mol. H_3AsO_4 in v litres are as follows:[3]

v (litres) .	8	16	32	64	128	256	512	1024
μ (mhos).	68·4	89·4	117·4	150·2	188·4	228·0	264·2	290·3

The three dissociation constants, k_1, k_2 and k_3, of arsenic acid, determined by means of the glass electrode, are[4] respectively $5{\cdot}6 \times 10^{-3}$, $1{\cdot}7 \times 10^{-7}$ and $3{\cdot}0 \times 10^{-12}$. During electrolysis reduction occurs, arsenic being deposited and arsine liberated at the negative electrode[5] and oxygen at the positive.[6] The amount of arsine produced depends on the nature of the electrode,[7] more being produced at a mercury cathode than at one of platinum; the quantity of arsine also increases with increasing concentration of arsenic acid.[8] The reduction proceeds more readily with an alternating current than with direct current.[9]

The oxidation-reduction potential of arsenious-arsenic acid solutions has been determined.[10] A small quantity of iodide was added as catalyst,[11] and it was found that true equilibrium values, varying normally with the concentration ratio, are obtained only if the solutions are acidified to an extent corresponding at least with N-HCl. For the cell

$$\text{Pt} \mid 0{\cdot}01\text{M-}H_3AsO_4,\ 0{\cdot}01\text{M-}H_3AsO_3,\ 0{\cdot}001\text{M-KI},\ \text{M-HCl} \vdots$$
$$NH_4NO_3 \text{ saturated solution} \vdots \text{M-}H_2SO_4,\ Hg_2SO_4 \mid \text{Hg}$$

E_0 at 18° C. is $+0{\cdot}574$ volt, and at higher acidities the value increases.[12]

The buffering power of arsenic acid towards alkali is considerable, and much greater than that of phosphate or citrate buffers.[13]

The absorption spectra of aqueous solutions have been examined.[14]

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[1] Astruc and Tarbouriech, *Compt. rend.*, 1901, 133, 36; Joly, *ibid.*, 1885, 100, 1221; 101, 1262; Blarez, *ibid.*, 1886, 103, 639, 1133.

[2] Thomsen, "*Thermochemistry*" (Longmans), 1908, pp. 131, 254. See also Baud and Astruc, *Compt. rend.*, 1904, 139, 202; 1907, 144, 1345.

[3] Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 56.

[4] Britton and Jackson, *J. Chem. Soc.*, 1934, p. 1048. See also Luther, *Zeitsch. Elektrochem.*, 1907, 13, 294; Washburn, *J. Amer. Chem. Soc.*, 1908, 30, 31; 1913, 35, 681; Blanc, *J. Chim. phys.*, 1920, 18, 28; Skrabal and Zahorka, *Zeitsch. Elektrochem.*, 1927, 33, 42; Hughes, *J. Chem. Soc.*, 1928, p. 491.

[5] Richter, "*Ueber die neuerer Gegenstande der Chemie*," Breslau, 1791, 1, 35.

[6] Bischof, *Kastner's Arch.*, 1825, 4, 13; 6, 438.

[7] Ramberg, *Arsskr. Lunds Univ.*, 1918, 14, 21.

[8] Lloyd, *Trans. Faraday Soc.*, 1931, 21, 89.

[9] Brochet and Petit, *Ann. Chim. Phys.*, 1905, [8], 5, 307, Lloyd, *loc. cit.*

[10] Foerster and Pressprich, *Zeitsch. Elektrochem.*, 1927, 33, 176.

[11] Loimaranta, *ibid.*, 1907, 13, 33.

[12] Luther (*loc. cit.*), from the conditions of equilibrium in the reduction of arsenic acid by hydriodic acid, obtained the value E_0 at 25° C. = $+0{\cdot}575$ volt. See also Roebuck, *J. Phys. Chem.*, 1905, 9, 127; Jellinek and Winogradoff, *Zeitsch. Elektrochem.*, 1924, 30, 483.

[13] Adova and Smorodincev, *Biochem. Zeitsch.*, 1931, 232, 159.

Arsenic acid in solution is readily reduced by nascent hydrogen, arsine being evolved; in the presence of alkali, however, this reduction does not take place.[1] When distilled with concentrated hydrochloric acid, arsenic trichloride is formed and passes into the distillate; the reaction is accelerated by the presence of organic matter[2] or other reducing agents, such as ferrous[3] or cuprous[4] salts. The reaction[5]

$$As_2O_5 + 10HCl \rightleftharpoons 2AsCl_3 + 2Cl_2 + 5H_2O$$

is the basis of a method used for separating arsenic from other elements which do not yield volatile chlorides under the same conditions.[6] The amount of trichloride produced increases with the concentration of the acid,[7] and a high yield is obtained when fuming hydrochloric acid is used.[8] Hydrobromic and hydriodic acids also reduce the pentoxide, but the products are arsenious acid and the free halogen; these reactions also are reversible[9] (see p. 143). When heated with potassium chloride, some arsenic trichloride distils over; potassium bromide has very little reducing action, but with alkali iodides, iodine is liberated and arsenious acid formed.[10] In the presence of dilute sulphuric acid the reaction with iodides is quantitative and proceeds according to the equation:

$$H_3AsO_4 + 2HI = H_3AsO_3 + I_2 + H_2O$$

This reaction may be employed for the determination of iodides;[11] the iodine is expelled by heating and the equivalent amount of arsenious acid in the solution determined.

The reaction of arsenic acid solutions with hydrogen sulphide has been the subject of much investigation and it is found that arsenic pentasulphide or arsenic trisulphide may be precipitated as the main product, according to conditions.[12] Thus, in an aqueous solution of the pentoxide at the ordinary temperature and in the presence of 8 to 14 per cent. of hydrochloric acid, the precipitate is the pentasulphide; as the concentration of hydrochloric acid is increased, the trisulphide and sulphur are also precipitated in increasing proportion, and at 32 to 33

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[1] Covelli, *Boll. Chim. Farm.*, 1909, 48, 623.

[2] Hehner, *Analyst*, 1892, 17, 268.

[3] Fischer, *Ber.*, 1880, 13, 1778; Hager, *Chem. Centr.*, 1881, p. 465.

[4] Clark, *J. Soc. Chem. Ind.*, 1887, 6, 352.

[5] Usher and Travers, *J. Chem. Soc.*, 1905, 87, 1370.

[6] Zenger, *Répert. Chim. Appl.*, 1862, 5, 203; Hufschmidt, *Ber.*, 1884, 17, 2245; Rohmer, *ibid.*, 1901, 34, 33; Gooch and Dammer, *Amer. J. Sci.*, 1891, [3], 42, 308; *Chem. News*, 1891, 64, 203; Field and Smith, *J. Amer. Chem. Soc.*, 1896, 18, 1051; Moyer, *ibid.*, 1899, 21, 1029; Fresenius and Hintz, *Zeitsch. anal. Chem.*, 1888, 27, 179; Travers and Lu, *Compt. rend.*, 1933, 196, 703.

[7] Fresenius and Souchay, *Zeitsch. anal. Chem.*, 1862, 1, 449; Mayrhofer, *Annalen*, 1871, 158, 329.

[8] Rose, *Pogg. Annalen*, 1858, 105, 573; 1859, 107, 186; Mayrhofer, *loc. cit.*

[9] Naylor, *Pharm. Trans.*, 1879, [3], 10, 441; Roebuck, *J. Phys. Chem.*, 1902, 6, 363; Bray, *ibid.*, 1905, 9, 573; Manchot and Oberhauser, *Zeitsch. anorg. Chem.*, 1923, 130, 163.

[10] Schonbein, *Pogg. Annalen*, 1849, 78, 514; Bunsen, *Annalen*, 1878, 192, 305.

[11] Gooch and Browning, *Amer. J. Sci.*, 1890, [3], 39, 188; 40, 66.

[12] Berzelius, *Pogg. Annalen*, 1826, 7, 2; Wackenroder, *J. prakt. Chem.*, 1834, [1], 2, 340; *Annalen*, 1835, 13, 241; Rose, *Pogg. Annalen*, 1858, 105, 573; 1859, 107, 186; Ludwig, *Arch. Pharm.*, 1859, [2], 97, 32; Parnell, *Chem. News*, 1870, 21, 133; McCay, *Chem. News*, 1886, 54, 287; *Amer. Chem. J.*, 1885, 7, 375; 1887, 9, 174; 1888, 10, 459; 1890, 12, 547; *Zeitsch. anal. Chem.*, 1887, 26, 635; 1888, 27, 632; *Zeitsch. anorg. Chem.*, 1901, 26, 329; 1902, 29, 46; *J. Amer. Chem. Soc.*, 1902, 24, 661.

per cent. HCl no pentasulphide is formed.[1] On the other hand, a cold solution of an arsenate containing not less than 29 per cent. of hydrochloric acid yields only the pentasulphide.[2] The formation of the latter is favoured by rapid passage of the hydrogen sulphide, whilst a rise in temperature above 50° C. favours reduction.[3] A sufficiently rapid introduction of the gas [4] into pure arsenic acid solutions always gives rise to arsenic pentasulphide, and the precipitation is progressively inhibited by hydrochloric acid in concentrations from N to 4N, but is promoted when the concentration exceeds 6N. If the addition of the hydrogen sulphide is interrupted before all the arsenic is precipitated, the solution is found to contain monothioarsenic acid, H_3AsO_3S, in amount corresponding with the incompleteness of the precipitation, and this acid is the primary product of the reaction, whether hydrochloric acid is present or not. The monothioarsenic acid under the influence of heat and mineral acids decomposes into free sulphur and arsenious acid, the latter with hydrogen sulphide then yielding arsenic trisulphide.[5]

From solutions of pure arsenic acid the pentasulphide separates in a highly disperse form which adsorbs arsenic acid so strongly that the last traces of the latter react with great difficulty at the ordinary temperature,[6] although this is not the case at 40° C. In the presence of salts of multivalent cations which by hydrolysis yield colloidal hydroxides, the arsenic pentasulphide is flocculated, but the completion of the reaction is greatly delayed owing to adsorption of the arsenic acid, especially at low temperatures.

If a solution of an alkali arsenate in moderately concentrated hydrochloric acid is saturated with hydrogen sulphide and heated in a sealed tube in the absence of air for one hour at 100° C., the arsenic is completely converted to the pentasulphide, no trisulphide or sulphur being formed.[7]

Solutions of arsenic acid are reduced to arsenious acid by sulphur dioxide, slowly in the cold but more rapidly when heated.[8] The rate of reduction depends upon the degree of acidity of the solution [9] and is complete only after prolonged heating or boiling unless the operation is carried out in a closed vessel.[10] Under the latter conditions the reaction may be used for the preparation of arsenious oxide.[11] The reduction is greatly retarded by the presence of vanadic acid in dilute sulphuric acid solution,[12] but proceeds rapidly if the mixture is heated with a trace of potassium iodide present. Complete reduction of the mixture to arsenious acid and a vanadyl salt may then be brought about by heating in a sealed vessel for about one hour on a water-bath.[13]

At room temperatures solutions of sodium monohydrogen arsenate

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[1] Usher and Travers, *J. Chem. Soc.*, 1905, 87, 1370.

[2] Neher, *Zeitsch. anal. Chem.*, 1893, 32, 45.

[3] Brauner and Tomíček, *Monatsh.*, 1887, 8, 627; *J. Chem. Soc.*, 1888, 53, 145.

[4] Foerster, Pressprich and Reuss, *Zeitsch. anorg. Chem.*, 1930, 188, 90. *Cf.* McCay and Foster, *Ber.*, 1904, 37, 573.

[5] McCay, *loc. cit.*; Foster, *J. Amer. Chem. Soc.*, 1916, 38, 52.

[6] Foerster and co-workers, *loc. cit.*

[7] McCay, *loc. cit.*

[8] Wohler, *Annalen*, 1839, 30, 224.

[9] Usher and Travers, *loc. cit.*

[10] Bunsen, *loc. cit.*; Brauner and Tomíček, *loc. cit.*; McCay, *loc. cit.*

[11] Norddeutsche Affinerie, *British Patent*, 372189 (1932).

[12] Browning and Goodman, *Amer. J. Sci.*, 1896, [4], 2, 355; Edgar, *ibid.*, 1909, [4], 27, 299; Trautmann, *Zeitsch. anal. Chem.*, 1911, 50, 371; Auger and Odinot, *Compt. rend.*, 1924, 178, 213.

[13] Gooch, "*Methods of Chemical Analysis*" (New York), 1912, p. 350.

and sulphurous acid react very slowly; the reaction is greatly accelerated by mineral acids and reaches a maximum in the presence of 0·13N-hydrochloric acid or 0·20 to 0·26N-sulphuric acid.[1]

Sodium thiosulphate also yields a precipitate of arsenic pentasulphide, slowly in the cold but more readily on heating and when hydrochloric acid is present; [2] pentathionic acid is formed in the solution.[3]

Hydrazine in the presence of sulphuric acid reduces arsenic acid to a slight extent to arsine, which is subsequently oxidised to arsenic; the reaction does not take place if a considerable concentration of hydrochloric acid is present.[4] Arsenites, in the absence of arsenates, are not reduced by hydrazine. An aqueous solution of arsenic acid is reduced to the trioxide by hydrazine salts only after prolonged boiling.[5]

Phosphine yields a copper-coloured precipitate, possibly an arsenide of phosphorus.[6] Phosphorus trichloride causes reduction to arsenic,[7] as also do the tribromide and triiodide, though less readily. Hypophosphorous acid causes a similar reduction to arsenic; [8] in hydrochloric acid solution the velocity of the reaction at various concentrations corresponds with that of a reaction of the second order and may be expressed by [9]

$$-\frac{dC_{H_3AsO_3}}{dt}=K.C_{H_3AsO_2}.C_{H_3PO_2}=KC_{H_3AsO_3}\{B-(C_0-C)\}$$

where B and C_0 are respectively the initial concentrations of hypophosphorous and arsenic acids and C is the concentration of the latter at time t.

Formic and oxalic acids and their salts in the presence of mineral acid reduce arsenic acid and arsenates; the reaction is accelerated by boiling.[10] Tartaric acid does not appear to form complexes with arsenic acid [11] such as are formed with arsenious acid. Certain sugars, namely fructose and less rapidly sucrose, but not glucose, maltose or lactose, form labile esters of arsenic acid during fermentation in the presence of this acid; the reaction is purely a chemical one and not biochemical.[12]

Many metals, including magnesium, aluminium,[13] zinc, tin and iron,[14] precipitate arsenic and liberate arsine from aqueous arsenic acid. When copper is placed in such a solution containing mineral acid, copper arsenide is formed on the metal; [15] this reaction is employed under the

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[1] Kurtenacker and Furstenau, *Zeitsch. anorg. Chem.*, 1933, 212, 289.

[2] Himly, *Annalen*, 1842, 43, 150; Chapin, *J. Agric. Research*, 1914, 1, 515.

[3] Vortmann, *Ber.*, 1889, 22, 1520.

[4] Kubina and Plichta, *Zeitsch. anal. Chem.*, 1928, 74, 235.

[5] Knövenagel and Ebler, *Ber.*, 1902, 35, 3055.

[6] Graham, *Phil. Trans.*, 1833, 123, 253.

[7] Sen, *Proc. Asiatic Soc. Bengal*, 1919, 15, 263.

[8] Thiele, *Apoth. Zeit.*, 1890, 5, 86; *Annalen*, 1891, 265, 55.

[9] Vozdvijenski and Gerasimov, *J. Russ. Phys. Chem. Soc.*, 1930, 62, 409.

[10] Hager, *Pharm. Centr.*, 1884, [3], 25, 443; *Jahresber.*, 1884, p. 1580; Patrouillard, *Pharm. Trans.*, 1875, [3], 6, 428; 1882, [3], 13, 362; *Jahresber.*, 1875, p. 939. See also Naylor and Braithwaite, *Pharm. Trans.*, 1882, [3], 13, 228, 464, 478.

[11] Britton and Jackson, *J. Chem. Soc.*, 1934, p. 1048.

[12] Braunstein, *Biochem. Zeitsch.*, 1934, 271, 285.

[13] Maack, *Thesis*, Göttingen, 1862, p. 35.

[14] Fischer, *Pogg. Annalen*, 1826, 9, 255; Mohr, *Annalen*, 1837, 23, 219.

[15] Reinsch, *Neues Jahrb. Pharm.*, 1861, 16, 135; Werther, *J. prakt. Chem.*, 1861, [1], 82, 286. See also Fresenius and von Babo, *Annalen*, 1844, 49, 291; Howe and Mertins, *J. Amer. Chem. Soc.*, 1896, 18, 953; Kenrick, *ibid.*, 1902, 24, 276.

name of Reinsch's test in the qualitative detection of arsenic. If an aqueous solution of arsenic acid is heated with copper in a sealed tube for 18 hours at 180° to 200° C., arsenious oxide and copper arsenate are formed.[1]

THE ARSENATES.

Salts corresponding to the ortho-, meta- and pyro-acids are generally known, although the acids themselves do not appear to exist as stable compounds. The close analogy between arsenic and phosphoric acids and their derivatives is seen in the isomorphism which exists between corresponding salts, for example: $Na_2HAsO_4.12H_2O$ and $Na_2HPO_4.12H_2O$ or $MgNH_4AsO_4.6H_2O$ and $MgNH_4PO_4.6H_2O$; and also in the formation of analogous heteropoly-acids and salts.

Aluminium Arsenates.—The *orthoarsenate*, $AlAsO_4$, is obtained[2] in the form of elongated lens-shaped crystals when normal sodium orthoarsenate is heated with an excess of aluminium sulphate in a sealed tube at 220° C. The crystals are hexagonal in structure, with $a_0 = 5{\cdot}030$ and $c_0 = 5{\cdot}612$ A.; the form is similar to that of quartz.[3]

A mixture of aluminium arsenate, lime and sand has been recommended as a hydraulic cement; on dehydration insoluble calcium arsenate is formed, which improves the resistance to disintegration.[4]

The addition of sodium monohydrogen arsenate to a solution of an aluminium salt results in the precipitation of a white powder which is probably *aluminium hydrogen arsenate*,[5] $Al_2(HAsO_4)_3$. The powder dissolves in acids and the solution in hydrochloric acid when boiled with ammonium sulphite yields a precipitate of aluminium hydroxide, the arsenic remaining in solution. When heated in a current of hydrogen, arsenic is volatilised.[6]

Aluminium Pyroarsenate, $Al_4(As_2O_7)_3$, is obtained[7] by fusing at as low a temperature as possible a mixture of alumina and 15 to 16 times its weight of sodium or potassium dihydrogen arsenate; colourless transparent crystals are formed on cooling. These dissolve only very sparingly in hot water, but are readily soluble in dilute acids.

Complex arsenates of sodium, potassium and barium with aluminium have been described; thus by dissolving alumina in a fused mixture of sodium or potassium dihydrogen arsenate with about 20 per cent. of the alkali chloride, transparent plates of composition, respectively, $Na_3Al_2(AsO_4)_3$ and $K_3Al_2(AsO_4)_3$, are obtained.[8] In the presence of sodium or barium hydroxide, arsenic pentoxide combines with aluminium hydroxide to form *alumini-arsenates*[9] of composition $NaH_2[Al(AsO_4)_2].0{\cdot}5H_2O$ and $BaH_4[Al(AsO_4)_3].H_2O$, analogous to the ferriphosphates.

Aluminium arsenate occurs in numerous minerals. *Liskeardite*, $(Al, Fe)AsO_4.8H_2O$, is found in Cornwall as a pale blue incrustation on

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[1] Coloriano, *Bull. Soc. chim.*, 1886, [2], 45, 707; *Ber.*, 1886, 19, 527.
[2] Coloriano, *Compt. rend.*, 1886, 103, 273.
[3] Machatschki, *Zeitsch. Krist.*, 1935, 90, 314; 1936, 94, 222.
[4] Robak, *Ind. Eng. Chem.* (News Edn.), 1936, 14, 151.
[5] Berthier, *Ann. Chim. Phys.*, 1843, [3], 7, 76.
[6] Rose, *Zeitsch. anal. Chem.*, 1862, 1, 416; Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 42.
[7] Lefèvre, *loc. cit.*
[8] Lefèvre, *Compt. rend.*, 1890, 111, 36; "*Sur les Arséniates cristallisés*," Paris, 1891; *Ann. Chim. Phys.*, 1892, [6], 27, 42.
[9] Rosenheim and Thon, *Zeitsch. anorg. Chem.*, 1927, 167, 1.

quartz;[1] *cærulite*, $CuO.2Al_2O_3.As_2O_5.8H_2O$, occurs in Chile in the form of a clay which consists of minute turquoise-blue crystals;[2] *liroconite*, $Cu_9Al_4(OH)_{15}(AsO_4)_5.20H_2O$, found in Cornwall and Hungary, is blue or green and occurs in monoclinic crystals;[3] a basic arsenate of composition $4CaO.5Al_2O_3.3As_2O_5.20H_2O$ occurs as an amorphous mineral associated with mercury ores in Utah.[4]

Ammonium Arsenates.—*Ammonium Orthoarsenate*, $(NH_4)_3AsO_4.3H_2O$, is precipitated on saturating an aqueous solution of arsenic acid, or of either ammonium mono- or di-hydrogen orthoarsenate, with ammonia;[5] or it may be obtained by cooling a warm concentrated solution of arsenic acid in aqueous ammonia. The deposit consists of rhombic crystals and may be recrystallised from hot aqueous ammonia. The salt rapidly loses ammonia both in air and in solution, the dihydrogen arsenate ultimately being formed. The *anhydrous salt*, $(NH_4)_3AsO_4$, is formed when the dry mono- or di-hydrogen salt absorbs ammonia under a pressure of 8 atmospheres; the absorption should be allowed to continue for 12 hours at about 50° C. This product also is unstable and rapidly loses ammonia to form the monohydrogen arsenate.

Ammonium Monohydrogen Orthoarsenate, $(NH_4)_2HAsO_4$, may be prepared by the addition of ammonia to a concentrated aqueous solution of arsenic acid, the precipitate first formed being dissolved by warming and the salt then obtained either by crystallisation[6] or by precipitation with ethyl alcohol.[7] The dry salt, when gently heated, loses ammonia to form the dihydrogen arsenate, as also does the aqueous solution; in the cold, however, the dry salt is stable in dry air. The crystals are monoclinic prisms,[8] with $a:b:c=0{\cdot}918:1:1{\cdot}1715$ and $\beta=91°\ 13'$; density 1·99.

Ammonium Dihydrogen Orthoarsenate, $NH_4H_2AsO_4$, may be prepared by mixing aqueous ammonia and arsenic pentoxide in theoretical proportions.[7] It has also been obtained by heating arsenious oxide with ammonium nitrate and by gently heating ammonium monohydrogen orthoarsenate.[9] It crystallises in long non-deliquescent[7] prisms belonging to the tetragonal system, the axial ratio[10] $a:c$ being 1 : 1·0035. The salt is isomorphous with the corresponding potassium salt and with the corresponding ammonium and potassium phosphates.[11] The density[12] at 20° C. is 2·340. When heated above 300° C. it loses

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[1] Maskelyne, *Nature*, 1878, 18, 426; Flight, *J. Chem. Soc.*, 1883, 43, 140. See also Lacroix, *Bull. Soc. franç. Min.*, 1901, 24, 27.

[2] Dufet, *ibid.*, 1900, 23, 147.

[3] Groth, "*Tabellarische Uebersicht der Mineralien*," Braunschweig, 1898, p. 98. See also Dana, "*System of Mineralogy*," New York, 1868, p. 567; Rammelsberg, "*Handbuch der Mineralchemie*," Leipzig, 1875, p. 352.

[4] Clarke, *J. Washington Acad.*, 1912, 2, 516.

[5] Matignon and de Passillé, *Compt. rend.*, 1934, 198, 777. See also Mitscherlich, *Ann. Chim. Phys.*, 1821, [2], 19, 350, 407; *Akad. Handl. Stockholm*, 1821, p. 4; *Quart. J. Sci.*, 1823, 14, 198, 415; Uelsmann, *Arch. Pharm.*, 1859, [2], 99, 145; Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 129.

[6] Scheele, *Svenska Akad. Handl.*, 1778, 40, 316; Mitscherlich, *loc. cit.*

[7] Matignon and de Passillé, *loc. cit.*

[8] Mitscherlich, *loc. cit.*; Rammelsberg, "*Handbuch der krystallographischen Chemie*," Berlin, 1855, p. 181; "*Handbuch der kryst. physikal. Chemie*," Leipzig, 1881, 1, 535.

[9] Macquer, *Mém. Paris Acad.*, 1745, p. 9; 1746, p. 223; 1748, p. 35.

[10] Töpsoe, *Sitzungsber. K. Akad. Wiss. Wien*, 1872, 66, 32; *Bull. Soc. chim.*, 1873, [2], 19, 246.

[11] Mitscherlich, *loc. cit.*; Hassel, *Zeitsch. Elektrochem.*, 1925, 31, 523.

[12] Matignon and de Passillé, *loc. cit.* See also Topsöe, *loc. cit.*; Muthmann, *Zeitsch. Kryst. Min.*, 1893, 22, 523; 1894, 23, 368; Gossner, *ibid.*, 1908, 44, 484.

ammonia and an almost insoluble *acid metarsenate*, $NH_4H(AsO_3)_2$, is obtained—[1]

$$2NH_4H_2AsO_4 = NH_3 + 2H_2O + NH_4H(AsO_3)_2$$

which is stable up to 425° C., no trace of arsenious oxide or arsenic being formed at this temperature. When boiled with water the metarsenate reverts to the orthoarsenate.

The solubility in water of ammonium dihydrogen orthoarsenate and the densities of the saturated solutions have been determined with the results shown in the following table : [1]

SOLUBILITY OF $NH_4H_2AsO_4$ IN WATER.

Temp., ° C.	g. per 100 g. H_2O.	Density.
0	33·74	1·1814
20	48·67	1·2280
40	63·83	1·2821
60	83·05	1·3464
80	107·25	1·4200
90	122·40	1·4623

The following values for the heats of neutralisation at 15° C. of arsenic acid by aqueous ammonia, and for the heats of dissolution of the ammonium arsenates, have been obtained.[2] The solutions of arsenic acid for the determination of the former contained $\frac{1}{6}$ mole of H_3AsO_4 per litre, and those of ammonia were of such concentrations that 1 volume of the acid was neutralised by an equal volume of the base.

Heats of Neutralisation.

$$H_3AsO_4.330H_2O + NH_3.330H_2O = NH_4H_2AsO_4.660H_2O + 13{,}750 \text{ calories}$$
$$H_3AsO_4.330H_2O + 2NH_3.330H_2O = (NH_4)_2HAsO_4.660H_2O + 24{,}300 \text{ calories}$$
$$H_3AsO_4.330H_2O + 3NH_3.330H_2O = (NH_4)_3AsO_4.660H_2O + 25{,}100 \text{ calories}$$

Heats of Dissolution.

$$NH_4H_2AsO_{4\,\text{solid}} + 660H_2O = NH_4H_2AsO_{4\,\text{dissolved}} - 4250 \text{ calories}$$
$$(NH_4)_2HAsO_{4\,\text{solid}} + 660H_2O = (NH_4)_2HAsO_{4\,\text{dissolved}} - 3150 \text{ calories}$$
$$(NH_4)_3AsO_{4\,\text{solid}} + 1500H_2O = (NH_4)_3AsO_{4\,\text{dissolved}} - 8400 \text{ calories}$$
$$(NH_4)_3AsO_4.3H_2O_{\text{solid}} + 1200H_2O = (NH_4)_3AsO_4.3H_2O_{\text{dissolved}} - 13{,}700 \text{ calories}$$

From the above data, and assuming the heat of dissolution of arsenic pentoxide to be +6000 calories (see p. 180), the following values for the heats of formation have been calculated : [3]

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[1] Matignon and de Passillé, *loc. cit.*

[2] de Passillé, *Compt. rend.*, 1935, 200, 1852.

Heats of Formation.

$$\tfrac{1}{2}(As_2O_{5\,\text{solid}} + 3H_2O_{\text{liquid}}) + NH_{3\,\text{gas}} = NH_4H_2AsO_{4\,\text{solid}} + 29{,}480 \text{ calories}$$
$$\tfrac{1}{2}(As_2O_{5\,\text{solid}} + 3H_2O_{\text{liquid}}) + 2NH_{3\,\text{gas}} = (NH_4)_2HAsO_{4\,\text{solid}} + 47{,}410 \text{ calories}$$
$$\tfrac{1}{2}(As_2O_{5\,\text{solid}} + 3H_2O_{\text{liquid}}) + 3NH_{3\,\text{gas}} = (NH_4)_3AsO_{4\,\text{solid}} + 61{,}940 \text{ calories}$$
$$\tfrac{1}{2}(As_2O_{5\,\text{solid}} + 3H_2O_{\text{liquid}}) + 3NH_{3\,\text{gas}} + 3H_2O_{\text{liquid}} = (NH_4)_3AsO_4.3H_2O_{\text{solid}} + 67{,}240 \text{ calories}$$

The values of Q_0 from Nernst's formula

$$\log p = -\frac{Q_0}{4{\cdot}57T} + 1{\cdot}75 \log T + 3{\cdot}3$$

for the di- and tri-ammonium salts[1] are respectively 15,500 and 13,070 calories; these values represent the heats liberated in fixing the second and third molecules of ammonia. A study of the dissociation of the triammonium arsenate suggests that the successive withdrawal of ammonia gives rise to equilibria which indicate the existence of the following compounds;[2] Q_0 represents the heat changes of the equilibria.

$$(NH_4)_6As_2O_8 \rightleftharpoons (NH_4)_5HAs_2O_8 + NH_3, \quad Q_0 = 13{,}000 \text{ cal.}$$
$$(NH_4)_5HAs_2O_8 \rightleftharpoons (NH_4)_4H_2As_2O_8 + NH_3, \quad Q_0 = 14{,}000 \text{ ,,}$$
$$(NH_4)_4H_2As_2O_8 \rightleftharpoons (NH_4)_3H_3As_2O_8 + NH_3, \quad Q_0 = 15{,}600 \text{ ,,}$$
$$(NH_4)_3H_3As_2O_8 \rightleftharpoons (NH_4)_2H_4As_2O_8 + NH_3, \quad Q_0 = 16{,}200 \text{ ,,}$$
$$(NH_4)_2H_4As_2O_8 \rightleftharpoons (NH_4)H_5As_2O_8 + NH_3, \quad Q_0 = 16{,}700 \text{ ,,}$$

Mixed orthoarsenates of ammonium and sodium have been obtained,[3] namely, *diammonium sodium orthoarsenate*, $(NH_4)_2NaAsO_4.4H_2O$, and *ammonium sodium hydrogen orthoarsenate*, $(NH_4)NaHAsO_4.4H_2O$. The latter forms monoclinic crystals when a solution containing equivalent quantities of ammonium and sodium monohydrogen arsenates is allowed to crystallise, or when an ammoniacal solution containing ammonium chloride and sodium dihydrogen arsenate (1 : 6) is concentrated. When ignited, water and ammonia are expelled and sodium metarsenate remains.[4] The diammonium sodium salt may be obtained by allowing to crystallise a solution of the ammonium sodium hydrogen salt in concentrated aqueous ammonia. The tabular crystals, when confined over dilute sulphuric acid, lose ammonia and revert to ammonium sodium hydrogen orthoarsenate.

Antimony Arsenates have not been prepared.[5]

Barium Arsenates.—Barium orthoarsenate, $Ba_3(AsO_4)_2$, is formed as large colourless plates when a mixture of barium oxide, alkali chloride and alkali hydrogen orthoarsenate is fused and allowed to cool.[6] It is also said to be formed[7] by the action of ammonia on an aqueous solution of barium hydrogen arsenate; the product, however, varies in composition, barium ammonium arsenate sometimes being formed and

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[1] Matignon and de Passillé, *loc. cit.*

[2] de Passillé, *Compt. rend.*, 1935, 201, 344.

[3] Uelsmann, *loc. cit.*

[4] Mitscherlich, *loc. cit.*

[5] See Berzelius, *Pogg. Annalen*, 1826, 7, 28; *Schweigger's J.*, 1821, 32, 162; Berthier, *Ann. Chim. Phys.*, 1823, [2], 22, 239; 1824, [2], 25, 379.

[6] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 17.

[7] Berzelius, *Pogg. Annalen*, 1826, 7, 137; Lefèvre, *loc. cit.*; Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 143.

barium orthoarsenate rarely.[1] The latter salt retains water, which may be expelled at 150° C.;[2] definite hydrates have not been obtained. It is only slightly soluble in cold water. The anhydrous orthoarsenate has density 5·095 and melts at 1605° C.[3] It is reduced by hydrogen at 400° to 450° C. to barium oxide, arsenic and water.

A study of the acid section of the system As_2O_5–BaO–H_2O at 30° C. shows[4] that the stable solid phases are barium monohydrogen orthoarsenate, $BaHAsO_4.H_2O$, barium dihydrogen orthoarsenate, $Ba(H_2AsO_4)_2.2H_2O$, and the (3, 5)-hydrate of arsenic pentoxide, $3As_2O_5.5H_2O$.

Barium Monohydrogen Orthoarsenate may be obtained[5] as a gelatinous precipitate by adding baryta-water drop by drop to aqueous arsenic acid until the solution is alkaline to phenolphthalein. On shaking, the precipitate becomes crystalline. Berzelius obtained this salt in the form of small crystalline scales by adding sodium hydrogen arsenate drop by drop to excess of barium chloride solution. The precipitate may be dried at 100° C. The crystals are transparent rhombic plates[6] of density 3·926 at 15° C.; from acetic acid it may be recrystallised in the form of octahedra.[7] When heated at 120° C. the salt loses its water of crystallisation, and at 320° C. it loses constitutional water and forms barium pyroarsenate.[8]

Barium Dihydrogen Orthoarsenate crystallises as the dihydrate from a solution of barium orthoarsenate or barium monohydrogen orthoarsenate in aqueous arsenic acid, or it may be precipitated by the addition of baryta-water or barium carbonate to aqueous arsenic acid.[9] The crystals are monoclinic, with axial ratios[10] $a:b:c=1\cdot160:1:0\cdot625$ and $\beta=108°\ 34'$. The salt is only slightly soluble in water and in the presence of excess of water changes to the monohydrogen arsenate. It is readily soluble in hydrochloric acid; less soluble in acetic acid. When heated, it loses water, and above 230° C. *barium metarsenate*, $Ba(AsO_3)_2$, remains.[11] The latter may also be obtained by evaporation of a solution of the pyroarsenate and calcination of the residue.[12]

Barium Pyroarsenate, $Ba_2As_2O_7$, is formed when barium monohydrogen orthoarsenate is ignited, or when barium oxide is fused with an alkali hydrogen arsenate.[13] In the latter case it may be extracted with anhydrous glycerol. In contact with cold water the *hexahydrate*, $Ba_2As_2O_7.6H_2O$, is formed; boiling water converts it to the orthoarsenate.[12]

Mixed orthoarsenates of composition $BaKAsO_4$,[12] $BaNaAsO_4.9H_2O$,[14] $Ba(NH_4)AsO_4.\frac{1}{2}H_2O$ and $Ba(NH_4)_2H_2(AsO_4)_2$[15] have been prepared,

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[1] Hendricks, *J. Physical Chem.*, 1926, 30, 248.

[2] Salkowski, *loc. cit.*; Field, *J. Chem. Soc.*, 1858, 11, 6.

[3] Guérin, *Compt. rend.*, 1936, 203, 997, 1163.

[4] Hendricks, *J. Physical Chem.*, 1926, 30, 248.

[5] Joly, *Compt. rend.*, 1886, 103, 746, 1197; 1887, 104, 1702.

[6] de Schulten, *Bull. Soc. franç. Min.*, 1904, 27, 104.

[7] Schiefer, *Jahresber.*, 1864, p. 237.

[8] Hormann, *Dissertation*, Erlangen, 1897.

[9] Berzelius, *loc. cit.*; Mitscherlich, *loc. cit.*; Hörmann, *loc. cit.*

[10] Rammelsberg, "*Handbuch der kryst. physikal. Chemie*," Leipzig, 1881, 1, 537.

[11] Mitscherlich, *loc. cit.*

[12] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 17.

[13] Lefèvre, *Compt. rend.*, 1889, 108, 1058.

[14] Joly, *loc. cit.*

[15] Abegg, "*Handbuch d. anorg. Chem.*" (Hirzel, Leipzig), 1907, III Bd., 3 Abt., p. 541. See Hendricks, *loc. cit.*

as also have complex alumini- and ferri-arsenates[1] of composition $BaH_4[Al(AsO_4)_3].H_2O$ and $Ba_3H_6[Fe(AsO_4)_3]_2$. *Barium chlorarsenoapatite*, $3Ba_3(AsO_4)_2.BaCl_2$, can be obtained by fusing a mixture of barium oxide, an alkali chloride and potassium or sodium metarsenate containing more than 60 per cent. of the arsenate.[2, 3] Bromo- and iodo-arsenoapatites are also known.[4]

Complex pyroarsenates of composition $BaCuAs_2O_7$ and $BaHgAs_2O_7.H_2O$ have been obtained[5] by heating aqueous solutions of arsenic acid with mixtures of barium hydroxide and the oxide or carbonate of the other metal at 180° to 200° C. Using copper carbonate and solutions of arsenic acid of 5 to 25 per cent. concentration, the barium-copper salt is formed quantitatively and the precipitate is of constant composition,[6] but outside the above limits of acid concentration the precipitate consists mainly of a mixture of orthoarsenates.

Beryllium Arsenates[7] are less stable than those of magnesium and readily form basic salts. *Beryllium orthoarsenate*, $Be_3(AsO_4)_2.15H_2O$, is obtained by drying in air the precipitate formed on mixing aqueous solutions of sodium monohydrogen arsenate and beryllium sulphate. The precipitate itself is probably *beryllium monohydrogen orthoarsenate*, $BeHAsO_4$, but this is readily hydrolysed and unless immediately removed from the solution forms a basic salt. It has been obtained in the form of a *dihydrate*, $BeHAsO_4.2H_2O$, as a viscous solid by dissolving beryllium hydroxide in arsenic acid and precipitating with alcohol, and in the *anhydrous* form by heating arsenic pentoxide and beryllium hydroxide together in a sealed tube at 220° C. *Beryllium dihydrogen orthoarsenate*, $Be(H_2AsO_4)_2$, is obtained as colourless hygroscopic tablets by the action of a hot saturated solution of arsenic acid on beryllium hydroxide and evaporation *in vacuo*.

By stirring beryllium oxide or carbonate with aqueous arsenic acid under carefully regulated conditions of concentration, acidity and temperature, Ephraim and Rosetti[8] have been able to isolate two arsenates of definite composition in a crystalline state, namely, $4{\cdot}5BeO.As_2O_5.9H_2O$ and $4BeO.As_2O_5.10H_2O$; whether these are to be considered basic salts or mixed acid salts (*cf.* p. 196) has not been determined.

Several double arsenates with alkali metals and ammonium have been described, but these are extremely unstable, undergoing ready hydrolysis to form basic salts.

Bismuth Arsenates.—*Bismuth Orthoarsenate* is obtained as a white crystalline precipitate by the action of arsenic acid or an alkali arsenate on a nitric acid solution of bismuth nitrate.[9] When dried at 100° to 120° C. the product is the *hemihydrate*, $BiAsO_4.\frac{1}{2}H_2O$, which loses water only at red heat. By evaporating the mixture on a water-bath, de Schulten[10] obtained a product which he described as the anhydrous

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[1] Rosenheim and Thon, *Zeitsch. anorg. Chem.*, 1927, 167, 1.

[2] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 17.

[3] Lefèvre, *Compt. rend.*, 1889, 108, 1058.

[4] Ditte, *Ann. Chim. Phys.*, 1886, [6], 8, 522, 529.

[5] Rosenheim and Antelmann, *Zeitsch. anorg. Chem.*, 1930, 187, 385.

[6] Rosenheim, *ibid.*, 1930, 193, 73.

[7] Bleyer and Muller, *ibid.*, 1912, 75, 285; Atterberg, *Bull. Soc. chim.*, 1875, [2], 24, 358; *Ber.*, 1876, 9, 864. See also Berzelius, *Ann. Chim. Phys.*, 1817, [2], 5, 179; 1819, [2], 11, 225; *Pogg. Annalen*, 1826, 7, 137.

[8] Ephraim and Rosetti, *Helv. Chim. Acta*, 1929, 12, 1025.

[9] Scheele, *Svenska Akad. Handl.*, 1778, 40, 316; Berzelius, *loc. cit.*; Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 170.

[10] de Schulten, *Bull. Soc. chim.*, 1903, [3], 29, 720.

salt; on adding water and keeping for a few days he obtained microscopic monoclinic prisms of density 7·142 at 15° C. The hemihydrate is usually obtained as microscopic spherical, stellate or octahedral crystals.[1] It is tasteless, sparingly soluble in water, soluble in dilute hydrochloric acid;[2] it melts only with difficulty.

A *basic arsenate*, $2BiAsO_4.3Bi_2O_3$, has been prepared by the action of sodium arsenate upon an ammoniacal solution of bismuth citrate.[3] It forms a gelatinous precipitate which resembles the corresponding phosphate in its chemical properties.

Basic arsenates of bismuth occur naturally in a number of minerals, especially in Saxony and Utah, the most noteworthy being *atelestite*, *rhagite*, *mixite* (containing copper) and *walpurgite* (containing uranium) (see p. 16).

Cadmium Arsenates.—The hydrated normal *cadmium orthoarsenate*, $2Cd_3(AsO_4)_2.3H_2O$, falls as a white voluminous precipitate on adding alkali to a solution of cadmium mono- or di-hydrogen arsenate in hydrochloric acid,[4] or on addition of sodium orthoarsenate to a solution of cadmium sulphate.[5] On drying at 100° C. the anhydrous salt remains.

Cadmium Monohydrogen Orthoarsenate, $CdHAsO_4.H_2O$, may be prepared by dissolving cadmium carbonate in aqueous arsenic acid.[6] The white crystalline substance dissolves easily in dilute hydrochloric acid, and it is decomposed by water to form a salt of composition $5CdO.2As_2O_5.5H_2O$. The existence of this salt appears to be well established[7] and it may be regarded as *cadmium dihydrogen tetra-orthoarsenate*, $Cd_3(AsO_4)_2.2CdHAsO_4.4H_2O$. It is formed as a precipitate when solutions of cadmium sulphate and sodium monohydrogen orthoarsenate are mixed.[8] If its saturated solution in arsenic acid is heated, the monohydrogen salt, $CdHAsO_4.H_2O$, separates,[9] the crystals of which have density 4·164 at 15° C. If, on the other hand, crystallisation of the solution occurs at ordinary temperatures, rhombic prisms of *cadmium dihydrogen orthoarsenate*, $Cd(H_2AsO_4)_2.2H_2O$, of density 3·241 at 15° C., separate. This salt is isomorphous with the corresponding phosphate, loses water with partial decomposition at 70° to 80° C., and with excess of water reverts to the acid salt, $5CdO.2As_2O_5.5H_2O$.[10]

Firm transparent jellies are produced[11] when solutions of potassium dihydrogen arsenate and cadmium sulphate, of suitable concentrations, are mixed. They are unstable and crystallise into $2Cd_3(AsO_4)_2.4CdHAsO_4.9H_2O$.

The following *double arsenates* have been described:[12] $Na_4Cd(AsO_4)_2$, $Na_8Cd_2As_2O_{11}$, $K_2Cd_2(AsO_4)_2$. *Cadmium chlorarsenoapatite*, $3Cd_3(AsO_4)_2.CdCl_2$, is produced by fusing normal ammonium arsenate or the acid

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[1] Haushofer, *Thesis*, Munchen, 1885, p. 140.

[2] Thénard, *Ann. Chim. Phys.*, 1804, [1], 50, 117.

[3] Cavazzi, *Gazzetta*, 1884, 14, 289.

[4] Demel, *Ber.*, 1879, 12, 1281.

[5] Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 162; *Ber.*, 1879, 12, 1447.

[6] Demel, *loc. cit.*

[7] Ephraim and Rosetti, *Helv. Chim. Acta*, 1929, 12, 1025.

[8] Salkowski, *loc. cit.*

[9] de Schulten, *Bull. Soc. chim.*, 1889, [3], 1, 473; *Bull. Soc. franç. Min.*, 1903, 26, 93.

[10] de Schulten, *loc. cit.*

[11] Klemp and Gyulay, *Kolloid-Zeitsch.*, 1921, 28, 262. See also Weiser and Bloxsom, *J. Physical Chem.*, 1924, 28, 26.

[12] Lefèvre, *Compt. rend.*, 1890, 110, 405; *Ann. Chim. Phys.*, 1892, [6], 27, 22.

salt $5CdO.2As_2O_5.5H_2O$ with excess of cadmium chloride. Its density at 15° C. is 5·865 and it resembles the corresponding phosphatic compound.[1] The analogous bromo-compound is similarly prepared as long yellow prisms of density 6·017.

Cadmium Metarsenate, $Cd(AsO_3)_2$, has been obtained by dissolving cadimum chloride in arsenic acid at 200° C. and drying the precipitate at 100° C.[2] When fused with cadmium oxide or carbonate, *cadmium pyroarsenate*, $Cd_2As_2O_7$, is obtained as colourless crystals.[3]

Cæsium Arsenate.—By adding excess of arsenic to a solution of cæsium hydroxide in nitric acid containing a little molybdic acid, white well-defined crystals of composition $Cs_2O.2As_2O_5.5H_2O$ have been obtained.[4]

Calcium Arsenates.—In a basic form calcium arsenate is an important commercial product and is used in the form of a spray or dust as an insecticide for plants (see Chapter XII). The commercial arsenates are usually mixtures and exhibit a wide variation in chemical and physical characteristics. The system $CaO–As_2O_5–H_2O$ has been investigated [5] at various temperatures, and equilibrium data, microscopic and X-ray examination point to the existence of the following compounds: $CaHAsO_4$, $Ca_5H_2(AsO_4)_4.5H_2O$, $Ca_3(AsO_4)_2.2H_2O$ and $4CaO.As_2O_5.xH_2O$.

The normal salt, *calcium orthoarsenate*, $Ca_3(AsO_4)_2$, may be obtained by the action of lime-water or milk of lime on arsenic acid, or by addition of aqueous calcium chloride to aqueous sodium monohydrogen arsenate; in the latter case if the solutions are alkaline a product of a high degree of purity is obtained.[6] Drying at 100° C. gives the dihydrate, $Ca_3(AsO_4)_2.2H_2O$, which loses its water of crystallisation at 175° C. The anhydrous salt melts at 1455° C.[7] It is reduced by hydrogen at 400° to 450° C. to calcium oxide, arsenic and water.[8] The density of the dihydrate [6] is 3·23, and of the anhydrous salt [7] 3·62. The solubility of the latter at 25° C. is 0·0133 grm. per 100 grm. of water.[6]

The commercial product is usually obtained either by adding arsenic acid to partly slaked lime containing sufficient quicklime to combine with the free water, thus yielding a dry product,[9] or by heating a mixture of lime and white arsenic in the presence of an oxidising medium, such as oxygen,[10] chlorine [11] or nitrates.[12] It is essential that the product

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[1] de Schulten, *loc. cit.*

[2] Salkowski, *loc. cit.*

[3] Lefèvre, *loc. cit.*; de Schulten, *loc. cit.*; Rosenheim, *Zeitsch. anorg. Chem.*, 1930, 193, 73.

[4] Ephraim and Herschfinkel, *Zeitsch. anorg. Chem.*, 1910, 65, 237.

[5] Pearce and Avens, *J. Amer. Chem. Soc.*, 1937, 59, 1258; Nelson and Haring, *ibid.*, 59, 2216; Smith, *ibid.*, 1920, 42, 259.

[6] Robinson, *J. Agric. Res.*, 1918, 13, 381. See *J. Soc. Chem. Ind.*, 1918, 37, 439 A; Guérin, *Bull. Soc. chim.*, 1937, [5], 4, 1249.

[7] Guérin, *Compt. rend.*, 1936, 203, 997.

[8] Guérin, *ibid.*, 1936, 203, 1163.

[9] Piver, *U.S. Patents*, 1667490–1 (1928); Schleicher, *U.S. Patent*, 1588499 (1926); Ellis and Stewart, *U.S. Patent*, 1690627 (1928); Széki and Romwalter, *Chem. Zentr.*, 1935, ii, 415.

[10] Rushton, *U.S. Patent*, 1624281 (1927). See also Bidaud, *U.S. Patent*, 1591958 (1926); Moore, *U.S. Patent*, 1619267 (1927).

should contain a minimum of soluble arsenic and that the presence of the more soluble acid arsenates should be avoided ; the commercial arsenate is generally slightly basic. The results of analyses of 16 samples showed [1] that the total As_2O_5 ranged only from 40·3 to 44·4 per cent. [As_2O_5 in $Ca_3(AsO_4)_2 = 57·7$ per cent.], and the average molecular quotient CaO/As_2O_5 was 3·4. The average commercial product contains 80 to 85 per cent. of what is probably a mixture of the normal arsenate and a basic arsenate, probably $4CaO.As_2O_5$, together with about 6·5 per cent. each of calcium hydroxide and calcium carbonate, and small quantities of other impurities. If varying quantities of arsenic acid are added to a saturated solution of lime, the ratio of $CaO : As_2O_5$ in the precipitate shows a continuous variation according to the quantity of arsenic acid added and under these conditions there is no evidence of the real existence of calcium orthophosphate, $Ca_3(AsO_4)_2$.[2]

An electrolytic method for the manufacture of calcium arsenate is as follows. A solution of arsenious oxide in caustic soda ($As_2O_3 : NaOH = 198 : 250$) is electrolysed between iron electrodes. Hydrogen and a small quantity of metallic arsenic are liberated at the cathode and very little oxygen at the anode, the basic arsenite in solution being oxidised to arsenate (see also p. 221). When this oxidation is complete, any arsenic is filtered off and the solution treated with milk of lime. A basic arsenate of extremely low solubility is precipitated and, after removal, is washed and dried.[3] The reactions involved are the following :

$$As_2O_3 + 2NaOH = 2NaAsO_2 + H_2O$$
$$2NaAsO_2 + 4NaOH = 2Na_3AsO_4 + 2H_2$$
$$2Na_3AsO_4 + 4Ca(OH)_2 = Ca_4As_2O_9 + 6NaOH + H_2O$$

Less basic arsenates may be obtained by precipitation with calcium chloride or nitrate.[4]

Calcium Monohydrogen Orthoarsenate, $CaHAsO_4$, may be prepared by treating calcium carbonate with arsenic acid, or by precipitation from solutions of calcium salts with sodium monohydrogen arsenate ; [5] both solutions should be acidified.[6] When dried at 100° C. the *monohydrate*, $CaHAsO_4.H_2O$, is obtained, but the water of crystallisation is expelled before the temperature of 175° C. is reached.[6] By placing a porous vessel containing sodium monohydrogen arsenate solution inside a vessel containing aqueous calcium nitrate, so that the two salts were able to mix by diffusion, well-defined monoclinic prisms of the *dihydrate*, $CaHAsO_4.2H_2O$, have been obtained.[7] These two hydrates occur in Nature, the monohydrate as *haidingerite* and the dihydrate as *pharmacolite*, and calcium arsenate is a constituent of many other minerals (see table, pp. 14-16). A third hydrate, $2CaHAsO_4.3H_2O$, has been described,[8] but its existence has not been confirmed.

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[1] Smith and Murray, *Ind. Eng. Chem.*, 1931, 23, 207.

[2] Clifford and Cameron, *ibid.*, 1929, 21, 69.

[3] Lloyd and Kennedy, *Chem. Met. Eng.*, 1925, 32, 624.

[4] Cambi and Bozza, *Giorn. Chim. Ind. Appl.*, 1925, 7, 687.

[5] Salkowski, *Jahresber.*, 1868, p. 231; Kotschoubey, *J. prakt. Chem.*, 1850, [1], 49, 182; *Annalen*, 1850, 76, 249; Dufet, *Compt. rend.*, 1888, 106, 1238; Des Cloiseaux, *ibid.*, 1888, 106, 1215.

[6] Robinson, *loc. cit.*

[7] Dufet, *Compt. rend.*, 1888, 106, 1238. See also Guérin, *Bull. Soc. chim.*, 1937, [5], 4, 1249.

[8] Debray, *Ann. Chim. Phys.*, 1861, [3], 61, 419; Kotschoubey, *loc. cit.*

A saturated solution of calcium monohydrogen arsenate contains at 25° C. 0·3108 grm. of the anhydrous salt per 100 grms. of solution.[1] The dihydrogen arsenate is sparingly soluble in cold water and is decomposed by hot water, yielding the monohydrogen salt and arsenic acid.

The heat developed by the saturation of a normal solution of arsenic acid with calcium hydroxide in aqueous solution is as follows : [2]

1st	equivalent CaO,	14,500	calories
2nd	,, ,,	12,500	,,
3rd	,, ,,	2,520	,,
4th	,, ,,	280	,,
5th	,, ,,	250	,,

With the addition of three equivalents the precipitate is variable in composition but approximates to the normal salt ; with 4 and 5 equivalents the precipitated arsenate is somewhat basic.

Calcium Dihydrogen Orthoarsenate has been obtained in the form of a monohydrate by adding nitric acid to a mixture containing equal proportions of calcium carbonate and arsenious oxide and allowing the solution to crystallise.[3] It may also be prepared by adding excess of arsenic acid to calcium carbonate or to the normal or monohydrogen orthoarsenate.[4] It forms colourless plates which lose their water at 180° C. and at 360° C. yield *calcium metarsenate*, $Ca(AsO_3)_2$, as a crystalline mass, insoluble in hydrochloric acid.

Calcium Pyroarsenate, $Ca_2As_2O_7$, in orthorhombic prisms, may be obtained by fusing calcium oxide with potassium monohydrogen arsenate,[5] or with a mixture of the latter with less than 40 per cent. of calcium chloride. When treated with cold water the prisms break up into minute crystals of the hexahydrate, $Ca_2As_2O_7.6H_2O$. By leaving in contact with water the salt is gradually transformed into calcium monohydrogen orthoarsenate, $CaHAsO_4.2H_2O$. The pyroarsenate undergoes reduction [6] when heated in hydrogen to above 400° C.

Several double orthoarsenates with the alkali metals are known : $CaKAsO_4$, $CaNaAsO_4$ and $Ca_3Na_6(AsO_4)_4$,[7] $Ca(NH_4)AsO_4.7H_2O$,[8] $Ca(NH_4)AsO_4.6H_2O$ [9] and $Ca_3(NH_4)H_2(AsO_4)_3.3H_2O$.[10] Lefèvre also isolated a calcium sodium pyroarsenate, $Ca_4Na_4(As_2O_7)_3$. Arsenoapatites similar to those of barium (p. 195) have been obtained.

Chromium Arsenates.—*Chromic Orthoarsenate*, $CrAsO_4$, is formed as an apple-green precipitate when potassium dihydrogen orthoarsenate is added to a solution of a chromic salt.[11]

Chromium Pyroarsenate, $Cr_4(As_2O_7)_3$, is produced when a small quantity of chromium sesquioxide is fused at a low temperature with sodium or potassium dihydrogen arsenate.[12] It yields green transparent

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[1] Robinson, *loc. cit.*
[2] Blarez, *Compt. rend.*, 1886, 103, 639.
[3] Bloxam, *Chem. News*, 1886, 54, 193.
[4] Hörmann, *Thesis*, Erlangen, 1897.
[5] Lefèvre, *Compt. rend.*, 1889, 108, 1058; *Ann. Chim. Phys.*, 1892, [6], 27, 5.
[6] Guérin, *Compt. rend.*, 1936, 203, 1163.
[7] Lefèvre, *loc. cit.*
[8] Bloxam, *Chem. News*, 1886, 54, 168, 193.
[9] Kotschoubey, *J. prakt. Chem.*, 1850, [1], 49, 182; *Annalen*, 1850, 76, 249.
[10] de Schulten, *Bull. Soc. franç. Min.*, 1903, 26, 18; Debray, *Ann. Chim. Phys.*, 1861, [3], 61, 419; Ditte, *ibid.*, 1886, [6], 8, 502; Lefèvre, *ibid.*, 1892, [6], 27, 5; Lechartier, *Compt. rend.*, 1867, 65, 172.
[11] Moser, *Schweigger's J.*, 1824, 42, 99.
[12] Lefèvre, *Compt. rend.*, 1890, 111, 36.

prisms, sometimes elongated, sometimes flattened, insoluble in dilute acids.

Double arsenates of chromium with the alkali metals have been described. When aqueous arsenious acid is added to a solution of potassium chromate, the liquid becomes green and soon coagulates to a tremulous jelly, which when dried at 100° C. yields a substance whose empirical formula is $4K_2O.3Cr_2O_3.3As_2O_5.10H_2O$.[1] The double arsenates $K_3Cr_2(AsO_4)_3$ and $Na_3Cr_2(AsO_4)_3$ have been prepared [2] by the addition of chromium sesquioxide to the fused alkali metarsenate. Crystallisation is accelerated by the addition of alkali chloride. Both compounds yield green transparent crystals. In the case of the potassium salt more than 7 per cent., and of the sodium salt more than 8 per cent., of the sesquioxide must be employed or a pyroarsenate is produced.

In the presence of alkali hydroxide, arsenic pentoxide forms with chromic hydroxide complex arsenates, analogous to the ferriphosphates, which have been formulated [3] $NaH_2[Cr(AsO_4)_2].H_2O$ and $KH_5[Cr(AsO_4)_3].7$ and $12H_2O$.

By allowing solutions containing molecular proportions of alkali arsenate and chromic oxide, or of arsenic pentoxide and alkali chromate or dichromate, to crystallise, the following *complex salts* have been obtained: [4]

$$2K_2O.As_2O_5.4CrO_3.H_2O$$
$$2(NH_4)_2O.As_2O_5.4CrO_3.H_2O$$
$$3(NH_4)_2O.As_2O_5.8CrO_3.H_2O$$

These compounds may be regarded as salts of two heteropoly-acids (*cf.* this Series, Vol. VII, Part III), and may be represented, respectively, according to the co-ordination theory by the formulæ:

$$R'_2H[AsO_2(CrO_4)_2]$$

and

$$R'_3[As(CrO_4)_4].0{\cdot}5H_2O$$

Cobalt Arsenates.—*Cobalt Orthoarsenate*, $Co_3(AsO_4)_2.8H_2O$, may be precipitated as pink microscopic needles by adding ammonium orthoarsenate to an aqueous solution of a cobalt salt,[5] or by stirring cobalt oxide or carbonate with aqueous arsenic acid.[6] It occurs widely distributed in Nature as the mineral *erythrite* or *cobalt bloom* (see p. 15) in the form of monoclinic crystals isomorphous with vivianite, $Fe_3(PO_4)_2.8H_2O$, and perhaps with nickel ochre, $Ni_3(AsO_4)_2.8H_2O$. Its crystallographic elements are [7] $a:b:c = 0{\cdot}7937:1:0{\cdot}7356$; $\beta = 74°\ 51'$. The indices of refraction along the three axes for sodium light are [8] $\alpha = 1{\cdot}629$, $\beta = 1{\cdot}663$ and $\gamma = 1{\cdot}701$. The mineral is soluble in hydrochloric acid forming a blue solution which reddens on dilution. A

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[1] Schweitzer, *J. prakt. Chem.*, 1846, [1], 39, 267.

[2] Lefèvre, *loc. cit.*

[3] Rosenheim and Thon, *Zeitsch. anorg. Chem.*, 1927, 167, 1.

[4] Friedheim, *ibid.*, 1894, 6, 273. See also Tarugi, *Gazzetta*, 1897, 27, 166; Meyerhofer, *Ber.*, 1897, 30, 1804, 1810.

[5] Ducru, *Ann. Chim. Phys.*, 1901, [7], 22, 185; *Compt. rend.*, 1900, 131, 675; *Thesis*, Paris, 1900.

[6] Ephraim and Rosetti, *Helv. Chim. Acta*, 1929, 12, 1025.

[7] Des Cloiseaux, *Bull. Soc. franç. Min.*, 1878, 1, 76; *Thesis*, Paris, 1867, p. 132. See also Brezina, *Tschermak's Mitt.*, 1872, [1], 2, 19.

[8] Larsen, *Bull. U.S. Geol. Survey*, 1921, p. 679. See also Gaubert, *Bull. Soc. franç. Min.*, 1907, 30, 107.

cobalt hydrogen arsenate of composition $Co_2H_2(AsO_4)_2.3{\cdot}5H_2O$ is precipitated by adding ether to a mixture of syrupy arsenic acid (2 parts) and alcoholic cobalt nitrate (3 parts).[1] The salt readily loses water. *Cobalt dihydrogen tetrarsenate*, $Co_3(AsO_4)_2.2CoHAsO_4.2H_2O$, has been obtained as red needle-shaped crystals by heating excess of arsenic acid with cobalt carbonate in a sealed tube at 235° C. It is insoluble in water and loses its water of crystallisation when heated.[2]

A *basic arsenate* of composition $Co_3(AsO_4)_2.CoO$ is obtained when sodium carbonate is added to a solution of cobalt orthoarsenate in nitric acid and the precipitate heated to fusion.[3] On cooling, deep blue prismatic crystals are formed which, when powdered, turn a rose-red colour. The product, which is soluble in acids, has been used as a pigment. An impure basic arsenate is known under the name of *zaffre* and is used in painting porcelain. It may be obtained by roasting iron-free cobaltite, or by addition of sodium carbonate to a solution of cobaltite in nitric acid, when the zaffre is obtained as a precipitate. A salt of composition $5CoO.2As_2O_5.15H_2O$ (and also with $28H_2O$) has been prepared.[4]

Cobalt Pyroarsenate, $Co_2As_2O_7$, is formed when cobalt oxide is fused with potassium metarsenate; violet crystals are obtained on cooling.[5] A *dihydrate*, $Co_2As_2O_7.2H_2O$, has also been described.[6]

Ammino-orthoarsenates of composition $Co_3(AsO_4)_2(NH_3).7H_2O$, $Co_3(AsO_4)_2(NH_3)_2.6H_2O$ and $Co_3(AsO_4)_2(NH_3)_3.5H_2O$ have been obtained by the interaction in solution of a cobalt salt, arsenic acid or an arsenate and free ammonia, ammonium salts being present.[7] The nature of the product depends on the amount of free ammonia present.

Colloidal cobalt arsenate has been obtained in the form of an opalescent jelly either by mixing in the cold a solution of a cobalt salt of a strong acid with potassium dihydrogen orthoarsenate,[8] or by successively treating an aqueous solution of a cobaltous salt with ammonium sulphate, acetic acid and an excess of sodium orthoarsenate.[9]

The following *mixed arsenates* have been prepared:[10] $NaCoAsO_4$, $KCoAsO_4$, $Na_4Co_4As_6O_{21}$. Complex salts corresponding to the ferriarsenates do not appear to be formed.[11]

Copper Arsenates.—Cupric orthoarsenate, $Cu_3(AsO_4)_2$, is formed when metallic copper is heated at 180° to 200° C. with aqueous arsenic acid in a sealed tube; after some hours the product consists of green triclinic crystals of the arsenate mixed with arsenious oxide and unchanged copper.[12] The *tetrahydrate*, $Cu_3(AsO_4)_2.4H_2O$, is produced by heating cupric nitrate solution with calcium arsenate,[13] by the interaction

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[1] Burghelle, *Bull. Soc. chim.*, 1935, [5], 2, 168.

[2] Coloriano, *Compt. rend.*, 1886, 103, 274; *Thesis*, Paris, 1900.

[3] Gentele, *Öfvers. Svenska Akad. Förh.*, 1851, p. 4.

[4] Ephraim and Rosetti, *loc. cit.*

[5] Lefèvre, *Compt. rend.*, 1890, 110, 407; *Thesis*, Paris, 1891.

[6] Goguel, *Thesis*, Paris, 1896.

[7] Ducru, *loc. cit.* See also Brintzinger and Osswald, *Zeitsch. anorg. Chem.*, 1935, 225, 365.

[8] Weiser and Bloxsom, *J. Physical Chem.*, 1924, 28, 26.

[9] Klemp and Gyulay, *Kolloid-Zeitsch.*, 1914, 15, 202; 1918, 22, 57.

[10] Lefèvre, *loc. cit.*

[11] Rosenheim and Thon, *Zeitsch. anorg. Chem.*, 1927, 167, 1.

[12] Coloriano, *Bull. Soc. chim.*, 1886, [2], 45, 241, 707, 709; Friedel and Sarasin, *ibid.*

of cupric chloride solution and silver arsenate,[1] or by the action of aqueous arsenic acid on copper oxide.[2] A *pentahydrate* is found in Nature as *trichalcite* (see p. 16).

Commercial methods of producing copper arsenate consist in heating copper arsenite at 600° to 700° C. in an oxygen-enriched atmosphere,[3] or in heating basic copper chloride with an arsenate or arsenic acid.[4]

When copper orthoarsenate is subjected to the action of hydrogen at high temperature and pressure it is reduced and a residue of approximate composition Cu_3As (*domeykite*) remains.[5]

Concentration at 70° C. of a solution of cupric carbonate in an excess of arsenic acid yields pale-blue leaflets of *cupric monohydrogen orthoarsenate*, $CuHAsO_4.H_2O$.[6] When boiled with water this yields a basic salt of composition $Cu_3(AsO_4)_2.CuO.H_2O$.[7]

Several other acid salts have been described,[8] including $2Cu_4H(AsO_4)_3.11H_2O$ and $Cu_5H_2(AsO_4)_4.xH_2O$ ($x = 2$, 7, $9\frac{1}{2}$ and $11\frac{1}{2}$). Many basic salts are also known and are found frequently in Nature. Thus *olivenite*, *clinoclasite*, *cornwallite* and *erinite* occur in Cornwall; *chalcophyllite*, *euchroite*, *leucochalcite* and *tyrolite* are also basic copper arsenates. The composition and properties of these minerals are given in the table on p. 14.

Ammino-arsenates of composition $Cu_3(AsO_4)_2(NH_3)_3.4H_2O$ and $CuHAsO_4(NH_3)_2$ (anhydrous and with $1H_2O$) have been prepared [9] by the action of alcoholic or aqueous ammonia on the respective arsenates. The compounds are stable at ordinary temperatures but lose water and ammonia when heated.

Complex orthoarsenates with the alkali metals, for example—$NaCuAsO_4$, $2Na_3AsO_4.Cu_3(AsO_4)_2$, $KCuAsO_4.Cu_3(AsO_4)_2$,[10] $Na_2HAsO_4.4Cu_3(AsO_4)_2.11H_2O$ and $NaH_2AsO_4.2Cu_3(AsO_4)_2.5H_2O$ [11]—and complex pyroarsenates of composition $MCuAs_2O_7$ ($M = Ca$, Sr or Ba), have been prepared (see p. 195).

Gold Arsenate is precipitated as a yellowish-white powder when sodium orthoarsenate is added to a hot solution of auric chloride.[12]

Hydroxylamine Orthoarsenate, $(NH_2OH)_3.H_3AsO_4$, is obtained [13] when aqueous arsenic acid is made alkaline with an excess of sodium carbonate and then treated with hydroxylamine hydrochloride until faintly acid. Microscopic rhombic prisms slowly form, which yield an acid solution in hot water, from which they may be recrystallised. The salt readily reduces ammoniacal silver nitrate and Fehling's solution.

Iridium Arsenate is said [14] to be precipitated when sodium orthoarsenate is added to a hot solution of iridium chloride.

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[1] Hirsch, *Dissertation*, Halle, 1890.

[2] Kosakewitsch, *Zeitsch. physikal. Chem.*, 1924, 108, 281.

[3] Soc. Chim. des Usines du Rhône, *Swiss Patent*, 122587 (1926).

[4] I.G. Farbenind. A.-G., *German Patent*, 428239 (1924).

[5] Ipatiev and Nikolaiev, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 698.

[6] Debray, *Ann. Chim. Phys.*, 1861, [3], 61, 419.

[7] Coloriano, *loc. cit.*

[8] Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 166; Hirsch, *loc. cit.*; Proust, *Ann. Chim. Phys.*, 1799, [1], 32, 26; 1806, [1], 60, 260; Simon, *Pogg. Annalen*, 1837, 40, 117.

[9] Gmelin, *ibid.*, 1825, 4, 157; Damour, *Compt. rend.*, 1845, 21, 1422; Girard, *ibid.*, 1853, 36, 794; Schiff, *Annalen*, 1862, 123, 42; Reichard, *Ber.*, 1894, 27, 1021.

[10] Lefèvre, "*Sur les Arséniates cristallisés,*" Paris, 1891; *Ann. Chim. Phys.*, 1892, [6], 27, 22.

[11] Hirsch, *loc. cit.* See also Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 166.

[12] Thomson, *Ann. Phil.*, 1814, 4, 171; 1820, 15, 81.

[13] Kohlschutter and Hofmann, *Annalen*, 1899, 307, 314.

[14] Thomson, *Ann. Phil.*, 1820, 15, 84.

Iron Arsenates.—*Ferrous Orthoarsenate*, $Fe_3(AsO_4)_2.6H_2O$, is obtained as a white precipitate when ammonium orthoarsenate [1] or sodium monohydrogen arsenate [2] is added to an aqueous solution of ferrous sulphate. In the latter case the reaction is stated to be:

$$4FeSO_4 + 4Na_2HAsO_4 = Fe_3(AsO_4)_2 + Fe(H_2AsO_4)_2 + 4Na_2SO_4$$

The precipitated *hexahydrate* gradually undergoes oxidation on exposure to moist air, yielding ferric arsenate and ferric oxide.[3] It is sparingly soluble in aqueous ammonia,[4] but is insoluble in the presence of ammonium salts.

Ferrous orthoarsenate occurs naturally as the mineral *symplesite* (see p. 16), which is the *octahydrate*, $Fe_3(AsO_4)_2.8H_2O$. This is found in pale blue or green prismatic or tabular crystals, probably isomorphous with vivianite and having axial ratios [5] $a : b : c = 0{\cdot}7806 : 1 : 0{\cdot}6812$, and $\beta = 72° 43'$. The mineral is decomposed by caustic alkali with formation of ferric hydroxide.[6]

Colloidal ferrous arsenate has been obtained [7] in the form of an opalescent jelly by successively treating an aqueous solution of a ferrous salt with ammonium sulphate, acetic acid and an excess of sodium orthoarsenate. The jelly cannot be kept indefinitely, but crystallises after a few weeks.

Ferrous Hydrogen Orthoarsenates have not been prepared in the pure state. According to Wittstein,[8] the dihydrogen arsenate remains in the mother liquor when the normal orthoarsenate is precipitated (see equation above); and when iron is acted upon by arsenic acid over a long period an asbestos-like deposit is formed which probably contains a ferrous hydrogen arsenate.[9]

Ferric Orthoarsenate.—The *dihydrate*, $FeAsO_4.2H_2O$, may be prepared by heating to 150° C. metallic iron and arsenic acid,[10] by heating at 80° C. in a sealed tube a mixture of anhydrous ferric arsenate and aqueous arsenic acid [11] or by crystallisation from a solution of ferric arsenate in aqueous hydrochloric acid. It is widely distributed in Nature as the mineral *scorodite* (see p. 16), which is usually greenish-brown and transparent. The crystals are rhombic, with axial ratios [12] $a : b : c = 0{\cdot}8785 : 1 : 0{\cdot}9550$, and the refractive indices [13] along the three axes are $\alpha = 1{\cdot}771$, $\beta = 1{\cdot}805$ and $\gamma = 1{\cdot}820$. The mineral is easily fused, dissolves in hydrochloric acid, and is decomposed by caustic alkali with formation of ferric hydroxide.[14] The solution in aqueous ammonia is red or yellow, but turns blue on acidifying.

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[1] Chenevix, *Phil. Trans.*, 1801, 91, 193.

[2] Wittstein, *Jahresber.*, 1866, 19, 243.

[3] Duncan, *Pharm. J.*, 1905, [4], 20, 71.

[4] Berzelius, *Akad. Handl. Stockholm*, 1824, p. 354; *Schweigger's J.*, 1821, 32, 162.

[5] Krenner, *Fermesz. Füzedek.*, 1886, 10, 83; *Zeitsch. Kryst. Min.*, 1888, 13, 70.

[6] Heide, *Zeitsch. Krist.*, 1928, 67, 33.

[7] Klemp and Gyulay, *Kolloid-Zeitsch.*, 1914, 15, 202; 1918, 22, 57; 1921, 28, 262. See also Weiser and Bloxsom, *J. Physical Chem.*, 1924, 28, 26; Prakash, *ibid.*, 1932, 36, 2483; Prakash and Dube, *Zeitsch. anorg. Chem.*, 1932, 208, 163.

[8] Wittstein, *Repert. Pharm.*, 1854, 63, 329; *Pharm. Vierteljahr.*, 1866, 15, 185.

[9] Fischer, *Pogg. Annalen*, 1827, 9, 262.

[10] Verneuil and Bourgeois, *Compt. rend.*, 1880, 90, 223.

[11] Metzke, *Neues Jahrb. Min.*, 1898, I, 169.

[12] Graham, *Trans. Roy. Soc. Canada*, 1913, [3], 7, 14. See also vom Rath, *Neues Jahrb. Min.*, 1876, p. 396; Groth, "*Tabellarische Uebersicht der Mineralien*," Braunschweig, 1898, p. 95.

[13] Ito and Shiga, *Mineral. Mag.*, 1932, 23, 130.

[14] Heide, *Zeitsch. Krist.*, 1928, 67, 33; Veichhertz and Kraschevskaja, *J. Appl. Chem. (U.S.S.R.)*, 1936, 9, 1909.

When hydrogen is allowed to react with an aqueous solution of an alkali arsenate containing ferric oxide at a temperature of 300° C. and under a pressure greater than 150 atmospheres, green crystals of scorodite are formed.[1] If the action is prolonged, elementary arsenic and ferric arsenides are produced.

A commercial method of utilising scorodite consists in roasting it and heating the residue with sulphuric acid, crystallising out the ferric sulphate and igniting the crystals to ferric oxide; the mother liquor, containing arsenious oxide and sulphuric acid, is used as a weed-killer.[2] Weed-killers consisting of mixtures of iron and calcium arsenates are made by causing a soluble iron salt to react with a soluble arsenate in solution and then adding a basic calcium arsenate.[3]

The *monohydrate*, $FeAsO_4.H_2O$, is formed when anhydrous ferric arsenate, arsenic acid, hydrogen peroxide and water are heated in a sealed tube for 14 days at 170° C.; a hemihydrate may be obtained in a similar manner by substituting precipitated ferric dihydrogen arsenate for the normal salt.

The monohydrate is a dull white insoluble substance which, when treated with aqueous sodium hydrogen carbonate, causes effervescence, a soluble double arsenate being produced. It would appear, therefore, that the hydrated salt is acidic, and determinations of its basicity[4] indicate that its formula is $FeO.AsO_2(OH)_2$.

Anhydrous Ferric Orthoarsenate, $FeAsO_4$, is obtained by heating the monohydrate at 100° C.[4] or the dihydrate at 220° to 250° C.[5] It yields black monoclinic prisms, with crystallographic elements $a:b:c = 0{\cdot}6155:1:0{\cdot}3221$, $\beta = 77° \, 8'$. The density is 4·32,[6] and the mean refractive index for sodium light 1·78.

When strongly heated, ferric orthoarsenate undergoes decomposition. The speed of the reaction in the presence of sodium chloride has been determined[7] at 700° to 1000° C. and the decomposition is found to be of the second order, and may be formulated

$$2FeAsO_4 \longrightarrow Fe_2O_3 + As_2O_5$$

Ferric Monohydrogen Orthoarsenate, $2Fe_2(HAsO_4)_3.9H_2O$, results when solutions of sodium monohydrogen arsenate and ferric chloride are mixed. The salt separates out as a white gelatinous precipitate, soluble in aqueous mineral acids forming yellow solutions and in ammonia forming a red solution.[8] If the gelatinous precipitate is thoroughly washed it may be peptized by a small quantity of aqueous ammonium hydroxide[9] to yield a stable colloid, which on long-continued dialysis forms a deep red gel. The composition of both sol and gel approximates closely to the formula, $FeAsO_4.Fe_2O_3.xH_2O$, the change in composition from that of the precipitated arsenate being due to removal of ammonium arsenate during dialysis.

[1] Ipatiev and Nikolaiev, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 698.

[2] Roberts, *Australian Patent*, 3833 (1926).

[3] Nisimura and Tani, *Japanese Patent*, 98955 (1933).

[4] Duncan, *Pharm. J.*, 1905, [4], 20, 71.

[5] Ito and Shiga, *loc. cit.*

[6] Ježek and Šimek, *Zeitsch. Kryst. Min.*, 1914, 54, 188.

[7] Adadurov and Gemet, *J. Phys. Chem.* (*U.S.S.R.*), 1932, 3, 507.

[8] Berzelius, *Schweigger's J.*, 1821, 32, 162; Metzke, *loc. cit.*; *Zeitsch. anorg. Chem.*, 1899, 19, 457.

[9] Holmes and Rindfusz, *J. Amer. Chem. Soc.*, 1916, 38, 1970. See also Ghosh and Prakash, *Kolloid-Zeitsch.*, 1933, 63, 315.

Ferric Dihydrogen Arsenate, $Fe(H_2AsO_4)_3.5H_2O$, is deposited when a solution of artificial pharmacosiderite (see below) in syrupy arsenic acid is heated. It is decomposed by water, and with acids and ammonia it yields solutions similar to those of the monohydrogen salt.[1]

A study of the viscosity of solutions of ferric oxide in aqueous arsenic acid at concentrations between 2·6 and 23·3 per cent. As_2O_5 shows[2] that two solid phases exist within these limits, the normal salt, $FeAsO_4.xH_2O$ (x about 3), which adsorbs arsenic acid, and an acid salt of composition $Fe_2O_3.2As_2O_5.8H_2O$, which has also been obtained by the action of excess of arsenic acid on a solution of ferric chloride.

On addition of sodium monohydrogen arsenate, Na_2HAsO_4, to ammonium iron alum, in the proportion of two mols. of the former to one of the latter, a precipitate of composition $Fe_2O_3.As_2O_5$ is obtained, which varies in tint according to circumstances.[3] Thus, on gradually adding the arsenate to the alum solution a white precipitate is obtained; but, on reversing the procedure, the precipitate is brownish. The white precipitate turns yellow, and finally brown, however, when washed with water. In the presence of large excess of either constituent the basic salt, $3Fe_2O_3.2As_2O_5$, is obtained. Other basic salts have been described, for example $4Fe_2O_3.3As_2O_5.nH_2O$ (with $n = 15{\cdot}4$, 20·5 and 33·5)[3] and $16Fe_2O_3.As_2O_5.24H_2O$.[4] The following minerals also contain basic ferric arsenates: *pharmacosiderite*, $Fe_4(OH)_3(AsO_4)_3.6H_2O$; *yukonite*, $(Ca_3, Fe_2)As_2O_8.2Fe(OH)_3.5H_2O$; *arseniosiderite*, $Ca_3Fe_4(OH)_9(AsO_4)_3$.

Pharmacosiderite may be obtained artificially[5] by heating ferric orthoarsenate and water in a sealed tube at 200° C. or by boiling the ferric salt with ammonium acetate solution acidified with acetic acid. The product contains considerably more water than the natural mineral, but loses it when strongly heated. The mineral loses 5 molecules of water up to 233 ± 1° C., when decomposition begins, the products being ferric and arsenic oxides.[6]

Mixed ortho- and pyro-arsenates with sodium and potassium of composition, respectively, $M_3Fe_2(AsO_4)_3$ and $MFeAs_2O_7$, have been described.[7] In the presence of alkali hydroxides, arsenic pentoxide reacts with ferric hydroxide to form complex ferri-arsenates analogous with alumini-arsenates (p.190) and with ferri-phosphates; the products so obtained[8] are formulated $NaH_2[Fe(AsO_4)_2].H_2O$; $KH_2[Fe(AsO_4)_2]$; $Ba_3H_6[Fe(AsO_4)_3]_2$. The products obtained by Curtman[9] by the action of potassium or ammonium monohydrogen arsenate on an acidified solution of ferric chloride and formulated $KH_2AsO_4.FeAsO_4$ and $(NH_4)H_2AsO_4.FeAsO_4$, are probably similar complexes.

Lead Arsenates.—*Lead Orthoarsenate*, $Pb_3(AsO_4)_2$, is formed when a mixture of arsenious oxide and lead monoxide is heated at 450° to 800° C.[10] It is difficult to obtain in a pure state by precipitation, but products approximating in composition to it are obtained when solutions

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[1] Metzke, *loc. cit.*

[2] Hartshorne, *J. Chem. Soc.*, 1927, p. 1759.

[3] Metzke, *loc. cit.*

[4] Berzelius, *loc. cit.*

[5] Metzke, *loc. cit.*

[6] Heide, *loc. cit.*; Adadurov and Gemet, *loc. cit.*

[7] Lefèvre, *Compt. rend.*, 1890, 111, 36; "*Sur les Arséniates cristallisés*," Paris, 1891.

[8] Rosenheim and Thon, *Zeitsch. anorg. Chem.*, 1927, 167, 1.

[9] Curtman, *J. Amer. Chem. Soc.*, 1910, 32, 626.

[10] Dubrovin, *J. Appl. Chem.* (*U.S.S.R.*), 1936, 9, 1049. See also Schairer, *Chem. Zeit.*, 1904, 28, 15; Brown and co-workers, *J. Ind. Eng. Chem.*, 1921, 13, 531.

of lead salts are added to alkali hydrogen arsenates.[1] It appears to be unstable and to exist only under limited conditions.[2]

The anhydrous salt yields yellowish-white crystals of density[2] 7·3 at 15° C. and melting point[3] 1042° C. The specific heat is[4] 0·0728 and the molar heat 65·4. The index of refraction is[2] 2·14. It is insoluble in water, aqueous ammonia and in solutions of ammonium salts,[5] and only slightly soluble in aqueous alkali or brine.[6] It is decomposed when heated with hydrogen chloride,[7] forming lead and arsenic chlorides, and in hot nitric acid it dissolves to form arsenic acid and lead nitrate, the latter being precipitated if the acid is sufficiently concentrated.[8]

Lead Monohydrogen Orthoarsenate, $PbHAsO_4$, is deposited in the form of white crystalline needles when a boiling solution of the normal arsenate in nitric acid is diluted with water[8] or treated with a dilute solution of ammonia.[9] It is also obtained by the prolonged action of arsenic acid and air upon metallic lead, or by decomposing aqueous lead nitrate with arsenic acid or sodium monohydrogen arsenate.[10] It has been found as a mineral in S.W. Africa[11] and named *schultenite* (see p. 16); the colourless monoclinic crystals have axial ratios $a : b : c = 0·8643 : 1 : 0·7181$, $\beta = 84^\circ 36'$, and indices of refraction along the three axes α 1·8903, β 1·9077 and γ 1·9765. When heated above 280° C. lead pyroarsenate is formed,[12] which fuses at a bright red heat.

The monohydrogen arsenate is insoluble in cold water and only very slightly soluble on long contact with boiling water, but the prolonged action of cold water converts it to a basic arsenate of composition[13] $Pb_5(OH)(AsO_4)_3$. It is attacked by halogen acids and salts and by nitric acid.

Commercial lead arsenate usually consists mainly of the monohydrogen arsenate, but may also contain the normal arsenate. It is in great demand as an insecticide (see p. 301). Many methods of manufacture are described in the patent literature,[14] some of the more recent being as follows: (1) Metallic lead and arsenious oxide are added to a concentrated solution of arsenic acid containing nitric acid;[15] lead arsenate is precipitated, the concentration of the arsenic acid remaining constant. At intervals the precipitate is removed and the arsenic acid solution again treated. (2) A solution of a soluble arsenate is treated

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[1] Graham, *Pogg. Annalen*, 1834, 32, 51; Holland and Reed, *Rep. Massachusetts Agric.*, 1912, 24, 204; Tartar and Robinson, *J. Amer. Chem. Soc.*, 1914, 36, 1843.

[2] McDonnell and Smith, *ibid.*, 1916, 38, 2027, 2366; 1917, 39, 938; *Amer. J. Sci.*, 1916, [4], 42, 139.

[3] Amadori, *Atti Ist Veneto*, 1917, 76, 419; *Gazzetta*, 1919, 49, i, 38.

[4] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129.

[5] Wittstein, "*Vollstandiges etymol.-chem. Handworterbuch*," München, 1851, 1, 389.

[6] Bradley and Tartar, *J. Ind. Eng. Chem.*, 1910, 2, 328.

[7] Smith and Hibbs, *J. Amer. Chem. Soc.*, 1895, 17, 685.

[8] Duvillier, *Compt. rend.*, 1875, 81, 1251; *Ber.*, 1876, 9, 189.

[9] de Schulten, *Bull. Soc. franç. Min.*, 1904, 27, 113; Tartar and Robinson, *loc. cit.*

[10] Pickering, *J. Chem. Soc.*, 1907, 91, 310; McDonnell and Smith, *loc. cit.*

[11] Spencer, *Nature*, 1926, 118, 411.

[12] Berzelius, *Schweigger's J.*, 1818, 23, 174; *Ann. Chim. Phys.*, 1819, [2], 11, 229; Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 129.

[13] McDonnell and Graham, *J. Amer. Chem. Soc.*, 1917, 39, 1912.

[14] For example, see Barstow, *American Patents*, 1014742, 1141920 (1911); Underwood, *ibid.*, 1512432 (1924); Kirby and others, *ibid.*, 1400167 (1921), 1398267 (1921); Allen, *ibid.*, 1427029 (1921); Butler, *ibid.*, 1324300 (1917).

[15] Mitchell and Toabe, *American Patent*, 1564093 (1925).

with lead chloride to cause partial conversion to lead arsenate and the reaction completed by adding lead nitrate.[1] (3) Steam is passed into a chamber in which a mixture of litharge and arsenious oxide is heated.[2] (4) Lead fluosilicate is heated with a metallic arsenate,[3] for example:

$$3PbSiF_6 + 2CaHAsO_4 = Pb_3(AsO_4)_2 + 2CaSiF_6 + H_2SiF_6$$

Lead arsenate may also be obtained electrolytically by the anodic dissolution of lead in the presence of an arsenate. An almost theoretical yield has been obtained[4] by using a diaphragm cell with an anolyte containing 20 g. sodium arsenite and 70 g. sodium nitrate per litre and sufficient acetic acid for neutralisation, and a catholyte consisting of a 30 per cent. solution of sodium nitrate. The anode should be of lead and the cathode of iron, and the current density 5·5 to 6 amps. per sq. dm.

Lead Dihydrogen Orthoarsenate, $Pb(H_2AsO_4)_2$, may be obtained[5] from the monohydrogen salt by boiling with a solution of arsenic acid of 86 per cent. concentration; the boiling temperature is about 130° C. and the crystals which form on cooling are removed by centrifuging, washed with alcohol and dried at 110° C. The product usually contains a slight excess of arsenic acid.

The crystals appear to be triclinic; the indices of refraction for sodium light at 20° C. are $\alpha = 1{\cdot}74$, $\beta = 1{\cdot}84$ and $\gamma = 1{\cdot}82$. The salt loses water when heated, the equivalent of 1 molecule being lost on prolonged heating at 150° C., when lead hydrogen pyroarsenate, $PbH_2As_2O_7$, is probably formed,[6] and the whole expelled below red heat; when fusion occurs some arsenious oxide vapour is emitted.

A phase rule study of the system $PbO–As_2O_5–H_2O$ has been made over the acid range at 25° C. and the conditions for the existence of the two acid lead arsenates defined.[7]

Lead Pyroarsenate, $Pb_2As_2O_7$, is formed when the monohydrogen orthoarsenate is heated above 280° C.,[8] or by fusing together lead oxide and arsenic pentoxide[9] or potassium metarsenate,[10] or by precipitating lead acetate solution by addition of sodium pyroarsenate.[11] The fused product forms colourless lamellæ of density 6·85 at 15° C.[9] and melting point 802° C.[12] In contact with water it becomes opaque and the monohydrogen orthoarsenate is formed.[9]

Lead Metarsenate, $Pb(AsO_3)_2$, is obtained by heating a mixture of arsenic pentoxide and lead monoxide, red lead or lead nitrate in suitable proportions.[9] A transparent glass is formed which, if broken up and heated to incipient fusion, crystallises as hexagonal tablets of density 6·42. The salt is decomposed by water.

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[1] Borchers, *German Patent*, 446409 (1926). See also Cambi and Bozza, *Giorn. Chim. Ind. Appl.*, 1925, 7, 687.

[2] Adati, *Japanese Patent*, 93352 (1931). See also Okada, *ibid.*, 98684 (1932).

[3] Meyerhofer, *Swiss Patent*, 122353 (1924).

[4] Plotnikov and Ivanenko, *Zeitsch. Elektrochem.*, 1931, 37, 88.

[5] McDonnell and Smith, *loc. cit.*; Tartar, Rice and Sweo, *J. Amer. Chem. Soc.*, 1931, 53, 3949.

[6] McDonnell and Smith, *loc. cit.*

[7] Tartar, Rice and Sweo, *J. Amer. Chem. Soc.*, 1931, 53, 3949.

[8] McDonnell and Smith, *loc. cit.* See also Tartar and Robinson, *J. Amer. Chem. Soc.*, 1914, 36, 1843.

[9] McDonnell and Smith, *loc. cit.*

[10] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 25; "*Sur les Arséniates cristallisés*," Paris, 1891.

[11] Pickering, *J. Chem. Soc.*, 1907, 91, 310.

[12] Amadori, *Atti Ist Veneto*, 1917, 76, 419; *Gazzetta*, 1919, 49, i, 38.

Mixed salts of composition $PbNaAsO_4$ and $PbKAsO_4$ have been obtained[1] by dissolving litharge in molten mixtures of the alkali orthoarsenate and chloride: from fused sodium metarsenate in which 15 per cent. of litharge was dissolved, crystals of composition $4PbO.2Na_2O.3As_2O_5$ or $Pb_4Na_4(As_2O_7)_3$ have been obtained.

The mineral *mimetite* (p. 15), $3Pb_3(AsO_4)_2.PbCl_2$, may be prepared artificially by fusing a mixture of its component salts.[2] It occurs in yellow to brown crystal aggregates or mammillary crusts. The crystals are hexagonal pyramids, $a : c = 0{\cdot}73147$, isomorphous with pyromorphite and the apatites.[3] It is widely distributed and has been found in Cornwall, Cumberland and Leadhills (Lanark).

Lithium Arsenates.—*Lithium Orthoarsenate* is obtained as the *hemihydrate*, $2Li_3AsO_4.H_2O$, by the action of lithium carbonate on arsenic acid and allowing the solution to crystallise.[4] The *anhydrous* salt is prepared by recrystallising this hydrate from fused lithium chloride;[5] rhombic crystals of density 3·07 at 15° C. are obtained. These are soluble in dilute acetic acid; they are extremely stable and may be heated to a white heat without fusion. With excess of arsenic acid the normal salt yields deliquescent rhombic prisms of *lithium dihydrogen arsenate*, $2LiH_2AsO_4.3H_2O$, which with water revert to the normal salt.[6]

Magnesium Arsenates.—*Magnesium Orthoarsenate* may be obtained in various hydrated forms. When solutions containing equivalent quantities of magnesium sulphate and normal sodium orthoarsenate are mixed, an amorphous precipitate forms which, on prolonged keeping in contact with the solution, becomes crystalline,[7] and on drying has the composition $Mg_3(AsO_4)_2.22H_2O$. The crystals are monoclinic and isomorphous with the corresponding phosphate.[8] The density[9] at 15° C. is 1·788, and the indices of refraction along the three axes $\alpha = 1{\cdot}548$ to $1{\cdot}563$, $\beta = 1{\cdot}556$ to $1{\cdot}571$ and $\gamma = 1{\cdot}574$ to $1{\cdot}596$. The *octahydrate*, $Mg_3(AsO_4)_2.8H_2O$, is obtained by mixing aqueous solutions of magnesium sulphate, sodium monohydrogen arsenate and sodium bicarbonate and keeping the amorphous precipitate in contact with the solution for 24 hours, when it becomes crystalline.[10] This hydrate is found in Nature as the mineral *hœrnesite*[11] (p. 15), the crystals of which are monoclinic and probably isomorphous with vivianite. The density of the mineral is 2·474;[12] that of the artificially prepared product is 2·609.[13] The *heptahydrate*, $Mg_3(AsO_4)_2.7H_2O$, is obtained if sodium dihydrogen arsenate is substituted for the monohydrogen salt in the above preparation.[14] The *decahydrate*, $Mg_3(AsO_4)_2.10H_2O$, is formed when potassium or ammonium magnesium

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[1] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 25.
[2] Lechartier, *Compt. rend.*, 1867, 65, 114.
[3] Brauns, *Centr. Min.*, 1909, p. 263.
[4] Rammelsberg, *Pogg. Annalen*, 1866, 128, 311.
[5] de Schulten, *Bull. Soc. chim.*, 1889, [3], 1, 479.
[6] Rammelsberg, *loc. cit.*
[7] Kinkelin, *Dissertation*, Erlangen, 1883.
[8] Haushofer, *Zeitsch. Kryst. Min.*, 1880, 4, 49.
[9] Larsen, *Bull. U.S. Geol. Survey*, 1921, p. 679.
[10] de Schulten, *Bull. Soc. franç. Min.*, 1903, 26, 81.
[11] Haidinger, *Sitzungsber. K. Akad. Wiss. Wien*, 1860, 40, 18.
[12] Haidinger, *loc. cit.*
[13] de Schulten, *loc. cit.*
[14] Chevron and Droixhe, *Bull. Acad. roy. Belg.*, 1888, [3], 16, 488.

orthoarsenate is digested with water for several hours.[1] On dehydration, hydrates containing 6, 5, 3, 2 and $1H_2O$ are obtained.[2] The anhydrous salt decomposes when heated above 1100° C. in a vacuum, magnesium and arsenious oxides and oxygen being formed.[2]

A light form of magnesium arsenate may be obtained by heating a slurry of magnesium hydroxide with the theoretical quantity of arsenic acid and 15 per cent. of the equivalent amount of sodium hydroxide in an autoclave at 180° C. until the filtrate contains less than 0·2 per cent. of arsenic pentoxide.[3]

Magnesium Monohydrogen Orthoarsenate, $MgHAsO_4.7H_2O$, may be prepared by adding the calculated amount of magnesium sulphate to a solution of sodium monohydrogen arsenate neutralised with acetic acid, and keeping the amorphous precipitate in contact with the solution for some days,[4] during which it becomes crystalline. It loses water when heated. This hydrate occurs in Nature as *roesslerite*[5] (p. 15), a fibrous mineral consisting of monoclinic crystals[6] with $a : b : c = 0{\cdot}4473 : 1 : 0{\cdot}2598$ and $\beta = 94° \ 26'$. A *hemihydrate*, $2MgHAsO_4.H_2O$, is obtained in the form of prismatic crystals by heating a solution of magnesium carbonate in excess of arsenic acid at 225° C. in a sealed tube.[7]

Magnesium Dihydrogen Orthoarsenate, $Mg(H_2AsO_4)_2$, has been described as a very deliquescent crystalline mass obtained by dissolving magnesium oxide in aqueous arsenic acid.[8] It is soluble in water.

Magnesium Pyroarsenate, $Mg_2As_2O_7$, results from ignition of the monohydrogen arsenate[9] or the double arsenate of magnesium and ammonium.[10] It is a white powder of density[11] 3·75 which, on ignition, melts but does not decompose. When heated above 800° C. in a vacuum it yields the normal orthoarsenate, arsenious oxide and oxygen.[12]

Several double arsenates of magnesium and the alkali metals, ammonium and calcium are known. The most important of these is *magnesium ammonium orthoarsenate*, $MgNH_4AsO_4.6H_2O$, which is obtained as a crystalline precipitate when ammonium orthoarsenate is added to a solution of a magnesium salt;[13] it may be dried over sulphuric acid. It is also formed when an alkali arsenate is added to a solution of a magnesium salt in the presence of an ammonium salt and ammonia.[14] When heated above 40° C. it loses ammonia and water and it is doubtful if any lower hydrate is formed, although such are described in the literature.[15] On strong ignition it forms the pyroarsenate, as stated above.

[1] Kinkelin, *loc. cit.*

[2] Guérin, *Compt. rend.*, 1937, 204, 1740.

[3] Heath, *American Patent*, 1737114 (1929).

[4] Kinkelin, *loc. cit.*

[5] Blum, *Jahrb. Min.*, 1861, p. 334.

[6] Haushofer, *Zeitsch. Kryst. Min.*, 1882, 7, 257.

[7] de Schulten, *Compt. rend.*, 1885, 100, 877.

[8] Schiefer, *Zeitsch. Ges. Naturw. Berlin*, 1864, 23, 363; Graham, *Phil. Trans.*, 1837, 127, 47.

[9] Graham, *loc. cit.*; Kinkelin, *loc. cit.*

[10] Levol, *Ann. Chim. Phys.*, 1846, [3], 17, 501; Fresenius, *J. prakt. Chem.*, 1852, [1], 56, 33; Wittstein, *Zeitsch. anal. Chem.*, 1863, 2, 19.

[11] Stallo, *Amer. J. Sci.*, 1877, [3], 14, 285.

[12] Guérin, *loc. cit.*

[13] Wach, *Schweigger's J.*, 1830, 59, 288.

[14] Levol, *loc. cit.*

[15] Chevron and Droixhe, *loc. cit.*; Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 55; Dehn and Heuse, *J. Amer. Chem. Soc.*, 1907, 29, 1137.

The solubility in water of magnesium ammonium arsenate is as follows (expressed in grams of $MgNH_4AsO_4.6H_2O$ per 100 grams of solution):[1]

Temp., °C.	0	20	40	50	60	70	80
Solubility	0·03388	0·02066	0·02746	0·02261	0·02103	0·01564	0·02364

It is less soluble in the presence of ammonia, 1 part of the anhydrous salt dissolving in about 15,800 parts of water containing 2·46 per cent. NH_3 (1 part of 0·96 ammonia to 3 parts H_2O).[2]

Magnesium can be estimated by precipitation as this double arsenate, which is then ignited or titrated.

Sodium Magnesium Arsenate, $NaMgAsO_4$, has been obtained[3] by dissolving magnesia in molten sodium dihydrogen arsenate, the alkali being removed from the residue by washing with very dilute nitric acid. By precipitation from magnesium sulphate with excess of sodium orthoarsenate, the *enneahydrate*, $NaMgAsO_4.9H_2O$, is obtained.[4] This loses water at 110° C. to give the *octahydrate*. In the presence of water the salt yields normal magnesium orthoarsenate. The corresponding potassium salt has been prepared, and also the more complex salts $Na_4Mg_4As_6O_{21}$, $K_4Mg_4As_6O_{21}$;[5] $Mg_2KH(AsO_4)_2.xH_2O$ ($x = 2$, 4, 5 and 15);[6] $Mg_2KNa(AsO_4)_2.14H_2O$.[7]

Certain magnesium calcium arsenates, sometimes associated with other metals, are found in Nature and are enumerated in the table of minerals, pp. 14–16.

Manganese Arsenates.—*Manganous Orthoarsenate*, $Mn_3(AsO_4)_2.H_2O$, is obtained as brown needles[8] when manganese sulphate is heated with sodium orthoarsenate in a sealed tube at 175° C.

Commercial manganese arsenate, consisting mainly of the normal salt, $Mn_3(AsO_4)_2$, is sometimes used, with or without diluents, for combating plant pests. It is obtained by the reaction between a manganous salt and normal sodium arsenate, by heating intimate mixtures of manganese compounds with arsenious oxide in the presence of an oxidising agent, or by treating arsenious oxide with manganese compounds having an oxidising action in the presence of water.[9]

Manganous Monohydrogen Orthoarsenate, $MnHAsO_4.H_2O$, is produced by saturating aqueous arsenic acid with manganese carbonate; it separates from solution as sparingly soluble rectangular tablets, and is more readily precipitated by addition of alcohol.[10] When heated to 140° C. it loses its water of crystallisation, and at a higher temperature

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[1] Wenger, *Thesis*, Geneva, 1911.

[2] Fresenius, *Zeitsch. anal. Chem.*, 1864, 3, 207; Puller, *ibid.*, 1871, 10, 68.

[3] Lefèvre, *loc. cit.*

[4] Kinkelin, *loc. cit.*

[5] Lefèvre, *loc. cit.*

[6] Kinkelin, *loc. cit.*; Chevron and Droixhe, *loc. cit.*

[7] Kinkelin, *loc. cit.*

[8] Coloriano, *Compt. rend.*, 1886, 103, 273; *Bull. Soc. chim.*, 1886, [2], 45, 707; *Thesis*, Paris, 1886.

[9] See, for example, Grasselli Chemical Co., Assees. of Tanner, *Canadian Patent*, 260934 (1924).

[10] See Schiefer, *Zeitsch. Ges. Naturw. Berlin*, 1864, 23, 347; Coloriano, *loc. cit.*; Amadori, *Atti Ist Veneto*, 1922, 81, 603.

it forms the pyroarsenate.[1] The solubility in water at the ordinary temperature is 0·013 gram of salt in 100 c.c. of water.[2] Hot water converts it to manganic arsenate. When heated in hydrogen or carbon monoxide, arsenic is volatilised and oxide of manganese remains.[3] It readily dissolves in arsenic acid to form *manganous dihydrogen orthoarsenate*, $Mn(H_2AsO_4)_2$, which crystallises in rectangular plates.[4] The latter may also be obtained from a solution of manganese carbonate in the theoretical quantity of arsenic acid. The crystals deliquesce in air. The *monohydrate*, $Mn(H_2AsO_4)_2.H_2O$, is formed in the presence of excess of arsenic acid, although if the latter is present in large excess the *acid salt*, $Mn(H_2AsO_4)_2.H_3AsO_4$, separates in micro-crystals.[5] Both salts are hydrolysed by water and are stable only in the presence of an excess of arsenic acid.[6]

Colloidal manganese arsenate may be obtained in an analogous way to that described for cadmium and cobalt arsenates.[7] If concentrated solutions of manganous chloride and potassium dihydrogen arsenate are mixed at the ordinary temperature, a solid jelly is formed, which remains stable for weeks; but finally, rose-coloured crystals separate and the jelly partly liquefies.[8] The essential constituent of the jelly appears to be the monohydrogen arsenate, $MnHAsO_4$, and the crystals are the monohydrate, $MnHAsO_4.H_2O$.

Manganous Pyroarsenate, $Mn_2As_2O_7$, results when manganous monohydrogen orthoarsenate or manganese ammonium arsenate is strongly ignited, or when the oxide or carbonate is dissolved in fused potassium dihydrogen orthoarsenate.[9] The tabular crystals are colourless, but when fused a red glass is formed.

Manganic Orthoarsenate, $Mn_2(AsO_4)_2.2H_2O$, may be prepared by treating a hot aqueous solution of arsenic acid with a concentrated solution of manganese nitrate.[10] It forms a dark grey powder which dissolves slowly in hydrochloric acid but is insoluble in nitric acid. When heated to redness it forms manganous pyroarsenate.

When manganous salts undergo oxidation in the presence of arsenic acid, a violet colour develops, due to the formation of *triarsenatomanganic acid*,[11] $H_6[Mn(AsO_4)_3].3H_2O$. This may be obtained in the form of violet-red crystals by dissolving manganic hydroxide or acetate in cold concentrated arsenic acid solution and allowing to evaporate, or by adding potassium permanganate to a solution of manganous

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[1] Scheele, *Svenska Akad. Handl.*, 1778, 40, 316.

[2] Amadori, *loc. cit.*

[3] Lefèvre, *Ann. Chim. Phys.*, 1892, [6], 27, 29; *Compt. rend.*, 1890, 110, 405.

[4] See Schiefer, *Zeitsch. Ges. Naturw. Berlin*, 1864, 23, 347; Coloriano, *loc. cit.*; Amadori, *Atti 1st Veneto*, 1922, 81, 603.

[5] Amadori, *loc. cit.*

[6] According to Grube, Heller and Herrmann (*Zeitsch. Elektrochem.*, 1936, 42, 223) a study of the ternary system Manganese arsenate–Arsenic acid–Water indicates the existence of 4 solid phases: $Mn_3(AsO_4)_2.H_2O$; $MnHAsO_4.4H_2O$; $H_4[Mn(AsO_4)_2].3H_2O$ and $H_4[Mn(AsO_4)_2]$.

[7] Klemp and Gyulay, *Kolloid-Zeitsch.*, 1914, 15, 202; Weiser and Bloxsom, *J. Physical Chem.*, 1924, 28, 26; Weiser, *Colloid Symposium*, Wisconsin Univ., 1923, p. 38.

[8] Deiss, *Kolloid-Zeitsch.*, 1914, 14, 139.

[9] Lefèvre, *loc. cit.*; Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 36; Reichard, *Ber.*, 1898, 31, 2165; Otto, *J. prakt. Chem.*, 1834, [1], 2, 414.

[10] Christensen, *ibid.*, 1883, [2], 28, 23.

[11] Deiss, *Zeitsch. anorg. Chem.*, 1925, 145, 365. See Barreswil, *Compt. rend.*, 1857, 44, 677.

dihydrogen arsenate in aqueous arsenic acid. The product may be recrystallised from aqueous acetic acid. Prolonged contact with water causes hydrolysis to arsenic acid and manganic orthoarsenate.

Mangani-arsenic Acid, $Mn(H_2AsO_4)_4$, containing quadrivalent manganese, may be prepared[1] by dissolving hydrated manganese dioxide in concentrated aqueous arsenic acid, or, more conveniently, by the action of arsenic acid on a permanganate, or by the interaction of arsenic acid with a mixture of manganous nitrate and a permanganate. It is a flesh-coloured microcrystalline powder, insoluble in water, but hydrolysed by prolonged contact to arsenic acid and hydrated manganese dioxide. An *ammonium mangani-arsenate*, of composition $(NH_4)_2H_2MnAs_2O_9$ or $O : Mn : [AsO_4(NH_4)H]_2$, has been obtained by adding aqueous ammonia to a suspension of the above acid in water.

Double salts with the alkali metals have been obtained,[2] and a number of mixed arsenates with calcium, magnesium, lead, iron and other metals occur in Nature, as also do several basic arsenates (see table, pp. 14–16).[3] An *acid arsenate* of composition $5MnO.2As_2O_5.6H_2O$ has been obtained in the crystalline form by stirring manganous carbonate with aqueous arsenic acid.[4]

Mercury Arsenates.—*Mercurous Orthoarsenate*, Hg_3AsO_4, is formed as an orange-yellow precipitate when a cold solution of mercurous nitrate is added to a large excess of aqueous sodium monohydrogen orthoarsenate.[5] If the mercury salt is in excess, the *basic double salt*, $3Hg_3AsO_4.2(HgNO_3.Hg_2O)$, separates which, when freshly precipitated and washed, is converted to the normal arsenate by treatment with aqueous sodium monohydrogen orthoarsenate. The double salt is white and soluble in hydrochloric acid. The normal arsenate may also be obtained by prolonged heating at 230° C. of a mixture of mercury and arsenic acid solution (containing 12·5 per cent. As_2O_5) in a sealed tube.[6]

Mercurous orthoarsenate yields orange rhombic prisms which are insoluble in water. Hydrochloric acid converts it into calomel and arsenic acid.

Mercurous Monohydrogen Orthoarsenate, $Hg_2HAsO_4.\frac{1}{2}H_2O$, is formed[7] when a concentrated solution of arsenic acid is treated with a solution of mercurous nitrate until the precipitate no longer redissolves. The product is white, but becomes red when dried. On further heating it loses water of crystallisation and at a higher temperature yields mercury and mercuric arsenate, the latter also decomposing at a still higher temperature to yield arsenious oxide, oxygen and mercury. The salt dissolves in cold nitric acid and may be reprecipitated by ammonia. Boiling nitric acid and cold concentrated hydrochloric acid decompose it.

Orange-red crystals of *dimercurous silver arsenate*, Hg_2AgAsO_4, have been obtained by adding hydrogen peroxide solution, free from chlorides, to a solution of silver nitrate, mercurous nitrate and potassium

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[1] Auger and Yakimach, *Compt. rend.*, 1928, 187, 603.

[2] Lefèvre, *Compt. rend.*, 1890, 110, 405; *Ann. Chim. Phys.*, 1892, [6], 27, 29; Reichard, *Ber.*, 1898, 31, 2165; Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 36.

[3] See also Aminoff and Blix, *K. Svenska Veten. Handl. Stockholm*, 1931, [3], 9, No. 5, 52; Palache and others, *ibid.*, 1933, [3], 11, No. 4, 32.

[4] Ephraim and Rosetti, *Helv. Chim. Acta*, 1929, 12, 1025.

[5] Haack, *Annalen*, 1891, 262, 181; *Thesis*, Halle, 1890, p. 35.

[6] Coloriano, *Bull. Soc. chim.*, 1886, [2], 45, 707; *Compt. rend.*, 1886, 103, 275; *Thesis*, Paris, 1886, p. 49; Goguel, *Thesis*, Paris, 1896.

[7] Simon, *Pogg. Annalen*, 1837, 40, 442; 1837, 41, 424.

arsenite in dilute nitric acid. The crystals are blackened by ammonium hydroxide solution owing to liberation of metallic mercury.[1]

Mercurous Metarsenate, $HgAsO_3$, has been obtained by prolonged heating in a sealed tube at 150° C. of a mixture of mercury and aqueous arsenic acid, the latter of 50 to 75 per cent. concentration,[2] and by boiling a mixture of mercuric oxide and aqueous arsenic acid until dry, thoroughly washing the residue with water and drying at 100° C.[3] It yields pale yellow hexagonal plates with axial ratio $a : c = 1 : 1{\cdot}5096$. The crystals blacken superficially in light. The salt decomposes on heating. It is insoluble in water, alcohol and acetic acid. It dissolves in dilute nitric acid and the addition of ammonia to the solution precipitates mercurous monohydrogen orthoarsenate.

Mercuric Orthoarsenate, $Hg_3(AsO_4)_2$, is obtained by precipitating a solution of mercuric nitrate with a solution of sodium mono- or dihydrogen arsenate, or by dropping aqueous arsenic acid into excess of mercuric nitrate solution.[4] It is a heavy citron-yellow powder. Hot water dissolves it slightly without decomposition, and shining crystals may separate from the cooled solution. Hydrochloric acid dissolves it freely, nitric acid less readily, and arsenic acid not at all. Brine solution converts it into red-brown mercury oxychloride. Potassium bromide solution colours it brown, and a yellow residue is ultimately left. Potassium iodide forms mercuric iodide.

Sodium dihydrogen arsenate or arsenic acid does not precipitate mercuric chloride solution, but the latter reacts with normal silver arsenate to form normal mercuric arsenate and silver chloride. Yellow precipitates containing normal mercuric arsenate, mercuric chloride and mercuric oxide are thrown down from mercuric chloride solution by a solution of sodium monohydrogen arsenate.

Basic mercuric sulphate is converted into mercuric orthoarsenate and mercuric oxide by warming with sodium monohydrogen arsenate solution. Hot acetic acid will extract the oxide.[5]

When mercuric oxide is treated with aqueous arsenic acid, the solid phase separates into two layers, one of which is mercuric oxide and the other a *basic mercuric arsenate* of composition $3HgO.Hg_3(AsO_4)_2$. When ammonium arsenate solution acts on mercuric oxide, a product of composition $Hg_2NH_2AsO_4$ is obtained.[6]

Complex *pyroarsenates* of composition $HgSrAs_2O_7$ and $HgBaAs_2O_7.H_2O$ have been prepared.[7]

In addition to the basic double salt with mercurous nitrate mentioned on p. 212, a double salt of composition $Hg_3AsO_4.2HgNO_3.2H_2O$ has been described as separating in warty masses or needle-shaped crystals when a solution of mercurous monohydrogen orthoarsenate in concentrated nitric acid is diluted with its own volume of water and then treated with aqueous ammonia and allowed to stand for a time.[8]

Colloidal mercuric orthoarsenate has been prepared[9] by adding

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[1] Jacobsen, *Bull. Soc. chim.*, 1909, [4], 5, 947.

[2] Goguel, *loc. cit.*

[3] Simon, *loc. cit.*

[4] Haack, *loc. cit.* See also Bergman, "*De arsenico*," Upsala, 1777; Goguel, *loc. cit.*

[5] Haack, *loc. cit.*

[6] Hirzel, *Jahresber.*, 1852, p. 420. Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 65.

[7] Rosenheim and Antelmann, *Zeitsch. anorg. Chem.*, 1930, 187, 385.

[8] Simon, *loc. cit.*

[9] Dexheimer, *Thesis*, Erlangen, 1910, p. 51.

mercuric chloride to a 10 per cent. solution of sodium protalbinate, dissolving the precipitate formed in aqueous sodium hydroxide and treating the latter solution with sodium monohydrogen arsenate. After dialysis, the solution is evaporated to dryness under reduced pressure, when an olive-green residue is obtained. This dissolves readily in water to give a colloidal solution which is olive-green in transmitted light and grey in reflected light.

Molybdenum Arsenates and **Molybdo-arsenates.**—*Molybdous Arsenate*, $Mo(HAsO_4)_2.nH_2O(?)$, is said [1] to be formed as a grey precipitate when molybdous chloride is treated with sodium monohydrogen arsenate; the precipitate first redissolves, but afterwards becomes permanent. *Molybdic arsenate*, obtained in a similar manner from molybdic chloride, has been described by Berzelius, who also considered that an acid salt was produced on dissolving the hydrate of molybdenum dioxide in excess of arsenic acid, since the solution turned blue on standing.[1]

Molybdic acid forms with arsenic acid a series of heteropoly-acids analogous to the molybdophosphoric acids. When a mixture of molybdic acid, arsenic acid and an ammonium salt is boiled for some time, a yellow crystalline precipitate is obtained of an ammonium molybdo-arsenate. To this compound Debray [2] gave the formula $3(NH_4)_2O.As_2O_5.20MoO_3$, and considered that on boiling with aqua regia and evaporating the solution, the residue contained two acids—one yellow, in which the ratio of As_2O_5 to MoO_3 was 1 : 20, and the other white, with $As_2O_5 : MoO_3 = 1 : 16$. This was contested by Seyberth,[3] who considered that both the precipitate and the acid obtained from it contained $As_2O_5 : MoO_3 = 1 : 7$. Various other acids and salts have been described in which the ratio of As_2O_5 to MoO_3 differs considerably, those compounds rich in molybdic acid generally being yellow in colour, while those containing less molybdic acid are white.[4] A satisfactory formulation of these compounds is due to the application of a modification of Werner's co-ordination theory suggested by Miolati [5] and extended by Rosenheim [6] (see Vol. VII, Part III, this Series).

According to this theory the complex molybdo-arsenic compounds may be considered as derived either from an acid containing a septavalent complex anion in which arsenic is the central atom with a co-ordination number of 6, or from an acid containing a tervalent anion in which arsenic has a co-ordination number of 4. The hypothetical parent compounds correspond therefore to $H_7[AsO_6]$ and $H_3[AsO_4]$.

12-Molybdo-arsenates.—The free acid corresponding to ordinary phosphomolybdic acid has not been prepared, but the two acid salts, $R'_3H_4[As(Mo_2O_7)_6].4H_2O$, where $R' = NH_4$ or K, have been obtained in the form of deep yellow crystalline precipitates by adding arsenic acid in small quantities to solutions of the molybdates previously made acid

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[1] Berzelius, *Pogg. Annalen*, 1826, 6, 346; "*Traité de Chimie*," 1847, 4, 498.

[2] Debray, *Compt. rend.*, 1874, 78, 1408. See also Struve, *J. prakt. Chem.*, 1853, [1], 58, 493.

[3] Seyberth, *Ber.*, 1874, 7, 391.

[4] See Debray, *loc. cit.*; Gibbs, *Amer. Chem. J.*, 1881–82, 3, 402; von der Pfordten, *Ber.*, 1882, 15, 1929; Pufahl, *ibid.*, 1884, 17, 217; Ditte, *Compt. rend.*, 1886, 102, 1021; Friedheim, *Zeitsch. anorg. Chem.*, 1892, 2, 314.

[5] Miolati and Pizzighelli, *J. prakt. Chem.*, 1908, [2], 77, 417.

[6] Rosenheim and Jänicke, *Zeitsch. anorg. Chem.*, 1917, 100, 304.

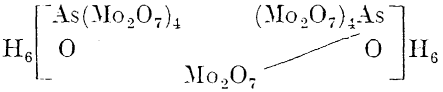
with nitric acid and containing the alkali nitrates. The ammonium salt serves for the analytical detection of arsenic acid, and the precipitation is quantitative[1] providing the concentration of hydrogen ion present is greater than 0·030 per cent., and that ammonium nitrate is present. In less acid or neutral solutions the precipitate is white, and contains less molybdenum than the yellow salt. The corresponding guanidinium salt has not been obtained, but when hydrochloric acid is added to a solution containing 12 gram-molecules of guanidinium molybdate and 1 gram-molecule of arsenic acid, deep yellow leaflets separate[2] consisting of the *10-molybdo-arsenate*, $(CH_5N_3)_3H_7[AsO(Mo_2O_7)_5].5H_2O$. By treating 1 gram-molecule of this salt with 2 gram-molecules of guanidinium carbonate, the heptabasic salt, $(CH_5N_3)_7H_7[AsO(Mo_2O_7)_5].6H_2O$, separates in the form of light yellow crystals which decompose when recrystallised. The conductivity corresponds with its formation as a normal salt. The free acid has not been prepared.

A series of compounds, free acids and ammonium salts of the types

$$H_7\left[\begin{array}{c}(Mo_2O_7)_x\\ As(W_2O_7)_y\\ (V_2O_6)_z\end{array}\right].nH_2O \quad \text{and} \quad (NH_4)_6H\left[\begin{array}{c}(Mo_2O_7)_x\\ As(W_2O_7)_y\\ (V_2O_6)_z\end{array}\right].nH_2O$$

in which $x+y+z=6$ and in which x or y may equal 0, has been prepared.[3] They are all more or less of an intense red colour, depending on the value of z. The crystals belong to the tetragonal system and are uniaxially birefringent. The individual salts are isomorphous and form mixed crystals, as they also do with the corresponding phospho-compounds.

9-Molybdo-arsenates.—In this series the complex anion is more stable than in the two preceding series. The salts are derived from the acid,[4]



$$H_6\left[\begin{array}{ccc}As(Mo_2O_7)_4 & & (Mo_2O_7)_4As\\ O & & O\\ & Mo_2O_7 & \end{array}\right]H_6$$

which is formed by agitation of a solution of normal sodium arsenate, saturated with molybdic acid, with hydrochloric acid and ether. It is very soluble in water and yields two hydrates: $H_{12}[As_2O_2(Mo_2O_7)_9].24H_2O$, red crystals, stable at ordinary temperatures; and $H_{12}[As_2O_2(Mo_2O_7)_9].34H_2O$, yellow crystals, stable below 8° C. On treating the solution with alkali hydroxide or carbonate, the alkali salts are obtained. The sodium salt, $Na_6H_6[As_2O_2(Mo_2O_7)_9].20H_2O$, is yellow, and is an acid salt, indicating[5] that the basicity of the acid is higher than 6. On standing, the crystals of this salt crumble and change into a colourless 25-hydrate. The corresponding yellow potassium salt, containing $11H_2O$, changes similarly into a colourless 25-hydrate. Normal salts, of composition $R'_{12}[As_2O_2(Mo_2O_7)_9].xH_2O$ $(R'=Cs, Ag, Tl, CH_6N_3)$, have been obtained by adding the metallic

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[1] Maderna, *Atti R. Accad. Lincei*, 1910, [5], 19, ii, 15.

[2] Rosenheim and Pinsker, *Zeitsch. anorg. Chem.*, 1911, 70, 73.

[3] Canneri, *Gazzetta*, 1926, 56, 871; Rodolico, *Atti R. Accad. Lincei*, 1926, [6], 4, 471. See also Cignoli, *Rev. centro. estud. farm. bioquím*, 1933, 22, 175.

or organic chloride to a solution of the yellow acid sodium salt, thus indicating that the basicity of the acid is 12.

Arsenic compounds corresponding to the 17-molybdo-2-phosphates (see Vol. VII, Part III) have not been prepared, but by mixing solutions of paramolybdates and alkali dihydrogen arsenates, white precipitates of composition $5R'_2O.As_2O_5.16MoO_3.xH_2O$ ($R' = NH_4$ or K) have been obtained,[1] which may be regarded as *8-molybdo-arsenates*, $R'_5[As(OH)_2(Mo_2O_7)_4].(x/2 - 1)H_2O$.

3-Molybdo-arsenates.—The complex anion of this series is the most stable of those derived from $[XO_4]'''$. The free acid, $H_3[AsO(MoO_4)_3]$, is tribasic, stronger than arsenic acid, and extremely stable, and is obtained on adding fuming nitric acid to a concentrated solution of arsenic acid saturated with molybdic acid. It readily dissolves in water, from which it may be crystallised in the form of white prisms.[2] The trisodium salt crystallises from water with $11{\cdot}5H_2O$, and the triguanidinium salt forms pale yellow anhydrous needles. Other salts have been described.[3]

Salts of acids containing less molybdic acid—for example, 2- and 1-molybdo-arsenates of the types $R'_2H[AsO_2(MoO_4)_2].xH_2O$ and $R'H_2[AsO_3(MoO_4)].xH_2O$—have been described,[4] as also have sulphur-containing compounds of the types $R'_4[As_2S_5(MoS_4)_2].xH_2O$ and $R'[AsS_2(MoS_4)].xH_2O$.

A compound of composition $[4MoO_3.MoO_2]_2.H_3AsO_4.4H_2O$ has been obtained[5] in the form of sapphire-blue hexagonal platelets by the addition of sodium monohydrogen arsenate to a solution of sodium molybdate acidified with sulphuric acid; the mixture was reduced by boiling under reflux with aluminium filings and, after cooling, extracted with ether. The extract was shaken with water and the blue compound passed into the water layer, from which it was obtained by evaporation in an atmosphere of carbon dioxide.

Nickel Arsenates.—*Nickel Orthoarsenate*, $Ni_3(AsO_4)_2$, is obtained when the octahydrate is heated or treated with nitric acid.[6] It occurs in Nature as the mineral *xanthiosite*[7] (p. 16). The *dihydrate*, $Ni_3(AsO_4)_2.2H_2O$, is precipitated when an alkali arsenate is added to a solution of a nickel salt.[8] It yields apple-green crystals which give up water on heating, turning red and at a high temperature yellow. It is soluble in mineral acids and in aqueous ammonia. The *octahydrate*, $Ni_3(AsO_4)_2.8H_2O$, occurs as the mineral *annabergite* near Annaberg in Saxony. It may be prepared by addition of ammonium orthoarsenate to a nickel salt, the solution being kept neutral.[8] If ammonia is present in excess, the molecules of water are partially replaced by ammonia, yielding hydrated *ammino-orthoarsenates*, which are insoluble in water but readily soluble in acids and in ammonia.[9] The following compounds have been distinguished: $Ni_3(AsO_4)_2.NH_3.7H_2O$; $Ni_3(AsO_4)_2.2NH_3.6H_2O$

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[1] Gibbs, *Amer. Chem. J.*, 1881–82, 3, 402; Friedheim, *Zeitsch. anorg. Chem.*, 1892, 2, 323.

[2] Rosenheim and Traube, *loc. cit.*

[3] Pufahl, *loc. cit.*

[4] Friedheim, *loc. cit.*

[5] Denigès, *Compt. rend.*, 1927, 185, 687.

[6] Girard, *Compt. rend.*, 1852, 34, 918.

[7] Adam, "*Tableau minéralogique*," Paris, 1869, p. 42.

[8] Tupputi, *Ann. Chim. Phys.*, 1811, [1], 78, 133; 79, 153.

[9] Ducru, *Compt. rend.*, 1900, 131, 702.

and $Ni_3(AsO_4)_2.3NH_3.5H_2O$. When heated to dull redness all these salts yield the anhydrous arsenate.

Nickel orthoarsenate also occurs in Nature associated with magnesium (*cabrerite*), cobalt (*forbesite*), copper (*lindackerite*) and other metals (see pp. 14, 15).

By treating nickel carbonate with arsenic acid at varying temperatures, precipitates of the following compositions have been obtained:[1] $4NiO.As_2O_5.14H_2O$, $3NiO.As_2O_5.11H_2O$, $2{\cdot}5NiO.As_2O_5.8H_2O$.

Nickel Monohydrogen Orthoarsenate, $NiHAsO_4.H_2O$, has been obtained[2] by heating in a sealed tube at 160° C. finely divided nickel and an excess of concentrated aqueous arsenic acid. The pale green rhombic prisms are soluble in water and, on strong ignition, lose their water of crystallisation. An acid salt of composition $5NiO.2As_2O_5.3H_2O$ has also been prepared.

Palladium Arsenate was reported by Berzelius[3] as a pale yellow precipitate formed when sodium orthoarsenate was added to a neutral solution of palladious nitrate.

Platinic Arsenate has been obtained[4] as red crystals by treating a solution of the hydroxyarsenide, Pt(OH)As, in aqua regia with potassium chloroplatinate. It was described by Thomson[5] as a pale brown precipitate obtained by double decomposition of sodium arsenate and platinic nitrate.

Neither of the above compounds has been further investigated.

Potassium Arsenates.—*Potassium Orthoarsenate*, K_3AsO_4, is formed when excess of potassium hydroxide reacts with aqueous arsenic acid[6] or from a mixture of potassium carbonate and potassium monohydrogen arsenate.[7] The salt crystallises in needles. The heat of formation is 396,200 calories.[8]

By subjecting potassium arsenate in a slowly moving stream of hydrogen to a silent electric discharge, reduction to arsenic occurs.[9] Suitable conditions for this result are to apply 80 volts to the primary circuit and 15,000 volts to the reaction vessel, using a transformer instead of an induction coil; the hydrogen should pass at the rate of 2 litres per hour.

The arsenate considerably accelerates the fermentation of hexose diphosphate,[10] and inhibits the combination of sucrose with phosphoric acid (phosphorylation).[11]

Potassium Monohydrogen Orthoarsenate, K_2HAsO_4, is formed[12] when potassium carbonate is added to aqueous arsenic acid until effervescence no longer occurs; on evaporating the solution to dryness a white residue is obtained. It is soluble in water[13] and may be crystallised in

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[1] Ephraim and Rosetti, *Helv. Chim. Acta*, 1929, 12, 1025.

[2] Coloriano, *Compt. rend.*, 1886, 103, 274; *Bull. Soc. chim.*, 1886, [2], 45, 240; *Thesis*, Paris, 1886.

[3] Berzelius, *Schweigger's J.*, 1813, 7, 66; *Pogg. Annalen*, 1828, 13, 454.

[4] Tivoli, *Gazzetta*, 1884, 14, 488.

[5] Thomson, *Ann. Phil.*, 1820, 15, 84.

[6] Graham, *Pogg. Annalen*, 1834, 32, 47.

[7] Mitscherlich, *Ann. Chim. Phys.*, 1821, [2], 19, 350, 407.

[8] Berthelot, "*Thermochimie*," 1897, 1, 193.

[9] Miyamoto, *J. Chem. Soc. Japan*, 1932, 53, 788.

[10] Mayer, *Biochem. Zeitsch.*, 1928, 193, 176.

[11] Neuberg and Kobel, *ibid.*, 1926, 174, 493.

[12] Scheele, *Svenska Akad. Handl.*, 1778, 40, 316.

the form of triclinic prisms of the *monohydrate*,[1] $K_2HAsO_4.H_2O$. These lose their water of crystallisation at 110° to 120° C. The heat of formation is 339,800 calories.[2] When ignited, fusion occurs and, on cooling, a white glass said to be *potassium pyroarsenate*, $K_4As_2O_7$, remains.[1]

Potassium Dihydrogen Orthoarsenate, KH_2AsO_4, is prepared by fusing together equal quantities of arsenious oxide and potassium nitrate, dissolving the product in water and allowing to crystallise; [3] or by adding sufficient aqueous arsenic acid to potassium carbonate to form a solution acid to litmus, when it may be crystallised from the solution.[4] It forms tetragonal crystals with axial ratio [5] $a : c = 1 : 0{\cdot}9380$, and isomorphous with the corresponding phosphates of potassium and ammonium.[6] The density is 2·851 at ordinary temperatures [7] and 2·8675 at 9·2° C.,[8] and the specific heat [9] is 0·175. The heat of formation is 234,000 calories.[10] When heated, the salt loses 1 molecule of H_2O at 240° to 290° C.,[11] and at a dull red heat fusion occurs and *potassium metarsenate* is formed.[11] The specific heat of the latter is 0·1563 between 17° and 99° C.[12] When dissolved in water the dihydrogen orthoarsenate is re-formed.[13]

The solubility of potassium dihydrogen orthoarsenate in water is 18·87 g. per 100 g. H_2O at 6° C. and increases with temperature.[14] The solution is acid to litmus.[15] The salt is insoluble in alcohol. The dielectric constant [16] is 31.

Arsenates of the Rare Earth Metals.—Only a few of these compounds have been prepared, and those described below have not been fully investigated, so that their composition, and even their existence, need confirmation.

Cerous Monohydrogen Orthoarsenate, $Ce_2(HAsO_4)_3$, is obtained as a white powder, insoluble in water, by digesting cerous oxide with aqueous arsenic acid.[17] It dissolves in excess of the latter and, if the solution is evaporated, a gelatinous mass, probably *cerous dihydrogen orthoarsenate*, $Ce(H_2AsO_4)_3$, is obtained.

Ceric Dihydrogen Orthoarsenate, $Ce(H_2AsO_4)_4.4H_2O$, may be prepared by heating cerous nitrate (1 g.-mol.) and arsenic acid (4 g.-mols.) with concentrated nitric acid for several hours, distilling off most of the nitric acid, and allowing the liquid to crystallise. The salt separates as

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[1] Hormann, *Inaug. Dissertation*, Erlangen, 1879.

[2] Berthelot, *loc. cit.*

[3] Glaser, *Mag. Pharm.*, 1826, 15, 132; Hormann, *loc. cit.*

[4] Mitscherlich, *loc. cit.*

[5] Topsöe, *Sitzungsber. K. Akad. Wiss. Wien*, 1872, 66, 32; *Bull. Soc. chim.*, 1873, [2], 19, 246.

[6] Muthmann, *Zeitsch. Kryst. Min.*, 1894, 22, 523; 23, 368; Hassel, *Zeitsch. Elektrochem.*, 1925, 31, 523.

[7] Schröder, "*Dichtigkeitsmessungen*," Heidelberg, 1873.

[8] Muthmann, *Zeitsch. Kryst. Min.*, 1894, 22, 497.

[9] Kopp, *Phil. Trans.*, 1865, 155, 71; *Annalen* (*suppl.*), 1865, 3, 289.

[10] Berthelot, "*Thermochimie*," 1897, 1, 193.

[11] Thomson, *Ann. Phil.*, 1820, 15, 85.

[12] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[13] Schiefer, *Zeitsch. Ges. Naturw. Halle*, 1864, 23, 350; Hormann, *loc. cit.*; Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 53.

[14] Thomson, *loc. cit.*

[15] Thomson, *Chem. News*, 1884, 49, 119; 1885, 52, 18, 29.

[16] Steulmann, *Zeitsch. Physik*, 1932, 77, 114.

[17] Hisinger and Berzelius, *Gehlen's J.*, 1804, 2, 397; *Schweigger's J.*, 1816, 17, 424.

white needles. When it is dissolved in the minimum quantity of concentrated nitric acid and the cold solution diluted with water, a white crystalline precipitate of *ceric monohydrogen orthoarsenate*, $Ce(HAsO_4)_2.6H_2O$, is formed.[1]

Transparent and opalescent jellies of ceric arsenate have been described.[2]

A gelatinous precipitate of *lanthanum monohydrogen orthoarsenate*, $La_2(HAsO_4)_3.nH_2O$, is formed when sodium monohydrogen orthoarsenate is added to a solution of lanthanum sulphate.[3] A similar product has been obtained with *didymium sulphate.*

Yttrium Orthoarsenate, $YAsO_4.nH_2O$, is formed as a white gelatinous precipitate[4] when sodium monohydrogen orthoarsenate is added to a solution of an yttrium salt, or when yttrium hydrogen arsenate is treated with ammonia. When dried, the precipitate forms a yellow horny mass which dissolves in nitric acid. *Yttrium monohydrogen orthoarsenate*, $Y_2(HAsO_4)_3.nH_2O$, is obtained in solution by dissolving yttria in aqueous arsenic acid.[5] When the solution is heated, arsenic acid is precipitated. *Yttrium dihydrogen orthoarsenate*, $Y(H_2AsO_4)_3.nH_2O$, is obtained as a white precipitate by adding an excess of sodium monohydrogen orthoarsenate to a solution of an yttrium salt.[6] The product dissolves in nitric acid.

Rhodium Arsenate.—A yellowish-white precipitate is formed when sodium orthoarsenate is added to a hot aqueous solution of sodium chlororhodate.[7] The precipitate is probably rhodium orthoarsenate, but its composition has not been confirmed.

Rubidium Arsenates.[8]—*Rubidium Orthoarsenate*, Rb_3AsO_4, is prepared by adding a solution of rubidium hydroxide to aqueous arsenic acid until the former is in excess. Very hygroscopic white lamellæ of the *dihydrate*, $Rb_3AsO_4.2H_2O$, are deposited on evaporation. The salt absorbs carbon dioxide from the air and its solution is alkaline in reaction. When heated, the water of crystallisation is lost at 100° C.

Rubidium Monohydrogen Orthoarsenate, Rb_2HAsO_4, is obtained by mixing aqueous solutions of rubidium hydroxide and rubidium dihydrogen orthoarsenate in molecular proportions; it forms white, hygroscopic lamellæ of the *monohydrate*, $Rb_2HAsO_4.H_2O$. It absorbs carbon dioxide slowly from the air, or more rapidly in aqueous solution. The crystals become anhydrous when heated and, above 150° C., *rubidium pyroarsenate*, $Rb_4As_2O_7$, is formed, which at a dull red heat decomposes to form a milky-white crystalline mass of *rubidium metarsenate*, $RbAsO_3$, which itself decomposes at a bright red heat.

Rubidium Dihydrogen Orthoarsenate, RbH_2AsO_4, is obtained in the anhydrous form by fusing together equal parts of arsenious oxide and rubidium nitrate, or by neutralising rubidium carbonate solution with arsenic acid using methyl orange as indicator; in the former method it yields tabular crystals and in the latter silky needles. At a dull red heat it forms the metarsenate.

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[1] Barbieri and Calzolari, *Ber.*, 1910, 43, 2214.

[2] Prakash, *J. Physical Chem.*, 1932, 36, 2483.

[3] Frerichs and Smith, *Annalen*, 1878, 191, 331.

[4] Berzelius, *Schweigger's J.*, 1816, 16, 250, 404; Berlin, *Pogg. Annalen*, 1838, 43, 105; Popp, *Annalen*, 1864, 131, 195.

[5] Ekeberg, *Scherer's J.*, 1800, 3, 189, 1803, 9, 597.

[6] Berlin, *loc. cit.*

[7] Thomson, *Ann. Phil.*, 1820, 15, 84.

[8] Bouchonnet, *Compt. rend.*, 1907, 144, 641.

Silver Arsenates.—Silver nitrate reacts with solutions of arsenic acid or arsenates, giving a chocolate-coloured precipitate of *silver orthoarsenate*, Ag_3AsO_4, containing a small proportion of silver nitrate, possibly in solid solution.[1] The adsorption of silver nitrate is prevented by the presence of ammonium nitrate. The precipitation is incomplete in acid solution.[2] The orthoarsenate cannot be completely dried except by fusion.

When precipitated from a boiling solution of silver nitrate by concentrated aqueous arsenic acid, the precipitate is deep purple in colour.[3] As usually prepared it forms cubic crystals, which may be tetra-, hexa- or dodeca-hedral. The unit cell contains [4] 2 molecules and has a side 6·12 A. The crystals have density 6·657 at 25° C.[5] The solubility in water at 20° C. is 0·0085 g. per litre.[6]

When heated, the salt first melts and at a higher temperature it decomposes to form silver;[7] reduction to the metal occurs more readily when heated with carbon.[8] Partial reduction also occurs when the orthoarsenate is treated with formaldehyde [9] or with ferrous sulphate solution;[10] in the former case silver is formed, but in the latter silver suboxide.

Silver orthoarsenate dissolves in hydrochloric acid, forming arsenic trichloride,[11] and in nitric acid with partial conversion to *nitrato-arsenate*,[12] which may be separated by fractional crystallisation, silver orthoarsenate crystallising out first and then the nitrato-arsenate; the latter, in contact with water, reverts to silver nitrate and silver orthoarsenate. The latter is also soluble in acetic acid, and in aqueous ammonia or ammonium carbonate. By crystallising the solution in ammonia over a mixture of quicklime and sal-ammoniac, colourless needles of *silver tetrammino-orthoarsenate*, $Ag_3AsO_4.4NH_3$, are obtained;[13] these lose ammonia in the air and turn reddish-brown.

When silver nitrate solution is dropped on a gelatin gel containing an alkali arsenate, periodic precipitation of silver orthoarsenate occurs only in darkness; if the gels are exposed to the light a continuous precipitate is formed.[14] *Colloidal silver orthoarsenate* has been prepared[15] by mixing solutions of silver nitrate and sodium protalbinate and dissolving the precipitate formed in dilute aqueous sodium hydroxide containing sodium monohydrogen orthoarsenate. After dialysis in the dark, the solution was evaporated *in vacuo* over sulphuric acid; the powder obtained gave a hydrosol which was dark green by reflected light and red by transmitted light.

Silver Monohydrogen Orthoarsenate, Ag_2HAsO_4, has not been obtained in the pure condition.

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[1] Graham, *Phil. Trans.*, 1833, 123, 253; Baxter and Coffin, *J. Amer. Chem. Soc.*, 1909, 31, 297; *Zeitsch. anorg. Chem.*, 1909, 62, 52.

[2] Scheele, *Svenska Akad. Handl.*, 1778, 40, 316.

[3] Kuhn, *Zeitsch. Pharm.*, 1857, 9, 24.

[4] Wyckoff, *Zeitsch. Kryst. Min.*, 1926, 62, 529; *Amer. J. Sci.*, 1925, [5], 10, 107.

[5] Baxter and Coffin, *loc. cit.*

[6] Whitby, *Zeitsch. anorg. Chem.*, 1910, 67, 107.

[7] Scheele, *loc. cit.*

[8] Simon, *Pogg. Annalen*, 1837, 40, 417; 41, 424.

[9] Zappi and Landaburu, *Anal. Soc. Quim. Argentine*, 1916, 4, 218; *Bull. Soc. chim.*, 1918, [4], 23, 318.

[10] Wohler, *Annalen*, 1839, 30, 1; 1860, 114, 119.

[11] Scheele, *loc. cit.*

[12] Setterberg, *Ofvers. Akad. Forh. Stockholm*, 1846, 3, 25; *J. Pharm. Chim.*, 1847, [3], 12, 142.

[13] Widman, *Bull. Soc. chim.*, 1873, [2], 20, 64.

[14] Duchemin, *Compt. rend.*, 1935, 200, 927.

[15] Dexheimer, *Thesis*, Erlangen, 1910, p. 53. See also Baxter and Coffin, *loc. cit.*

Silver Dihydrogen Orthoarsenate, AgH_2AsO_4, is readily obtained as white monoclinic crystals from a solution of arsenic acid (of composition $H_3AsO_4.H_2O$) saturated with silver orthoarsenate.[1] If the solution is saturated with the silver orthoarsenate at a temperature a little below 100° C., it deposits orange-red hexagonal prisms similar to those of silver monohydrogen phosphate; these are probably the monohydrogen arsenate, but they decompose rapidly in the presence of water. Also when the dihydrogen arsenate is heated to 100° C. it first turns red, probably forming the monohydrogen salt, but rapidly loses water to form *silver metarsenate*, $AgAsO_3$, as a white powder.

When a syrupy solution of silver orthoarsenate in arsenic acid is heated above 100° C. it yields a white granular powder of composition $Ag_2O.2As_2O_5$, which is decomposed by water into silver orthoarsenate and arsenic acid.[2]

Sodium Arsenates.—*Sodium Orthoarsenate*, Na_3AsO_4, is formed when excess of sodium hydroxide reacts with arsenic acid.[3] It is usually manufactured by causing arsenious oxide, sodium hydroxide or carbonate and a reducible metallic oxide, for example antimony trioxide, to react in the fused condition, the sodium arsenate being extracted from the melt with water and crystallised from the resulting solution.[4] The process may be performed in the presence of molten lead to alloy the antimony which is formed. Metallic arsenic may be used instead of arsenious oxide.[5] Or, arsenious oxide vapour mixed with excess of air or oxygen is passed over the alkali at about 500° C.[6] The mixture of alkali and arsenious oxide may be oxidised with nitric acid, but large quantities of nitrous vapours are evolved during the reaction. An improved method is to use sodium peroxide as the oxidising agent.[7]

The arsenate may be prepared, however, without the presence of an oxidiser other than arsenious oxide if excess of the latter be used. Thus, sodium carbonate with excess of arsenious oxide heated at 500° to 550° C. yields the arsenate by the following reaction:[8]

$$9Na_2CO_3 + 5As_2O_3 = 6Na_3AsO_4 + 4As + 9CO_2$$

Sodium orthoarsenate is also obtained electrolytically by the method described under calcium arsenate (p. 198). Yields up to 100 per cent. may be obtained[9] by employing a cell with a diaphragm between iron electrodes. The anolyte should contain sodium arsenite, or sodium hydroxide and arsenious oxide (equivalent to 150 g. As_2O_3 per litre), and the catholyte sodium hydroxide (150 g. per litre). With a current density of 3 amps. per sq. dm. the current efficiency is 100 per cent. A solid crust of sodium arsenate forms around the anode. The process may be rendered continuous by circulating the anolyte and removing the precipitated arsenate. Iron or nickel electrodes are

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[1] Joly, *Compt. rend.*, 1886, 103, 1071. See also Setterberg, *loc. cit.*; Dufet, *Bull. Soc. franç. Min.*, 1886, 9, 36.

[2] Joly, *loc. cit.*; Hurtzig and Geuther, *Annalen*, 1859, 111, 168.

[3] The system Na_2O–As_2O_5–H_2O has been studied in the region from NaH_2AsO_4 up to high alkalinity at 0°, 20° and 50° C. See Menzel and Hagen, *Zeitsch. anorg. Chem.*, 1937, 233, 49.

[4] Burkey, *American Patents*, 1654527–8 (1928); Kirsebom, *Canadian Patent*, 307091 (1930).

[5] Kirsebom, *British Patent*, 851653 (1929).

[6] Britzke, *German Patent*, 443286 (1925).

[7] Bellon, *Ann. hyg. publ. ind. sociale*, 1931, p. 335.

[8] Reissaus, *German Patent*, 544195 (1930).

[9] Essin, *Zeitsch. Elektrochem.*, 1929, 35, 234; Plotnikov and Ivanenko, *ibid.*, 1931, 37, 88.

satisfactory; the latter yield a purer product, but iron has the advantage of hindering the formation of arsine. Electrodes of Acheson graphite may also be used with advantage.[1] The diaphragm should be of asbestos cement.

The density[2] of anhydrous sodium orthoarsenate is 2·835. From solution it crystallises as the *dodecahydrate*, $Na_3AsO_4.12H_2O$, of density[3] 1·76 and melting point 85·5° C. The crystals are hexagonal prisms, isomorphous with the corresponding phosphate. The following refractive indices have been determined:[4]

	Li	Na	Tl
$Na_3AsO_4.12H_2O$ ω .	1·4553	1·4589	1·4624
ϵ .	1·4630	1·4669	1·4704

The molecular refraction[5] is 61·4.

The salt dissolves in water yielding a strongly alkaline solution. Reliable determinations of the solubility have not been made; Graham stated[6] that at 13·5° C. 100 parts of water dissolve 28 parts of the crystallised salt, but Schiff gave a much lower value.[7]

The densities of solutions of various concentrations at 17° C. have been determined as follows:[8]

Concentration. Parts per 100 Parts Solution.		Density.
$Na_3AsO_4.12H_2O$	Na_3AsO_4	
2	0·981	1·0167
4	1·962	1·0215
6	2·944	1·0325
8	3·925	1·0435
10	4·906	1·0547
12	5·887	1·0659
14	6·868	1·0773
16	7·850	1·0887
18	8·831	1·1003
20	9·812	1·1120

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[1] Brown, Hatfield and Church, *Trans. Electrochem. Soc.*, 1936, 70, Preprint 2, 31.

[2] Clarke, "*Constants of Nature*," Washington, 1888 (2nd Ed.), I, 121.

[3] Dufet, *Bull. Soc. franç. Min.*, 1887, 10, 77; *Zeitsch. Kryst. Min.*, 1888, 14, 610. See also Schiff, *Annalen*, 1859, 112, 92; 1860, 113, 196; Playfair and Joule, *Mem. Chem. Soc.*, 1845, 2, 401.

[4] Baker, *J. Chem. Soc.*, 1885, 47, 356; Dufet, *loc. cit.* The ordinary ω values correspond to light vibrating along directions perpendicular to the optic axis; the extraordinary ϵ values correspond to light vibrating parallel to the optic axis.

[5] Doumer, *Compt. rend.*, 1890, 110, 41.

[6] Graham, *Pogg. Annalen*, 1834, 32, 33.

[7] Schiff, *loc. cit.*

[8] Schiff, *Annalen*, 1860, 113, 196; von Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 286.

The heat of formation of sodium orthoarsenate in aqueous solution from the elements is 381,500 calories,[1] and that of the solid 360,800 calories.[2] The heat of neutralisation ($3NaOH.H_3AsO_4.aq.$) is 35,920 calories,[3] and the heat of formation from the oxides is : [2]

$$3Na_2O + As_2O_5 = 2Na_3AsO_4 + 202,800 \text{ calories}$$

Other hydrates of sodium orthoarsenate have been obtained. The *decahydrate*, $Na_3AsO_4.10H_2O$, crystallises from a solution containing sodium monohydrogen orthoarsenate (100 g.) in 150 c.c. of 50 per cent. sodium hydroxide after keeping for some time at about 77° C. ; [4] or it may be prepared by treating a saturated solution of arsenious oxide with an excess of sodium peroxide in the cold, and concentrating on a water-bath, the crystals being deposited on cooling.[5] The decahydrate is efflorescent in dry air. The crystals are regular, resemble those of the corresponding vanadate, and have melting point 85° C. A *(2, 9)-hydrate*, $2Na_3AsO_4.9H_2O$, is deposited from a solution containing 100 g. of the monohydrogen arsenate in 40 c.c. of 50 per cent. sodium hydroxide when allowed to crystallise at about 86° C.[4]

In cold aqueous solution, sodium orthoarsenate reacts with sodium hydrosulphite to form *sodium arsenohydrosulphite*,[6] $Na_3As(S_2O_4)_3$, a creamy white granular powder. In the presence of sodium sulphite this compound decomposes, forming sodium arsenothiosulphate, an unstable intermediate product, and finally arsenious sulphide.[7] If the reduction by sodium hydrosulphite takes place in the presence of hydrochloric acid, some arsenic subsulphide, As_3S, is also precipitated,[8] and this product is also obtained when the orthoarsenate in aqueous solution is treated with phosphorus trichloride and the mixture saturated with sulphur dioxide.[9]

Sodium Monohydrogen Orthoarsenate, Na_2HAsO_4, is produced when aqueous arsenic acid is mixed with a large excess of sodium carbonate,[10] or when the normal orthoarsenate is treated in solution with a dilute acid or chlorine.[11] It is prepared on a large scale by dissolving arsenious oxide in aqueous sodium hydroxide and adding sodium nitrate. The mixture is concentrated by boiling and finally heated in a furnace until dry and the residue calcined ; this residue is extracted with dilute alkali and allowed to crystallise. The product is used in calico-printing as a substitute for cow-dung, which was formerly used for clearing the cloth after mordanting with either iron or aluminium acetate (the use of dung originated in India and its action has not been satisfactorily explained).

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[1] Thomsen, "*Thermochemische Untersuchungen*," 1886, 1, 299.

[2] Mixter, *Amer. J. Sci.*, 1909, [4], 28, 103.

[3] Thomsen, "*Thermochemistry*" (translated by Burke) (Longmans Green and Co., London), 1908, p. 254.

[4] Hall, *J. Chem. Soc.*, 1887, 51, 95.

[5] Schairer, *Chem. Zeit.*, 1904, 28, 15.

[6] Farmer and Firth, *J. Chem. Soc.*, 1927, p. 2019.

[7] *Cf.* Jellinek, *Zeitsch. physikal. Chem.*, 1911, 76, 257; von Szilágyi, *Zeitsch. anorg. Chem.*, 1920, 113, 69.

[8] Farmer and Firth, *J. Chem. Soc.*, 1926, p. 119.

[9] Scott, *ibid.*, 1900, 77, 651.

[10] Mitscherlich, *Ann. Chim. Phys.*, 1821, [2], 19, 350, 407; Wagner, *Dingl. poly. J.*, 1865, 176, 134.

[11] Graham, *Phil. Trans.*, 1833, 123, 253; *Phil. Mag.*, 1844, [3], 24, 401.

The *anhydrous* salt is obtained[1] by heating the crystals to 120° C. If crystallisation takes place at the ordinary temperature, the *dodecahydrate*, $Na_2HAsO_4.12H_2O$, is obtained; while if the crystals are formed above 36° C. the *heptahydrate*, $Na_2HAsO_4.7H_2O$, is produced. The transition point determined from the solubility curve of sodium monohydrogen arsenate in water[2] is at 22° C.

The dodecahydrate is efflorescent at room temperature in air. At 22° C. it becomes damp and the dampness increases as the temperature rises until finally the salt becomes completely liquid. A definite melting point is not exhibited.[3] The liquid becomes clear at 56·2° C. and is then a true solution of the heptahydrate. When this is supercooled to about 40° C. and seeded with a crystal of the salt, crystals of the heptahydrate are deposited and the temperature rises to 56·2° C. A similar evolution of heat, but less marked, occurs at 22° C. The heptahydrate does not effloresce appreciably at room temperature in air.

The dissociation pressures of the two hydrates have been determined[4] by a dynamical method with the following results:

For the reaction $Na_2HAsO_4.12H_2O \longrightarrow Na_2HAsO_4.7H_2O + 5H_2O$, at 14·9° C., 5·24 mm.; and at 20° C., 7·36 mm.

For the reaction $Na_2HAsO_4.7H_2O \longrightarrow Na_2HAsO_4 + 7H_2O$, at 24·92° C., 9·98 mm.; at 30° C., 14·39 mm.; and at 35° C., 20·73 mm.

The dissociation pressure-temperature curves confirm the transition point as very near 22° C.

The heats of hydration of the above reactions at various temperatures have been calculated with the aid of the Clapeyron-Clausius and the Nernst equations:[5]

Reaction.	Temperature, ° C.	Q, calories.
$Na_2HAsO_4.12H_2O$ . . . . . $\longrightarrow Na_2HAsO_4.7H_2O + 5H_2O(liq.)$	14·9 to 20	2,895
$Na_2HAsO_4.7H_2O$ . . . . . $\longrightarrow Na_2HAsO_4 + 7H_2O(liq.)$ . .	24·92 to 30	21,455
	30 to 35	21,644

The specific heats of the hydrates over the range +16° to −12° C. have been found to be approximately:[5] $Na_2HAsO_4.12H_2O$, 0·414 calorie per gram; $Na_2HAsO_4.7H_2O$, 0·350 calorie per gram; the respective molecular heats being 166·3 and 109·3 calories.

The solubility expressed in grams of anhydrous salt per 100 g. of solution has been determined[6] up to 34° C. as follows:

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[1] Partington and Winterton, *J. Chem. Soc.*, 1930, p. 637.

[2] Rosenheim and Thon, *Zeitsch. anorg. Chem.*, 1927, 167, 7.

[3] Partington and Winterton, *loc. cit.* *Cf.* Tilden, *J. Chem. Soc.*, 1884, 45, 269; Lescœur, *Compt. rend.*, 1887, 104, 1171; *Ann. Chim. Phys.*, 1890, [6], 21, 556.

[4] Partington and Winterton, *loc. cit.* See also Partington and Huntingford, *J. Chem. Soc.*, 1923, 123, 160; Menzies, *J. Amer. Chem. Soc.*, 1920, 42, 978, 1951.

[5] Partington and Winterton, *loc. cit.*

[6] Rosenheim and Thon, *loc. cit.* See also Tilden, *J. Chem. Soc.*, 1884, 45, 409.

Temperature, ° C.	Solubility.	Solid Phase.
0	5·46	$Na_2HAsO_4.12H_2O$
8·6	9·66	
11·8	12·53	
16·0	17·30	
21·0	25·75	
22·5	26·75	$Na_2HAsO_4.7H_2O$
28·0	30·48	
30·1	32·34	
34·0	35·09	

Both hydrates crystallise in the monoclinic system, the crystal elements being[1]

$$Na_2HAsO_4.12H_2O, \quad a:b:c=1{\cdot}7499:1:1{\cdot}4121\,;\ \beta=121^\circ\ 49'$$
$$Na_2HAsO_4.\ 7H_2O, \quad a:b:c=1{\cdot}2294:1:1{\cdot}3526\,;\ \beta=\ 97^\circ\ 14'$$

and the densities respectively[2] 1·67 and 1·88.

The refractive indices for light of various wavelengths along the three crystal axes are as follows:[3]

		Li	Na	Tl
$Na_2HAsO_4.12H_2O$	α .	1·4420	1·4453	1·4482
	β .	1·4462	1·4496	1·4513
	γ .	1·4480	1·4513	1·4545
$Na_2HAsO_4.7H_2O$	α .	1·4587	1·4622	1·4655
	β .	1·4623	1·4658	1·4689
	γ .	1·4746	1·4782	1·4812

The equivalent conductivity is as follows[4] (for solutions containing $\frac{1}{2}Na_2HAsO_4$ in v litres):

v . .	32	64	128	256	512	1024	∞
Λ . .	79·0	84·7	88·8	92	94·4	95·9	103·8

An investigation[5] of the temperature-concentration curves of the system Na_2HAsO_4-H_2O over the range $< 0^\circ$ to 120° C. reveals transition points which indicate the existence of the anhydrous salt and hydrated forms containing 0·5, 5, 7 and $12H_2O$. The normal boiling point of the saturated solution is 116° C. The existence of a *hemihydrate* has not been confirmed, but Menzel and Hagen state[6] that a

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[1] Dufet, *Zeitsch. Kryst. Min.*, 1888, **14**, 610; *Bull. Soc. franç. Min.*, 1887, **10**, 77.

[2] Dufet, *loc. cit.*; Schiff, *Annalen*, 1860, **113**, 196.

[3] Dufet, *loc. cit.*

[4] Walden, *Zeitsch. physikal. Chem.*, 1888, **2**, 53.

[5] Chrétien and Genet, *Compt. rend.*, 1935, **200**, 834.

[6] Menzel and Hagen, *Zeitsch. anorg. Chem.*, 1937, **233**, 209.

monohydrate exists, and have determined the following transition points: anhyd. $\rightleftharpoons$ $1H_2O$, 99·5° C.; anhyd. (metastable) $\rightleftharpoons$ $5H_2O$, 68·0° C.; $1H_2O \rightleftharpoons 5H_2O$, 67·4° C.; $5H_2O \rightleftharpoons 7H_2O$, 56·3° C.; $7H_2O \rightleftharpoons 12H_2O$, 20·5° C. The cryohydric point is −1·138° C.

Sodium Dihydrogen Orthoarsenate, NaH_2AsO_4, is formed when an aqueous solution of sodium carbonate is treated with arsenic acid until the solution gives no precipitate with barium chloride;[1] after concentration and cooling thoroughly, crystals of the *monohydrate*, $NaH_2AsO_4.H_2O$, slowly separate. The crystals may also be obtained by fusing together equivalent quantities of arsenious oxide and sodium nitrate, dissolving the residue in water and allowing to crystallise.[2] Rhombic crystals, isomorphous with those of the corresponding phosphate, are obtained, the axial ratios[3] being $a:b:c=0·9177:1:1·6039$. The salt is dimorphous,[4] however, and crystallisation from warm solutions yields monoclinic crystals with $a:b:c=1·087:1:1·1588$ and $\beta=92° 22'$. These crystals are unstable at the ordinary temperature, rapidly becoming turbid and passing to the rhombic form without change in weight. The indices of refraction of the latter for sodium light are $\alpha=1·5382$, $\beta=1·5535$ and $\gamma=1·5607$. The density[5] is 2·67. The aqueous solution, when concentrated until the density is 1·7, deposits rhombic octahedra of the *dihydrate*, $NaH_2AsO_4.2H_2O$.[6] These are isomorphous with those of the corresponding phosphate and have axial ratios $a:b:c=0·9177:1:1·6039$ and density 2·309. The indices of refraction for sodium light are $\alpha=1·4794$, $\beta=1·5021$ and $\gamma=1·5265$. The dihydrate is efflorescent in air.

The monohydrate loses water of crystallisation at 130° C. and on further heating yields a product which has been described[7] as *sodium metarsenate*, $NaAsO_3$, but which dissolves in water to form sodium dihydrogen orthoarsenate. Similarly, when sodium monohydrogen orthoarsenate is strongly heated (above 250° C.) the product appears to be *sodium pyroarsenate*, $Na_4As_2O_7$, and this re-forms the orthoarsenate on dissolution in water.[8] The existence of the meta- and pyro-arsenates is not established (*cf.* p. 182). Both products when heated in hydrogen or carbon monoxide yield volatile arsenic.[9]

Complex salts of composition $Na_3H_3(AsO_4)_2.3H_2O$, $Na_3K_3H_6(AsO_4)_4.9H_2O$ and $Na_3(NH_4)_3H_6(AsO_4)_4.6H_2O$ have been described,[10] as also have $NaKHAsO_4.nH_2O$[11] ($n=7–9$), $Na(NH_4)HAsO_4.4H_2O$[11] and $Na(NH_4)_2AsO_4.4H_2O$.[12]

In the presence of sodium hydroxide, arsenic pentoxide reacts with

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[1] Mitscherlich, *Ann. Chim. Phys.*, 1821, [2], 19, 350, 407.

[2] Hörmann, *Thesis*, Erlangen, 1879.

[3] Joly and Dufet, *Compt. rend.*, 1886, 102, 259, 1391; *Bull. Soc. franç. Min.*, 1886, 9, 194.

[4] Dufet, *ibid.*, 1887, 10, 77.

[5] Dufet, *loc. cit.* Schiff (*Annalen*, 1859, 112, 92; 1860, 113, 196) gave 2·535.

[6] Joly and Dufet, *loc. cit.*

[7] Hörmann, *loc. cit.*; Streng, *Berg. Hütt. Zeit.*, 1860, 19, 128; *Annalen*, 1864, 129, 241: Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 53.

[8] Hörmann, *loc. cit.*; Walden, *loc. cit.*; Clark, *Edin. J. Sci.*, 1827, 7, 298, 309, 311, 314; Marx, *Kastner's Arch.*, 1824, 2, 18; Schiefer, *Zeitsch. Ges. Naturw. Halle*, 1864, 23, 350.

[9] Lefèvre, *Thesis*, Paris, 1891; *Ann. Chim. Phys.*, 1892, [6], 27, 19; Soubeiran, *ibid.*, 1830, [2], 43, 407.

[10] Filhol and Senderens, *Compt. rend.*, 1881, 93, 388; 1882, 95, 343; 1883, 96, 1051.

[11] Mitscherlich, *loc. cit.*

[12] Uelsmann, *Arch. Pharm.*, 1859, [2], 99, 145.

the hydroxides of aluminium, chromium and ferric iron to form complex salts of composition $NaH_2[Al(AsO_4)_2].0{\cdot}5H_2O$, $NaH_2[Cr(AsO_4)_2].H_2O$ and $NaH_2[Fe(AsO_4)_2].H_2O$, respectively.[1] Corresponding salts of bismuth, cobalt, thallium or lanthanum are not formed under the same conditions.

Strontium Arsenates.—*Strontium Orthoarsenate*, $Sr_3(AsO_4)_2$, may be prepared by neutralising aqueous arsenic acid with strontia-water,[2] or by adding ammonia to a solution of strontium monohydrogen arsenate in dilute hydrochloric acid;[3] in either case the precipitate is separated and well washed with water. The salt may also be obtained by fusing together equal quantities of sodium chloride and sodium orthoarsenate and adding the required proportion of strontium oxide; after cooling, the sodium salts are removed by washing with water.[4] Colourless rhombic crystals of density 4·601 are obtained, readily soluble in dilute acids. The salt melts[5] at 1635° C. When heated at 400° to 450° C. in hydrogen, reduction occurs to give strontium oxide, arsenic and water.[6]

Strontium Monohydrogen Arsenate, $SrHAsO_4$, may be prepared as follows:[7] Strontium hydroxide is added slowly and with stirring to a solution of arsenic acid (containing 75 g. As_2O_5 in 1·5 litres H_2O) until a slight turbidity appears. Sodium hydroxide, free from carbonate, is then added to bring the pH to about 5·4, the faintly turbid solution heated in portions of about 150 c.c. and stirred until the monohydrogen orthoarsenate separates in fine crystals. The supernatant liquid is removed, again treated with sodium hydroxide and heated to give a further yield. The crystals are washed with alcohol and dried in air. They usually contain a slight excess of arsenic acid.

The salt may also be obtained by the action of hot water on strontium dihydrogen orthoarsenate[8] or on the pyroarsenate;[9] or by the action of ammonia on a hot solution in hydrochloric acid of the precipitate obtained by mixing solutions of strontium chloride and sodium monohydrogen orthoarsenate.[10] In the last case the anhydrous salt crystallises out, but if the mother liquor is kept in an atmosphere of ammonia, the *monohydrate*, $SrHAsO_4.H_2O$, crystallises out. The density of the latter is 3·606 at 15° C. and of the anhydrous salt 4·035. The monohydrate becomes anhydrous at 130° C. and at a higher temperature yields the pyroarsenate.[11]

Strontium Dihydrogen Orthoarsenate, $Sr(H_2AsO_4)_2$, may be prepared[12] by adding 24 g. of strontium hydroxide to an aqueous solution of arsenic acid (containing 60 g. As_2O_5 in 90 c.c.) and heating until a

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[1] Rosenheim and Thon, *Zeitsch. anorg. Chem.*, 1927, 167, 1.

[2] Blarez, *Compt. rend.*, 1886, 103, 639.

[3] Kotschoubey, *J. prakt. Chem.*, 1850, [1], 49, 189.

[4] Lefèvre, *Compt. rend.*, 1889, 108, 1058; *Thesis*, Paris, 1891; *Ann. Chim. Phys.*, 1892, [6], 27, 22.

[5] Guérin, *Compt. rend.*, 1936, 203, 997.

[6] Guérin, *Compt. rend.*, 1936, 203, 1163.

[7] Tartar, Rice and Sweo, *J. Amer. Chem. Soc.*, 1931, 53, 3949.

[8] Hormann, *Thesis*, Erlangen, 1897.

[9] Lefèvre, *loc. cit.*

[10] de Schulten, *Bull. Soc. franç. Min.*, 1903, 26, 18; 1904, 27, 104. See also Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 143; Joly, *Compt. rend.*, 1886, 103, 746, 1197; 1887, 104, 1702.

[11] Salkowski, *loc. cit.*; Hormann, *loc. cit.*

[12] Tartar, Rice and Sweo, *loc. cit.*

clear solution is obtained. On prolonged boiling, much of the dihydrogen salt crystallises out and, after filtration, a further crop may be obtained from the mother liquor. The crystals should be washed with alcohol and dried. Like the monohydrogen salt they usually contain a slight excess of arsenic acid.

The *dihydrate*, $Sr(H_2AsO_4)_2.2H_2O$, may be obtained by treating strontium carbonate with an excess of arsenic acid.[1] The crystals lose their water of crystallisation at 240° to 250° C. and on further heating yield *strontium metarsenate*, $Sr(AsO_3)_2$.

Strontium Pyroarsenate, $Sr_2As_2O_7$, is formed when the monohydrogen orthoarsenate is heated above 360° C.[1] or when potassium monohydrogen orthoarsenate is fused with strontium oxide or carbonate.[2] It is slightly soluble in mineral acids.

A *basic arsenate* of composition $3Sr_3(AsO_4)_2.Sr(OH)_2$ has been obtained[3] as a fine flaky precipitate by the action of sodium hydroxide and strontia-water on an acidified solution of sodium monohydrogen orthoarsenate, care being taken to ensure the absence of carbonate.

Salts of the type $MSrAsO_4$ (where $M = NH_4$, K or Na) have been obtained,[4] as also have the following pyroarsenates,[5] $SrCuAs_2O_7$ and $SrHgAs_2O_7$ (*cf.* p. 195).

Thallium Arsenates.—*Thallous Orthoarsenate*, Tl_3AsO_4, has been obtained by the action of ammonia on a solution of the dihydrogen salt.[6] It separates as white silky needles.

Thallous Monohydrogen Orthoarsenate, Tl_2HAsO_4, has been prepared by dissolving thallium in aqueous arsenic acid,[7] or by saturating a boiling solution of the latter with thallous carbonate.[8] It separates on cooling as long transparent needle-shaped crystals, soluble in water. When heated, the salt melts at 120° C. and at a higher temperature decomposes to form thallous oxide and arsenious oxide. *Thallous dihydrogen orthoarsenate*, TlH_2AsO_4, is formed by boiling thallic oxide in aqueous arsenious acid; on cooling the solution colourless glittering needle-shaped crystals separate.[9] The salt is readily soluble in water and may be heated to 150° C. without decomposition.

Thallic Orthoarsenate, $TlAsO_4.2H_2O$, separates as a lemon-yellow gelatinous mass when aqueous arsenic acid is added to a solution of thallic nitrate.[9] It is insoluble in boiling water, readily soluble in hydrochloric acid and decomposed by aqueous alkali or ammonia with formation of thallic hydroxide or a basic salt.

Thorium Arsenates.—When solutions of thorium salts are treated with aqueous arsenic acid, the precipitates vary in composition according to conditions.[10] The normal orthoarsenate has not been prepared. *Thorium monohydrogen orthoarsenate*, $Th(HAsO_4)_2.6H_2O$, is obtained[11] as a crystalline precipitate by adding aqueous arsenic acid (40 per cent.)

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[1] Hörmann, *loc. cit.*

[2] Lefèvre, *loc. cit.*

[3] Tartar, Rice and Sweo, *loc. cit.*

[4] Lefèvre, *loc. cit.*; Baumann, *Arch. Pharm.*, 1844, [1], 36, 299; 39, 10.

[5] Rosenheim and Antelmann, *Zeitsch. anorg. Chem.*, 1930, 187, 385.

[6] Willm, *Ann. Chim. Phys.*, 1865, [4], 5, 5.

[7] Oettinger, *Thesis*, Berlin, 1864, p. 64.

[8] Lamy, *Ann. Chim. Phys.*, 1865, [4], 5, 410, 421; *Thesis*, Paris, 1863.

[9] Willm, *loc. cit.*

[10] Berzelius, *Pogg. Annalen*, 1829, 16, 412; Barbieri, *Atti R. Accad. Lincei*, 1910, [5], 19, ii, 642.

[11] Barbieri, *loc. cit.*

to a boiling solution of thorium nitrate (≡ 2 per cent. ThO_2). If the solutions are more dilute, amorphous or gelatinous precipitates of variable composition are formed. The crystals readily lose water in air. They are gradually decomposed in contact with water, owing to hydrolysis. The salt is insoluble in dilute nitric acid.

Thorium Dihydrogen Orthoarsenate, $Th(H_2AsO_4)_4.4H_2O$, is obtained in a manner similar to the above, using 50 per cent. aqueous arsenic acid and thorium nitrate solution containing the equivalent of 5 per cent. thoria. It separates as colourless crystals. The salt is converted to the monohydrogen salt by the action of water.

Thorium arsenate gels have been prepared.[1]

Tin Arsenates.—The arsenates of tin are not well-defined. *Stannous monohydrogen orthoarsenate*, $SnHAsO_4.0{\cdot}5H_2O$, separates as a white bulky precipitate when a solution of potassium orthoarsenate in concentrated acetic acid is gradually added to stannous chloride solution.[2] On heating it decomposes into stannic oxide and arsenious oxide, and a trace of arsenic is liberated. *Stannic orthoarsenate*, $Sn_3(AsO_4)_4.6H_2O$, has been obtained[3] in the form of a gel by adding stannic chloride to moderately concentrated aqueous arsenic acid; the mixture gradually thickens and after some weeks becomes set. On dialysis it yields a transparent colourless gel of density 1·135. It is slowly soluble in water and is reprecipitated on addition of mineral acids or certain salts, such as chloride of ammonium, calcium or iron or silver nitrate, but not by mercuric chloride, alkali carbonate, acetic acid or alcohol. Concentrated acids and alkalies readily dissolve the gel. It is decomposed on heating, much water being expelled at 100° C. but a little being retained even above 200° C.; arsenious oxide is liberated below a dull red heat.

A basic stannic pyroarsenate, $SnAs_2O_7.SnO_2.10H_2O$, is obtained when the white gelatinous precipitate formed by boiling a solution containing sodium stannate, excess of sodium orthoarsenate and nitric acid, is dried at the ordinary temperature.[4] The salt becomes anhydrous at 120° C.

By mixing sodium stannate and sodium orthoarsenate in alkaline solution, or by dissolving stannic orthoarsenate in sodium hydroxide and allowing to crystallise, the compound $Na_2SnO_3.5Na_3AsO_4.60H_2O$ has been obtained[5] as white needle-shaped crystals. The compound $6Na_2O.SnO_2.2As_2O_5.50H_2O$ has also been described.[4]

Titanyl Arsenate has been described[6] as a flocculent precipitate formed by adding aqueous arsenic acid to a solution of titanic acid in hydrochloric acid made as nearly neutral as possible. It is soluble in excess of either titanic or hydrochloric acid. The composition of the product has not been verified.

Tungsto-arsenic Acids and **Tungsto-arsenates.**—These compounds are analogous to the phosphotungstic acids and their salts (see this Series, Vol. VII, Part III), but the complex anions are

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[1] Prakash and Dhar, *J. Indian Chem. Soc.*, 1929, 6, 391, 587; 1930, 7, 367, 417, 591; Prakash, *ibid.*, 1932, 9, 193; *J. Physical Chem.*, 1932, 36, 2483; *Zeitsch. anorg. Chem.*, 1931, 201, 301; *J. Soc. Chem. Ind.*, 1931, 50, 387T.

[2] Lenssen, *Annalen*, 1860, 114, 113. See also Scheele, *Svenska Vet. Akad. Handl.*, 1775, 36, 265.

[3] Williams, *Proc. Manchester Lit. Phil. Soc.*, 1876, 15, 67.

[4] Haeffely, *Phil. Mag.*, 1855, [4], 10, 290.

[5] Prandtl and Rosenthal, *Ber.*, 1907, 40, 2133.

[6] Rose, "*Ausführliches Handbuch der analytischen Chemie*," Braunschweig, 1851, 1, 283.

essentially more unstable than those of the phosphorus compounds. They are analogous also to the molybdo-arsenates (see p. 214). The investigation of these acids and salts is as yet very incomplete.[1]

12-Tungsto-arsenates.—Only the *ammonium salt*, $(NH_4)_3H_4[As(W_2O_7)_6].4H_2O$, has been prepared. It separates as a white crystalline precipitate when a solution containing normal sodium tungstate (8 gram-molecules) and arsenic acid (1 gram-molecule) is acidified with hydrochloric acid, treated with solid ammonium chloride, and boiled.[2] The free acid is unstable and undergoes hydrolysis in solution.

11-Tungsto-arsenates.—These are completely analogous to the 11-tungstophosphates. The *barium salt*, $7BaO.As_2O_5.22WO_3.54H_2O$ or $Ba_{3.5}[As(OH)(W_2O_7)_5]–W_2O_7–[(W_2O_7)_5(OH)As]Ba_{3.5}.53H_2O$, is obtained by adding a 5 per cent. solution of ammonium carbonate to a suspension of the ammonium 12-tungsto-arsenate in boiling water until a clear solution results, when, on adding barium chloride, the salt crystallises in double pyramids isomorphous with the corresponding phosphate. Other salts of the series may be obtained from the barium salt by double decomposition. As indicated by the co-ordination formula, the molecule is considered to contain two nuclei joined by an outer bridge.

9-Tungsto-arsenic acid (*luteo-arsenotungstic acid*) may be obtained by saturation of a boiling solution of an alkali arsenate with tungstic anhydride and allowing the mixture to stand for several weeks until the reactions of the 12-tungsto-arsenate have disappeared; or by acidifying a solution of one of its salts and shaking out with ether. The acid is isomorphous with the corresponding phosphoric acid and has the composition $H_5[As(OH)(W_2O_7)_4–W_2O_7–(W_2O_7)_4(OH)As]H_5.36H_2O$, the two nuclei being joined by an inner bridge. It melts at 26° C. Only the tribasic ammonium and potassium salts of this series have been prepared. These are obtained by adding arsenic acid to a boiling solution of alkali tungstate until the colour becomes deep yellow, and then treating with ammonium or potassium chloride. On evaporation the solution yields lemon-yellow crystals of composition $3R_2O.As_2O_5.18WO_3.xH_2O$ ($R = NH_4$, K).

17 : 2-Tungsto-arsenates.—Solutions of the 9-tungsto-arsenates, when treated with the corresponding carbonates until the yellow colour disappears, yield colourless crystalline precipitates of salts belonging to this series, isomorphous with the corresponding phosphates and of composition $5(NH_4)_2O.As_2O_5.17WO_3.16H_2O$ and $5K_2O.As_2O_5.17WO_3.22H_2O$.

Alumino-tungsto-arsenates of composition $6(NH_4)_2O.2Al_2O_3.3As_2O_5.18WO_3.14H_2O$, $4BaO.2Al_2O_3.3As_2O_5.18WO_3.12H_2O$ and $4CdO.2Al_2O_3.3As_2O_5.18WO_3.17H_2O$, have been described.[3]

According to Jander and his co-workers,[4] the gradual addition of

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[1] See Gibbs, *Amer. J. Sci.*, 1877, [3], **14**, 61; *Proc. Amer. Acad.*, 1880, **16**, 134; *Amer. Chem. J.*, 1885–86, **7**, 313; Lefort, *Compt. rend.*, 1881, **92**, 1461; *Ann. Chim. Phys.*, 1882, [5], **25**, 200; Fremery, *Ber.*, 1884, **17**, 296; *Bull. Soc. chim.*, 1884, [2], **42**, 457; Kehrmann, *Annalen*, 1888, **245**, 52; *Bull. Soc. chim.*, 1889, [3], **2**, 19; *Zeitsch. anorg. Chem.*, 1900, **22**, 290; Sweeney, *J. Amer. Chem. Soc.*, 1916, **38**, 2377; Cignoli, *Rev. centro. estud. farm. bioquim*, 1933, **22**, 175.

[2] Rosenheim and Janicke, *Zeitsch. anorg. Chem.*, 1917, **101**, 235.

[3] Daniels, *J. Amer. Chem. Soc.*, 1908, **30**, 1846.

[4] Jander, Mojert and Aden, *Zeitsch. anorg. Chem.*, 1929, **180**, 129; Jander and Banthien, *ibid.*, 1935, **225**, 162.

hydrochloric acid to a solution of an alkali tungstate produces first a polymerisation to hexatungstic acid—

$$6WO_4^{=} + 6H^+ \rightleftharpoons W_6O_{21}^{VI} + 3H_2O$$

the salts of which are identical with the paratungstates. With addition of more acid, further polymerisation occurs to metatungstic acid, which is probably a diparatungstic acid, and in the presence of arsenic acid an heteropoly-acid is formed, thus:

$$H_2WO_4 \longrightarrow H_6[W_6O_{21}] \longrightarrow H_8[As_2(W_2O_7)_9]$$

The existence of such an acid or of derived salts lacks confirmation, however.

Uranium Arsenates.—*Uranous Monohydrogen Orthoarsenate*, $U(HAsO_4)_2.2H_2O$, may be prepared by digesting freshly precipitated uranous hydroxide with cold dilute arsenic acid;[1] or by adding arsenic acid to a solution of the hydroxide in sulphuric acid. It yields pale green needle-shaped crystals, insoluble in water but soluble in excess of arsenic acid. A *tetrahydrate*, $U(HAsO_4)_2.4H_2O$, is formed as a green precipitate when an alkali arsenate is added to a solution of a uranous salt.[2]

Uranyl Orthoarsenate, $(UO_2)_3(AsO_4)_2.12H_2O$, occurs in Nature as *trögerite*. It is yellow in colour, but on heating turns reddish-brown, with loss of water; on cooling, the product again becomes yellow.[3] It breaks down when heated with water, yielding micaceous leaflets. The compound has been produced artificially.[4]

Uranyl Monohydrogen Orthoarsenate, $UO_2HAsO_4.4H_2O$, is obtained[5] as a pale yellow powder by the addition of uranyl acetate to a solution of arsenic acid or sodium arsenate. It is insoluble in water and acetic acid.

Uranyl Dihydrogen Orthoarsenate, $UO_2(H_2AsO_4)_2.3H_2O$, separates in small yellow crystals when a solution of uranyl acetate or nitrate containing an excess of arsenic acid is concentrated.[6] The crystals lose their water of crystallisation at 150° C.

Uranyl Pyroarsenate, $(UO_2)_2As_2O_7$, remains as a yellow powder when the arsenate, $UO_2HAsO_4.4H_2O$, or ammonium uranyl arsenate (see below), is heated.[7]

Several double arsenates occur in Nature (see p. 16), for example: *zeunerite*, $Cu(UO_2)_2(AsO_4)_2.8H_2O$; *uranospinite*, $Ca(UO_2)_2(AsO_4)_2.8H_2O$, corresponding to the phosphates chalcolite and autunite; and *walpurgite*, a basic bismuth uranyl arsenate. Compounds having the same composition as zeunerite and uranospinite may be formed artificially[8] by mixing a solution of precipitated copper carbonate, or of lime, in excess of arsenic acid with a solution of uranyl acetate or nitrate; on allowing to crystallise, rectangular laminæ are obtained. By similar means the ammonium salt, $NH_4UO_2AsO_4$, containing 3 and $5H_2O$, has been prepared.[9] The potassium salt is not easily obtained, since the

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[1] Aloy, *Bull. Soc. chim.*, 1899, [3], **21**, 613.

[2] Rammelsberg, *Pogg. Annalen*, 1842, **55**, 318; **56**, 125.

[3] Winkler, *J. prakt. Chem.*, 1873, [2], **7**, 7.

[4] Goldschmidt, *Chem. Zentr.*, 1899, [2], 785; Kraft, *Compt. rend.*, 1938, **206**, 57.

[5] Werther, *Annalen*, 1848, **68**, 313; Kraft, *loc. cit.*

[6] Werther, *loc. cit.*

product resulting from the reaction between potassium arsenate and a uranyl salt varies in composition with the concentration of the solutions.[1] The salt, $KUO_2AsO_4.3{\cdot}5H_2O$, has been obtained [2] by the prolonged action of arsenic acid on potassium uranate as a yellow powder, stable towards water.

Vanado-arsenates.—These compounds are analogous to the molybdo- and tungsto-arsenates (see pp. 214, 229). They are derived from the hypothetical arseno-acid $H_7[AsO_6]$. The salts which have hitherto been prepared are all of low vanadium pentoxide content compared with the amount of arsenic pentoxide present, and correspond therefore to the *luteo* vanado-phosphates (see Vol. VI, Part III). Three series are known. The first has the general formula $2R''O.V_2O_5.As_2O_5.xH_2O$ or $R''\left[\mathrm{As}^{\mathrm{VO_3}}_{\mathrm{O_3}}\right].x, 2H_2O$, where R″ may be Mg, Zn, Cu or Co. They form yellow crystals which are obtained by the addition of arsenic pentoxide to solutions of the respective vanadates, or by the action of the carbonate of the metal on the free vanado-arsenic acid (see below). Of the second series only the *ammonium* and *potassium* salts are known, viz. $(NH_4)_2O.2V_2O_5.As_2O_5.5H_2O$ or $(NH_4)\left[\mathrm{As}^{\mathrm{(VO_3)_2}}_{\mathrm{O_2}}\right].2{\cdot}5H_2O$, and $K_2O.2V_2O_5.As_2O_5.5H_2O$ or $K\left[\mathrm{As}^{\mathrm{(VO_3)_2}}_{\mathrm{O_2}}\right].2{\cdot}5H_2O$. These also give rise to yellow crystals. The third series has the general formula $2R'_2O.2V_2O_5.3As_2O_5.xH_2O$, where R'_2 may be $(NH_4)_2$, 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.[3]

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 $V_2O_5.As_2O_5.10H_2O$ or $H_2\left|\mathrm{As}^{\mathrm{VO_3}}_{\mathrm{O_3}}\right|.4H_2O$. Recrystallisation of this hydrate from concentrated nitric acid gives a *dihydrate*, $V_2O_5.As_2O_5.2H_2O$, which can be looked upon as the acid $H_2\left[\mathrm{As}^{\mathrm{VO_3}}_{\mathrm{O_3}}\right]$. The *anhydride*, $V_2O_5.As_2O_5$, is obtained by heating the dihydrate to 440° C.

Molybdo-vanadoarsenates. A number of compounds have been described which are analogous to the molybdo-vanadophosphates, and which contain arsenic for the nuclear atom of the complex anion. In many cases these compounds approximate to the general formula $R'_6H\left[\mathrm{As}^{(V_2O_6)_x}_{(Mo_2O_7)_y}\right].nH_2O$, 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.[4]

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[1] Werther, *loc. cit.* See Abegg-Auerbach, "*Handbuch der anorganischen Chemie*," Leipzig, 1921, IV, 1, ii, 951.

[2] Rimbach, with Burgher and Grewe, *Ber.*, 1904, 37, 461.

[3] Fernandez, *Ber.*, 1884, 17, 1632; Gibbs, *Amer. Chem. J.*, 1886, 7, 209; Ditte, *Compt. rend.*, 1886, 102, 757, 1019; Friedheim and Schmitz-Dumont, *Ber.*, 1890, 23, 1530, 2600; Schmitz-Dumont, *Dissertation*, Berlin, 1891.

[4] Canneri, *Gazzetta*, 1923, 53, 773; 1926, 56, 871.

Tungsto-vanadoarsenates.—These are comparable to the molybdo-vanadoarsenates, and can be represented generally as

$$R'_6H\left[As^{(V_2O_6)_x}_{(W_2O_7)_y}\right].nH_2O$$

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, whence 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:

$$(NH_4)_6H\left[As^{(V_2O_6)_2}_{(W_2O_7)_4}\right].nH_2O\ ; \qquad (NH_4)_6H\left[As^{(V_2O_6)_3}_{(W_2O_7)_3}\right].25H_2O\ ;$$

$$(NH_4)_6H\left[As^{(V_2O_6)_4}_{(W_2O_7)_2}\right].25H_2O$$

Barium and *thallium salts* have also been described, and some of the free acids have been isolated.[1]

Canneri [2] 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 $(Mo_2O_7)''$.[3]

Tungsto-vanadoarsenophosphates.—Several ammonium salts have been prepared, which are most probably isomorphous mixtures of arsenates and phosphates.[4]

Vanado-tungstomolybdoarsenophosphates have been described; these are also isomorphous mixtures of simpler compounds.[5]

Zinc Arsenates.—*Zinc Orthoarsenate*, $Zn_3(AsO_4)_2$, has been obtained in the anhydrous form by heating zinc carbonate with aqueous arsenic acid to 200° C.[6] or by fusing a mixture of zinc chloride and arsenic pentoxide.[7] The latter process yields prismatic crystals of density 4·913 at 15° C. The *trihydrate*, $Zn_3(AsO_4)_2.3H_2O$, is precipitated

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[1] Gibbs, *loc. cit.*; Rogers, *J. Amer. Chem. Soc.*, 1903, 25, 298; Canneri, *Gazzetta*, 1923, 53, 773, 779; 1925, 55, 883; 1926, 56, 871; Rodolico, *Atti R. Accad. Lincei*, 1926, [6], 4, 471.

[2] Canneri, *Gazzetta*, 1926, 56, 871.

[3] Rodolico, *loc. cit.*

[4] Rogers, *loc. cit.*; Rodolico, *loc. cit.*; Canneri, *loc. cit.*

[5] Rogers, *J. Amer. Chem. Soc.*, 1903, 25, 312; Rodolico, *loc. cit.*; Canneri, *loc. cit.*

[6] Friedel, *Ber.*, 1876, 9, 734.

from zinc sulphate solutions by normal sodium orthoarsenate.[1] The same substance is precipitated in a white voluminous form when excess of alkali is added to solutions of acid zinc arsenates in hydrochloric acid.[2] The *octahydrate*, $Zn_3(AsO_4)_2.8H_2O$, occurs naturally, associated with cobalt and nickel ores, as *köttigite* (see p. 15), a pinkish mineral found in Germany in the massive form or in crystalline crusts with a fibrous structure; the crystals are isomorphous with vivianite.[3] The octahydrate may be obtained artificially by adding a soluble arsenate to a solution of a zinc salt, the quantity added being insufficient to remove completely the acidity of the solution;[4] or by mixing solutions of zinc monohydrogen orthoarsenate and zinc sulphate.[5] The precipitate formed is amorphous but, if kept in contact with the solution for some days, the crystalline octahydrate is formed.

Zinc Monohydrogen Orthoarsenate, $ZnHAsO_4.H_2O$, is obtained as a jelly by treating zinc with excess of aqueous arsenic acid, heating, and filtering at 100° C.;[6] or by mixing solutions of potassium dihydrogen orthoarsenate and zinc sulphate in appropriate proportions.[7] The jelly gradually crystallises on keeping, or when treated with hot water; the crystals are either rhombic or monoclinic. Small white tabular or needle-like crystals of this salt may be prepared by dissolving zinc oxide in aqueous arsenic acid.[8] The salt has also been obtained by prolonged contact between zinc orthophosphate trihydrate and aqueous arsenic acid,[9] and by prolonged digestion at 100° C. of the precipitate obtained by adding ammonium arsenate to a solution of a zinc salt.[10]

An *acid salt*, of composition $5ZnO.2As_2O_5.4H_2O$, has been obtained as a precipitate by mixing aqueous solutions of zinc sulphate and sodium orthoarsenate.[11] It loses one quarter of its water at 100° C. By heating the monohydrogen orthoarsenate in a sealed tube at 200° C. rhombic crystals of composition $5ZnO.2As_2O_5.nH_2O$, probably $Zn_3(AsO_4)_2.2ZnHAsO_4.(n-1)H_2O$, are obtained.[12]

Zinc Metarsenate, $Zn(AsO_3)_2$, has been described as a heavy white powder formed by allowing zinc orthoarsenate trihydrate to remain in contact with aqueous arsenic acid for more than a year and then filtering the solution.[13]

Zinc Pyroarsenate, $Zn_2As_2O_7$, is obtained by dissolving zinc oxide in molten potassium metarsenate.[14] It yields tabular crystals isomorphous with manganese pyroarsenate. The salt is decomposed by water. A basic salt, of composition $Zn(OH)_2.Zn_2As_2O_7.7H_2O$, has been obtained[12] by mixing solutions of zinc orthoarsenate and zinc acetate, and boiling the precipitate with water for several weeks; silky crystalline needles are finally obtained, from which all the water may be expelled at 300° C.

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[1] Salkowski, *J. prakt. Chem.*, 1868, [1], **104**, 129.

[2] Demel, *Ber.*, 1879, **12**, 1279.

[3] Groth, "*Die Mineraliensammlung der Universitat Strassburg*," 1878, p. 166.

[4] Skey, *Chem. News*, 1870, **22**, 61.

[5] de Schulten, *loc. cit.*

[6] Coloriano, *Bull. Soc. chim.*, 1886, [2], **45**, 709.

[7] Klemp and Gyulay, *Kolloid-Zeitsch.*, 1918, **22**, 57.

[8] Demel, *Ber.*, 1879, **12**, 1279.

[9] Debray, *Compt. rend.*, 1864, **59**, 40.

[10] Debray, *loc. cit.*

[11] Salkowski, *J. prakt. Chem.*, 1868, [1], **104**, 129.

[12] Goguel, *Thesis*, Bordeaux, 1896.

[13] Salkowski, *Ber.*, 1879, **12**, 1446.

[14] Lefèvre, *Compt. rend.*, 1890, **110**, 405; "*Sur les Arséniates cristallisés*," Paris, 1891; *Ann. Chim. Phys.*, 1892, [6], **27**, 22.

The *basic salt* $4ZnO.As_2O_5.H_2O$ is produced when zinc monohydrogen orthoarsenate crystals are heated with water.[1] It occurs naturally as *adamite* (see p. 14), which may be green, yellow, violet or colourless and is usually formulated $Zn(Zn.OH)AsO_4$. *Legrandite*,[2] a bright yellow transparent mineral associated with massive blende in Mexico, has a composition approximating to $Zn_{14}(OH)(AsO_4)_9.12H_2O$.

The following *double arsenates* have been described: $NaZnAsO_4$, $Na_2ZnAs_2O_7$, $K_2Zn_2As_2O_8$ [3] and NH_4ZnAsO_4.[4]

Zirconium Arsenates.—*Zirconium Orthoarsenate*, $Zr_3(AsO_4)_4.5H_2O$, has been obtained[5] as a voluminous white precipitate by adding sodium monohydrogen orthoarsenate to a solution of zirconyl fluoride in hydrochloric acid. *Zirconium monohydrogen orthoarsenate*, $Zr(HAsO_4)_2$, appears to be formed slowly by adsorption of arsenic acid by zirconium dioxide.[6]

Zirconyl Pyroarsenate, $(ZrO)_2As_2O_7.nH_2O$, is obtained as a white precipitate when sodium monohydrogen orthoarsenate is added to a solution of zirconium sulphate.[7] When dried at 110° C. the monohydrate, $(ZrO)_2As_2O_7.H_2O$, remains. It is insoluble in water, but readily dissolves in hydrochloric acid.

PERARSENATES.

Perarsenic acid has not been isolated, but by the action of hydrogen peroxide or of metallic peroxides on the alkali arsenates, products are obtained which contain peroxidic oxygen. Whether these products are to be regarded as true perarsenates or as additive compounds of the arsenates with hydrogen peroxide has not been satisfactorily elucidated.

The alkali "perarsenates" may be obtained by evaporating under reduced pressure an aqueous solution of the arsenate containing hydrogen peroxide.[8] The product with normal sodium orthoarsenate has been formulated[9] $3Na_3AsO_4.5H_2O_2.16H_2O$. By the action of sodium peroxide on a cooled solution of sodium monohydrogen orthoarsenate in aqueous alcohol, a precipitate is obtained which, after drying *in vacuo* in the presence of phosphorus pentoxide, yields a product which was described by Alvarez[10] as the perarsenate, $NaAsO_4$. Coons,[11] however, found that the precipitate varied in composition and, after excess of water was removed over concentrated sulphuric acid under reduced pressure, approximated to $2Na_3AsO_4.7Na_2O_2.2NaOH.75H_2O$. He also found that when the monohydrogen salt was treated with 5 per cent. hydrogen peroxide[12] no compound containing active oxygen was formed, but with 30 per cent. hydrogen peroxide a residue whose composition

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[1] Coloriano, *loc. cit.* According to Demel (*loc. cit.*), $5ZnO.2As_2O_5.5H_2O$ is produced by the action of water on $ZnHAsO_4.H_2O$.

[2] Drugman and Hey, *Mineralog. Mag.*, 1932, 23, 175.

[3] Lefèvre, *loc. cit.*

[4] Meade, *J. Amer. Chem. Soc.*, 1900, 22, 354.

[5] Weibull, *Acta Univ. Lund.*, 1882, 18, 21; *Ber.*, 1887, 20, 1394.

[6] Wedekind and Wilke, *Kolloid-Zeitsch.*, 1924, 34, 83.

[7] Kulka, *Thesis*, Berne, 1902; Paykull, *Bull. Soc. chim.*, 1873, [2], 20, 67; *Ofvers. Akad. Förh.*, 1873, p. 22.

[8] Askenasy, *German Patents*, 296796, 296888, 299300 (1914).

[9] Petrenko, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 391.

[10] Alvarez, *Chem. News*, 1906, 94, 269; *Ann. Chim. anal. appl.*, 1906, 11, 401.

[11] Coons, *Iowa State Coll. J. Sci.*, 1932, 6, 419.

[12] See also Münzberg, *Lotos*, 1928, 76, 351.

corresponded with the formula $25Na_2HAsO_4.32H_2O_2.16H_2O$ was produced. Both the above products were probably mixtures.

When an alkaline earth peroxide is dissolved in arsenic acid and the solution is evaporated under reduced pressure at a low temperature, a perarsenate is said to be produced,[1] and if an alkali sulphate is added to the solution before evaporation, a solution of the alkali perarsenate is obtained. The latter may be obtained with scarcely any loss of active oxygen by careful evaporation to dryness under reduced pressure. Using the above method of desiccation, however, Coons [2] could not obtain any compound containing active oxygen either by this method or by the electrolytic method.

When an alkali perarsenate is added to aqueous solutions of metallic salts, precipitates containing active oxygen are obtained ; thus salts of the alkaline earths, zinc, cadmium, silver, mercurous mercury, lead and bismuth yield white precipitates, mercuric salts give red precipitates, copper blue, manganese pink, nickel greenish-white and ferrous salts bluish-green. With auric chloride oxygen is liberated, and with ferric chloride ferric hydroxide is precipitated.

Magnesium ammonium orthoarsenate can combine additively with hydrogen peroxide.[3]

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[1] Askenasy, *loc. cit.*

[2] Coons, *loc. cit.*

[3] Münzberg, *loc. cit.*

CHAPTER IX.

ARSENIC AND SULPHUR.

THE occurrence in Nature and the historical importance of the two sulphides, realgar, As_2S_2, and orpiment, As_2S_3, have already been discussed (pp. 9, 23). The existence of a third sulphide, arsenic pentasulphide, As_2S_5, is also well-established, and two others of composition As_3S and As_4S_3 probably exist as definite compounds. Berzelius[1] reported several other products which he assumed to be sulphides. Three of these approximated in composition to the formulæ $As_{12}S$, As_2S_{10} and As_2S_{18}, but they were undoubtedly mixtures of arsenic sulphides with arsenic or sulphur.[2] Investigations of the system As–S have so far established only the existence of the di- and tri-sulphides (see below). A study of the photochemical reaction between yellow arsenic and sulphur dissolved in carbon disulphide,[3] which results in the formation of insoluble products, suggests the possibility of the existence of other sulphides, probably similar to those of phosphorus. The properties of the precipitates are neither those of known sulphides of arsenic nor of mixtures of the two elements. The composition of the products varies with the proportions of arsenic and sulphur dissolved.

The system As–S has been studied by Borodowski[4] and Jonker.[5] The freezing point curve (fig. 11) determined by the former is not continuous, because mixtures containing 20 to 60 per cent. of arsenic were so viscid that definite solidifying points could not be obtained. The form of the curve shows that both orpiment and realgar exist in two forms. The yellow or α-form of orpiment is stable at low temperatures and is converted at 170° C. into the red β-form, which melts at 300° C. The stable α-form of realgar is red and changes at 267° C. into the black β-form, which melts at 307° C. and boils at 565° C. (at 760 mm.). β-realgar forms a discontinuous series of mixed crystals with arsenic, and apparently orpiment and sulphur form mixed crystals. A break in the curve at 301° C. may be due to transformation of α- to β-arsenic, or to the formation of the unstable subsulphide As_3S. The existence of tetrarsenic trisulphide, As_4S_3, is not indicated.

The sublimation curve[6] of the system As–S (fig. 12) was obtained from analyses of the vapour in contact with the boiling liquid. A saturated solution of arsenic in realgar boils at 534° C. and a liquid of composition As_2S_3 resembles natural orpiment in boiling at 707° C.

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[1] Berzelius, *Schweigger's J.*, 1822, 34, 46; *Pogg. Annalen*, 1826, 7, 137.

[2] Kuhn, *Arch. Pharm.*, 1852, [2], 71, 1.

[3] Haenny, *Helv. Chim. Acta*, 1930, 13, 725.

[4] Borodowski, *Sitzungsber. Naturf. Ges. Dorpat.*, 1905, 14, 159; *Chem. Zentr.*, 1906, [2], 297.

[5] Jonker, *Zeitsch. anorg. Chem.*, 1909, 62, 89.

[6] Jonker, *loc. cit.*

The form of the sublimation curve shows that the vapour of the disulphide, As_2S_2, is largely dissociated, whilst the trisulphide, As_2S_3, distils unchanged. This is not in accordance with the work of Szarvasy and Messinger[1] who, from vapour density determinations, concluded that the vapour of the disulphide was considerably associated. The sublimation curves do not show any indication of the formation of a pentasulphide.

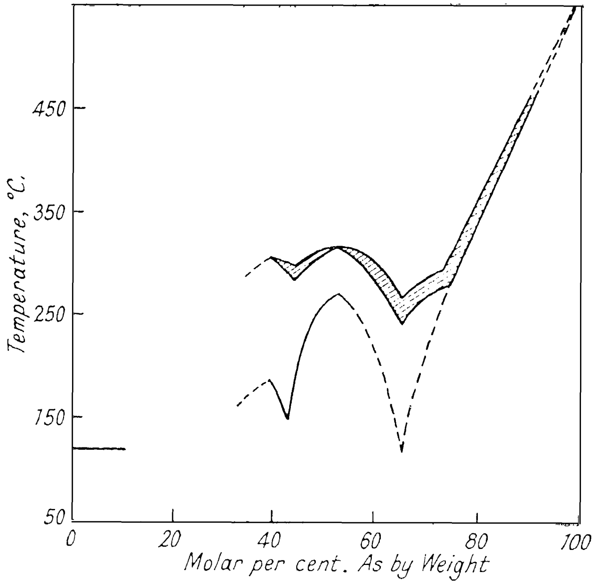

FIG. 11.—Freezing Point Curves of Binary System As–S.

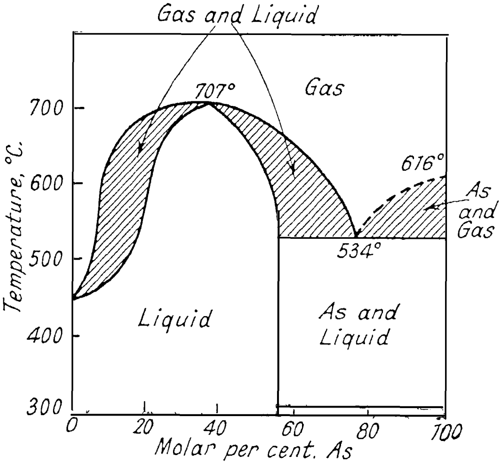

FIG. 12.—Boiling Point Curves of Binary System As–S.

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[1] Szarvasy and Messinger, *Ber.*, 1897, 30, 1343.

Arsenic Subsulphide (*Arsenic Tritasulphide*), As_3S, was first obtained in 1900 by Scott,[1] who treated an aqueous solution of an alkali arsenate with phosphorus trichloride and, after filtering, saturated the mixture with sulphur dioxide. The method of procedure was as follows: 150 c.c. of phosphorus trichloride were added to a solution containing 200 g. of sodium arsenate crystals dissolved in 3·5 litres of water; when cold, the mixture was filtered and sulphur dioxide was passed in. The product was kept for two days, when the supernatant liquor was poured off and the precipitate washed first with water and then with aqueous ammonia. It was then digested for an hour or so with a more concentrated solution of ammonia, hydrogen sulphide being passed into the liquid. Finally the precipitate was washed, first with water and then with alcohol and dried in a vacuum. The subsulphide may be obtained in a similar manner from arsenites, but owing to the precipitation of much arsenious oxide from the strongly acid solution the yield of subsulphide is very much smaller.

By the reducing action of sodium hydrosulphite, $Na_2S_2O_4$, on arsenious oxide or alkali arsenites, in moderately acid solutions, precipitates are obtained,[2] insoluble in colourless ammonium sulphide and containing about 12·7 per cent. of sulphur. These appear to consist of arsenic subsulphide ($As_3S = 12{\cdot}45$ per cent. S) with a small amount of arsenious sulphide. Compounds containing quinquevalent arsenic under similar treatment yield products which approximate in composition to $As_2S_3.As_3S$; in strongly acid solution the precipitates are mainly As_2S_3. In neutral solution only arsenates yield products containing the subsulphide, those from arsenites containing only 6 to 7 per cent. of sulphur; in alkaline solution precipitation occurs only at the boiling point and no subsulphide is produced. In the formation of the subsulphide, intermediate complex compounds of the types $Na_3As(S_2O_4)_3$, sodium arsenohydrosulphite, and $Na_3As(S_2O_3)_3$, sodium arsenothiosulphate, appear to be produced.[3] In no case is the arsenic completely precipitated from the solution.

Arsenic subsulphide is a dark brown powder. It is insoluble in carbon disulphide, in aqueous ammonia and in colourless ammonium sulphide. It dissolves, however, in yellow ammonium sulphide, which is at the same time decolorised, and the addition of an excess of hydrochloric acid to the solution precipitates arsenious sulphide. It is decomposed by caustic alkali. When heated, arsenic subsulphide is resolved into realgar and arsenic.

Tetrarsenic Trisulphide (*Arsenic Tritetritasulphide*), As_4S_3, is obtained by fusing together realgar and an excess of arsenic;[4] after cooling, the product is crushed and extracted with carbon disulphide, or allowed to sublime in a vacuum. Yellow orthorhombic prisms are obtained. This sulphide is also formed in small quantity during the photochemical disintegration of realgar (see p. 242).

The crystals have density 3·60 at 19° C.[4] According to Krenner,[5] the sublimed crystals have axial ratios $a:b:c = 0{\cdot}58787:1:0{\cdot}88258$; the optic axial angle $2H_a = 108°\,46'$ and the optical character is positive.

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[1] Scott, *J. Chem. Soc.*, 1900, 77, 651.

[2] Farmer and Firth, *J. Chem. Soc.*, 1926, p. 119.

[3] Farmer and Firth, *J. Chem. Soc.*, 1927, p. 2019.

[4] Schüller, *Ber. Math. Naturw. Ungarn.*, 1894, 12, 255; *Zeitsch. Kryst. Min.*, 1896, 27, 97.

[5] Krenner, *ibid.*, 1907, 43, 476.

The density of this product he gives as 2·60 at 19° C., a much lower value than that above. On warming, the crystals darken to an orange colour. The vapour dissociates at high temperatures, as is shown by the following values of the vapour density :[1] at 792° C., 8·204 ; at about 1000° C., 6·59 ; ($As_4S_3 = 13·67$).

Minute orange-yellow crystals, of density 3·58, corresponding in composition with As_4S_3, were obtained from a fumarole in Italy by Schacci[2] and named by him *dimorfina*, which later became *dimorphin* or *dimorphite*.[3] It was described as occurring in two crystalline forms, α- and β-dimorphite, both rhombic, but the α-form is probably identical with orpiment (Dana). The nature of the β-form has not been elucidated and it may be a definite species.[4]

Arsenic Disulphide (*Realgar*), As_2S_2, the *sandarach* of Pliny, is also known as the *red sulphide of arsenic* and in the native form as *ruby sulphur*.[5] Although it occurs as a mineral, the realgar of commerce is usually produced artificially. A mixture of mispickel and iron pyrites is distilled in a clay retort, the proportions in the mixture being such that the product will contain excess of arsenic. The condensers are operated at a temperature above the melting point of realgar so that most of the product is obtained in the fused state and any pulverulent material can be re-treated.[6] The fused condensate is allowed to set, crushed to a powder, mixed with additional sulphur to give the composition which will produce the colour tint required, and again fused. To obtain a rich red-coloured product it is not necessary that the elements should be present in stoichiometrical proportions. In fact, although realgar may be produced by fusion of such mixtures of sulphur and arsenic, or sulphur and arsenious oxide,[7] it is better to have the latter in each case in excess or some arsenious sulphide is formed ; the equation for the reaction in the second case is

$$2As_2O_3 + 7S = 2As_2S_2 + 3SO_2$$

It may also be obtained by fusion of a mixture of arsenic and arsenious sulphide[8] in the calculated proportions. A fiery red product is formed by melting arsenious oxide or arsenic pentoxide with sodium thiosulphate.[9] The red sulphide has also been found mixed with other sulphides in the flue dusts obtained during the roasting of arsenical ores.[10]

Realgar may also be prepared in the laboratory by heating arsenious sulphide with an aqueous solution of sodium bicarbonate in a sealed tube at a temperature of 150° C. ; the sulphide dissolves and, on cooling, realgar crystallises from the solution.[11] The same result is obtained by

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[1] Szarvasy and Messinger, *Ber.*, 1897, 30, 1345.

[2] Schacci, *Compt. rend.*, 1850, 31, 263; *Mem. Geol. Campania*, Napoli, 1849, p. 116.

[3] Dana, "*System of Mineralogy*," Wiley, 1914, p. 35.

[4] Krenner, *Zeitsch. Kryst. Min.*, 1907, 43, 476; Kenngott, *Neues Jahrb. Min.*, 1870, p. 537; Stevanovic, *Zeitsch. Kryst. Min.*, 1904, 39, 18.

[5] For the occurrence and history of realgar, see pp. 240–244.

[6] Hayward, "*Outline of Metallurgical Practice*," van Nostrand, New York, 1929, p. 322; Hausmann, *Annalen*, 1850, 74, 197; Kast and Brauning, *Jahresber. Techn.*, 1871, p. 195.

[7] Berzelius, *Schweigger's J.*, 1823, 34, 46; *Pogg. Annalen*, 1826, 7, 137; *Ann. Chim. Phys.*, 1819, [2], 11, 225; 1826, [2], 32, 166; Gélis, *ibid.*, 1873, [4], 30, 114; Nilson, *J. prakt. Chem.*, 1875, [2], 12, 295.

[8] Thénard, *Ann. Chim.*, 1806, [1], 59, 284.

[9] Faktor, *Pharm. Post.*, 1905, 38, 527.

[10] Reich, *Berg. Hütt. Ztg.*, 1864, 23, 115; Fuchs, *Dissertation*, Haarlem, 1872, p. 50.

[11] de Sénarmont, *Ann. Chim. Phys.*, 1851, [3], 32, 159.

dissolving arsenious sulphide in a boiling concentrated aqueous solution of sodium carbonate and cooling the liquid.[1] The disulphide dissolves in hot carbon disulphide and can be recrystallised therefrom.[2] Black needle-shaped crystals of realgar were obtained by Borodowski[3] by heating in a sealed tube at 150° to 300° C. a mixture of arsenic and sulphur in atomic proportions with a 10 per cent. aqueous potassium carbonate solution, and cooling the resulting clear solution.

Properties.—Realgar, both natural and artificial, varies considerably in colour according to the conditions of formation; it may be red, orange-red or orange-yellow, or even black. It forms short, transparent or translucent, prismatic crystals, with axial ratios[4] 0·7201 : 1 : 0·4872 and β 66° 11′. According to Beijerinck,[5] the crystals are pleochroic, being red in the direction of the axis and yellow in the direction of the base. The faces in the prismatic zone are striated vertically. The (010)-cleavage is almost perfect; the (100)-, (001)-, (210)- and (110)-cleavages are somewhat less clear. The hardness is 1·5 to 2·0 and the density[6] 3·2 to 3·5. Borodowski, whose investigation is described above (p. 237), gave $D^{19^\circ}_{19^\circ}$ 3·506 for α-As_2S_2, 3·254 for β-As_2S_2 and 3·161 for the amorphous form. The optical character is negative.[7] The optic axial angle 2H = 96° 20′ for red light and 92° 58′ for yellow light.

In powder form realgar is usually orange-red; when heated the colour darkens to brown, but on cooling returns to the original.[8] The compound melts, according to Borgström,[9] at 310° C. Below this temperature it may be sublimed in a vacuum, and under ordinary pressure out of contact with air it sublimes without change well below red heat.[10] The vapour is yellowish-green and the sublimate reddish-yellow. The following values of the vapour density, determined by Szarvasy and Messinger,[11] show that there is considerable association at lower temperatures:

Temperature, ° C.	450	503	513	574	588	1000 (approx.)	2000 (approx.)
Vapour Density .	19·16	18·5	15·9	13·89	12·52	7·51	6·95

(Theory: As_2S_2 = 7·40)

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[1] Nilson, *J. prakt. Chem.*, 1875, [2], 12, 327; 1876, [2], 13, 1.

[2] Schuller, *loc. cit.*

[3] Borodowski, *Sitzungsber. Naturf. Ges. Dorpat.*, 1905, 14, 159.

[4] Liffa and Emszt, *Foldt. Kozl.*, 1920, 50, 21; Pilz, Schroder and Thost, *Zeitsch. Kryst. Min.*, 1912, 51, 132. *Cf.* Des Cloiseaux, "*Nouvelles Recherches sur les Propriétés optiques des Cristaux*," Paris, 1865, p. 166.

[5] Beijerinck, *Neues Jahrb. Min.*, 1897, 11, 423.

[6] Mohs, "*Grundr. der Mineralogie*," Dresden, 1824, 2, 616; Neumann, *Pogg. Annalen*, 1831, 23, 1; Bottger, "*Tabulated Densities*," Frankfort, 1837.

[7] Des Cloiseaux, *loc. cit.*

[8] Houston, *Chem. News*, 1871, 24, 177.

[9] Borgstrom, *Ofvers. Finska Vet. Soc. Forh.*, 1915, 57, 24. Borodowski (*loc. cit.*) gave 307° C.; Jonker (*Zeitsch. anorg. Chem.*, 1909, 62, 89), 320° C.

[10] Nilson, *J. prakt. Chem.*, 1875, [2], 12, 327; 1876, [2], 14, 19; *Akad. Handl. Stockholm*, 1871, 10, 2; *Ofvers. Akad. Stockholm*, 1871, 28, 303; Saito, *Sci. Rep. Tohoku Univ.*, 1927, 16, 37.

[11] Szarvasy and Messinger, *Ber.*, 1897, 30, 1344.

The boiling point is 565° C. at 760 mm.[1] According to Britzke and his co-workers,[2] the vapour begins to dissociate into its elements between 781° and 830° C., and then contains As_2S_2, As_4, As_2 and S_2 molecules; the dissociation is complete at 1076° C.

The molar heat of formation from solid arsenic and rhombic sulphur has been calculated [3] to be 28,900 calories. This value differs considerably from earlier determinations.[4] From diatomic gaseous sulphur and solid arsenic the heat of formation is calculated [5] to be 51,430 calories.

Under the influence of light, realgar disintegrates to a reddish-yellow powder which consists of arsenious sulphide and arsenious oxide, together with some tetrarsenic trisulphide. It was observed by Weigel [6] that the incidence of light affects the electrical conductivity of the crystals, which is very small [7] but which varies with the wavelength of the incident light, showing maxima at 5300 and 5500 A. Thus, fragments of realgar exposed to direct sunlight for 112 hours behind sheets of glass of various colours show the greatest change with a green glass of maximum transparency near 5200 A. Wiegel concluded that the photochemical disintegration is due to the separation of electrons and the loosening of the atomic linkings, thus facilitating oxidation of the arsenic.

Realgar is less diamagnetic than orpiment both in the solid form and in colloidal solution.[8] The mineral is opaque to X-rays.[9]

Arsenic disulphide is reduced to arsenic when heated in hydrogen; the reaction, which is reversible,

$$As_2S_2 + 2H_2 \rightleftharpoons 2H_2S + As_2$$

commences at about 300° C.[10] In air, oxidation occurs slowly at ordinary temperatures [11] and oxide usually occurs on the surface of natural sulphides, being produced by the reaction

$$6As_2S_2 + 3O_2 = 4As_2S_3 + 2As_2O_3$$

When heated to 215° C., realgar decreases in weight owing to oxidation to arsenious oxide and sulphur dioxide; [12] the reaction becomes more rapid with rise in temperature, and the sulphide finally inflames and burns with a bluish flame.[13] The heat of the reaction representing the roasting process has been given as [14]

$$[As_2S_2] + 3{\cdot}5(O_2) = [As_2O_3] + 2(SO_2) + 271{,}370 \text{ cal.}$$

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[1] Borodowski, *loc. cit.*

[2] Britzke and others, *J. Chem. Ind.* (*U.S.S.R.*), 1931, 8, No. 19, 1; *Zeitsch. anorg. Chem.*, 1932, 205, 95.

[3] Britzke and others, *ibid.*, 1933, 213, 58; *J. Phys. Chem.* (*U.S.S.R.*), 1934, 5, 91.

[4] Britzke and others, *J. Chem. Ind.* (*U.S.S.R.*), 1931, 8, No. 19, 1. Also Jellinek and Zadowsky, *Zeitsch. anorg. Chem.*, 1925, 142, 1.

[5] Britzke and others, *J. Chem. Ind.* (*U.S.S.R.*), 1931, 8, No. 19, 1.

[6] Weigel, *Tsch. Min. Petr. Mitt.*, 1925, 38, 288.

[7] Case, *Phys. Review*, 1917, [2], 9, 305; Beijerinck, *Neues Jahrb. Min.*, 1897, 11, 424.

[8] Bhatnagar and Bhatia, *Proc. 15th Indian Sci. Congress*, 1928, p. 141.

[9] Doelter, *Neues Jahrb. Min.*, 1896, [ii], 91.

[10] Nilson, *J. prakt. Chem.*, 1875, [2], 12, 327; 1876, [2], 14, 19; Pélabon, *Compt. rend.*, 1900, 131, 416; 1901, 132, 774; 1903, 136, 812.

[11] Nilson, *loc. cit.*; Schuller, *Ber. Math. Naturw. Ungarn.*, 1894, 12, 255.

[12] Saito, *Sci. Rep. Tohoku Univ.*, 1927, 16, 37.

[13] Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 536.

[14] Britzke and others, *J. Chem. Ind.* (*U.S.S.R.*), 1931, 8, No. 19, 1.

When oxygen under pressure acts upon an aqueous suspension of realgar, some sulphuric acid is produced but no arsenic acid can be detected.[1]

Water does not sensibly attack realgar (at boiling temperature a little arsenious oxide and hydrogen sulphide are produced[2]), but steam reacts at red heat to give a sublimate of arsenious oxide and arsenious sulphide.[3]

The sulphide is decomposed by chlorine.[4] In a rapid stream of the gas it inflames and yields a yellowish-brown liquid which, on fractionation, yields sulphur monochloride and arsenic trichloride. Bromine water oxidises realgar to arsenic acid.[5] When fused with iodine, arsenious iodide and sulphur are formed : [6]

$$As_2S_2 + 3I_2 = 2AsI_3 + 2S$$

The same reaction occurs if realgar is added to a solution of iodine in an organic solvent such as carbon disulphide, and the solution is decolorised.

Dilute aqueous ammonia has no action on realgar ; more concentrated solutions cause a dulling of the surface.[7] Liquid ammonia dissolves it.[8] Heated with a mixture of ammonium chloride and ammonium nitrate, realgar yields arsenic trichloride.[9] When boiled with aqueous alkali, realgar reacts to yield the trisulphide and a precipitate of arsenic, thus—[10]

$$3As_2S_2 = 2As_2S_3 + 2As$$

No arsine is evolved, but probably a trace of hydrogen results from the decomposition of water by the finely divided arsenic. The latter gradually encrusts the remaining realgar and prevents the reaction from proceeding to completion. It was the residue from this reaction that Berzelius[11] regarded as $As_{12}S$ (see p. 237).

If finely powdered realgar is heated with aqueous sodium sulphide in a sealed tube at 100° C., a thioarsenate is formed and arsenic, which may be contaminated with sulphur, is precipitated.[12] Heated with arsenious oxide, metallic arsenic sublimes and sulphur dioxide is evolved.[13]

Strong oxidising agents convert realgar into sulphuric and arsenic acids ; thus, in an atmosphere of oxygen under a pressure of 20 atm. and at 120° C., aqueous nitric acid (10 per cent.) completely oxidises half its weight of realgar in 30 minutes.[14] With no oxygen present, a larger amount of nitric acid is required. Boiling with 5 per cent. nitric acid produces some hydrogen sulphide, but with more concentrated acid, oxides of nitrogen are evolved. Nitric oxide is evolved

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[1] Askenasy, Elod and Zieler, *Zeitsch. anorg. Chem.*, 1927, 162, 161.

[2] de Clermont and Frommel, *Compt. rend.*, 1878, 87, 331 : *Ann. Chim. Phys.*, 1879, [5], 18, 192, 202.

[3] Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 364.

[4] Rose, *Pogg. Annalen*, 1837, 42, 536; Nilson, *loc. cit.*

[5] Schuller, *loc. cit.*

[6] Schneider, *J. prakt. Chem.*, 1886, [2], 34, 505.

[7] Gélis, *Ann. Chim. Phys.*, 1873, [4], 30, 114.

[8] Gore, *Proc. Roy. Soc.*, 1872, 20, 441 : 1873, 21, 140.

[9] Fresenius, *Zeitsch. anal. Chem.*, 1886, 25, 200.

[10] Kühn, *Arch. Pharm.*, 1852, [2], 71, 1 ; Nilson, *loc. cit.*

[11] Berzelius, *Ann. Chim. Phys.*, 1819, [2], 11, 225 ; 1826, [2], 32, 166.

[12] Geuther, *Annalen*, 1887, 240, 221.

[13] Nilson, *loc. cit.*

[14] Askenasy, Elod and Zieler, *loc. cit.*

from a cold agitated mixture of realgar and 40 per cent. nitric acid. A mixture of nitre and realgar can be detonated, and the addition of sulphur to these two provides a mixture much used in pyrotechny for producing a white light of bluish tint; the so-called *Indian fire* and *Bengal lights* or "*blue light*" generally contain the ingredients in the proportions: realgar 2, sulphur 7, nitre 24. A mixture of these three substances was also employed by the Germans during the Great War in smoke candles;[1] these on ignition gave off a heavy yellowish smoke.

Realgar is employed as a depilatory in tanning, its red colour being a desirable feature in the treatment of hides and skins. It has been used as a paint pigment under the name of *arsenic orange*, but it is not too permanent and is now seldom used. Its early use as a remedy for asthma, etc., has been mentioned (p. 23). Unless carefully prepared, the commercial product is liable to contain white arsenic, and the poisonous nature of the latter tends to limit the applications of realgar.

Arsenic Trisulphide (*Arsenious Sulphide, Orpiment*), As_2S_3, occurs in Nature as a yellow mineral which was well known in early times (see pp. 23, 24). It may be formed artificially by heating together arsenious oxide and sulphur[2] in the requisite proportions, when it sublimes; or by melting together realgar and sulphur[3] in suitable proportions (see p. 240). It may be produced as a precipitate by the action of hydrogen sulphide or an alkali sulphide on a solution in hydrochloric acid of arsenious oxide, an arsenite or an arsenate.[4] In the latter case the reaction is slow but may be accelerated by the presence of a soluble iodide,[5] which facilitates the reduction of the arsenate probably in the following manner:

$$H_3AsO_4 + 2HI = H_3AsO_3 + H_2O + I_2$$
$$H_2S + I_2 = 2HI + S$$

With arsenious oxide the product has a high degree of purity if precipitation is not allowed to proceed to completion. The presence of hydrochloric acid is not necessary and the arsenious oxide may be suspended in water or in a salt solution, in which case the liquid should be warmed as the hydrogen sulphide is passed in.[6]

The arsenious sulphide may be formed as a crystalline precipitate under favourable conditions. When hydrogen sulphide is passed into a 0·2N solution of arsenious oxide in water, golden-yellow leaflets are formed in small quantity,[7] and the amount increases with the concentration up to 0·3N. Beyond this concentration the amount of crystalline sulphide produced diminishes whilst, with very dilute solutions (0·05N), traces only are formed. The crystalline form is also obtained by heating in a sealed tube a mixture of arsenious oxide, ammonium thiocyanate and hydrochloric acid.[8] If arsenic acid is used in place of the oxide, sulphur is also precipitated. A convenient

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[1] Alexander, "*Colloid Chemistry*" (Chemical Catalog Co., N.Y.), 1931, III, 247.

[2] Guibourt, *J. Chim. Méd.*, 1826, [1], 2, 55, 106; Buchner, *Sitzungsber. K. Akad. Wiss. Wien*, 1868, 57, 404; *Repert. Pharm.*, 1868, 17, 386; *Zeitsch. anal. Chem.*, 1871, 10, 308.

[3] Thénard, *Ann. Chim. Phys.*, 1825, [2], 29, 284.

[4] Nilson, *Akad. Handl. Stockholm*, 1871, 10, 2; *Öfvers. Akad. Stockholm*, 1871, 28, 303; *J. prakt. Chem.*, 1875, [2], 12, 327; 1876, [2], 14, 19.

[5] Reedy, *J. Amer. Chem. Soc.*, 1921, 43, 2419.

[6] I.-G. Farbenind. A.-G., Assees. of U. Dreyer, *German Patent*, 432358 (1925).

[7] Winter, *Zeitsch. anorg. Chem.*, 1905, 43, 228.

[8] Weinschenk, *Zeitsch. Kryst. Min.*, 1890, 17, 499.

method for obtaining the crystalline sulphide is first to obtain the double sulphide, $As_2S_3.C_4H_{10}N_2.H_2S$, which is formed by the prolonged action of hydrogen sulphide on the solution obtained by boiling arsenious oxide with piperazine;[1] if this is treated with cold dilute hydrochloric acid or sodium hydroxide, crystalline arsenious sulphide is formed.

Sodium hydrosulphite reduces arsenates and arsenites, yielding precipitates containing sulphides the composition of which varies with conditions. In strongly acid solutions arsenic trisulphide is the main product.[2] Sodium thiosulphate also precipitates arsenic as the trisulphide from acid solutions,[3] but the amount of precipitation depends on the nature and concentration of the acid present. Thus, with hydrochloric, perchloric or sulphuric acid, the precipitation reaches a maximum of 50 to 80 per cent. for 0·1N acid,[4] and above this concentration the amount of precipitation falls to zero with hydrochloric acid but passes through a minimum with perchloric acid at N concentration and with sulphuric acid at 2 to 3N concentration. At still higher acid concentrations precipitation becomes almost quantitative.

If arsenopyrite is allowed to stand in aqueous hydrochloric acid for some time, the formation of arsenic trisulphide may be observed.[5]

When yellow arsenious sulphide, obtained by precipitation from the colloidal solution (see p. 258) by addition of an electrolyte, is heated in an air oven at 100° C., it is converted into a red vitreous mass.[6] If hydrochloric acid is present, this must first be removed before the change will take place. The red form may also be obtained by evaporation of the colloidal solution on a water-bath, or by freezing the colloidal solution, when a mixture of ice and the red form separates. The red form is gradually transformed to the yellow by exposure to air for 5 to 6 weeks at the ordinary temperature, or the change may be brought about more rapidly by heating for some time at 150° to 160° C. When the yellow precipitated arsenious sulphide is dried in a current of dry air, the product is pale yellow and, according to Spring,[7] has the composition $As_2S_3.6H_2O$. Its density is 1·8806 at 25·6° C. It is decomposed by a pressure of 6000 to 7000 atm. into the sulphide and water. Spring also observed that the precipitated sulphide becomes microcrystalline if kept for some days at 150° C.

Physical Properties.—Arsenic trisulphide crystallises in short octahedral prisms which were at first described as rhombic[8] but which Groth described as monoclinic.[9] The crystals are greasy and possess a lustre which is nacreous at the plane of cleavage. The cleavage on the (010)-face is perfect, while that on the (100)-face shows in traces. The (001)-face is a gliding plane.[10] The optical character is negative.[11] The

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[1] Debucquet and Velluz, *Bull. Soc. chim.*, 1932, [4], 51, 1565, 1571.

[2] Farmer and Firth, *J. Chem. Soc.*, 1926, p. 119.

[3] Vohl, *Annalen*, 1855, 96, 238.

[4] Kurtenacker and Fürstenau, *Zeitsch. anorg. Chem.*, 1933, 215, 257. See Hansen, *Ber.*, 1934, 67, B, 1418; Metallges., *English Patent*, 349472 (1930).

[5] Gages, *J. Geol. Soc. Dublin*, 1860, 8, 243. For extraction from copper sulpharsenate ores, see Széki and Romwalter, *Chem. Zentr.*, 1935, ii, 415.

[6] Winter, *loc. cit.*

[7] Spring, *Zeitsch. physikal. Chem.*, 1895, 18, 556; *Zeitsch. anorg. Chem.*, 1895, 10, 185; *Bull. Acad. roy. Belg.*, 1895, [3], 30, 199.

[8] Phillips, "*Introduction to Mineralogy*," London, 1823, p. 227; Mohs, "*Grundriss der Mineralogie*," Dresden, 1824, 2, 613.

[9] Groth, *Chem. Kryst.*, 1906, I. 159.

[10] Mugge, *loc. cit.*

[11] Des Cloiseaux, *Bull. Soc. franç. Min.*, 1882, 5, 108.

colour of the crystals varies from lemon-yellow to deep orange, whilst the precipitated sulphide, when dried, may be of any shade from yellow, through orange, to red according to the conditions of precipitation. The lighter shades result when hydrogen sulphide acts upon a solution of arsenious oxide or an arsenite containing sufficient acid or other electrolyte to cause immediate precipitation.[1] The darker shades are obtained when the tervalent arsenic is first converted to arsenious sulphide sol and this is subsequently coagulated by the addition of an excess of an electrolyte. The red colour has been variously attributed to polymorphism,[2] to the presence of realgar [3] or of a red thioarsenite.[4] Weiser, however, considers [5] that the variation in colour is due to differences in the physical nature of the precipitated sulphide. Direct precipitation in the presence of a foreign electrolyte yields a flocculent precipitate of relatively large particles or loose aggregates which disintegrate on drying to an impalpable yellow to orange-yellow powder. On the other hand, coagulation of a sol gives a gelatinous precipitate consisting of aggregates of ultramicroscopic particles which on drying coalesce to give a red glassy mass. The latter, by grinding or by heating below the sintering temperature, disintegrates and becomes yellow, whilst heating the yellow sulphide at about 175° C. causes it to sinter, contract and assume an orange to brown colour, depending on the temperature and time of heating. The density of arsenic trisulphide varies from 3·44 to 3·48 according to its origin.[6] The hardness of natural orpiment is 1·5 to 2, and of the artificial vitreous form, 3.

The suggestion of Winter that two distinct forms of the sulphide do exist was supported by the work of Borodowski (p. 237). The former gave the transition point as 150° to 160° C. If the yellow form, α-As_2S_3, is heated for some time at 170° in carbon disulphide vapour, it changes to the red β-form, but there is no change below that temperature. Weiser[7] observed, however, that the red form is stable at ordinary temperatures in the dark and when thoroughly dry is not affected by light. The presence of light and moisture causes a superficial chemical disintegration and the red sulphide becomes coated with a yellow film of sulphur and sulphide. This photochemical action is similar to that on As_2S_3 sols (see p. 268).

When heated, arsenious sulphide readily sublimes and fusion occurs, according to Borgström,[8] at 320° C. Earlier determinations have put the melting point at 310°,[9] 300°[10] and 325° C.[11] Air must be excluded or oxidation occurs. Some degree of volatilisation may be observed at the ordinary temperature.[12] According to Schüller,[13] when

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[1] Weiser, *J. Physical Chem.*, 1930, 34, 1021.

[2] Winter, *Zeitsch. anorg. Chem.*, 1905, 43, 228.

[3] Bhatnagar and Rao, *Kolloid-Zeitsch.*, 1923, 33, 159.

[4] Semler, *ibid.*, 1924, 34, 209.

[5] Weiser, *loc. cit.*

[6] Guibourt, *J. Chim. Méd.*, 1826, [1], 2, 55, 106; Karsten, *Schweigger's J.*, 1832, 65, 394; Mohs, *loc. cit.*

[7] Weiser, *loc. cit.*

[8] Borgstrom, *Öfvers. Finska Vet. Soc. Forh.*, 1915, 47, 24.

[9] Jonker, *Zeitsch. anorg. Chem.*, 1909, 62, 89.

[10] Borodowski, *Sitzungsber. Nat. Ges. Dorpat.*, 1905, 14, 159.

[11] Cusack, *Proc. Irish Acad.*, 1891, 4, 399.

[12] Zenghelis, *Zeitsch. physikal. Chem.*, 1905, 50, 219.

[13] Schuller, *Ber. Math. Naturw. Ungarn.*, 1894, 12, 255.

heated in a vacuum volatilisation begins only after melting. In the vacuum of the cathode light, sublimation begins at a temperature just above 220° C. and the sulphide distils unchanged.[1] Vapour density determinations between 820° and 1150° C. indicate that dissociation occurs and that the vapour probably contains molecules of As_2S_3, As_2S_2, As_4, As_2 and S_2.[2]

The crystals exhibit pleochroism, being greenish and reddish-yellow[3] in the direction of the *a* and *c* axes, respectively; on gentle heating, the pleocroism resembles that of realgar but, if the temperature is not allowed to exceed 150° C., the original state is recovered on cooling. A suggested explanation of this is that the reversible change

$$3As_2S_3 \rightleftharpoons 2As_2S_2 + As_2S_5$$

occurs.[4]

Arsenic trisulphide does not conduct electricity at the ordinary temperature,[5] but if heated above 60° C. conductivity becomes appreciable. The incidence of light appears to be without effect.[6] The sulphide exhibits no fluorescence in ultraviolet light;[7] it is opaque to X-rays.[8]

The molar heat of formation from solid arsenic and rhombic sulphur has been calculated to be 34,700 calories.[9]

Chemical Properties.—Arsenic trisulphide may be reduced to arsenic by heating in a stream of hydrogen; the arsenic sublimes. The reaction begins at about 300° C.,[10] but proceeds more readily if the sulphide is first fused with an alkali carbonate.[11] A similar reduction occurs when the sulphide is heated with a mixture of charcoal and alkali carbonate[12] or lime; when heated with potassium cyanide,[13] an oxalate[14] or with a metal such as silver or iron; the latter if in excess yields arsenide.

In moist air the sulphide undergoes slow oxidation.[15] As the temperature is raised, oxidation is appreciable at about 200° C. and complete at 750° C., arsenious oxide and sulphur dioxide being produced.[16] When ignited, the sulphide burns with a pale lilac flame. With the sulphide in neutral or acid solution, oxidation by means of atmospheric oxygen under pressure proceeds only very slowly, but in alkaline

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[1] Merz, *Thesis*, Heidelberg, 1905; Krafft, *Ber.*, 1907, 40, 4778.

[2] Britzke and others, *J. Chem. Ind.* (*U.S.S.R.*), 1931, 8, No. 19, 1; *Zeitsch. anorg. Chem.*, 1932, 205, 95. See also Szarvasy and Messinger, *Ber.*, 1897, 30, 1344.

[3] Weinschenk, *Zeitsch. Kryst. Min.*, 1890, 17, 499.

[4] Hintze, "*Handb. der Mineralogie*," Leipzig, 1904, I, [i], 360.

[5] Beijerinck, *Neues Jahrb. Min.*, 1897, II, 424; Case, *Phys. Review*, 1917, [2], 9, 305; Tubandt and Haedicke, *Zeitsch. anorg. Chem.*, 1927, 160, 297. See also Jannettaz, *Compt. rend.*, 1893, 116, 317.

[6] Case, *loc. cit.*

[7] Robl, *Zeitsch. angew. Chem.*, 1926, 39, 608.

[8] Doelter, *Neues Jahrb. Min.*, 1896, ii, 91.

[9] Britzke and others, *J. Phys. Chem.* (*U.S.S.R.*), 1934, 5, 91; *Zeitsch. anorg. Chem.*, 1933, 213, 58.

[10] Pélabon, *Compt. rend.*, 1903, 136, 454, 812.

[11] Berzelius, *Schweigger's J.*, 1823, 34, 46; *Pogg. Annalen*, 1826, 7, 137; *Ann. Chim. Phys.*, 1819, [2], II, 225; 1826, [2], 32, 116.

[12] Liebig, *Pogg. Annalen*, 1828, 13, 433.

[13] C. R. Fresenius and von Babo, *Annalen*, 1844, 49, 298; Haidlen and C. R. Fresenius, *ibid.*, 1842, 43, 129; W. Fresenius, *Zeitsch. anal. Chem.*, 1881, 20, 522.

[14] Rose, *Pogg. Annalen*, 1837, 42, 536; 1853, 90, 194, 565; 1858, 105, 577; Duflos, *Breslau Schles. Ges.*, 1835, p. 65.

[15] Polacci, *Boll. Chim. Farm.*, 1908, 47, 363.

[16] Saito, *Sci. Rep. Tohoku Univ.*, 1927, 16, 37.

media oxidation occurs more readily—under such conditions the process of dissolution of the sulphide in aqueous sodium hydroxide is extremely complex and consists of a number of successive reactions which at 100° to 110° C. may be represented[1] summarily by the equation

$$2As_2S_3 + 8NaOH + 5O_2 = 4NaAsO_2 + 2Na_2S_2O_3 + 2S + 4H_2O$$

and at 150° to 300° C. by

$$As_2S_3 + 10NaOH + 7O_2 = 2Na_2HAsO_4 + 3Na_2SO_4 + 4H_2O$$

with Na_2HAsS_3 in both cases as an intermediate product. The reaction is catalysed by copper sulphate to an extent increasing with rise of temperature. If a suspension of the sulphide in 4N-sodium hydroxide is heated for two hours at 150° C. and 25 to 50 atm., colloidal sulphur is formed, which may be precipitated by the addition of aqueous carbon dioxide or sulphuric acid, the amount obtained being 50 to 75 per cent. of that originally present as arsenious sulphide.[2]

The sulphide is only slightly attacked by water at the ordinary temperature, and even on prolonged boiling only a little arsenious oxide passes into solution, whilst a trace of hydrogen sulphide is evolved.[3] With the freshly precipitated sulphide the hydrolysis is more rapid,[4] possibly owing to the physical condition allowing greater contact with the water. It has been suggested that the accelerated reaction may be due to the more ready formation of an intermediate hydroxysulphide by the fresh precipitate;[5] the presence of arsenious oxide, which forms an oxysulphide, retards the reaction, however. According to Regnault,[6] steam reacts to form an arsenic oxysulphide of variable composition. If the sulphide is boiled with water *in vacuo*, decomposition commences at 22° C.[7]

The solubility of arsenic trisulphide in pure water at 0° C. has been determined[8] by digesting the mixture for several days, filtering through an ultra-filter, and estimating the dissolved arsenic iodometrically; a value of 0·89 mg. As_2S_3 per litre was obtained. In the presence of 0·002 per cent. of hydrogen sulphide the solubility was reduced to 0·23 mg. per litre. With higher concentrations of hydrogen sulphide the solubility increased, but this increase did not occur in the presence of hydrochloric acid and the trisulphide may be precipitated quantitatively by saturation of the solution in hydrochloric acid with hydrogen sulphide. Arsenic trisulphide dissolves readily in solutions of alkali hydroxides,[9] carbonates[10] or sulphides.[11] Thus with alcoholic sodium

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[1] Razuvaiev, Malinovski and Lopatina, *J. Appl. Chem.* (*U.S.S.R.*), 1933, 6, 206.

[2] Lopatina, *ibid.*, 1933, 6, 803.

[3] Decourdemanche, *J. Chim. Méd.*, 1827, [1], 3, 229; *J. Pharm. Chim.*, 1827, [1], 13, 217; Hünefeld, *J. prakt. Chem.*, 1836, [1], 7, 235.

[4] de Clermont and Frommel, *Compt. rend.*, 1878, 86, 828; 87, 230; Ward, *Jahresber.*, 1873, p. 235; Cross and Higgin, *Ber.*, 1883, 16, 1195; Linder and Picton, *J. Chem. Soc.*, 1892, 61, 114; Spring, *Bull. Acad. roy. Belg.*, 1895, [3], 30, 199; Vorlander and Haberle, *Ber.*, 1913, 46, 1612; Schmidt, *Arch. Pharm.*, 1917, 255, 45.

[5] Chodounsky, *Chem. Listy*, 1889, 13, 114; de Clermont and Frommel, *loc. cit.*

[6] Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 384.

[7] de Clermont and Frommel, *loc. cit.*

[8] Holtje, *Zeitsch. anorg. Chem.*, 1929, 181, 395.

[9] Berzelius, *loc. cit.*

[10] Biltz, *Zeitsch. anorg. Chem.*, 1870, 9, 410; Nilson, *J. prakt. Chem.*, 1875, [2], 12, 327; 1876, [2], 14, 19.

[11] Puller, *Zeitsch. anal. Chem.*, 1871, 10, 41.

hydroxide, arsenate and mono- and di-thioxyarsenates result.[1] With alcoholic sodium hydroxide, arsenate, mono- and di-thioxyarsenates are formed. A solution in sodium carbonate, saturated at 80° C., yields crystals of the trisulphide on cooling, but if heated to 100° C. a thioarsenite is formed in solution. In yellow ammonium sulphide, ammonium thioarsenate is formed—

$$3(NH_4)_2S + 2S + As_2S_3 = 2(NH_4)_3AsS_4$$

while in an aqueous solution of sodium sulphide a thioarsenite is produced :

$$Na_2S + As_2S_3 = 2NaAsS_2$$

In ammoniacal solution, arsenic trisulphide is oxidised by hydrogen peroxide to arsenic and sulphuric acids.[2]

Arsenic trisulphide reacts readily with the halogens. When exposed to chlorine, considerable heat is evolved and a liquid product containing arsenic trichloride and sulphur dichloride is obtained.[3] In an aqueous medium oxidation to quinquevalent arsenic occurs.[4] Oxidation also results when the sulphide is heated with hydrochloric acid and potassium chlorate,[5] some arsenic trichloride being vaporised during the process.[6] Bromine water, or a solution of bromine in hydrochloric acid or in aqueous potassium bromide, reacts similarly, quinquevalent arsenic and arsenic tribromide being formed in solution.[7] Iodine in carbon disulphide solution reacts with the freshly precipitated sulphide, though not with natural orpiment, to form arsenic triiodide and sulphur.[8] The same products result when a mixture of the sulphide and iodine is gently heated, but at a higher temperature the reaction is reversible :

$$As_2S_3 + 3I_2 \rightleftharpoons 2AsI_3 + 3S$$

When arsenic trisulphide is exposed to dry hydrogen chloride or hydrogen bromide, it liquefies at the ordinary temperature and on heating complete volatilisation occurs.[9] It is not readily attacked by halogen acids. When boiled with concentrated hydrochloric acid it is decomposed, but with great difficulty, and the hydrogen sulphide and arsenious chloride evolved reproduce arsenious sulphide in the receiver.[10] A similar reaction occurs when heated with a chloride in the presence of concentrated sulphuric acid, but the decomposition is incomplete.[11] The reaction is facilitated by the presence of cuprous chloride or ferric chloride. Only a slight reaction is observed with dilute acid,[12] and the

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[1] Weinland and Lehmann, *Zeitsch. anorg. Chem.*, 1901, 26, 322; Berzelius, *loc. cit.*

[2] Classen and Bauer, *Ber.*, 1883, 16, 1061.

[3] Rose, *Ann. Chim. Phys.*, 1839, [2], 70, 278; Nilson, *J. prakt. Chem.*, 1875, [2], 12, 327; 1876, [2], 14, 19; Baudrimont, *Compt. rend.*, 1867, 64, 368.

[4] Bunsen, *Annalen*, 1858, 106, 10; 1878, 192, 317.

[5] Fresenius and von Babo, *ibid.*, 1844, 49, 298.

[6] Bunsen, *loc. cit.*

[7] Reichardt, *Arch. Pharm.*, 1880, 217, 1; de Koninck, *Zeitsch. anal. Chem.*, 1880, 19, 468.

[8] Schneider, *J. prakt. Chem.*, 1881, [2], 23, 486; 1887, [2], 36, 498.

[9] Kelley and Smith, *Amer. Chem. J.*, 1896, 18, 1096.

[10] Gmelin, "*Handbook of Chemistry*" (London), 1850, 4, 274.

[11] Becker, *Pogg. Annalen*, 1848, 74, 303; Fyfe, *Phil. Mag.*, 1851, [4], 2, 487; Wallace and Penny, *ibid.*, 1852, [4], 4, 361; Lintner, *Repert. Pharm.*, 1852, [4], 1, 314; Kaiser, *Zeitsch. anal. Chem.*, 1875, 14, 259; Beckurts, *Arch. Pharm.*, 1884, 222, 654.

[12] Schmidt, *ibid.*, 1917, 255, 45.

trisulphide is quite insoluble in, and unacted upon by, aqueous hydrochloric acid of density 1·16, providing the liquid is saturated with hydrogen sulphide.[1] Metallic chlorides, notably mercuric chloride, react directly on heating to produce arsenic trichloride.

When finely divided arsenic trisulphide is exposed to gaseous ammonia, the latter is slowly absorbed until, after about three weeks, the composition of the product corresponds[2] with $As_2S_3.NH_3$; this loses ammonia on exposure to air, whilst water converts it to ammonium arsenite and thioarsenite. The trisulphide dissolves readily in aqueous ammonia and is slightly soluble in liquid ammonia.[3] It is decomposed by nitric acid or aqua regia. A few drops of fuming nitric acid on melted orpiment produce a deflagration,[4] whilst nitric acid of density 1·42 causes separation of sulphur, which melts and may form a protective film on some of the sulphide particles, thus preventing complete oxidation.[5] The presence of hydrazine effectively retards the oxidising action of nitric acid on arsenic trisulphide, both with acid of concentration 1 to 4N at boiling temperature, and with 6 to 10N acid (density 1·2 to 1·3) at 20° to 22° C.[6] The reaction velocity depends upon the amount of sulphide in solution, and a gradual oxidation occurs which, even in the presence of large amounts of hydrazine, reaches equilibrium after several days, during which the components are destroyed in the proportions of 1 mole of hydrazine to 4 equivalents of arsenic trisulphide. In the presence of oxygen under a pressure of 20 atm. and of twice its weight of 40 per cent. nitric acid, orpiment is completely oxidised at 120° C. to arsenic and sulphuric acids in 15 minutes;[7] this amount of nitric acid, as in the case of realgar (p. 243), is less than that theoretically needed in the absence of oxygen. Oxygen alone acts on an aqueous suspension of the sulphide to oxidise some of the sulphur to sulphuric acid, but no arsenic acid is formed.

Arsenic trisulphide is not dissolved by dry liquid hydrogen sulphide.[8] The precipitated sulphide obtained by the action of hydrogen sulphide on solutions of arsenious oxide in aqueous hydrochloric or acetic acid is found to contain an amount of sulphur in excess of that required by the formula As_2S_3, but which cannot be extracted with carbon disulphide. This has been attributed to the formation of a hydrosulphide since, if the precipitate is dried in a vacuum and then heated at 115° C., hydrogen sulphide is evolved. The products vary in composition, but that produced in presence of hydrochloric acid approximates to $16As_2S_3.H_2S$ and that from acetic acid solutions to $8As_2S_3.H_2S$.[9]

The trisulphide reacts with sulphur dioxide at temperatures between 300° and 800° C. to form sulphur and a sulphate,[10] whilst if the sulphide is digested with an aqueous solution of sulphur dioxide, or of potassium hydrogen sulphite, it dissolves and the solution when boiled evolves

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[1] Lang and Carson, *J. Soc. Chem. Ind.*, 1902, 21, 1018.

[2] Berzelius, *Ann. Chim. Phys.*, 1819, [2], 11, 225; 1826, [2], 32, 116; Bineau, *ibid.*, 1839, [2], 70, 264; Morita, *J. Chem. Soc. Japan*, 1935, 56, 325.

[3] Gore, *Proc. Roy. Soc.*, 1872, 20, 441; 1873, 21, 140; Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 820.

[4] Proust, *J. Physique*, 1801, 53, 89; *Nicholson's J.*, 1802, 1, 109.

[5] Bunsen, *loc. cit.*

[6] Kešāns, *Acta Univ. Latviensis, Kim. Fakult. Serija*, 1933, 2, 311, 317.

[7] Askenasy, Elöd and Zieler, *Zeitsch. anorg. Chem.*, 1927, 162, 161.

[8] Biltz and Keunecke, *ibid.*, 1925, 147, 171.

[9] Linder and Picton, *J. Chem. Soc.*, 1892, 61, 114.

[10] Milbauer and Tucek, *Chem. Zeit.*, 1926, 50, 323.

sulphur dioxide, and arsenate, thiosulphate and free sulphur are formed.[1] Concentrated sulphuric acid also dissolves the trisulphide to form arsenious oxide and sulphur dioxide.[2] Sulphur monochloride, when heated with the sulphide, yields a molten mixture of arsenic trichloride and sulphur;[3] decomposition is complete at about 140° C.[4] Sulphur iodides react similarly.[5] Thionyl chloride also attacks the trisulphide when the mixture is heated in a sealed tube at 150° C.[6]

Arsenic trisulphide is insoluble in benzene or carbon disulphide: it is soluble in an aqueous solution of citric acid or of an alkali citrate.[7] An aqueous solution of borax (2 per cent.) dissolves the sulphide slowly in the cold, more rapidly on heating.[8]

Arsenious sulphide reacts with metallic sulphides as an acid thioanhydride and forms a series of complex salts known as thioarsenites. These may be considered to be derived from the following hypothetical acids:[9]

Orthothioarsenious acid, H_3AsS_3
Metathioarsenious acid, $HAsS_2$
Pyrothioarsenious acid, $H_4As_2S_5$
Metathiotriarsenious acid, HAs_3S_5
Orthothiotetrarsenious acid, $H_6As_4S_9$
Metathiotetrarsenious acid, $H_2As_4S_7$
Metathio-octo-arsenious acid, $H_2As_8S_{13}$
Metathioennea-arsenious acid, HAs_9S_{14}
Metathiododeca-arsenious acid, $H_2As_{12}S_{19}$

These acids are supposed to be formed from $H_{3n}As_nS_{3n}$ by loss of H_2S; thus the last of the series is equivalent to $H_{36}As_{12}S_{36}-17H_2S$.

Many of these compounds have been described in the literature,[10] but in only a few cases have the conditions been such as to produce pure compounds. Many thioarsenites occur in Nature (see p. 13).[11]

The salts are usually prepared by the interaction of arsenious sulphide with the metallic sulphide, hydrosulphide or carbonate, taking care to exclude air to prevent the formation of thioarsenates. Thus, Nilson[12] obtained the salts of the alkali and alkaline earth metals by dissolving arsenious sulphide in the aqueous solutions of the respective hydrosulphides and concentrating *in vacuo*.

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[1] Bunsen, *Annalen*, 1858, 106, 8.

[2] Rose, *Ann. Chim. Phys.*, 1839, [2], 70, 278.

[3] Baudrimont, *Compt. rend.*, 1867, 64, 368; Feigel, *Thesis*, Erlangen, 1905.

[4] Kelley and Smith, *loc. cit.*

[5] Schneider, *J. prakt. Chem.*, 1887, [2], 36, 498.

[6] North and Connor, *Amer. J. Sci.*, 1915, [4], 40, 640; *J. Amer. Chem. Soc.*, 1915, 37, 2486.

[7] Spiller, *J. Chem. Soc.*, 1858, 10, 110.

[8] Materne, *Bull. de Belg.*, 1906, 20, 46.

[9] Hilger and Weinland, "*Gmelin's Handbuch der anorganischen Chemie*," Heidelberg, 1897, 2, ii, 590.

[10] See Berzelius, *Ann. Chim. Phys.*, 1819, [2], 11, 225; 1826, [2], 32, 166; *Schweigger's J.*, 1823, 34, 46; *Svenska Akad. Handl.*, 1825, 295. Also see Mellor, "*Comprehensive Treatise on Inorganic and Theoretical Chemistry*" (Longmans), 1929, 9, 289–305.

[11] See Zambonini, *Riv. Min. Crist. Ital.*, 1912, 41, 3; 1916, 47, 40; Cesaro, *Bull. Soc. franç. Min.*, 1915, 38, 38; Wherry, *J. Washington Acad.*, 1920, 10, 487; 1921, 11, 1; Foshag, *Amer. J. Sci.*, 1921, [5], 1, 444; Niggli, *Zeitsch. Kryst. Min.*, 1924, 60, 477.

[12] Nilson, *J. prakt. Chem.*, 1875, [2], 12, 295; 1876, 13, 1; 14, 145; 1877, 16, 93; *Ofvers. Akad. Stockholm*, 1871, 28, 303; 1877, 34, 5.

Wünschendorff,[1] using carefully purified arsenious sulphide and the alkali sulphide, prepared the following compounds :

Potassium metathioarsenite, $KAsS_2$, red rhombic crystals ;
Potassium metathiotriarsenite, $KAs_3S_5.1{\cdot}5H_2O$, an insoluble red granular powder ;
Potassium metathiotetrarsenite, $K_2As_4S_7.2H_2O$, red crystalline needles.

The ortho- and pyro-thioarsenites could not be obtained in the solid condition, their solutions decomposing into the orthothioarsenate and arsenic when concentrated. Berzelius [2] described products obtained by precipitation with alcohol from solutions of arsenious sulphide in alkali sulphides as orthothioarsenites, R_3AsS_3 ($R = K$, Na, NH_4) ; and pyrothioarsenites, $R_4As_2S_5$, were said to be obtained by heating the corresponding pyrothioarsenates. Nilson [3] obtained the *orthothiotetrarsenite*, $K_6As_4S_9.8H_2O$, as a blood-red gelatinous mass by evaporation of the mother liquor from the metathiotetrarsenite, after separating the latter from a solution of arsenious sulphide in potassium hydrosulphide.

Five sodium salts may be prepared by Wünschendorff's method :[4]

Sodium metathioarsenite, $NaAsS_2$, brown prismatic crystals ;
Sodium metathiotriarsenite, $NaAs_3S_5.3H_2O$, brown spherites ;
Sodium metathiotetrarsenite, $Na_2As_4S_7.2H_2O$, brown prisms ;
Sodium pyrothioarsenite, $Na_4As_2S_5.H_2O$, dark orange prisms ;
Sodium orthothioarsenite, Na_3AsS_3.

The last two compounds are extremely unstable and decompose rapidly to form arsenic and sodium orthothioarsenate.

Only two ammonium salts have been prepared by the above method :

Ammonium metathioarsenite, NH_4AsS_2, yellow needles, very unstable ;
Ammonium metathiotetrarsenite, $(NH_4)_2As_4S_7$, red needles, stable.

The ortho-salt was reported by Berzelius (see above), and Nilson obtained *ammonium metathiotriarsenite*, $NH_4As_3S_5.2H_2O$, by evaporation of a saturated solution of arsenious sulphide in ammonium hydrosulphide.

The following other salts have been obtained by Wünschendorff :[5]

$Ca(AsS_2)_2.8H_2O$, yellow prisms ;
$Ca_2As_2S_5.9H_2O$, yellow triclinic crystals, unstable ;
$Sr(AsS_2)_2.2H_2O$, yellow amorphous powder ;
$Sr_2As_2S_5.7H_2O$, orange triclinic crystals ;
$Sr_3(AsS_3)_2.6H_2O$, yellowish-white scales ;
$Ba_3As_4S_9.6H_2O$, brownish-yellow crystals ;
$Ba_2As_2S_5.5H_2O$, yellow crystals ;
$Ba_3(AsS_3)_2.8H_2O$, yellow prisms ;
$Ba(AsS_2)_2.0{\cdot}5H_2O$, an insoluble brown precipitate ;
$AgAsS_2$; Ag_3AsS_3 ; KAg_2AsS_3 ; $M_3(AsS_3)_2$ and $KMAsS_3$ ($M =$ Zn, Pb, Mn). The corresponding salts of iron, cobalt and nickel were apparently formed, but were unstable and could not be purified.

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[1] Wünschendorff, *Bull. Soc. chim.*, 1929, [4], 45, 889.
[2] Berzelius, *loc. cit.*
[3] Nilson, *J. prakt. Chem.*, 1876, [2], 13, 1.
[4] Wunschendorff, *loc. cit.*
[5] Wünschendorff, *loc. cit.*; Wunschendorff and Valier, *Bull. Soc. chim.*, 1933, [4], 53, 1525, 1529.

Thioarsenites of the heavy metals may be prepared in a dry way by heating together arsenious sulphide and the metallic chloride in suitable proportions.[1] For example, a mixture containing $3AgCl : As_2S_3$ yields the ortho-salt Ag_3AsS_3, the reaction commencing at 150° C.: the product is a brittle reddish-black lustrous mass. From $3AgCl : 2As_2S_3$ reddish-black crystals of the meta-salt, $AgAsS_2$, are obtained, the reaction commencing at 170° C. The pyro-salt, $Ag_4As_2S_5$, is obtained from a mixture of composition $12AgCl : 5As_2S_3$: it is a lustrous black solid. In a similar manner the following lead salts have been obtained: $Pb(AsS_2)_2$; $Pb_2As_2S_5$ and $Pb_3(AsS_3)_2$. Copper thioarsenites of definite composition cannot be obtained by this method, although Sommerlad obtained a product which approximated to $Cu_4As_2S_5$.

Thioarsenite solutions may be employed in the purification of coal-gas for the removal of hydrogen sulphide. When saturated with the latter the purifier may be recovered by aeration, until precipitation of sulphur ceases, and saturation of the filtered solution with carbon dioxide, which yields a yellow precipitate containing most of the arsenic; this is redissolved in sodium hydroxide or carbonate, with aeration, and the solution returned to the purifying circuit.[2]

In experiments with proustite, Ag_3AsS_3, Coblentz observed [3] that at temperatures from +20° to −50° C. the spectrophotoelectric sensitivity curve showed a slight maximum at about 6100 A. and a marked sensitivity with a maximum in the extreme violet. As the temperature is lowered to −100° C. the maximum in the violet is more or less obliterated by a new maximum (the 6100 A. band) which occurs at about 5800 A. The position of this new maximum remains quite constant as the temperature is further lowered to −170° C. No photoelectric sensitivity is observed for radiation stimuli of wavelengths extending from 10,000 to 20,000 A. in the infra-red.

Few *oxythioarsenites* have been prepared. A *sodium* compound of composition $Na_8As_{18}O_7S_{24}.30H_2O$ has been obtained by several methods, for example: by boiling a mixture of arsenious sulphide and aqueous sodium carbonate;[4] by boiling a mixture of arsenious oxide and sodium hydrosulphide, adding alcohol to the filtered solution and allowing the alcoholic extract to crystallise;[5] by evaporation of the mother liquor from sodium sulphite produced by interaction of sodium thiosulphate and sodium dihydrogen orthoarsenite.[6] It crystallises as deep red hexagonal plates, which decompose in the presence of water, acids and alkalis. A *barium* salt, $Ba_5As_4O_2S_9.6H_2O$, has also been described.[7]

Colloidal Arsenic Trisulphide.

It was observed by Berzelius that arsenious sulphide, obtained by precipitation from aqueous arsenious oxide with hydrogen sulphide, after it had been washed with cold water, dissolved to a slight extent in hot water forming a yellow solution. Water containing hydrogen

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[1] Sommerlad, *Zeitsch. anorg. Chem.*, 1897, 15, 173; 1898, 18, 420.

[2] Gollmar, *American Patent*, 1827082 (1931).

[3] Coblentz, *Phys. Review*, 1921, [2], 17, 245.

[4] Nilson, *J. prakt. Chem.*, 1875, [2], 12, 297; 1876, 14, 10; 1877, 16, 93.

[5] Preis, *Annalen*, 1890, 257, 178.

[6] Weinland and Gutmann, *Zeitsch. anorg. Chem.*, 1898, 17, 409; Gutmann, *Thesis*, München, 1897.

[7] Nilson, *loc. cit.*

sulphide did not dissolve it. On keeping, the yellow solution gradually deposited the sulphide. Moreover, whilst hydrogen sulphide immediately and almost completely precipitates the sulphide from a saturated solution of arsenious oxide, if the gas or its aqueous solution is added to a *dilute* aqueous solution of the oxide[1] a clear yellow solution results which, after excess of hydrogen sulphide has been removed by passing oxygen or hydrogen through it, gives on addition of hydrochloric acid complete precipitation of the arsenic as trisulphide.[2] Thus, although the hydrogen sulphide causes no precipitation, the arsenic is quantitatively converted to trisulphide, which remains in colloidal solution. This hydrosol has been the subject of much classical investigation, especially as regards the conditions governing its stability and coagulation, for it was early observed that the sulphide separated in yellow flakes when the liquid was heated[3] or frozen,[4] or on adding to it certain electrolytes[5] or even insoluble powders such as charcoal, copper oxide, glass powder or powdered Iceland spar.[6]

In order to prepare the hydrosol free from electrolytes, pure arsenious oxide should be dissolved in "conductivity water" which is kept boiling and the solution obtained allowed to flow into a saturated solution of hydrogen sulphide through which a current of the gas is continuously passing.[7] The uncombined hydrogen sulphide is subsequently removed by passing a current of hydrogen, preferably with exclusion of light, and the liquid is finally filtered. Or, hydrogen sulphide gas may be passed into the saturated solution of arsenious acid until the latter can no longer be detected in the filtrate after precipitation with an electrolyte.[8] There is a limit to the concentration of the sols thus prepared, owing to the sparing solubility of arsenious oxide; but by passing hydrogen sulphide and then dissolving more arsenious oxide, and so repeating several times, a sol containing as much as 37·46 per cent. As_2S_3 has been obtained.[9] Much of the water may be eliminated under reduced pressure and any large particles removed by energetic centrifuging.[10] Such a sol has the appearance of an intensely yellow milk, but is transparent under the microscope. Dilute hydrosols of arsenious sulphide prepared from more concentrated sols by dilution are more turbid than dilute sols of the same concentration prepared directly, and are more yellow than the latter, which have a reddish-yellow tint.

According to Gazzi,[11] the most highly purified sols contain an excess of arsenious oxide since, on analysis of the hydrosol, the quantity of oxide obtained is always much greater than that which could result from the complete hydrolysis of soluble arsenic trisulphide. Gazzi found the solubility of the precipitated trisulphide to be 0·5166 mg.

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[1] *E.g.* 0·2 per cent.

[2] Bischof, *Brande's Arch.*, 1826, 17, 239; Gmelin, "*Handbook of Chemistry*," London, 1850, 4, 274; Küster and Dahmer, *Zeitsch. anorg. Chem.*, 1902, 33, 105; 1903, 34, 410.

[3] Boutigny, *J. Chim. Méd.*, 1832, [1], 8, 449.

[4] Pfaff, *Schweigger's J.*, 1825, 45, 95.

[5] Boutigny, *loc. cit.*

[6] Küster and Dahmer, *Zeitsch. anorg. Chem.*, 1903, 34, 410.

[7] Linder and Picton, *J. Chem. Soc.*, 1892, 61, 137.

[8] Chaudhury and Kundu, *Quart. J. Indian Chem. Soc.*, 1926, 3, 345.

[9] Schulze, *J. prakt. Chem.*, 1882, [2], 25, 431.

[10] Boutaric and Simonet, *Bull. Acad. roy. Belg.*, 1924, [5], 10, 150.

[11] Gazzi, *Zymologica*, 1927, 2, 1; *Ber. ges. Physiol. exp. Pharmakol.*, 1927, 41, 425; *Chem. Zentr.*, 1927, ii, 26.

per litre (*cf.* p. 248), and this quantity would yield 0·4154 mg. of the trioxide per litre. In sols prepared by passing hydrogen sulphide through aqueous solutions of arsenious oxide, and after addition of two drops of dilute sulphuric acid, filtering and removing excess of hydrogen sulphide either by dialysis, boiling or passing hydrogen with exclusion of light, the arsenious oxide content was 1·5 to 3·0 mg. per litre for the dialysed sols, and with the others the amount increased with the duration of boiling or passing hydrogen. Chaudhury and Kundu[1] found the atomic ratio of As : S in sols containing excess of arsenious acid to be 1 : 1·46, agreeing with the composition As_2S_3, but in sols which were purified from arsenious acid and hydrogen sulphide the ratio was 1 : 2, possibly corresponding with $As_2S_3.H_2S$ or $As_2S_3.As_2S_5$, the former being the more probable.

In sols purified by electrodecantation the concentration of hydrogen ion calculated from the results of electrometric titration is greater than that given by the conductivity, whereas the converse is true of the liquid separated from a coagulum obtained by freezing the sol.[2] The coagulum has the composition As_2S_3 but retains adsorbed stabilising groups from which H^+ may be liberated by treatment with a barium salt. Both the original sol and the intermicellar liquid may be shown by conductometric titration and by analysis to contain the acid H_3AsO_4 and a salt, probably $H_2(AsO)AsO_4$, which are formed by oxidation of the S-containing stabilising complex. Sulphur is absent from the intermicellar liquid.

The arsenic trisulphide hydrosols, if carefully protected from air and light, are very stable, and may be kept for considerable periods with little deposition; Linder and Picton[3] record no change in a 2 per cent. sol over three years, and Dumanski[4] made the observation that during four years the rate of fall, due to gravity, of the particles of arsenic trisulphide was on the average 0·031 cm. per day. The sols, however, undergo oxidation in the presence of atmospheric oxygen, the products after prolonged action being arsenious acid, free sulphur and sulphuric acid.[5] The last-named has a precipitative influence on the colloid present and may be a disturbing factor in experimental determinations carried out in the presence of air. The presence in the sol of electrolytes, non-electrolytes and protective colloids, has each a marked effect on the stability of the colloid and is discussed below.

The colour of arsenic trisulphide hydrosols varies from pale yellow to orange-red, dependent to some extent apparently on the size of the colloid particles.[6] The coarser suspensions are usually orange-red, whilst with sols in the highest degree of fine division there is only slight milkiness by transmitted light. According to Menon,[7] light refracted by freshly prepared sols is almost completely plane-polarised. Bhatnagar,[8] however, does not agree with the view that the difference

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[1] Chaudhury and Kundu, *loc. cit.*

[2] Pauli and Laub, *Kolloid-Zeitsch.*, 1937, 78, 295.

[3] Linder and Picton, *J. Chem. Soc.*, 1892, 61, 137.

[4] Dumanski, *Kolloid-Zeitsch.*, 1925, 36, 98.

[5] Swiderska and co-workers, *Rocz. Chem.*, 1929, 9, 411, 416.

[6] Peskoff, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 1619: *Kolloid-Zeitsch.*, 1923, 32, 24, 163, 238; Semler, *ibid.*, 1924, 34, 209.

[7] Menon, *Kolloid-Zeitsch.*, 1936, 76, 9.

[8] Bhatnagar, *J. Physical Chem.*, 1931, 35, 1803. See also Bhatnagar and others, *ibid.*, 1924, 28, 387.

in colour is due only to difference in physical character, but states that the reddish precipitate separated from a sol has a more complex composition than is indicated by the formula As_2S_3. The size of the colloid particles increases with the concentration of the arsenious oxide solution employed in the preparation of the sol;[1] thus when the concentration was 10^{-2} N, Börjeson[2] found the mean radius of the sulphide particles to be 39 $\mu\mu$; with 5×10^{-4} N arsenious oxide, the mean radius was 16 $\mu\mu$, and with 10^4 N the value was 11 $\mu\mu$. According to Boutaric and Semelet,[3] an orange-coloured fine-grained sol is obtained by a rapid flow of hydrogen sulphide through aqueous arsenious acid, whereas with a slow supply a yellow coarse-grained sol is produced. The mean magnitude also increases to a slight extent with rise in temperature and may be further increased by protracted boiling of the sol at constant volume.[4] The colour of the sol usually darkens on boiling, the opacity increases and precipitation occurs. The Brownian movement may be observed in suspensions where the radius of the particles is less than 2·5 μ. From the examination of freshly prepared sols by means of X-rays and the ultramicroscope, it has been concluded[5] that the particles of arsenic trisulphide are amorphous and nearly spherical.

The density of the hydrosols varies linearly with the concentration up to about 9 per cent. As_2S_3, but beyond this the increase is more rapid.[6] Linder and Picton[7] showed that at low concentrations the density could be calculated by the law of mixtures, thus:

As_2S_3 per cent.	*D* (obs.).	*D* (calc.).
4·4	1·033810	1·033810
2·2	1·016880	1·016905
1·1	1·008435	1·008440
0·01719	1·000137	1·000134

The solid sulphide obtained from the sol by rapid centrifuging was found by Dumanski[8] to have density 2·938. The viscosity also depends on the concentration of the sol and, according to Boutaric and Simonet,[9] if η and η_0 represent respectively the viscosities of the sol and of the dispersive medium, both at 20° C., and ϕ the ratio of the volume of the disperse substance to that of the suspension, the value of

$$k = (\eta - \eta_0)/\eta_0\phi \text{ (Einstein's equation)}$$

approaches 2·5 as dilution approaches infinity. The addition of an

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[1] Linder and Picton, *loc. cit.*; Boutaric and Vuillaume, *Compt. rend.*, 1924, 178, 938; *J. Chim. phys.*, 1924, 21, 247.

[2] Borjeson, *Kolloid-Zeitsch.*, 1920, 27, 18.

[3] Boutaric and Semelet, *J. Chim. phys.*, 1929, 26, 195.

[4] Boutaric and Vuillaume, *loc. cit.* *Cf.* Kruyt and van der Spek, *Kolloid-Zeitsch.*, 1919, 25, 1.

[5] Freundlich, *Trans. Faraday Soc.*, 1927, 23, 614; *Ber.*, 1928, 61 B, 2219. *Cf.* Menon, *Proc. 15th Indian Sci. Cong.*, 1928, p. 72.

[6] Boutaric and Simonet, *Bull. Acad. roy. Belg.*, 1924, [5], 10, 150.

[7] Linder and Picton, *J. Chem. Soc.*, 1895, 67, 71.

[8] Dumanski, *Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 262.

[9] Boutaric and Simonet, *Bull. Acad. roy. Belg.*, 1924, [5], 10, 150. See Einstein, *Ann. Physik*, 1911, 34, 591.

electrolyte generally causes a change in the viscosity: thus, small quantities of potassium chloride or cadmium chloride cause an increase to a maximum,[1] after which the viscosity falls off with further addition. Such changes are not observed, however, on addition of mercuric chloride.[2] The surface tension of the hydrosol is the same as that of water.[3] The diffusibility of the sol into water was studied by Linder and Picton,[4] who confirmed Graham's view that colloids, no less than electrolytes, diffuse considerably, although the rate is very slow. The dialysis is influenced by the presence of other substances; thus the presence of a soluble tartrate accelerates, while the presence of a gel[5] retards, the speed of diffusion, the extent of the effect depending on the concentration of the added substance. The molecular weight derived from the diffusion constant[6] is greater than 6000. Osmotic pressure measurements give very variable values which are always small, and the sol has no effect on the freezing point of water.

The particles of the colloid are electronegatively charged, so that during cataphoresis they are transported towards the anode. The velocity of migration of particles suspended in a liquid is, according to Smoluchowski,[7] given by the formula $\zeta H\epsilon/4\pi\eta$, where ζ is the potential difference of the double layer, H the fall of potential (volts per cm.), ϵ the dielectric constant and η the viscosity; putting $\zeta = 0{\cdot}05$ volt, the value for glass and water, Smoluchowski calculated the velocity under a potential fall of 1 volt per cm. to be 34×10^{-5} cm. per sec. For an arsenic trisulphide sol containing particles of diameter 50 $\mu\mu$ the value 22×10^{-5} was obtained by Linder and Picton,[8] while Kruyt and van der Willigen[9] determined the velocity to be 31×10^{-5} cm. per sec. The electrical conductivity has been determined[10] as 136×10^{-6} mho. The cataphoretic speed is influenced by the presence of electrolytes, the effect usually being a fall with low concentrations, but a gradual increase as the amount of electrolyte increases; on the other hand, the decrease in cataphoretic speed may continue to high concentrations of the electrolyte[11] until the flocculation point is reached (see below). With acids and alkalies the migration velocity may be at a high value, and in some cases almost equal to that in the original sol, when precipitation occurs. This is probably due to the high adsorption at the surface of the particles increasing the dielectric constant, and while the cataphoretic velocity remains high, the critical potential at which precipitation results is lowered.[12] The velocity increases with increase in concentration of univalent cations and does not pass through a maximum; this again appears to depend on high adsorbability. With the alkali chlorides at 0·0002N concentration the cataphoretic speeds indicate the following order of adsorption:[13] $K^+ > Na^+ > Li^+$, but the

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[1] Tendeloo, *Kolloid-Zeitsch.*, 1927, 41, 290. *Cf.* Dhar and Chakravarti, *ibid.*, 1927, 42, 120.

[2] Kulkarni, *J. Indian Chem. Soc.*, 1936, 13, 439.

[3] Linder and Picton, *loc. cit.* See Rossi and Marescotti, *Gazzetta*, 1929, 59, 313.

[4] Linder and Picton, *J. Chem. Soc.*, 1892, 61, 187.

[5] Bechhold and Ziegler, *Zeitsch. physikal. Chem.*, 1906, 56, 105.

[6] Thovert, *Compt. rend.*, 1901, 133, 1197; 1902, 134, 507; 135, 579.

[7] Smoluchowski, *Bull. Acad. Sci. Cracow*, 1903, p. 182.

[8] Linder and Picton, *J. Chem. Soc.*, 1897, 71, 568.

[9] Kruyt and van der Willigen, *Zeitsch. physikal. Chem.*, 1927, 130, 170.

[10] Dumanski, *Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 262.

[11] Mukherjee and co-workers, *J. Indian Chem. Soc.*, 1933, 10, 27.

[12] Kruyt and Briggs, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 384.

[13] Mukherjee and co-workers, *loc. cit.*

order of adsorption of cations varies with conditions. The addition of arsenious oxide to the hydrosol decreases the cataphoretic speed, the effect depending on the amount of oxide added.[1] If potassium chloride is already present, the arsenious oxide causes a decrease in speed, but the effect for increasing oxide passes through a maximum; in the presence of barium chloride the decrease is greater with increasing concentration of the latter. It will readily be understood that the migration velocity, depending as it does on the charge on the colloid particle, will vary considerably with the method of preparation of the sol, the nature of the ions present, and their relative adsorbability. Acids with smaller dielectric constants, such as acetic and formic acids, are more highly adsorbed and lower the charge to a greater extent than acids of higher dielectric constant, such as oxalic and hydrochloric acids.[2] The coagulating power of these acids is the reverse of their capacity to diminish the charge. The cataphoretic speed varies with the period of dialysis and has been observed[3] to decrease up to 8 days, increase up to 28 days and then to decrease; the effect is attributed to changes in the composition of the sol during dialysis.

The fact that the addition of acids or salts to the hydrosol caused coagulation of the arsenic trisulphide particles was first recorded in 1832 by Boutigny,[4] who observed that the mineral acids were most effective, but that weak organic acids, such as oxalic and acetic acids, and even carbonic acid, caused some precipitation. Such weak acids as boric, tartaric, benzoic and salicylic acids, when added in cold solution, do not cause precipitation. Salts which are strong electrolytes readily cause precipitation, and Schulze[5] observed that the concentration required depended on the ion whose charge was of opposite sign to that of the colloid, the coagulating power of the ion being greater the higher the valency. This was confirmed in an extensive series of experiments carried out by Freundlich,[6] some results of which are given in the table opposite. The precipitation values were compared by determining the concentration of the salt solution that, within a given time and under otherwise equal conditions, caused a separation of flocks large enough to be completely kept back by a filter of standard type.

There is a limiting concentration necessary for complete precipitation, and also a limiting concentration below which no coagulation occurs even after a long interval of time. Thus, with a hydrosol containing 9·57 millimoles of arsenious sulphide per litre, to portions of which potassium chloride was added in concentrations of 1·22, 2·44 and 3·90 millimoles per litre, respectively, no precipitation had occurred in the first two cases after 340 days, whereas in the third almost complete precipitation took place in that time.[7]

The anion is not completely without influence on the precipitating power of the electrolyte. Solutions of chlorides, bromides, iodides and nitrates, if the cations are of equivalent concentrations, show the same coagulating power, and the same relation obtains for the free acids.

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[1] Mukherjee, *Kolloid-Zeitsch.*, 1930, 53, 159; Mukherjee and Ganguly, *J. Indian Chem. Soc.*, 1930, 7, 465.

[2] Mukherjee and co-workers, *ibid.*, 1925, 2, 296; 1933, 10, 27.

[3] Joshi, Barve and Desai, *Proc. Indian Acad. Sci.*, 1936, 4, A 590.

[4] Boutigny, *J. Chim. Méd.*, 1832, [1], 8, 449.

[5] Schulze, *J. prakt. Chem.*, 1882, [2], 25, 431; Hardy, *Zeitsch. physikal. Chem.*, 1900, 37, 385.

[6] Freundlich, *ibid.*, 1903, 44, 129.

[7] Freundlich, *loc. cit.*

PRECIPITATION VALUES OF ELECTROLYTES FOR ARSENIOUS SULPHIDE HYDROSOL (7·54 MILLIMOLES PER LITRE).

Electrolyte.	Concentration (millimoles per litre).	Electrolyte.	Concentration (millimoles per litre).
Univalent Cations :		*Bivalent Cations :*	
HCl . .	30·8	$MgSO_4$ . .	0·810
$\frac{1}{2}H_2SO_4$ . .	30·1	$MgCl_2$ . .	0·717
$\frac{1}{2}K_2SO_4$ . .	65·5	$CaCl_2$ . .	0·649
KCl . .	49·5	$SrCl_2$ . .	0·635
KNO_3 . .	50·0	$BaCl_2$ . .	0·691
NaCl . .	51·0	$Ba(NO_3)_2$ . .	0·687
LiCl . .	58·5	$ZnCl_2$ . .	0·685
K formate .	86		
K acetate .	110	*Tervalent Cations :*	
$\frac{1}{3}K_3$ citrate .	240	$AlCl_3$ . .	0·093
		$Al(NO_3)_3$ . .	0·095

With anions of higher valency, however, the salt concentration necessary to precipitate the trisulphide within a given time increases with the valency of the anion, and the effect is more marked with fairly complex anions, such as in benzoates and ferrocyanides.[1] This is shown in the table of results (see p. 260) which were obtained with sols containing 39·8 millimoles of arsenic trisulphide per litre ; *a* is the dilution of the electrolyte in litres containing 1 gram-equivalent after mixing ; *b* is the concentration of the cation in gram-ions per litre at 18° C. (or * at 25° C.) ; the relative times of coagulation were observed by passing a definite current (0·2 amp.) through a straight filament 4-volt lamp placed at a fixed distance from the cell containing the colloid. As coagulation proceeded, the sol became more and more opaque and the light of the lamp viewed through the cell diminished in intensity ; the time at which the filament became invisible was determined, at least six observations being made in each case.

The influence of the anion, however, is relatively unimportant and the valency has little effect ; the complexity appears to be an influencing factor.

The process of coagulation is greatly affected by the quality and concentration of the sol and by the concentration of the electrolyte. It may be studied photometrically by periodically measuring the coefficient of absorption, which first increases rapidly and then reaches a limiting value. The speed of the flocculation by alkali chlorides and by aluminium chloride is greatly retarded by the presence of a slight excess of hydrogen sulphide in the sol, but precipitation with calcium, strontium and barium chlorides is accelerated, whilst there is little effect on the precipitation with manganese or magnesium chloride. The presence of

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[1] Mukherjee and Chaudhury, *J. Chem. Soc.*, 1924, 125, 794; Ghosh and Dhar, *Kolloid-Zeitsch.*, 1925, 36, 129.

INFLUENCE OF ANION ON TIME OF COAGULATION OF As_2S_3 SOL.

Electrolyte.	*a*.	*b*.	Time.
(i) Potassium salts:			
Chloride . .	24	0·0373	7 min. 29 sec.
Sulphate . .	22	0·035	25 ,, 20 ,,
Oxalate . .	16	0·049	11 ,, 43 ,,
Benzoate . .	16	. .	100 ,, 0 ,,
(ii) Potassium salts:			
Chloride . .	14	0·061	8 ,, 7 ,,
Sulphate . .	14	0·053	28 ,, 11 ,,
Benzoate . .	8	. .	68 ,, 0 ,,
Ferrocyanide .	8	0·069*	29 ,, 59 ,,
(iii) Acids:			
HCl . . .	34	0·0275	10 ,, 52 ,,
$\frac{1}{2}H_2SO_4$ . .	24·4	0·0271	9 ,, 44 ,,
$\frac{1}{2}H_2C_2O_4$ . .	8	0·0345	7 ,, 2 ,,
$CH_2Cl.COOH$.	2	0·075	7 ,, 14 ,,
$CCl_3.COOH$.	26	0·0361	1 ,, 4 ,,

an excess of arsenious oxide, on the other hand, increases the flocculating power of univalent and bivalent ions, thus sensitising the sol, but the effect is less than that caused by hydrogen sulphide.[1] In comparing the effects of electrolytes on the sol, the latter should be carefully freed from both these impurities. Hydrogen sulphide itself is liable to cause considerable coagulation if a sol containing it is heated to 180° C.,[2] whilst if the hydrogen sulphide is first removed no precipitation is apparent at this temperature. The rapidity of coagulation with potassium and barium chlorides diminishes as the colloid particles increase in size, but the inverse is the case with aluminium and thorium chlorides.[3] The increase of particle size by boiling makes sols more stable at first towards potassium and barium chlorides and then less stable; the stability towards aluminium chloride is practically unaffected.[4] The sols on dialysis become more stable towards potassium chloride and less stable towards barium and aluminium chlorides. A smaller minimum quantity of thorium chloride is necessary for precipitation of a coarse-grained than for a fine-grained sol.

With constant quantities of electrolyte and colloid, the velocity of flocculation diminishes at first as dilution of the electrolyte increases, but tends towards a limit when the dilution reaches a certain value.[5]

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[1] Boutaric and Vuillaume, *Compt. rend.*, 1921, 172, 1293; *J. Chim. phys.*, 1924, 21, 247; Mukherjee and Ganguly, *J. Indian Chem. Soc.*, 1930, 7, 465.

[2] Katsurai, *Bull. Chem. Soc. Japan*, 1932, 7, 257.

[3] Boutaric and Vuillaume, *Compt. rend.*, 1924, 178, 938; Boutaric and Semelet, *J. Chim. phys.*, 1929, 26, 195.

[4] Boutaric and Morizot, *Bull. Soc. chim.*, 1934, [5], 1, 153.

[5] Boutaric and Vuillaume, *Compt. rend.*, 1921, 173, 229.

In comparing velocities of flocculation by different electrolytes it is therefore necessary to ensure in every case that the electrolyte is sufficiently diluted to give the limiting velocity. When the amount of added electrolyte is varied, but the concentration is kept constant, the velocity of flocculation increases with the amount of electrolyte used. The velocity of flocculation increases as the concentration of the colloid increases with potassium, barium, magnesium and manganese chlorides, but diminishes with aluminium and cadmium chlorides.[1] Moreover, the amount of the electrolyte necessary to cause flocculation varies with the concentration of the colloid and also with the valency of the cation. Thus, with sols [2] containing, respectively, 0·027 and 0·00337 g. As_2S_3 per c.c. the concentration of the electrolyte required to coagulate a given amount of disperse phase, for univalent ions, K^+, Li^+, increased with decreasing concentration of the colloid; for bivalent ions, Mg^{++}, Ba^{++}, the concentration necessary was almost constant and independent of the concentration of the colloid; for tervalent ions, Al^{+++}, La^{+++}, the concentration necessary varied almost directly with that of the colloid, and for quadrivalent ions, Zr^{++++} and Ce^{++++}, it decreased much more rapidly than the concentration of the colloid. Hazel and McQueen [3] showed that the position of some ions in the lyotropic series, *i.e.* the order of precipitating power, was altered in going from high to low concentrations of the sol; thus, for high concentrations the order is Th > Cr > Al > Fe > Ba > K and for low concentrations Th > Cr > Fe > Al > Ba > K. The order of the coagulating power of the alkali sulphates is Cs > Rb > K > Na > Li.[4] Mukherjee and Ganguly [5] found that dilution of arsenious sulphide sols, whether arsenious oxide was present or not, stabilised the sol towards hydrochloric acid or lithium, potassium and barium chorides; but, as regards the last-named, this is not in agreement with the observations of Burton, Dhar and their co-workers. Ghosh and Dhar [6] ascribe the stabilisation towards univalent ions on dilution to hydrolysis and to the peptising effect of the hydrogen sulphide thus formed being greater than the coagulating effect of arsenious acid. Rossi and Marescotti agree that dilution of the sol increases greatly the degree of dispersion of the arsenious sulphide.[7]

The temperature also affects the process of coagulation.[8] With the chlorides of potassium, sodium, lithium and ammonium the velocity of flocculation varies inversely as the temperature;[9] with the chlorides of barium, strontium, calcium, magnesium and cadmium the velocity varies directly as the temperature; with aluminium chloride it is independent of the temperature. Heating thus stabilises the sol towards univalent cations but diminishes the stability towards bivalent ions.[10] The

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[1] Boutaric and Vuillaume, *ibid.*, 1922, 174, 1351.

[2] Burton and Bishop, *J. Physical Chem.*, 1920, 24, 701; Burton and MacInnes, *ibid.*, 1921, 25, 517.

[3] Hazel and McQueen, *ibid.*, 1933, 37, 553.

[4] Mukherjee and Chaudhury, *J. Chem. Soc.*, 1924, 125, 794.

[5] Mukherjee and Ganguly, *J. Indian Chem. Soc.*, 1930, 7, 465.

[6] Ghosh and Dhar, *Kolloid-Zeitsch.*, 1925, 36, 129.

[7] Rossi and Marescotti, *Gazzetta*, 1929, 59, 319.

[8] Linder and Picton, *J. Chem. Soc.*, 1905, 87, 1906; Paine, *Proc. Camb. Phil. Soc.*, 1912, 16, 430.

[9] Boutaric and Vuillaume, *Compt. rend.*, 1922, 174, 1351.

[10] Mukherjee, *J. Chem. Soc.*, 1920, 117, 350. Ghosh and Dhar (*Kolloid-Zeitsch.*, 1925, 36, 129) state that heating increases the stability of the sol towards uni- and bi-valent ions.

stability is also diminished towards hydrochloric and sulphuric acids.[1] The effects of temperature are small compared with valency and concentration effects, and with aluminium sulphate and thorium nitrate both increase and decrease in stability may be met with, according to the quality of the sol and the concentration of the electrolyte. The influence of temperature depends also on the concentration of the sol when the concentration of the coagulating electrolyte is constant.[2] The addition of the electrolyte lowers the critical temperature of stability, that is, the temperature below which the sol is indefinitely stable, by weakening the repulsive forces.[3]

The age of the sol may also affect the observations,[4] the sol generally becoming less stable on ageing.[5] Thus the precipitation value of barium chloride decreases with time;[6] but ageing may cause either an increase or a decrease of stability towards a particular electrolyte, according as the micelles contain excess of arsenious oxide or of hydrogen sulphide.[7] Ageing, especially under the influence of light, results in a decrease in the amount of disperse phase, an increase in the amount of arsenious acid in the dispersion medium, and the production of colloidal sulphur. These factors influence the stability of the sol to an extent which varies with different electrolytes.

Since the precipitating influence of an electrolyte is mainly determined by the electric charge on the ion with opposite charge to that on the colloid particle, the effect appears to be a consequence of the reduction or elimination of the potential difference between the disperse phase and the medium. If it is assumed that the negative charge on the arsenious sulphide particle is due to adsorption of anions, then the neutralisation of this charge, and consequently precipitation, can be brought about by adsorption of cations. As seen in the table on p. 259, the hydrogen ion, which is readily adsorbed, has a greater coagulating power than other univalent ions, and this is generally true, any readily adsorbable ion having a lower precipitating value than other ions of the same valency.[8] The organic ions are generally readily adsorbed and their precipitating values, given opposite, for an arsenic trisulphide sol containing 7·54 millimoles per litre should be compared with the values for inorganic ions given in the table on p. 259.

Moreover, the adsorbability of an ion is generally greater the greater the valency. Matsuno[9] used the precipitating values of cobaltammines to determine the valency of the complex ions, employing the equation, deduced from Freundlich's adsorption hypothesis, $S_N = S/N^4$, where S_N is the equivalent concentration of an N-valent ion, N being the valency of the complex ion, and S the precipitating value of a univalent ion. The results confirmed those obtained by spectroscopic and conductivity methods.

The way in which the precipitating electrolyte is added has a notable

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[1] Mukherjee, *loc. cit.*; Joshi and Phansalkar, *J. Indian Chem. Soc.*, 1932, 9, 157. *Cf.* Linder and Picton, *loc. cit.*

[2] Joshi and Phansalkar, *loc. cit.*

[3] Deacon and Annetts, *Trans. Roy. Can. Inst.*, 1931, 18, i, 33.

[4] Mukherjee and Sen, *J. Chem. Soc.*, 1919, 115, 462.

[5] Ghosh and Dhar, *Kolloid-Zeitsch.*, 1925, 36, 129.

[6] Kruyt and Briggs, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, 32, 384.

[7] Krestinskaja, *Kolloid-Zeitsch.*, 1934, 66, 58.

[8] Weiser, *J. Physical Chem.*, 1926, 30, 1526. Also *ibid.*, 1921, 25, 399, 655; 1924, 28, 237; 1925, 29, 955, 1253; 1926, 30, 20.

[9] Matsuno, *J. Coll. Sci. Tokyo*, 1921, 41, [11], 1–15.

PRECIPITATION VALUES OF ORGANIC ELECTROLYTES FOR ARSENIOUS SULPHIDE HYDROSOL[1] (7·54 MILLIMOLES PER LITRE).

Electrolyte.	Concentration (millimoles per litre).	Electrolyte.	Concentration (millimoles per litre).
Univalent Cations :		*Bivalent Cations :*	
Guanidine nitrate	16·4	Quinine sulphate	0·24
Strychnine nitrate	8·0	Benzidine nitrate	0·087
Aniline chloride .	2·52		
Toluidine sulphate	1·17		
p-Chloraniline chloride	1·08		

effect, and the slower the addition, the longer the time and the greater the quantity of the reagent required for complete precipitation.[2] The hydrosol may thus appear to become "acclimatised" to the coagulant. The first effect of adding the electrolyte is the neutralisation of the colloid charge, and the delay in precipitation on slow addition is due to adsorption of the precipitating ion by the neutralised particles. It was suggested by Mines[3] that the precipitant reverses the sign of part of the disperse phase, which then mutually precipitates with uncharged particles; when slowly added, time is afforded for all the particles to be equally affected and there is therefore no precipitation. According to Ghosh and Dhar,[4] the phenomenon is to be traced to adsorption of ions carrying the same charge as the sol particles. Krestinskaja and Jakovleva[5] studied the effect of slowly adding barium chloride solution to the sol, and concluded that the Ba^{++}-ions react with the hydrolysis products of the arsenious sulphide, so quickening the hydrolysis. The hydrolysis products are arsenious acid and hydrogen sulphide, and an outer layer of the latter in the micelle gives a negative charge to it. The barium sulphide formed is adsorbed by the colloid and consequently the Ba^{++}-ion concentration of the solution is diminished; thus the critical amount of barium chloride required for coagulation is increased. This explanation is supported by the fact that hydrochloric acid, which does not accelerate the hydrolysis of arsenious sulphide, does not show the "acclimatisation" phenomenon. If this acid is added to the hydrosol in amounts insufficient to cause coagulation, a stabilising or a destabilising effect may result as regards the precipitating action of the hydrochloric acid itself. The effect depends on the quantity added and is accompanied by a change in the degree of dispersion of the sol—an increase or a decrease according as the sol is stabilised or destabilised.[6]

When the addition of acids is spread over several days, small amounts being added at intervals, the quantity required to effect coagulation is

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[1] Freundlich, *Zeitsch. physikal. Chem.*, 1903, 44, 129.

[2] Freundlich, *ibid.*, p. 143.

[3] Mines, *Jahrb. Miner.*, 1893, 2, 147.

[4] Ghosh and Dhar, *J. Physical Chem.*, 1925, 29, 435.

[5] Krestinskaja and Jakovleva, *Kolloid-Zeitsch.*, 1928, 44, 141.

[6] Rossi and Marescotti, *Gazzetta*, 1930, 60, 993.

less than that required when added all at once.[1] This phenomenon, which has been termed "negative acclimatisation," is more marked in dilute solutions. It appears to originate from the checking by the acid of hydrolysis of the sol, and is observed only where adsorption of oppositely charged ions is very high and that of similarly charged ions is negligible. The "positive acclimatisation" described above involves the adsorption of similarly charged ions. The "negative acclimatisation" also occurs when univalent electrolytes such as potassium chloride or nitrate are added to arsenious sulphide sols in the presence of strong acids, the diminution of hydrolysis due to the latter resulting in a decrease of peptisation.[2] Also, smaller quantities of crystal violet, strychnine or quinine hydrochloride are required to coagulate the sol if the electrolyte is added slowly than if rapidly.

The above explanation of "acclimatisation" is supported by the results obtained on adding mixtures of electrolytes to the hydrosol. Hydrolysis of the coagulating electrolyte has a pronounced influence and the presence of one electrolyte may diminish the coagulating power of another. More magnesium chloride is required to coagulate a sol containing lithium chloride than is required in the absence of lithium chloride. Also in the presence of sodium benzoate or sodium nitrite, more than the calculated quantity of potassium or barium chloride is required for precipitation.

An examination of the changes in hydrogen ion concentration during coagulation of the hydrosol led Rabinowitsch[3] to suggest that the latter behaved as a fairly strong complex acid, ionising as follows:

$$(As_2S_3)_n.SH_2 \rightleftharpoons (As_2S_3)_n.SH^- + H^+ \rightleftharpoons (As_2S_3)_n.S^= + 2H^+$$

the second ionisation constant being less than the first. The hydrogen ion concentrations of the sol and of the filtrate after precipitation by means of barium chloride were measured and the latter was found to be the greater after correcting for dilution.[4] The increase in acidity rises with concentration of the sol. The coagulum contained Ba^{++}-ions but no Cl^--ions. When an arsenious sulphide sol is titrated with barium chloride, the conductivity increases, and the increase is due in part to the presence of the added electrolyte and partly to the liberation of the more mobile H^+-ions. This increase in acidity appears to be general, and the addition of an electrolyte to the sol causes at first a rapid increase in conductivity, which gradually slows down and becomes linear. The initial increase is ascribed to the displacement of the H^+-ions by the cations of the electrolyte, a process which ceases as the conductivity curve becomes linear. In order to produce coagulation, a cation must partly or completely displace the H^+-ions which are attached to the colloid particles; a certain excess of cations is also necessary, which is the greater the lower the valency of the ion.[5] The adsorption of cations of different valencies by the colloid particles reaches a maximum at approximately the same equivalent concentration, but the quantities adsorbed vary. The process of coagulation thus takes place in two stages: (i) the exchange of added cations with

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[1] Prakash, Ghosh and Dhar, *J. Indian Chem. Soc.*, 1928, 5, 313.

[2] Ghosh, Battacharya and Dhar, *Kolloid-Zeitsch.*, 1926, 38, 141.

[3] Rabinowitsch, *Zeitsch. physikal. Chem.*, 1925, 116, 97; *J. Russ. Phys. Chem. Soc.*, 1926, 58, 849.

[4] See also Rabinowitsch and Burstein, *Chem. Zentr.*, 1927, ii, 1007.

[5] Rabinowitsch and Dorfmann, *Zeitsch. physikal. Chem.*, 1928, 131, 313.

the H^+-ions of the sol particles; (ii) visible clotting of the particles.[1] The action of dilute solutions of potassium, barium and aluminium chlorides on arsenious sulphide hydrosol enclosed in sealed tubes was observed over a period of 4 to 9 months, and the time noted at which precipitation suddenly increased.[1] The concentration required to cause coagulation was not equivalent to the concentration of H^+-ion liberated from the sol; the K^+-ion displaces the H^+-ion only slowly, while the Al^{+++}-ion tends to cause coagulation before the exchange adsorption is complete; the displacing power and consequently the precipitating power of the Ba^{++}-ion is intermediate between these two. The second stage, the clotting of the particles, is ascribed by Rabinowitsch to electrostatic compression. Weiser and Gray [2] followed the changes in hydrogen ion concentration by means of the glass electrode during the stepwise addition of metallic chlorides to the hydrosol, and showed that the H^+-ion displacement curve resembles an adsorption curve. The displacement is relatively greater at lower concentrations and reaches a maximum at or below the precipitation value. The total displaced H^+-ion amounts to 20 to 40 per cent. of the total hydrogen ion concentration of the supernatant liquid after coagulation, the actual proportion depending on the conditions of formation of the sol. The amount of H^+-ion displaced is less than the amount of precipitating ion adsorbed. The order of displacing power of the chlorides examined was $Al > Ba$ or $Sr > Ca > NH_4$, which is also the order of their precipitating power and the order of their adsorption below the precipitation value. Ghosh [3] found, however, that the order of the precipitating values of the alkali and alkaline earth metals, determined by measuring the velocity of increase in turbidity, was the inverse of their adsorption values, thus: $Li > Na > K > NH_4 > H$; and $Mg > Ca > Sr > Ba$.

The pH value at which an arsenious sulphide sol flocculates infinitely slowly is approximately the same for different strong acids.[4] Thus for a sol containing 1·55 g. As_2S_3 per litre the pH was 1·22, but the value varies with the concentration of the sol. Weak acids fail to cause precipitation of the sol of the concentration mentioned; with more concentrated sols weak acids cause precipitation, but the limiting pH shows a minimum value, less acid being required for very dilute and for very concentrated sols than for sols of intermediate concentrations. On dilution or neutralisation by potassium hydroxide, the pH value of an arsenious sulphide sol varies in a similar manner to the pH under similar conditions in the case of a weak acid, such as acetic acid, except that equilibrium is attained only after 1 to 3 days, indicating an evolution in the structure of the micelles.

Coagulation is supposed to occur when the potential of the electrical double layer is decreased to a certain critical value. The potential is directly proportional to the cataphoretic speed, but Mukherjee and Raichoudhuri [5] assert that there is no critical potential at which coagulation takes place.

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[1] Rabinowitsch and Vassiliev, *Kolloid-Zeitsch.*, 1932, 60, 268.

[2] Weiser and Gray, *J. Physical Chem.*, 1932, 36, 2796.

[3] Ghosh, *J. Indian Chem. Soc.*, 1932, 9, 591.

[4] Boutaric and Perreau, *Bull. Acad. roy. Belg.*, 1928, [5], 14, 666; *Bull. Soc. chim.*, 1929, [4], 45, 701.

[5] Mukherjee and Raichoudhuri, *Nature*, 1928, 122, 960. Mukherjee, *Kolloid-Zeitsch.*, 1930, 53, 159. See also Jabłczyński, *ibid.*, 1931, 54, 164; Joshi and Prabhu, *J. Indian Chem. Soc.*, 1931, 8, 337.

Changes in conductivity, pH value and stability result on filtering arsenious sulphide sols, probably owing to dissolution of electrolytes from the paper, or to adsorption of H^+-ions by the paper.[1] Similar changes occur also on dialysis, the conductivity showing at first a sharp decrease, followed by a slow increase probably due to slow ionisation.[2]

When arsenious sulphide is precipitated from a solution containing a barium salt, the adsorbed barium cannot be removed from the precipitate by washing with aqueous sodium or potassium chloride, but if washed with a solution of a tervalent metal, such as iron, aluminium or chromium, interchange of barium with the metal takes place.[3] After precipitating an arsenious sulphide hydrosol with barium chloride, Pauli and Semler [4] found that the precipitate contained 4 equivalents of barium for each equivalent of H^+-ion found in the sol, and suggested as a possible composition of the colloid, $[x\mathrm{As_2S_3.H_2As_2S_4.HAs_2S_4}]\mathrm{H}$, one hydrogen atom only being ionised in solution, but all four being replaceable on precipitation.

It was observed by Kruyt and van Duin [5] that the addition of an alcohol or phenol to the hydrosol influenced the coagulation by electrolytes, sensitising the sol (*i.e.* diminishing the limiting concentration of electrolytes necessary for coagulation) towards uni- and ter-valent cations, and stabilising the sol towards bi- and quadri-valent cations. The observations of subsequent workers indicate that the behaviour of the coagulating ion in the presence of a non-electrolyte cannot be predicted from its valency, nor does the adsorbability of the ion run parallel to the tendency to coagulation. Small amounts of alcohols sensitise the sol towards sodium chloride, the effect increasing with increased molecular weight of the alcohol.[6] Higher concentrations caused stabilisation until a maximum was reached, when further alcohol sensitised the sol again. Ethyl alcohol stabilises the sol towards barium chloride over a wide range of concentration.[7] With aluminium chloride, the coagulation concentration diminishes with increasing concentration of alcohol. With sodium sulphate, a large concentration of ethyl alcohol compared with that of the electrolyte sensitises the sol; whilst a little alcohol stabilises the sol towards ceric and thorium chlorides. Methyl alcohol sensitises the sol towards barium chloride, and both alcohols sensitise it towards hydrochloric acid and reduce the cataphoretic velocity. Weak organic acids act in a similar manner to alcohols. The effects appear to be due (i) to a decrease in the dielectric constant of the medium, so that coagulation takes place at a higher particle charge and the sol is sensitised, and (ii) to a change in the interfacial tension, which also affects the potential at which coagulation takes place.[8] That the change in dielectric constant

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[1] Annetts, *J. Physical Chem.*, 1932, 36, 2936.

[2] Pauli and Semler, *Kolloid-Zeitsch.*, 1924, 34, 145.

[3] Charriou, *Compt. rend.*, 1923, 176, 1890.

[4] Pauli and Semler, *Kolloid-Zeitsch.*, 1924, 34, 145. *Cf.* Bhatnagar and Rao, *ibid.*, 1923, 33, 159.

[5] Kruyt and van Duin, *Koll. Beihefte*, 1914, 5, 269. See also Boutaric and Semelet, *J. Chim. phys.*, 1929, 26, 195.

[6] Janek and Jirgensons, *Kolloid-Zeitsch.*, 1927, 41, 40.

[7] Mukherjee and co-workers, *Quart. J. Indian Chem. Soc.*, 1926, 3, 349; Dumanski and Bondarenko, *J. Gen. Chem.* (*U.S.S.R.*), 1931, 1, 937. See also Lepeshkin, *Kolloid-Zeitsch.*, 1926, 36, 41.

[8] Chaudhury, *J. Physical Chem.*, 1928, 32, 1481; Mukherjee and co-workers, *loc. cit.* *Cf.* Weiser, *J. Physical Chem.*, 1925, 29, 955, 1253; 1926, 30, 20.

alone is insufficient to account for the influence of non-electrolytes on coagulation is the conclusion arrived at by Bikermann[1] after a study of the coagulation of organosols of arsenic trisulphide by certain electrolytes; the electrokinetic potential at which coagulation occurred was almost independent of the nature of the dispersion medium, and its value did not vary more than 20 per cent. in sols whose dielectric constants showed a 5-fold variation.

When two colloids of opposite electric charges are mixed, mutual precipitation may occur. Thus the gradual addition of ferric hydroxide or aluminium hydroxide hydrosol to arsenic trisulphide hydrosol causes instability in the system, the cataphoretic speed is lowered and a point is reached at which complete precipitation occurs. Mixtures containing higher proportions of the positive sol move towards the cathode during cataphoresis, so that the mobilities of the mixtures lie between those of the pure colloids.[2] Billiter[3] made the following observations of the appearance and behaviour of mixtures of ferric hydroxide and arsenic trisulphide hydrosols:

BEHAVIOUR OF MIXED SOLS OF ARSENIC TRISULPHIDE AND FERRIC HYDROXIDE.

Composition of Mixture (mg. in 10 c.c.).		Cataphoresis.	Coagulating Effect.
As_2S_3	Fe_2O_3		
20·3	0·61	To anode	Opalescence
16·6	6·08	,,	Immediate precipitation
14·5	9·12	No movement	Complete ,,
10·4	15·2	To cathode	Immediate ,,
4·14	24·3	,,	Slight opalescence
2·07	27·4	,,	No change

The amount of a positive sol necessary for complete precipitation is not the chemical equivalent of the arsenic trisulphide present and the requisite amounts of various positive sols differ considerably. This is shown in the following list of optimum quantities required for the precipitation of a hydrosol containing 24 mg. of arsenic trisulphide:[4]

Positive sol .	Fe_2O_3	ThO_2	CeO_2	ZrO_2	Al_2O_3	Cr_2O_3
Milligrams .	13	6	4	2	2	0·5

The decreased stability of the system results from mutual adsorption by the two colloids, with consequent unequal redistribution of the total

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[1] Bikermann, *Zeitsch. physikal. Chem.*, 1925, 115, 261.

[2] Hazel and McQueen, *J. Physical Chem.*, 1933, 37, 553.

[3] Billiter, *Zeitsch. physikal. Chem.*, 1905, 51, 142. *Cf.* Boutaric and Dupin, *Bull. Soc. chim.*, 1928, [4], 43, 44.

[4] Biltz, *Ber.*, 1904, 37, 1095. See Lottermoser and May, *Kolloid-Zeitsch.*, 1932, 58, 61.

charges round the aggregates; chemical reactions between the stabilising ions do not appear to have an important effect.[1]

The addition of a protective colloid, such as gelatin or agar-agar, to a hydrosol of arsenious sulphide results in stabilisation of the sol towards the precipitative action of electrolytes.[2] If only a trace of gelatin is added, however, precipitation is facilitated, that is, a smaller quantity of the electrolyte effects precipitation.[3] This appears to be due to the interaction of the gelatin with the traces of stabilisers present in the hydrosol, resulting either in adsorption of the stabilisers by the gelatin, or in diminution of the gelatin concentration by the precipitative action of the stabilisers.[4] Larger quantities of gelatin hinder precipitation, probably owing to the formation of a film of gelatin particles round the particles of arsenic sulphide, thus preventing their coalescence. The following example illustrates this protective action. To coagulate 300 c.c. of a hydrosol containing 0·2872 g. of arsenious sulphide, 12·87 millimoles of hydrochloric acid were necessary; but after addition of 12 g. of gelatin, 300 millimoles of hydrochloric acid were necessary.[5] If the gelatin is added slowly, drop by drop, to the hydrosol, the latter is less stable towards electrolytes than when the protective colloid is added all at once;[6] this is a parallel of the "acclimatisation" phenomenon mentioned on p. 263. Protective action is also exerted by soaps, and with these it is generally increased by rise in temperature.[7]

On exposure to light, arsenic trisulphide hydrosols show an increase in electrical conductivity, the rate of change increasing with decreasing concentration of the sol.[8] The charge on the colloid particle decreases and the conductivity increases with an increase in the period of exposure. After a short exposure the hydrosol is stabilised towards uni- and bi-valent electrolytes, but it becomes unstable on prolonged exposure. According to Joshi and his co-workers, there is no preliminary stabilisation towards magnesium chloride. Ganguly and Dhar[9] observed that the sols coagulated on exposure to tropical sunlight. The hydrosols are photochemically active, the oxidation of certain coloured compounds, such as eosin and malachite green, being sensitised by them in light.[10] Peskoff[11] observed that in the light the addition of anthracene to the sol caused precipitation after a few hours, but in the dark there was no change after 17 days. The increase in electrical conductivity and the photochemical activity are attributed to increased hydrolysis in light of the arsenic trisulphide, free arsenious acid and hydrogen sulphide being formed.[12] The latter is oxidised to sulphur and a thionic acid by

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[1] Hazel and McQueen, *J. Physical Chem.*, 1933, 37, 571. *Cf.* Thomas and Johnson, *J. Amer. Chem. Soc.*, 1923, 45, 2532; Joshi and Panikkar, *J. Indian Chem. Soc.*, 1936, 13, 309.

[2] Müller and Artmann, *Oesterr. Chem. Zeit.*, 1904, 7, 149; Traube and Rackwitz, *Kolloid-Zeitsch.*, 1925, 37, 131.

[3] Billiter, *Zeitsch. physikal. Chem.*, 1905, 51, 129.

[4] Peskoff, *J. Russ. Phys. Chem. Soc.*, 1917, 49, 1.

[5] Rossi and Marescotti, *Gazzetta*, 1929, 59, 313.

[6] Rao, *J. Indian Chem. Soc.*, 1931, 8, 621.

[7] Papaconstantinou, *J. Physical Chem.*, 1925, 29, 323.

[8] Murphy and Mathews, *J. Amer. Chem. Soc.*, 1923, 45, 16; Roy, *J. Indian Chem. Soc.*, 1929, 6, 431; Joshi, Barve and Desai, *Current Sci.*, 1934, 3, 105.

[9] Ganguly and Dhar, *Kolloid-Zeitsch.*, 1922, 31, 16.

[10] Freundlich and Nathansohn, *Kolloid-Zeitsch.*, 1920, 28, 258.

[11] Peskoff, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 1619; *Kolloid-Zeitsch.*, 1923, 32, 24, 163, 238.

[12] Freundlich and Nathansohn, *loc. cit.*; Murphy and Mathews, *loc. cit.*

the sensitising action of the micelles of arsenic trisulphide. A reaction between the thionic acid and hydrogen sulphide, which provide stabilising ions for the micelles of arsenic trisulphide and sulphur, results in their removal and the destabilisation of the two colloids, which are consequently precipitated. The greater activity of the dilute sol is attributed to greater dispersion. When colloidal sulphur is added to colloidal arsenic trisulphide, the mixture is unstable, although both sols are negatively charged. The particles rapidly increase in size and the precipitation values of hydrochloric acid and aluminium nitrate are less than half the values for the individual sols. The instability is due probably to the reaction between pentathionic acid contained in the sulphur sol with hydrogen sulphide in the arsenic sulphide sol; so that the formation of sulphur micelles in colloidal arsenic trisulphide sols will always tend towards instability.

The earlier stages of the process of coagulation may be studied by measurement of the rate of change of the intensity of the scattered and transmitted light. By this means evidence has been obtained that after addition of traces of the precipitating electrolyte, a series of equilibrium states may be set up, so that coagulation occurs by stages.[1] Boutaric and Bouchard have examined the effect of visible and ultraviolet light on the rate of coagulation by electrolytes of arsenious sulphide hydrosols in fluorescent media,[2] such as fluorescein, eosin and erythrosin. In all cases illumination decreased the time required for coagulation, the effect being greater in ultraviolet light than in visible light freed from infrared. Thus the time was lowered by 15 to 30 minutes on exposure to light, and by 35 to 63 minutes by ultraviolet rays. Sulphuric acid and potassium sulphate, which inhibit the fluorescence of the dyes, also suppress the effect of light. The difference, Δt, between the time required for flocculation in the dark and in daylight or ultraviolet, is approximately proportional to the logarithm of the fluorescing power of the mixture of fluorescein and the electrolyte. Sulphuric acid gives the greatest inhibiting effect; lithium chloride has no effect, but tannin, hydroquinone, phenol or cresol, in the presence of lithium chloride, reduce both the fluorescing power and Δt. Eosin and erythrosin, which have absorption bands close to that of fluorescein, reduce the fluorescence of the latter and also reduce its effect on the flocculation. The addition of sucrose and glycerol to an arsenic trisulphide sol containing fluorescein and potassium chloride reduces the fluorescence by increasing the viscosity of the sol, and the effect on the flocculation time is consequently diminished.

Exposure to light, including ultraviolet and infra-red, has little effect either on the cataphoretic speed or the rate of coagulation of arsenious sulphide sols.[3] The absorption spectrum of the hydrosol has been studied [4] and shows that there is simple absorption which increases with the size of the particles, and also a selective absorption in the region

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[1] Burton and Annetts, *J. Physical Chem.*, 1931, 35, 48; Ghosh, *J. Indian Chem. Soc.*, 1932, 9, 591. See also Menon, *Proc. 15th Indian Sci. Cong.*, 1928, p. 72.

[2] Boutaric and Bouchard, *Compt. rend.*, 1931, 192, 95, 357; 193, 45; *Bull. Soc. chim.*, 1932, [4], 51, 757; Boutaric, *Annales Guebhard-Séverine*, 1935, 11, 25.

[3] Schaum and Friedrich, *Zeitsch. wiss. Photochem.*, 1924, 23, 98. The action of light was also studied by Bhatnagar and co-workers, *J. Physical Chem.*, 1924, 28, 387, 730; *J. Indian Chem. Soc.*, 1927, 4, 209; Lange, *Zeitsch. physikal. Chem.*, 1928, 132, 1.

[4] Boutaric and Vuillaume, *J. Chim. phys.*, 1924, 21. 247; *Compt. rend.*, 1923, 177, 259.

6200 A. which is due to reflection of the incident rays from the surfaces of the colloid particles, and which decreases with increase in the size of the particles. The product of the refractive index and the specific volume is a linear function of the concentration.[1]

If a mixture containing sols of silver and arsenic trisulphide is kept in the dark, the colour changes from golden-brown through greenish-brown to lilac, whilst in the light the colour goes through green to golden-yellow.[2] The former change appears to be due to direct interaction between the sol particles, but the latter involves oxygen, with the probable formation of a silver thioarsenite. Both changes are prevented by the addition of gelatin gel.

Periodic coagulation of arsenic trisulphide has been effected by diffusing a solution of ferric chloride or of aluminium sulphate into the sol contained in an agar gel.[3]

Many attempts have been made to elucidate the constitution of the colloidal aggregates in the arsenic trisulphide hydrosols. Linder and Picton [4] observed that the sols contained an excess of hydrogen sulphide which was not removable by hydrogen, and considered this to be an essential constituent of the colloid, to which they assigned the formula $8As_2S_3.H_2S$. When coagulated by an electrolyte some of the metal is carried down with the precipitate, replacing the hydrogen, thus—

$$mAs_2S_3.H_2S + 2KCl \rightleftharpoons mAs_2S_3.K_2S + 2HCl$$

but Pauli and Semler found that four equivalents of the metal were removed for each equivalent of H^+-ion present in the sol and gave the formula $[xAs_2S_3.H_2As_2S_4.HAs_2S_4]H$ (see p. 266), while Rabinowitsch (see p. 264) considered it to be a fairly strong acid which he formulated $(As_2S_3)_n.SH_2$. Bhatnagar and Rao stated[5] that when hydrogen sulphide was removed from the sol the composition was more nearly $(AsS)_x$, and that if the red colloidal solution (see p. 255) is heated it yields the yellow sol and a precipitate of sulphur, the change involving oxygen, thus :

$$As_2S_2.xH_2S + xO = As_2S_3 + xH_2O + (x-1)S$$

If the hydrogen sulphide content is small, no sulphur is precipitated. These authors considered it probable that the red variety was identical in properties with realgar and the yellow with orpiment, and that the action of light and heat consists mainly in the transformation of one variety into the other, thus :

$$As_2S_2 + H_2S + O = As_2S_3 + H_2O$$

Chaudhury and his co-workers [6] showed that the composition of the hydrosol varied according to the method of its formation, but that arsenious acid was usually present. This they considered to be a normal constituent of the sol, and the many irregularities observed in different sols were attributed to interaction of H^+-ions and polythionic

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[1] Lifschitz and Beck, *Kolloid-Zeitsch.*, 1920, 26, 10; 1922, 31, 13.
[2] Freundlich and Moor, *Kolloid-Zeitsch.*, 1925, 36, 17.
[3] Hedges and Henley, *J. Chem. Soc.*, 1928, p. 2714.
[4] Linder and Picton, *ibid.*, 1892, 61, 128.
[5] Bhatnagar and Rao, *Kolloid-Zeitsch.*, 1923, 33, 159.
[6] Mukherjee and Chaudhury, *J. Indian Chem. Soc.*, 1925, 2, 296; Chaudhury and Kundu, *ibid.*, 1926, 3, 345.

acids present. The constitution of a sol containing excess of arsenious acid was given as As_2S_3, but in a sol containing no free arsenious acid or hydrogen sulphide the probable composition was thought to be $As_2S_3.H_2S$ or $As_2S_3.As_2S_5$ (see p. 255). Murphy and Mathews[1] suggested that a complex compound of the type $As_2O_3(As_2S_3)_x$ existed in the solution; Gazzi,[2] however, maintained that all the arsenious oxide may be removed by dialysis, and that the oxide and sulphide are present as a mixture.

Reversal of the electric charge on the colloid particle may be accomplished[3] by the adsorption of a large quantity of positive ions, and by employing a thorium salt a positively charged arsenic trisulphide sol has been obtained.

The addition of alkali to the arsenic trisulphide hydrosol causes a solvent action on the sol particles, the rate of dissolution depending on the alkali used and increasing in the order Li^+, Na^+, K^+, Rb^+, Cs^+.[4] The addition of ammonium hydroxide, however, greatly decreases the rate of dissolution. The coagulated sulphide is dissolved by alkalis in exactly the same order as above, so that the action is manifest with all degrees of dispersion.

Various organosols of arsenic trisulphide have been described. Bikermann[5] prepared stable sols in nitrobenzene and ethyl acetoacetate by passing dry H_2S through solutions of arsenic trichloride in the anhydrous liquids, the excess of hydrogen sulphide and the hydrogen chloride formed being removed by a current of dry air. Concentrations up to 29 millimoles As_2S_3 per litre were obtained. The sols were precipitated by dissolved salts at a definite potential which was practically independent of the solvent and the concentration of the sol; also the valency rule as to precipitating power held as for hydrosols. Concentrated sols in pure or aqueous glycerine, preferably in the presence of a protective colloid, are obtained[6] by the action of hydrogen sulphide on arsenious oxide dissolved in the medium.

Stable sols of arsenic trisulphide in concentrated acids, including sulphuric, phosphoric, acetic and trichloracetic acids, have been prepared.[7] In such sols coagulation occurs if a certain degree of ionisation of the acid is reached.

Arsenic Pentasulphide, As_2S_5.—When arsenic is fused with an excess of sulphur the product contains arsenic, sulphur and arsenic pentasulphide; the last-named may be extracted with liquid ammonia[8] or, by careful fractionation, the arsenic and sulphur may be removed, leaving the sulphide. If the elements are fused together in stoichiometric proportions, a greenish-yellow plastic mass is obtained which gradually hardens and becomes lemon-yellow: if this product is powdered and digested with aqueous ammonia, a yellow solution results and insoluble sulphur remains. After filtering, the addition of an acid to the yellow solution precipitates the pentasulphide.

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[1] Murphy and Mathews, *J. Amer. Chem. Soc.*, 1923, 45, 16.

[2] Gazzi, *Zymol. chim. colloidi*, 1927, 2, 10; *Chem. Zentr.*, 1927, [2], 27.

[3] Dhar and Sen, *J. Physical Chem.*, 1923, 27, 376; Mukherjee and Roy, *J. Chem. Soc.*, 1924, 125, 476.

[4] Peskoff, *Kolloid-Zeitsch.*, 1923, 32, 163.

[5] Bikermann, *ibid.*, 1927, 42, 293; *Zeitsch. physikal. Chem.*, 1925, 115, 261.

[6] Faust, *German Patent*, 424141 (1925).

[7] Wannow, *Kolloid-Zeitsch.*, 1936, 77, 251; Ostwald and Wannow, *ibid.*, 1936, 76, 159.

[8] Géhs, *Ann. Chim. Phys.*, 1873, [4], 30, 114.

Borodowski[1] failed to obtain evidence of the formation of this sulphide in his study of the freezing point curves (see p. 237) because, with mixtures containing 20 to 60 molar per cent. of arsenic, the products are viscous and do not give definite freezing points.

Arsenic pentasulphide may also be prepared from aqueous arsenic acid or a solution of an arsenate by the action of hydrogen sulphide, but the nature of the product depends upon conditions. Berzelius reported[2] the formation of the pentasulphide when the gas acted on a moderately concentrated solution of arsenic acid, but Wackenroder stated[3] that the arsenic acid was first reduced by hydrogen sulphide to arsenious acid, even in the presence of hydrochloric acid, and that a mixture of arsenic trisulphide and sulphur was then precipitated. Rose,[4] after passing hydrogen sulphide into a solution of arsenic acid, heated the solution and filtered off the precipitate, and then by the addition of silver nitrate showed that both arsenious and arsenic acids were present in the filtrate. It was therefore accepted that reduction takes place and the reaction was represented thus :

$$2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O$$

Bunsen[5] showed that the passage of a rapid stream of hydrogen sulphide through a hot solution of an alkali arsenate acidified with hydrochloric acid produced a precipitate of arsenic pentasulphide, and that this was a satisfactory method of determining arsenic quantitatively. These results were confirmed by McCay,[6] and led to more systematic investigation of the subject,[7] the result of which showed that the conditions favourable for the formation of arsenic pentasulphide, when hydrogen sulphide acts on aqueous arsenic acid or acid solutions of arsenates, are (*a*) a considerable excess of hydrochloric acid present, (*b*) a rapid passage of the gas, and (*c*) a comparatively low temperature—the liquid should be warm, as precipitation is extremely slow in the cold. Under these conditions arsenic pentasulphide alone is formed :

$$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$$

When these conditions are not fulfilled, in addition to the above, a secondary reaction occurs which proceeds in two stages, thus :

$$H_3AsO_4 + H_2S = H_3AsO_3 + S + H_2O$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$

Thus, in the absence of hydrochloric acid, a solution containing 0·6 per cent. of arsenic pentoxide gave a precipitate which, after removing the free sulphur, contained 85 per cent. of the pentasulphide. In the presence of 8 per cent. of hydrochloric acid the precipitate consisted of the pure pentasulphide. Solutions containing 0·3664 per cent. of As_2O_5 and varying quantities of hydrochloric acid, after treatment with

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[1] Borodowski, *Sitzungsber. Naturf. Ges. Dorpat.*, 1905, 14, 159; *Chem. Zentr.*, 1906, [2], 297.

[2] Berzelius, *Pogg. Annalen*, 1826, 7, 2.

[3] Wackenroder, *Annalen*, 1835, 13, 241. See also Ludwig, *Arch. Pharm.*, 1859, [2], 97, 32; Parnell, *Chem. News*, 1870, 21, 133.

[4] Rose, *Pogg. Annalen*, 1858, 105, 573; 1859, 107, 186.

[5] Bunsen, *Annalen*, 1878, 192, 305.

[6] McCay, *Chem. News*, 1887, 54, 287.

[7] Brauner and Tomíček, *J. Chem. Soc.*, 1888, 53, 145.

hydrogen sulphide for 12 hours at 15° C., gave precipitates which, after removal of free sulphur, had the following compositions :[1]

HCl, per cent. .	1·8	7·9	10·76	14·34	25·1	32·27
As_2O_5, ,, .	91	100	100	100	58	0
As_2O_3, ,, .	9	0	0	0	42	100

A boiling dilute aqueous solution of an alkali thioarsenate on addition of hydrochloric acid yields a precipitate which contains arsenic pentasulphide and may contain sulphur.[2] Under ordinary conditions the precipitation is not quantitative[3] and the excess of sulphur is difficult to remove ;[4] for complete precipitation the liquid should be kept overnight before filtration.[5]

A convenient method of preparing arsenic pentasulphide is to boil arsenic pentoxide with piperazine, when a solution is obtained which, by the prolonged action of hydrogen sulphide, yields the compound $As_2S_5.3C_4H_{10}N_2.3H_2S$; if this is treated with cold dilute hydrochloric or acetic acid, crystals of arsenic pentasulphide are formed.[6]

Properties.—Arsenic pentasulphide is usually obtained as an amorphous lemon-yellow powder. It is stable in air up to a temperature of about 95° C., but above this temperature a surface film of the trisulphide is formed ;[7] nevertheless, it may be dried at about 110° C. without sensible decomposition.[8] At a higher temperature it melts, the melting point being somewhat higher than that of sulphur.[9] The liquid is rather deeper in colour than the solid. On distillation, the vapour contains arsenic trisulphide and sulphur and the residue becomes continually richer in arsenic trisulphide.[10] The pentasulphide is very slightly soluble in pure water, 1 litre of which at 0° C. dissolves 1·36 mg. of As_2S_5.[11] It is much less soluble in the presence of hydrogen sulphide, and 1 litre of water containing 0·002 per cent. of the gas dissolves only 0·27 mg. As_2S_5. It is insoluble in alcohol or carbon disulphide, but is soluble in aqueous ammonia, alkali hydroxides or alkali sulphides, forming thioarsenates and oxythioarsenates. It also dissolves in aqueous solutions of citric acid and alkali citrates.[12] When the pentasulphide is boiled with water, a solution of arsenic trioxide is obtained, with separation of sulphur.[13] The pentasulphide is insoluble in hydrochloric acid and also in dilute nitric acid ; it is attacked by more concentrated nitric acid with evolution of nitric oxide. With acid of 20 to

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[1] Usher and Travers, *J. Chem. Soc.*, 1905, 87, 1370. See also le Roy and McCay, *Amer. Chem. J.*, 1887, 9, 174; 1888, 10, 459; 1890, 12, 547; Thiele, *Annalen*, 1892, 265, 65; Neher, *Zeitsch. anal. Chem.*, 1893, 32, 45.

[2] Berzelius, *loc. cit.*; Fuchs, *Zeitsch. anal. Chem.*, 1862, 1, 189.

[3] Nilson, *J. prakt. Chem.*, 1876, [2], 14, 145.

[4] Bunsen, *loc. cit.*; Brauner and Tomíček, *Monatsh.*, 1887, 8, 607.

[5] Holtje, *Zeitsch. anorg. Chem.*, 1929, 181, 395.

[6] Debucquet and Velluz, *Bull. Soc. chim.*, 1932, [4], 51, 1565, 1571.

[7] Nilson, *loc. cit.*

[8] Bunsen, *loc. cit.*; Brauner, *J. Chem. Soc.*, 1895, 67, 532.

[9] Berzelius, *loc. cit.*

[10] Gélis, *Ann. Chim. Phys.*, 1873, [4], 30, 114; *Compt. rend.*, 1873, 76, 1205; V. and C. Meyer, *Ber.*, 1879, 12, 1112.

[11] Höltje, *loc. cit.*

[12] Spiller, *J. Chem. Soc.*, 1858, 10, 110.

[13] de Clermont and Frommel, *Compt. rend.*, 1878, 87, 330.

40 per cent. concentration the action is observed only on boiling or vigorous agitation; with 60 per cent. acid the reaction proceeds in the cold.[1] Ammonia is absorbed by the pentasulphide, but is again liberated on exposure to air.[2] Arsenic pentasulphide is readily reduced by heating in hydrogen or with carbon, or when fused with a mixture of alkali cyanide and carbonate.[3]

THIOARSENATES.

Arsenic pentasulphide acts as an acid thioanhydride and with metallic sulphides yields salts known as thioarsenates. These may be regarded as derivatives of the following hypothetical acids:

H_3AsS_4, *Orthothioarsenic acid*
$H_4As_2S_7$, *Pyrothioarsenic acid*
$HAsS_3$, *Metathioarsenic acid*

and of two more complex acids of empirical composition $H_5As_3S_{10}$ and $H_{10}As_4S_{15}$.

The alkali salts are generally formed when arsenic pentasulphide is dissolved in an aqueous solution of the hydrosulphide and the mixture evaporated or precipitated with alcohol, or when a solution of an arsenate is treated with hydrogen sulphide under suitable conditions. The thioarsenates of the heavy metals (except silver, see p. 279) may be formed by the action of an excess of an alkali thioarsenate on a salt of the heavy metal; if the latter is in excess the sulphide is formed.[4]

The thioarsenates vary in colour, being yellow, red or brown and, in Nature, black. They possess an unpleasant bitter taste. The ortho-salts are generally well crystallised, but the other thioarsenates are not. The ortho-salts of the alkali metals and barium may be heated out of contact with air to a white heat without decomposition and, on cooling, a completely soluble yellow mass is obtained. Mercury orthothioarsenate sublimes without decomposition. The ortho-salts of other metals, and ammonium, decompose on heating. Meta- and pyrothioarsenates lose sulphur and form thioarsenites when heated.

The salts of the alkali and alkaline earth metals, as well as of gold, magnesium, beryllium and yttrium, are soluble in water, the solutions being colourless or pale yellow. They gradually decompose, however, when kept, with deposition of sulphur, arsenic and arsenic pentasulphide. The following thioarsenates have been described.

Ammonium Thioarsenates. *Ammonium Orthothioarsenate*, $(NH_4)_3AsS_4$, separates as colourless prisms when alcohol is added to a hot solution containing arsenic pentasulphide and excess of ammonium hydrosulphide.[5] The crystals gradually turn yellow in air and, when heated, melt and decompose, yielding ammonium sulphide, arsenious sulphide and sulphur.

Ammonium Pyrothioarsenate, $(NH_4)_4As_2S_7$, has been described as a reddish-yellow mass obtained by evaporation of an ammoniacal solution

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[1] Zieler, *Zeitsch. anorg. Chem.*, 1927, 162, 161.

[2] Berzelius, *loc. cit.*

[3] Rose, *loc. cit.*

[4] Berzelius, *Ann. Chim. Phys.*, 1819, [2], 11, 225; 1826, [2], 32, 166; *Schweigger's J.*, 1822, 34, 46; *Pogg. Annalen*, 1826, 7, 1; Nilson, *Akad. Handl. Stockholm*, 1871, 10, 2;

of arsenic pentasulphide. It is stable at the ordinary temperature, but decomposes on heating. If the ammoniacal solution is filtered and evaporated *in vacuo*, the composition of the yellow residue is $(NH_4)_5As_3S_{10}$.[1] According to McCay and others,[2] the solution of arsenic pentasulphide in ammonia contains the orthothioarsenate and thioxyarsenates. The yellow solution on keeping becomes almost colourless and slightly turbid, owing to separation of sulphur produced by decomposition of the thioxyarsenates.

Antimony Thioarsenate.—When sodium orthothioarsenate is added to a solution of an antimonious salt, a brownish-yellow precipitate is produced.[3]

Barium Thioarsenates.—*Barium Orthothioarsenate*, $Ba_3(AsS_4)_2.nH_2O$, may be obtained by digesting barium sulphide with an aqueous solution of barium pyrothioarsenate and precipitating the resulting clear liquid with alcohol; or the pyro-salt may be heated to redness, when arsenious sulphide and sulphur are expelled.[3] The salt does not decompose on heating. When barium hydrosulphide and arsenic pentasulphide are heated together in solution, double salts composed of thioarsenate and thioarsenite, such as $2Ba_3AsS_4.Ba_2As_2S_5$, are formed.[4]

Barium Pyrothioarsenate, $Ba_2As_2S_7.nH_2O$, is obtained as a lemon-yellow mass when sodium pyrothioarsenate is added to a solution of a barium salt and the liquid concentrated by evaporation.[3]

The metathioarsenate has not been isolated.

Beryllium Thioarsenate is formed in solution when arsenic pentasulphide and beryllium hydroxide are boiled with water for some time.[3]

Bismuth Thioarsenate.—When sodium orthothioarsenate is added to a solution of a bismuth salt, a dark brown precipitate of *bismuth pyrothioarsenate*, $Bi_4(As_2S_7)_3$, is formed.[3]

Cadmium Thioarsenates.—*Cadmium Orthothioarsenate*, $Cd_3(AsS_4)_2$, is obtained as a pale yellow precipitate when a solution of a cadmium salt is treated with sodium orthothioarsenate[5] or with a solution of ammonium hydrosulphide saturated with arsenious sulphide.[3] The addition of sodium pyrothioarsenate to a solution of a cadmium salt yields a yellow precipitate of *cadmium pyrothioarsenate*,[3] $Cd_2As_2S_7$.

Calcium Thioarsenates.—*Calcium Orthothioarsenate*, $Ca_3(AsS_4)_2.20H_2O$, may be prepared by the methods described for the corresponding barium salt. It yields pale yellow rhombic crystals which are soluble in water. Unlike the barium salt, it decomposes when heated.

Calcium Pyrothioarsenate, $Ca_2As_2S_7.nH_2O$, is obtained by addition of sodium pyrothioarsenate to a solution of a calcium salt and evaporation of the solution. The residue is yellow and opaque, soluble in water or alcohol. It loses water at 60° C. but absorbs it from the air again on cooling. It loses sulphur on heating to form thioarsenite. When arsenic pentasulphide is dissolved in warm aqueous calcium hydrosulphide and the solution concentrated *in vacuo*, crystals of the salt, $Ca_5As_4S_{15}.12H_2O$ (or $5CaS.2As_2S_5.12H_2O$), are obtained.[6]

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[1] Nilson, *J. prakt. Chem.*, 1876, [2], 14, 159.

[2] McCay, *Chem. Zeit.*, 1891, 15, 476; *Zeitsch. anorg. Chem.*, 1900, 25, 459; Weinland and Lehmann, *Zeitsch. anorg. Chem.*, 1901, 26, 322; Fluckiger, *Pharm. Viertelj.*, 1863, 12, 330.

[3] Berzelius, *loc. cit.*

[4] Nilson, *loc. cit.*

[5] Heubach, *Thesis*, Berlin, 1890.

[6] Nilson, *loc. cit.*

Cerium Thioarsenates.—The addition of sodium orthothioarsenate to an aqueous solution of a cerous salt produces a pale yellow precipitate of cerous orthothioarsenate.[1] With sodium hydrogen orthothioarsenate the precipitate approximates in composition to cerous pyrothioarsenate. Ceric salts also give pale yellow precipitates, probably ceric orthothioarsenate. Thioarsenates of other rare earth metals have not been described.

Chromium Thioarsenate.—Sodium orthothioarsenate gives a yellow precipitate when added to an aqueous solution of a chromic salt.[1]

Cobalt Thioarsenate.—With solutions of cobalt salts, sodium orthothioarsenate gives a dark brown precipitate of cobalt pyrothioarsenate, $Co_2As_2S_7$, soluble in excess of the reagent.[1]

Copper Thioarsenates.—*Cupric Orthothioarsenate*, $Cu_3(AsS_4)_2$, is formed as a dark brown precipitate when sodium orthothioarsenate is added to a solution of a cupric salt.[2] The reaction, however, is complex, sulphides of copper and arsenic also being formed.[3] A similar precipitate is formed when ammonium hydrosulphide or hydrogen sulphide is added to a solution of arsenic acid and a copper salt,[4] and the proportion of sulphide and thio-salt in the precipitate varies with the concentration of the reactants. Copper hydroxide reacts with alkali thioarsenates to form copper sulphide and alkali arsenate, but some copper orthothioarsenate is formed and remains in solution in excess of alkali thioarsenate.[5]

Cuprous Orthothioarsenate, Cu_3AsS_4, occurs widely distributed as the minerals *enargite* and *clarite* (see p. 13). These occur in massive or granular form or in greyish-black monoclinic or rhombic crystals.

Gold Thioarsenates.—*Auric Orthothioarsenate*, $AuAsS_4$, and *auric pyrothioarsenate*, $Au_4(As_2S_7)_3$, are obtained as brown precipitates when solutions of gold salts are precipitated respectively with sodium ortho- and pyro-thioarsenates.[6] Both salts are soluble in water.

Iron Thioarsenates.—Both ferrous and ferric salts, when treated with a solution of sodium orthothioarsenate, yield brown precipitates which are soluble in excess of the reagent. The *ferric salt* is stable in air and may be heated to fusion without decomposition; at a higher temperature sulphur is expelled. The *ferrous salt* decomposes on drying in the air, ferric hydroxide and thioarsenate being formed.[6] Ferrous sulphide dissolves in an aqueous solution of an alkali thioarsenate.[7]

Lead Thioarsenates.—The *ortho*- and *pyro*-salts are obtained as red and deep brown precipitates when solutions of lead salts are treated respectively with sodium ortho- and pyro-thioarsenates.[6] The mineral *reniformite* (p. 13), occurring in Japan, is probably a thioarsenate of composition $Pb_3(AsS_4)_2.2PbS$.[8]

Lithium Thioarsenates.—*Lithium Orthothioarsenate*, $Li_3AsS_4.nH_2O$, is precipitated when alcohol is added to an aqueous solution of

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[1] Berzelius, *loc. cit.*

[2] Preis, *Annalen*, 1890, 257, 178.

[3] Heubach, *Thesis*, Berlin, 1890.

[4] Berzelius, *Pogg. Annalen*, 1826, 7, 29; Anthon, *Repert. Pharm.*, 1836, 76, 125; Carnot, *Compt. rend.*, 1887, 105, 121.

[5] Berzelius, *loc. cit.*; Storch, *Ber.*, 1883, 16, 2015.

[6] Berzelius, *Ann. Chim. Phys.*, 1819, [2], 11, 225; 1826, [2], 32, 166; *Schweigger's J.*, 1822, 34, 46; *Pogg. Annalen*, 1826, 7, 4.

[7] Storch, *loc. cit.*

[8] Kawai, *J. Geol. Soc. Tokyo*, 1925, 32, 106.

the pyro-salt; it forms colourless crystals which are soluble in water. If alcohol is added to the solution of the ortho-salt, *lithium metathioarsenate*, $LiAsS_3$, is precipitated. *Lithium pyrothioarsenate*, $Li_4As_2S_7$, separates as citron-yellow crystals when an aqueous solution of lithium monohydrogen orthoarsenate, saturated with hydrogen sulphide, is allowed to evaporate. The crystals are stable in the air.[1]

Magnesium Thioarsenates.—*Magnesium Orthothioarsenate*, $Mg_3(AsS_4)_2.nH_2O$, is obtained by heating the pyro-salt, or by treating a hot solution of the latter with magnesium hydrosulphide until hydrogen sulphide is no longer liberated. On cooling or evaporation *in vacuo*, colourless hygroscopic crystals are formed. *Magnesium pyrothioarsenate*, $Mg_2As_2S_7.nH_2O$, is obtained by the action of sodium pyrothioarsenate on a solution of a magnesium salt. It is an amorphous, lemon-yellow mass, soluble in water and in aqueous alcohol.[1] A thioarsenate of composition $Mg_5As_4S_{15}.3H_2O$ remains as a mass of crystals when a solution of magnesium hydrosulphide saturated with arsenic pentasulphide is evaporated in a vacuum.[2] Like the corresponding calcium salt (p. 275), it is readily soluble in water and is decomposed by hot hydrochloric acid.

A solution containing magnesium and ammonium orthothioarsenates yields, on the addition of alcohol, needle-shaped crystals of the double salt $Mg(NH_4)AsS_4.nH_2O$. The salt is unstable in air, hydrogen sulphide and ammonia being given off.

Manganese Thioarsenates.—Manganese salts do not yield precipitates with alkali orthothioarsenates. The *pyrothioarsenate*, $Mn_2As_2S_7$, and some orthoarsenate, are formed when manganese carbonate and arsenic pentasulphide are digested with water; and when freshly precipitated manganese sulphide and arsenic pentasulphide are suspended in water, some pyrothioarsenate is precipitated but redissolved when more water is added.[3] Evaporation of the solution causes decomposition. A brick-red basic salt is formed when the pyrothioarsenate is boiled with concentrated aqueous ammonia.

Mercury Thioarsenates.—When an alkali orthothioarsenate is added to an aqueous solution of a mercurous salt, a black precipitate of mercurous sulphide separates and a thioarsenate is formed in solution. Berzelius [3] thought this to be the pyro-salt which, when obtained by evaporation and heated, lost mercury and formed the mercuric pyro-salt. Heubach,[4] however, stated that mercurous orthothioarsenate was formed and that this was decomposed by excess of mercurous salt to mercurous sulphide and arsenic acid. The mercuric salts are more stable.

Mercuric Orthothioarsenate, $Hg_3(AsS_4)_2$, is formed as an orange-coloured precipitate by treating mercuric chloride solution with sodium orthothioarsenate.[5] It may be dried at 100° C. and sublimed without decomposition. *Mercuric pyrothioarsenate* is obtained as a dark yellow precipitate when mercuric chloride solution is treated with sodium meta- or pyro-thioarsenate.[3] The salt decomposes on heating with loss of arsenic and sulphur.

[1] Berzelius, *loc. cit.*

[2] Nilson, *J. prakt. Chem.*, 1876, [2], 14, 159.

[3] Berzelius, *loc. cit.*

Molybdenum Thioarsenates.—Berzelius stated that *molybdic orthothioarsenate* was formed in solution when sodium orthothioarsenate was added to a solution of a molybdic salt. A series of *complex thio-salts* of arsenic and molybdenum has been prepared,[1] most of which appear to be derived from a hypothetical acid of composition $H_4As_2S_7.(MoS_3)_2$, or may be regarded as double salts of metathioarsenic and pyrothiomolybdic acids: $2HAsS_3.H_2Mo_2S_7$. The alkali salts are best prepared by adding salicylic acid to a solution of molybdenum trisulphide in aqueous alkali orthothioarsenate, the three compounds being in molecular proportions, and precipitating with alcohol. The *sodium salt*, $Na_4As_2S_7.(MoS_3)_2.14H_2O$, crystallises in lustrous, dark red, hexagonal prisms, and the *potassium salt*, $K_4As_2S_7.(MoS_3)_2.8H_2O$, in bright red needles. Both are readily soluble in water, are not hygroscopic, but decompose on keeping or when acted upon by mineral acids. The *ammonium salt*, $(NH_4)_4As_2S_7.(MoS_3)_2.5H_2O$, is obtained by adding salicylic acid to a concentrated solution of ammonium thiomolybdate and pyrothioarsenate and precipitating with alcohol. It yields scarlet, needle-shaped crystals, which are very unstable and are difficult to obtain pure. The aqueous solution decomposes with evolution of hydrogen sulphide and ammonia. The *barium salt*, $Ba_2As_2S_7.(MoS_3)_2.14H_2O$, crystallises in red needles from a solution of arsenic pentasulphide in aqueous barium thiomolybdate cooled at −15° C. The corresponding salts of cobalt, copper, bivalent mercury, nickel, silver and zinc are obtained as red or brown precipitates by adding the potassium salt to an aqueous solution of a salt of the metal. When the potassium salt is triturated in the presence of water with salicylic acid, in molecular proportions 2 : 3, and the mixture heated at about 50° C. until clear and then precipitated with alcohol, a brick-red amorphous powder of composition $KAsS_3.MoS_3.4H_2O$ is obtained. It is insoluble in water, but soluble in aqueous alkali or ammonia. The *sodium salt*, $NaAsS_3.MoS_3.6H_2O$, is obtained in a similar manner and resembles the potassium salt in properties.

Nickel Thioarsenates.—*Nickel Orthothioarsenate*, $Ni_3(AsS_4)_2$, and *nickel pyrothioarsenate*, $Ni_2As_2S_7$, are formed as dark brown precipitates when aqueous solutions of a nickel salt are precipitated with sodium ortho- and pyro-thioarsenates, respectively.[2]

Platinic Thioarsenate is obtained as a deep yellow precipitate when a solution of hydrochloroplatinic acid is treated with sodium ortho- or meta-thioarsenate.[2]

Potassium Thioarsenates.—*Potassium Orthothioarsenate*, $K_3AsS_4.H_2O$, may be obtained by treating an aqueous solution of the pyro-salt with alcohol and evaporating the mixture,[2] or by adding excess of potassium sulphide or hydrosulphide to a solution of arsenious sulphide in the aqueous reagent, and evaporating in a vacuum.[3] It crystallises in pale yellow, four-sided prisms, which are hygroscopic. *Potassium pyrothioarsenate*, $K_4As_2S_7$, crystallises in rhombic plates[2] when an aqueous solution of potassium monohydrogen orthoarsenate is saturated with hydrogen sulphide and allowed to evaporate. If carbon dioxide is passed into the solution, arsenic pentasulphide separates. The

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[1] Weinland and Sommer, *Zeitsch. anorg. Chem.*, 1897, 15, 42.

[2] Berzelius, *Ann. Chim. Phys.*, 1819, [2], 11, 225; 1826, [2], 32, 166; *Schweigger's J.*, 1822, 34, 46; *Pogg. Annalen*, 1826, 7, 4.

[3] Nilson, *J. prakt. Chem.*, 1875, [2], 12, 295; 1876, [2], 14, 145.

addition of alcohol to an aqueous solution of the ortho-salt precipitates *potassium metathioarsenate*,[1] $KAsS_3$. The ortho-salt is not decomposed on heating, but both the pyro- and meta-salts are converted to thioarsenites, with loss of sulphur.

Silver Thioarsenates.—*Silver Orthothioarsenate*, Ag_3AsS_4, is formed as a dark brown precipitate when an aqueous solution of silver nitrate is treated with sodium orthothioarsenate.[1] If, however, silver nitrate is added to a solution of sodium orthothioarsenate, silver orthothioarsenate is not formed but silver sulphide is precipitated and arsenious acid, nitric acid and sodium nitrate are formed in solution.[2] The reactions involved probably take the following course:[3]

$$2Na_3AsS_4 + 6AgNO_3 = 3Ag_2S + As_2S_5 + 6NaNO_3$$
$$As_2S_5 + 10AgNO_3 + 8H_2O = 5Ag_2S + 2H_3AsO_4 + 10HNO_3$$

the nitric acid then liberates hydrogen sulphide from the thioarsenate and this reduces the arsenic acid:—

$$2Na_3AsS_4 + 6HNO_3 = 3H_2S + As_2S_5 + 6NaNO_3$$
$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S$$

the sulphur being partly oxidised to sulphuric acid, which is also found in the solution. The presence of mineral acid in the thioarsenate solution favours the above decomposition; in ammoniacal solution arsenic acid remains in the solution and no arsenious acid is formed.

Silver orthothioarsenate readily decomposes on heating, yielding sulphides of silver and arsenic and free sulphur. It is found in Nature as a yellow or orange-red mineral, generally in the form of powder, known as *xanthoconite* (see p. 13), and sometimes associated with selenium as *rittingerite*.

Sodium Thioarsenates.—*Sodium Orthothioarsenate*, Na_3AsS_4, may be prepared by dissolving arsenic pentasulphide or sodium pyrothioarsenate in a hot aqueous solution of sodium hydrosulphide and evaporating *in vacuo*;[4] by adding alcohol to an aqueous solution of the pyro-salt; by passing hydrogen sulphide into a solution of sodium orthoarsenate,[5] or into an alkaline solution of sodium monohydrogen orthoarsenate and pouring the clear liquid into alcohol.[6] It yields pale yellow monoclinic crystals with axial ratios[7] $a:b:c = 0{\cdot}6676:1:1{\cdot}0393$, and $\beta = 100°\ 0'$. It is stable in air but, on heating, gives off its water of crystallisation, undergoing partial hydrolysis:[5]

$$Na_3AsS_4 + 4H_2O = Na_3AsO_4 + 4H_2S$$

At a higher temperature it turns yellow and a little hydrogen sulphide is given off; finally it melts to a red liquid which, on cooling, yields a residue which consists mainly of the anhydrous salt.[8] It is soluble in water and the solution on boiling gives off hydrogen sulphide. When added to solutions of the salts of heavy metals, precipitates of the thioarsenates of the latter are formed. The passage of carbon dioxide

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[1] Berzelius, *loc. cit.*

[2] Nilson, *loc. cit.*; Preis, *Annalen*, 1890, 257, 196.

[3] Heubach, *Thesis*, Berlin, 1890.

[4] Berzelius, *loc. cit.*; Nilson, *loc. cit.*

[5] Heubach, *loc. cit.*

through the solution expels hydrogen sulphide and causes precipitation of sulphur and arsenic pentasulphide.

Sodium Pyrothioarsenate, $Na_4As_2S_7$, is obtained as a pale yellow residue when an aqueous solution of sodium monohydrogen arsenate is saturated with hydrogen sulphide and allowed to evaporate.[1] On heating it melts and, at a higher temperature, loses sulphur, forming thioarsenite. *Sodium metathioarsenate*, $NaAsS_3$, according to Berzelius, is precipitated when alcohol is added to an aqueous solution of the ortho-salt.

The *double salt*, $Na_3(NH_4)_3(AsS_4)_2$, is obtained when alcohol is added to a mixture of the two thioarsenates in molecular proportions, or when a solution containing ammonium chloride and sodium orthothioarsenate is allowed to evaporate; it crystallises as pale yellow hexagonal prisms. A corresponding sodium-potassium salt is obtained by evaporation of a solution of the mixed orthothioarsenates.[1]

Strontium Thioarsenates.—*Strontium Orthothioarsenate*, $Sr_3(AsS_4)_2.nH_2O$, may be prepared[2] by digesting strontium sulphide with an aqueous solution of strontium pyrothioarsenate and, after filtering, either adding alcohol or evaporating to crystallisation. *Strontium pyrothioarsenate*, $Sr_2As_2S_7.nH_2O$, is obtained by mixing aqueous solutions of a strontium salt and sodium pyrothioarsenate, and evaporating the liquid. Both salts resemble the analogous calcium salts in properties. A crystalline *double salt* containing orthothioarsenate and pyrothioarsenite, and of composition $Sr_3(AsS_4)_2.Sr_2As_2S_5.8H_2O$, has been obtained[3] by evaporating *in vacuo* a saturated solution of arsenic pentasulphide in aqueous strontium hydrosulphide.

Thallium Orthothioarsenate, Tl_3AsS_4, may be obtained[4] by passing hydrogen sulphide into an alkaline solution containing an arsenate and a thallous salt. It forms an orange-coloured precipitate, decomposed by acids and on boiling with concentrated alkali sulphides. It is stable in air, but undergoes partial decomposition on heating.

Tin Thioarsenates.—By double decomposition with sodium orthothioarsenate, stannous and stannic salts yield, respectively, chestnut-brown and pale yellow precipitates.[5]

Uranyl Thioarsenate is also obtained by double decomposition. It is formed as a dirty yellow precipitate, soluble in excess of the alkali orthothioarsenate.[5]

Yttrium Thioarsenate.—Yttrium does not form an insoluble thioarsenate but, if yttrium hydroxide and arsenic pentasulphide are digested with water, thioarsenate is formed in solution. The compound is unstable, however, and gradually decomposes, with separation of sulphur and arsenic.[5]

Zinc Thioarsenates.—*Zinc Orthothioarsenate*, $Zn_3(AsS_4)_2$, is precipitated in yellow flakes from a cold solution of zinc sulphate by addition of an alkali orthothioarsenate.[6] *Zinc pyrothioarsenate*, $Zn_2As_2S_7$, is also obtained by double decomposition.[5] *Zinc metathioarsenate*, $Zn(AsS_3)_2$, is precipitated when hydrogen sulphide is passed into a solution containing zinc in the presence of an excess of arsenic

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[1] Berzelius, *loc. cit.*

[2] Berzelius, *loc. cit.*

[3] Nilson, *loc. cit.*

[4] Hawley, *J. Amer. Chem. Soc.*, 1907, 29, 1013.

[5] Berzelius, *loc. cit.*

[6] Preis, *Annalen*, 1890, 257, 196; Berzelius, *loc. cit.*

acid and of sulphuric or hydrochloric acid;[1] under these conditions the precipitation is quantitative.

Zirconium Thioarsenate is obtained as a lemon-yellow precipitate when sodium orthothioarsenate is added to a solution of a zirconium salt.[2]

Oxythioarsenates.

Intermediate compounds between the arsenates and thioarsenates are known, and are derived from the acids H_3AsO_3S, $H_3AsO_2S_2$ and H_3AsOS_3. These acids are very unstable and have not been isolated, but the first and second have been obtained in dilute aqueous solution.

Trioxythioarsenic Acid, H_3AsO_3S, is formed in solution when hydrogen sulphide is passed into a cold, dilute, acidified solution of potassium orthoarsenate.[3] Excess of the gas should be avoided but, if present, may be removed either by immediate addition of copper sulphate, or by a vigorous stream of air. Any opalescence due to sulphur may be removed by adding asbestos and filtering. The solution obtained gives no immediate precipitate with hydrogen sulphide, but sulphur ultimately appears. When the solution is boiled, pure sulphur is precipitated, but no hydrogen sulphide or sulphur dioxide is evolved; on cooling, passage of hydrogen sulphide gives an immediate precipitate of arsenious sulphide.

Trioxythioarsenates of ammonium, the alkali metals and the alkaline earth metals have been prepared. Those of the heavy metals are unstable and difficult to isolate; the precipitates obtained when the salts of such metals are treated with a solution of an alkali trioxythioarsenate undergo immediate decomposition, yielding sulphides.

Ammonium Trioxythioarsenate, $(NH_4)_3AsO_3S.3H_2O$, may be obtained by heating under pressure on a water-bath an aqueous solution of ammonium arsenite containing the calculated amount of fine sulphur; thioarsenate and arsenate are also formed and the thioxy-salt may be separated by fractional crystallisation from aqueous alcohol.[4] It yields small, colourless plates, which are readily soluble in water. The crystals lose ammonia when kept in air, and the solution also loses ammonia on boiling, the salt being decomposed with formation of arsenious oxide and sulphur. A *tetrahydrate*, $(NH_4)_3AsO_3S.4H_2O$, has been obtained[5] by melting together equal parts of arsenious oxide and sulphur and digesting the residue with aqueous ammonia; after keeping the liquid for 24 hours, it was filtered and the filtrate treated with alcohol. An oil separated which, when cooled in ice, set to a white crystalline mass, with properties similar to the trihydrate. The mother liquor from which the oil had separated, on addition of more alcohol, yielded a crystalline precipitate of *ammonium monohydrogen trioxythioarsenate*, $(NH_4)_2HAsO_3S$. The crystals turned yellow in air with loss of ammonia, but in an atmosphere of ammonia the white colour was restored.

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[1] Wohler, *Berzelius' Jahresber.*, 1842, 21, 150.

[2] Berzelius, *loc. cit.*

[3] McCay, *Amer. Chem. J.*, 1888, 10, 459; *Zeitsch. anal. Chem.*, 1888, 27, 632. Compare Brauner and Tomíček, *J. Chem. Soc.*, 1888, 53, 145; Bouquet and Cloez, *Ann. Chim. Phys.*, 1845, [3], 13, 44.

[4] Weinland and Rumpf, *Ber.*, 1896, 29, 1008, *Zeitsch. anorg. Chem.*, 1897, 14, 52. See also McCay, *Chem. Zeit.*, 1891, 15, 476.

[5] McLauchlan, *Ber.*, 1901, 34, 2167.

The normal *sodium* and *potassium salts*, $Na_3AsO_3S.12H_2O$ and $K_3AsO_3S.2H_2O$, may be prepared [1] by treating a concentrated solution of the alkali arsenite with sodium thiosulphate at the ordinary temperature. Heat is developed and, in the case of the sodium salt, the trioxythioarsenate crystallises out and sodium sulphite remains in the solution:

$$Na_3AsO_3 + Na_2S_2O_3 = Na_3AsO_3S + Na_2SO_3$$

A small quantity of arsenic also separates. In the case of the potassium salt, however, the sulphite is first crystallised out and the trioxythioarsenate then obtained by evaporating the mother liquor over sulphuric acid. The alkali monohydrogen arsenites also yield the above salts, in the cold, with sodium thiosulphate.

Sodium Monohydrogen Trioxythioarsenate, $Na_2HAsO_3S.8H_2O$, has been obtained [2] as colourless triclinic crystals by fractionally crystallising the liquid resulting when arsenious oxide is boiled with aqueous sodium sulphide; the normal trioxythioarsenate, as well as *sodium dioxythioarsenate*, $Na_3AsO_2S_2.10H_2O$, and sodium orthoarsenate, were also obtained from the solution. The corresponding *potassium salt*, $K_2HAsO_3S.2{\cdot}5H_2O$, has been prepared [3] by adding a slight excess ($\frac{1}{7}$ more than the theoretical quantity) of potassium hydroxide to a solution of the dihydrogen salt and allowing the mixture to crystallise over sulphuric acid and potassium hydroxide. It yields colourless, very hygroscopic prisms.

Sodium Dihydrogen Trioxythioarsenate, $NaH_2AsO_3S.H_2O$, is formed when the normal salt, $Na_3AsO_3S.12H_2O$ (1 mol.), is triturated, without addition of water, with salicylic acid (2 mols.) and the product treated with alcohol in a closed vessel until the presence of salicylic acid can no longer be detected.[4] The salt is freed from any remaining normal salt by levigation. It forms colourless prismatic crystals which give an acid reaction with moist litmus paper. It is unstable and decomposes with separation of sulphur, both in the dry state and in the presence of water:

$$NaH_2AsO_3S = NaAsO_2 + H_2O + S$$

The decomposition is accelerated by heat. The corresponding *potassium* salt, $KH_2AsO_3S.H_2O$, has been obtained by the action of hydrogen sulphide on a cold aqueous solution of potassium mono- or di-hydrogen orthoarsenate,[5] and also by digesting arsenious sulphide in a concentrated solution of potassium carbonate,[6] or by the method described above for the sodium salt. The salt is colourless, stable in air, sparingly soluble in cold water but more soluble in hot. It loses water when heated at 170° C. and at a higher temperature melts and then decomposes. The hot solution also undergoes some decomposition.

Dioxydithioarsenic Acid, $H_3AsO_2S_2$, has been obtained in dilute aqueous solution by the action of a large excess of hydrogen sulphide on aqueous arsenic acid, and by passing hydrogen sulphide into a solution

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[1] Weinland and Gutmann, *Zeitsch. anorg. Chem.*, 1898, 17, 409; Weinland and Rumpf, *loc. cit.*

[2] Preis, *Annalen*, 1890, 257, 180.

[3] Weinland and Rumpf, *loc. cit.*

[4] Weinland and Rumpf, *Zeitsch. anorg. Chem.*, 1897, 14, 57.

[5] Bouquet and Cloez, *Ann. Chim. Phys.*, 1845, [3], 13, 44; McCay, *Amer. Chem. J.*, 1888, 10, 463.

[6] Nilson, *J. prakt. Chem.*, 1876, [2], 14, 155.

of sodium orthoarsenate acidified with mineral acid.[1] Normal salts only of this acid have been prepared.

Sodium Dioxydithioarsenate, $Na_3AsO_2S_2$, may be obtained by the action of aqueous sodium sulphide on arsenious oxide,[2] or of the disulphide on sodium metarsenite—[3]

$$Na_2S_2 + NaAsO_2 = Na_3AsO_2S_2$$

or on sodium trioxythioarsenate. It has also been prepared by adding sodium hydroxide to a hot solution of sodium thioarsenate—[4]

$$Na_3AsS_4 + 4NaOH = Na_3AsO_2S_2 + 2Na_2S + 2H_2O$$

and by the action of sodium carbonate on barium dioxydithioarsenate.[5] It yields rhombic crystals with axial ratios $a : b : c = 0{\cdot}769 : 1 : 0{\cdot}555$. It is soluble in water; hydrochloric acid decomposes it, giving a yellow precipitate and evolution of hydrogen sulphide. Barium chloride gives a white precipitate of *barium dioxydithioarsenate*, $Ba_3(AsO_2S_2)_2.4$ or $6H_2O$. This salt is also obtained[6] when a solution of sodium thioarsenate is boiled with baryta-water. Silver nitrate gives a black precipitate.

The *potassium salt*, $K_3AsO_2S_2.nH_2O$, is unstable. It has been obtained in an impure form by treating the precipitate resulting from the action of hydrogen sulphide on aqueous potassium orthoarsenate with potassium hydroxide.[6] On evaporation of the solution, the salt separates in yellow, hygroscopic crystals which cannot be recrystallised owing to decomposition to orthoarsenate and thioarsenate.

Oxytrithioarsenic Acid, H_3AsOS_3, has not been prepared. The *sodium* and *potassium* salts have been obtained by the action of magnesia on freshly prepared arsenic pentasulphide, suspended in water, and removing the magnesium by means of the alkali hydroxide, when the oxytrithioarsenate remains in solution.[7] By adding alcohol to the cold solution, the salt slowly separates. The sodium salt can be recrystallised from water containing a little alkali, when it yields feathery crystals of composition $Na_3AsOS_3.11H_2O$. It is unstable and is acted on by light at the ordinary temperature with the probable formation of monothio- and dithio-arsenates. It is decomposed by hydrochloric acid with evolution of hydrogen sulphide. Silver nitrate gives a black precipitate. The potassium salt, $K_3AsOS_3.7H_2O$, separates as a yellow oil which crystallises at $-20°$ C.

By the action of alkaline earth chlorides on the sodium and potassium salts, the following have been obtained:

$Ca_3(AsOS_3)_2.20H_2O$, unstable needles.
$NaSrAsOS_3.10H_2O$, white crystals gradually turning yellow.
$Na_2Ba_7As_5O_7S_{14}.12H_2O$(?).
$KBaAsOS_3.7H_2O$, yellow crystals.

A series of complex *arsenothiomolybdates* has been described.[8]

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[1] McCay, *Ber.*, 1899, 32, 2474; *Zeitsch. anorg. Chem.*, 1902, 29, 46; *J. Amer. Chem. Soc.*, 1902, 24, 661.
[2] Preis, *Annalen*, 1890, 257, 178.
[3] Weinland and Rumpf, *loc. cit.*
[4] Preis, *loc. cit.*
[5] McCay, *loc. cit.*
[6] Weinland and Rumpf, *loc. cit.*
[7] McCay and Foster, *Zeitsch. anorg. Chem.*, 1904, 41, 452: *Ber.*, 1904, 37, 573.
[8] Weinland and Sommer, *Zeitsch. anorg. Chem.*, 1897, 15, 42.

Sulphato-compounds of Arsenic.

Arsenious oxide dissolves in hot concentrated or fuming sulphuric acid to form compounds of composition $As_2O_3.nSO_3$ ($n = 1$ to 8), which separate as crystals on cooling.[1] Two members of the series, $As_2O_3.SO_3$ and $As_2O_3.3SO_3$, have been detected in deposits from the flues of the pyrites burners of lead chamber plant.[2] The compounds readily lose sulphur trioxide on heating, and in contact with water form sulphuric acid and arsenious oxide. This behaviour and the fact that they cannot be prepared by the agency of dilute sulphuric acid, suggests that they should not be considered as sulphates.

Arsenic Monosulphatotrioxide, $As_2O_3.SO_3$, sometimes called **arsenyl sulphate,** $(AsO)_2SO_4$, is obtained by dissolving arsenious oxide in warm concentrated sulphuric acid, the concentration of which should be between $H_2SO_4.H_2O$ and $9H_2SO_4.2H_2O$, and evaporating until sulphur trioxide is no longer expelled.[3] On cooling, tabular crystals separate, which in air become moist and form sulphuric acid and arsenious oxide. This compound is somewhat more stable than those with higher sulphur trioxide content and, on gently heating, some volatilisation without decomposition occurs; at 225° C. it begins to lose sulphur trioxide; finally, on heating, fused arsenious oxide remains. From sulphuric acid of weaker concentration than $H_2SO_4.H_2O$, no sulphato-compound can be obtained.

Arsenic Disulphatotrioxide, $As_2O_3.2SO_3$, is similarly prepared[4] from a saturated solution of arsenious oxide in 98 per cent. sulphuric acid, or from a solution of the trisulphato-compound in concentrated sulphuric acid. It is stable on gently heating, but decomposes at 170° C.

Arsenic Trisulphatotrioxide, $As_2O_3.3SO_3$, sometimes called **arsenic sulphate,** $As_2(SO_4)_3$, is obtained[5] by heating arsenious oxide with sulphur trioxide at 100° C. and maintaining the mixture at this temperature until excess of the latter oxide is expelled. It may also be separated from the mother liquor from the preparation of the tetrasulphato-compound.[4] The trisulphato-compound is less stable than the mono- and di-compounds described above.

Arsenic Tetrasulphatotrioxide, $As_2O_3.4SO_3$, separates as glistening needles from a solution of arsenious oxide in sulphuric acid containing 88·3 per cent. of sulphur trioxide.[6]

Arsenic Hexasulphatotrioxide, $As_2O_3.6SO_3$, is obtained by heating a mixture of arsenious oxide and sulphur trioxide at 60° C.[7]

Arsenic Octasulphatotrioxide, $As_2O_3.8SO_3$, is formed when a mixture of the two oxides is heated in a sealed tube at 100° C.[8]

Complex salts containing arsenic tri- or pent-oxide and sulphur

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[1] Adie, *J. Chem. Soc.*, 1889, 55, 157; Karl, *Thesis*, Geneva, 1908. See also Buchholz, *Schweigger's J.*, 1815, 15, 337; Vogel, *J. prakt. Chem.*, 1835, [1], 4, 232.

[2] Schafthaütl, *B.A. Rep.*, 1840, p. 69; Ulrich, *Berg.- u. hütt. Zeit.*, 1854, p. 98; Reich, *J. prakt. Chem.*, 1863, [1], 90, 176; Stavenhagen, *Zeitsch. angew. Chem.*, 1893, 6, 284.

[3] Adie, *loc. cit.*; Stavenhagen, *loc. cit.*; Reich, *loc. cit.*

[4] Adie, *loc. cit.*

[5] Weber, *Ber.*, 1886, 19, 3186.

[6] Schultze-Sellac, *Ber.*, 1871, 4, 112; Adie, *loc. cit.*

[7] Weber, *loc. cit.*

[8] Adie, *loc. cit.*

trioxide, apparently in a complex anion, have been described. The following are examples:

$2K_2O.As_2O_3.4SO_3$	Prepared[1] by heating solutions of the metallic sulphate and arsenious oxide in concentrated sulphuric acid.
$CaO.As_2O_3.3SO_3$	
$PbO.As_2O_3.2SO_3$	
$2K_2O.As_2O_5.2SO_3.3H_2O$	Obtained[2] from solutions of the alkali dihydrogen orthoarsenate in sulphuric acid.
$2(NH_4)_2O.As_2O_5.2SO_3.3H_2O$	
$2Na_2O.As_2O_5.2SO_3.3H_2O$	
$3Ag_2O.As_2O_5.SO_3$ . . .	Obtained by dissolving silver orthoarsenate in sulphuric acid.[3]

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[1] Kühl, *Arch. Pharm.*, 1907, 245, 377. See also Stavenhagen, *loc. cit.*

[2] Friedheim and Mozkin, *Zeitsch. anorg. Chem.*, 1894, 6, 273; 1911, 69, 262.

[3] Setterberg, *Öfvers. Vet. Akad. Förh.*, 1846, 3, 25; *J. Pharm. Chim.*, 1847, [3], 12, 142.

CHAPTER X.

ARSENIC AND THE ELEMENTS OF GROUPS V, IV AND III.

Arsenic and Nitrogen.

Arsenic Nitride, AsN, has been described as an orange-red powder obtained by heating at 250° C., preferably in a vacuum, the imide described below.[1] Attempts to prepare it by heating arsenious oxide in ammonia or with a cyanide were not successful.[2]

Arsenic Imide, $As_2(NH)_3$, is obtained by heating to 60° C. the amide described below. It is a pale yellow amorphous powder, stable in air up to 100° C., but above that temperature it decomposes forming the nitride. It is slowly decomposed by water into arsenious oxide and ammonia.[3]

Arsenic Amide, $As(NH_2)_3$, is formed by the action of ammonia on arsenic trichloride, tribromide or triiodide at $-35°$ to $-40°$ C., the ammonium halide being removed from the residue by washing with liquid ammonia, in which the amide is insoluble.[3] It is a greyish-white powder, stable in dry air below 0° C., but above this temperature it begins to decompose, yielding the imide and, at higher temperatures, the nitride. It may be kept at ordinary temperatures in an atmosphere of ammonia without decomposition. Water readily converts it into arsenious oxide and ammonia.

Arsenic and Phosphorus.

Arsenic Phosphides.—Black or brown products of indefinite character, to which have been ascribed the formulæ As_2P [4] and AsP,[5] have been obtained by various methods, such as (1) by heating the elements together,[6] (2) by allowing phosphorus to stand in solutions of arsenious acid,[7] and (3) by the action of phosphine on arsenic halides.[8] The properties of these substances resemble in general those which would be possessed by mixtures of the two elements; thus, they burn in air to give the mixed oxides, decompose on heating with vaporisation of first phosphorus and then arsenic, and are oxidised by nitric acid.

Oxyphosphides of composition $As_3P_2O_2$ [9] and As_4PO_2 [10] are obtained by the action of water on the above products.

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[1] Hugot, *Compt. rend.*, 1904, 139 54.

[2] Bachmann, *Amer. Chem. J.*, 1888, 10, 42.

[3] Hugot, *loc. cit.*

[4] Ritter, *Bull. Soc. chim.*, 1874, [2], 21, 151; *Jahresber.*, 1874, p. 224.

[5] Janowsky, *Ber.*, 1873, 6, 216; 1875, 8, 1636.

[6] Landgrebe, *Schweigger's J.*, 1830, 60, 184.

[7] Blondlot and Thénard, *Compt. rend.*, 1874, 78, 1130.

[8] Besson, *ibid.*, 1890, 110, 1260; Janowsky, *loc. cit.*

[9] Janowsky, *loc. cit.*

Arsenic Phosphate, $AsPO_4$, has been prepared[1] by heating pyrophosphoric acid at 230° to 245° C., adding arsenious oxide in small portions, and further heating the mixture at 280° C. until it solidified as a hard mass of white microscopic needles. It is hygroscopic and, when exposed to moist air, arsenious oxide separates. Using an excess of pyrophosphoric acid, a compound of composition $4AsPO_4.3H_4P_2O_7$ was similarly prepared. It formed a hygroscopic mass of white microscopic needles which melted above 400° C.

Arsenic Thiophosphate, $AsPS_4$, has been obtained by heating together arsenious sulphide and phosphorus pentasulphide.[2]

ARSENIC AND CARBON.

Arsenic Tricarbide, AsC_3, is formed[3] as a brown amorphous precipitate when a solution of arsenic trichloride reacts with the double compound of magnesium carbide and iodide :[4]

$$2AsCl_3 + 3Mg_2C_2I_2 = 2AsC_3 + 3MgI_2 + 3MgCl_2$$

The product resembles the corresponding phosphorus carbide. It is insoluble in acids and alkalis, and when heated or rubbed it explodes with liberation of carbon and arsenic.

Arsenic carbonate has not been prepared, but arsenic salts of several organic acids, including arsenic cyanide, thiocyanate, acetate and tartrate, are known. Arsenic chromithiocyanate, $As[Cr(SCN)_6]$, has also been described.[5]

ARSENIC AND SILICON.

Arsenic does not combine directly with silicon to form a silicide.

Arsenic Pentasilicide, $AsSi_5$, has been prepared,[6] however, by the action of hydrochloric acid on zinc silico-arsenide. The product was very impure, containing zinc, silica and arsenic monohydride ; the last was removed by heating in a stream of hydrogen, and the zinc and silica were removed by treating with boiling nitric acid and aqueous alkali respectively. It remained as microscopic dark grey needles, stable when heated in air, and unattacked by concentrated acids or aqua regia.

A series of complex **silico-arsenides** has been obtained[6] by melting metals with silicon and an excess of arsenic under a layer of molten cryolite and sodium chloride. The following have thus been prepared : *copper silico-arsenide*, a grey crystalline brittle mass ; *zinc silico-arsenide*, which behaved as above with hydrochloric acid ; *iron, cobalt* and *nickel silico-arsenides*, of composition $M_2Si_9As_4$, similar in appearance to the copper compound. When *platinum* was treated in the same way, a hard white product of indefinite composition was obtained, almost insoluble in nitric acid.

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[1] Horsch and Betsis, *Praktika Akad. Athenon*, 1928, 3, 216; *Chem. Zentr.*, 1928, [2], 2632; Ghiron and Mangili, *Gazzetta*, 1935, 65, 1244.

[2] Glatzel, *Zeitsch. anorg. Chem.*, 1893, 4, 186.

[3] de Mahler, *Bull. Soc. chim.*, 1921, [4], 29, 1071.

ARSENIC AND BORON.

An arsenide of boron has not been obtained.

Boron Arsenate, $BAsO_4$, has been prepared by evaporating to dryness an aqueous solution of boric and arsenic acids and igniting the residue.[1] The product is a mixed anhydride. The crystal structure[2] resembles that of boron phosphate, being of the silica type, the arsenic and boron atoms being surrounded tetrahedrally by oxygen, each atom of which belongs to two tetrahedra. The space group is S_4^2; each cell, space-centred, has two molecules and has $a = 4{\cdot}459 \pm 0{\cdot}006$ and $c = 6{\cdot}796 \pm 0{\cdot}006$ A., $c/a = 1{\cdot}524$; arsenic is in position *a* and boron in position *c*.

The arsenate is reduced when heated with aluminium or calcium silicide. Two hydrates have been obtained,[3] $BAsO_4.3H_2O$ and $BAsO_4.6H_2O$, and by extracting either of these with liquid ammonia, the compound $BAsO_4.3H_2O.NH_3$ has been isolated. This appears to be an acid salt of a complex arsenoboric acid of structure $H_2[BAsO_3(OH)_4]$, corresponding with the trihydrate, and the hexahydrate appears to be a trihydrate of this acid. Potentiometric titration indicates that in aqueous solution a mixture of boric and arsenic acids is obtained.

Calcium Boroarsenate occurs in New Jersey as the mineral *cahnite*[4] (see p. 14); it forms white, vitreous, tetragonal sphenoids, occurring in characteristic interpenetrating twins. The refractive index is 1·662.

The **compound** $BCl_3.AsH_3$ is formed[5] at −80° C. by mixing liquid boron trichloride with liquid arsine in an atmosphere of hydrogen, or by passing arsine entrained in hydrogen through the liquid boron trichloride. It yields white crystals, dissociating at −40° C., decomposing at room temperature in a sealed tube to boron trichloride, hydrogen and arsenic, and with water yielding boric and hydrochloric acids and arsine.

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[1] Berger, *Compt. rend.*, 1920, 170, 1492.

[2] Schulze, *Naturwiss.*, 1933, 21, 562.

[3] Gruner, *Zeitsch. anorg. Chem.*, 1934, 219, 181.

[4] Palache and Bauer, *Amer. Min.*, 1927, 12, 77, 149.

[5] Stieber, *Compt. rend.*, 1932, 195, 610.

CHAPTER XI.

PHYSIOLOGICAL PROPERTIES OF ARSENIC COMPOUNDS.

Arsenicals have long been considered the most important of toxic inorganic compounds and it is not surprising that, to the lay mind, the name itself suggests poison. In spite of the ease with which it may be detected if suspicion is aroused, the deliberate use of white arsenic as a homicidal poison is still prevalent, especially in Europe,[1] probably owing to the ease with which it may be administered, its resemblance to flour, and the fact that it is odourless and practically tasteless; moreover, it has been easily obtainable, both directly and surreptitiously, from sources such as fly-papers, insect powders[2] and weed-killers. The incidence of arsenical poisoning was greatly reduced by the Arsenic Act of 1851 (14 Vict. cap. xiii), which restricted the sale of white arsenic and prescribed its admixture with soot or indigo if sold in quantities of less than 10 lbs.; prior to this 34 per cent. of all cases of poisoning in England were due to this substance. This act was repealed by the Pharmacy and Poisons Act of 1933, which stipulated rules for colouring of arsenic, provision being made for the addition of a dye to arsenical poisons.

Accidental poisoning, however, provides a more important problem, and the widespread distribution of arsenic, its frequent occurrence as a by-product in industry, and its use for a great variety of purposes, constitute a source of danger.[3] The most frequent sources of arsenical poisoning are food contamination and occupational contact. An outbreak affecting 6000 persons, including 70 fatal cases, occurred in Lancashire in 1900 and was traced to beer made from glucose in the preparation of which arsenical sulphuric acid had been employed. Confectionery and many food ingredients have been found to be similarly contaminated, but modern methods of sulphuric acid manufacture (see this Series, Vol. VII, Part II) have considerably lessened the likelihood of contamination from this source. An interesting case of cocoa to which potassium carbonate had been added to improve its solubility is cited by Monier-Williams;[4] the carbonate had been made by calcining the residues left after cleaning wool from sheep which had been washed with arsenical insecticide.

The occurrence of arsenic in shell-fish has been described (p. 19). The amounts present vary within wide limits and the element appears

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[1] Beothy, *Deut. Zeitsch. für die Gesamte Gerichtl. Med.*, 1934, 23. Heft 3; Martin, *Police J.*, 1935, 8, 215.

[2] Sartori, *Chem. Zeit.*, 1931, 55, 105; 1932, 56, 316.

[3] See Amor, *Chemistry and Industry*, 1931, 50. 475.

[4] Monier-Williams, "*Food and the Consumer,*" *Inst. of Chem. Publication*, London, 1935.

to be in a form only slightly toxic, but there may be sufficient to affect a person who cannot tolerate arsenic.[1]

Cases of poisoning by drinking water contaminated with arsenic have been reported.[2]

In prepared foods there is a permissible limit to the amount of arsenic which may be present; this limit, 0·01 grain per lb., was recommended by a Royal Commission in 1903 and is generally accepted, although it is not laid down by Statute.

Pollution of the atmosphere is a frequent cause of trouble; thus in 1929 the cattle dipping truck yards at Julia Creek, Queensland, were removed owing to contamination of the town atmosphere, dust samples from which disclosed 10 to 12 parts of arsenic per million.[3] Chronic poisoning has also resulted from the inhalation of the fumes liberated on burning "mosquito incense" made from orpiment and sawdust.[4] A systematic clinical and X-ray examination of furnace workers at the arsenic works at Freiberg, Saxony, revealed that the majority suffered from pustular and eczematous conditions of the skin and 80 per cent. showed ulceration and perforation of the septum of the nose, in spite of the provision of sponge respirators and protective clothing;[5] arsenic was present in the hair and nails.

All the organic arsenicals which find important therapeutic application in certain blood diseases and syphilis are synthetic products[6] and are only feebly poisonous. In time, however, arsenious acid may be formed in the tissues and cause typical symptoms of poisoning.[7] The possible formation of injurious volatile alkylarsines is discussed on p. 292.

The important inorganic toxic compounds to be considered in the following pages are arsine, arsenic trichloride, white arsenic, arsenites and arsenates and arsenic sulphides. Metallic arsenic itself is not poisonous, and the intravenous injection of a colloidal solution of this substance has been found[8] to benefit greatly a case of bone sarcoma of the femur which did not respond to X-ray treatment.

Arsenic trihydride, or *arsine*, is a powerful blood poison, 1 part in 20,000 parts of air being sufficient to produce symptoms. Inhalation of the gas appears to cause a lysis of the red corpuscles, hæmoglobin being excreted in the urine; symptoms of suffocation result, the anæmia may affect the kidneys and jaundice result; the victim suffers severe pain in the lower chest and upper abdominal regions, accompanied by rigor and spasms, and finally collapse and death occur about the ninth day.[9] The usual effects of arsenical poisoning (see p. 295) may also be present, but the gastro-intestinal symptoms may be slight or absent. The

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[1] Chapman, *Analyst*, 1926, 51, 548.

[2] Mackenzie, *Med. J. Australia*, 1931, I, 317.

[3] Committee of Public Health, Queensland, Australia, *Annual Report*, 1929.

[4] Li and Yang, *Chinese Med. J.*, 1933, 47, 979.

[5] Saupe, *Arch. Gewerbepath. Gewerbehyg.*, 1930, I, 582; *Bull. Hyg.*, 1931, 6, 470.

[6] Morgan, "*Organic Compounds of Arsenic and Antimony*," 1918; Goddard, *This Series*, Vol. XI, Part II.

[7] Kerr, "*Forensic Medicine*" (Black, London), 1935.

[8] Hendrick and Burton, *Can. Med. Assoc. J.*, 1933, 28, 192. See Labes, *Arch. exp. Path. Pharm.*, 1928, 131, 322.

[9] Vogel, *Brit. For. Med.-Chir. Rev.*, 1854, p. 279; Vilette, *Lyon Méd.*, 1870, p. 440; Cöster, *Cent. fur d. med. Wiss.*, 1884, 26, 461; Guy and Ferrier, "*Principles of Forensic Medicine*," 7th Ed., revised Smith (Henry Renshaw), 1895; Meyer and Heubner, *Biochem. Zeitsch.*, 1929, 206, 212; Kerr, *loc. cit.*; Kogan, *Arch. exp. Path. Pharm.*, 1931, 161, 310.

treatment consists in administering oxygen, repeated blood transfusions and saline injections.

Experiments show that arsine acts on the red blood cells only where oxidative processes are occurring.[1] Thus if oxygen is removed from a suspension of the red corpuscles by a current of an inert gas such as hydrogen or nitrogen, or by reduction with sodium sulphite or a culture of paramœcia, hæmolysis does not occur. In arsine-hæmolysis the oxygen is supplied by the oxyhæmoglobin. Arsenites and arsenates do not act thus on the blood elements. Following inhalation by cats, dogs and rabbits, Thauer found [2] arsenic in the non-hæmolysed blood corpuscles but not in the plasma. Methæmoglobin formation is noticeable. The arsenic content of the organs was relatively low, the highest occurring in the spleen (from blood degradation), liver and kidney. Rapid excretion, mainly in the urine, occurs. The animals were not all equally susceptible to the poison.

The chemist Gehlen, after inhaling the gas, died on the ninth day, and many cases have occurred of men being overcome by the impure gas generated in industrial processes. Among recent cases recorded are those in which the gas resulted from the sprinkling of water on to the dross, containing aluminium arsenide, remaining after tin refining,[3] and when the zinc slimes, from the recovery of gold by the cyanide process, were treated with sulphuric acid.[4] The distribution of the arsenic (in parts per million) in the bodies of two fatal cases from the latter cause was as follows: brain 1·4, 1·0; lungs 2·59, 2·3; stomach and contents 0·1, 0·3; spleen 0·48, 2·2; kidney 0·36, 1·3; liver 6·90, 4·4.

Very dilute crude sulphuric acid in contact with iron or steel, in the presence of reducible arsenic compounds, may generate arsine even at ordinary temperatures. Sufficient arsenic may be derived from impurities in either the acid or the metal, and the presence of small quantities of nitric acid in technical sulphuric acid does not prevent the reaction.[5] The use of acid containing more than 1 p.p.m. of As_2O_3 should be avoided. A German patent [6] suggests that a safeguard in treating industrial materials containing arsenic with acid is always to carry out the operation in the presence of an oxidising agent such as chlorine water.

There is evidence [7] that repeated exposure to low concentrations of arsine results in a cumulative effect, leading to severe poisoning. Following exposure there is generally a delay in the onset of symptoms and it is difficult to state with certainty the concentration which it is safe to breathe; but it has been concluded from available data that the

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[1] Labes, *Deut. med. Wochschr.*, 1926, **52**, 2152; *Arch. exp. Path. Pharm.*, 1928, **127**, 125; **131**, 322; Hilterhaus, *Arch. Gewerbepath. Gewerbehyg.*, 1935, **6**, 70.

[2] Thauer, *Arch. exp. Path. Pharm.*, 1934, **176**, 531. See also Fretwurst, Horwitz and Rosenbaum, *Zeitsch. klin. Med.*, 1933, **123**, 703; *Chem. Zentr.*, 1933, [2], 1212.

[3] Manceau, *Lyon Pharm.*, 1929, **39**, 203; Kremer, *Gasmaske*, 1931, **3**, 109; Bomford and Hunter, *Lancet*, 1932, II, 1446; Loning, *Deut. Arch. klin. Med.*, 1932, **173**, 177; Nuck and Jaffe, *Arch. Gewerbepath. Gewerbehyg.*, 1932, **3**, 496.

[4] Grigg, *Analyst*, 1929, **54**, 659. See also Grassmann, *Arch. Gewerbepath. Gewerbehyg.*, 1930, **1**, 197; *Chem. Zentr.*, 1930, [1], 2923.

[5] Leymann and Weber, *Chim. et. Ind.*, 1930, **24**, 832. See also *J. Ind. Hyg.*, 1928, **10**, 137.

[6] Bencker and Heinze, *German Patent*, 524803 (1930). See also Koch, *Metall u. Erz*, 1931, **28**, 429.

[7] Davidson Pratt, "*Protection against Toxic Gases in Industry*," *Inst. of Chem. Publication*, 1936, p. 15.

permissible concentration for an unprotected person for a single period of 4 to 6 hours' exposure should not exceed 1 in 200,000 (0·0005 per cent.).

Numerous cases of poisoning have occurred attributed to wall-papers containing an arsenical pigment such as Schweinfurt Green or Scheele's Green. The use of these pigments for colouring papers and boards is now discontinued and, in England, more than 2 to 3 parts of arsenic per million is rarely present, there being a provisional agreement that not more than 10 parts per million is permissible,[1] while in certain continental countries the permissible limit is 5 mg. per sq. m.[2] The symptoms arising from this source are [3] sneezing, lachrymation and cough, nausea, sickness and diarrhœa, dry throat and tongue with thirst, colic pains, cramps and spasms, depression and extreme weakness. In most wall-paper cases the poisonous effects were first attributed to the presence in the air of arsenical dust, but it has been shown that the action of moisture and organic matter such as starch paste and gelatin on free arsenious acid may produce a volatile compound presumed to be an alkylarsine,[4] and after removal of all dust from such air, passage through aqueous silver nitrate shows that arsenic is still present.[5] Gosio [6] discovered that, in the presence of organic matter containing arsenic, certain moulds, under suitable conditions, were able to synthesise volatile arsenic compounds having an intense garlic odour. The most active organisms are *Penicillium brevicaule* and *Penicillium divaricatum*, and the action of the first is used for the detection of small quantities of arsenic in organic matter (see p. 322), the test being known as Abba's test.[7] The presence of carbohydrate appears to be necessary.[8] With the *Penicillium divaricatum* it is possible to detect as little as 0·00008 per cent. of arsenic.[9] Compounds of selenium and tellurium similarly yield volatile compounds by the action of such organisms and, in the latter case, the odour resembles that due to arsenic.[10] The nature of the volatile compound has not been conclusively demonstrated, being variously described as arsine,[11] diethylarsine,[12] trimethylarsine [13] and diethylcacodyl oxide;[14] possibly more than one such compound may be produced. Lerrigo [15] experimented with garden soils to which arsenic had been added, but was unable to show that volatile compounds were produced by the agency of soil bacteria.

In the investigation of a number of cases of fatal poisoning attributed to wall coverings, the evidence has led to the plaster as being the source of the trouble.[16] Thus, in a case in which two children died at Cinderford, Forest of Dean, in 1932, the paper from a dry part of the wall contained 8·3 parts As_2O_3 per million, a sample where mould was most

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[1] Stern, *Analyst*, 1928, 53, 83.

[2] Scheringa, *Pharm. Weekblad*, 1928, 65, 677.

[3] Guy and Ferrier, *loc. cit.*

[4] Fleck, *Zeitsch. f. Biol.*, 1873, 8, 444; Selmi, *Gazzetta*, 1881, 11, 437; Husemann, *Arch. Pharm.*, 1881, [3], 16, 169. *Cf.* Tonegutti, *J. Chem. Soc.*, 1909, A ii, 700; *Boll. Chim. Farm.*, 1909, 48, 259, 370.

[5] Hamburg, *Pharm. J.*, 1874, [3], 4, 81; Bartlett, *Analyst*, 1880, 5, 81.

[6] Gosio, *Ber.*, 1897, 30, 1024. *Cf.* Emmerling, *ibid.*, 1896, 29, 2728.

[7] Abba, *Centralbl. Bakteriol.*, 1898, ii, 4, 806; Gosio, *L'Orosi*, 1900, 23, 361.

[8] Markmann, *Chem. Zentr.*, 1900, [2], 1187.

[9] Thom, "*The Penicillia,*" 1930, p. 92.

[10] Rosenheim, *Proc. Chem. Soc.*, 1902, 18, 138; Maasen, *Chem. Zentr.*, 1902, [1], 1245.

[11] Markmann, *loc. cit.*

[12] Biginelli, *Atti R. Accad. Lincei*, 1900, [5], 9, 210.

[13] Challenger, *Ind. Chem.*, 1933, 9, 134.

[14] Klason, *Ber.*, 1914, 47, 2634.

[15] Lerrigo, *Analyst*, 1932, 57, 155.

[16] Vervloet, *Pharm. Weekblad*, 1933, 70, 578.

pronounced 2·3 parts, an unused roll of wall-paper purchased when the wall was papered 4·4 parts, and the plaster (composed of coke breeze and cement) 91 parts. It was concluded [1] that the arsenic present in the paper was an impurity and that that present in the plaster dissolved in moisture coming through the wall from a bank of soil outside and was converted to a volatile compound by the mould on the paper. The arsenic in the air could not be detected by simple aspiration, but filter papers saturated with silver nitrate placed near the walls for 7 and 9 days collected sufficient to be detected by the electrolytic Marsh test (see p. 317). In another case, where the odour of alkylarsines was reported, the outer papers gave a negative test for arsenic, but older paper beneath gave a strong positive test, the arsenic being almost completely soluble in water.[2] It was revealed, however, that the paperhanger, 15 years previously, had mixed rat poison with the paste in order to prevent mice from gnawing the paper! Re-papering from time to time had evidently furnished nutrient material for the fungi which converted the arsenic to volatile compounds.

According to Foulkes,[3] experiments with arsine for war purposes suggested that the toxicity was less than usually supposed. A pig in a trench exposed to a high concentration of the gas appeared unaffected, and of two officers who entered the trench, which smelt very strongly of garlic, one only suffered ill-effects. Such compounds as diphenylchlorarsine and diphenylamine-chlorarsine were employed during the Great War as lachrymators, sternutators and respiratory irritants, one part of the latter in 25 million of air being sufficient to produce intolerable conditions; chloroform gave immediate relief and the effects were only temporary.

Arsenic trichloride is highly toxic and inhalation of the fumes rapidly causes acute arsenical poisoning, the symptoms including laryngeal obstruction, dyspnœa and convulsions. During the Great War, shells containing the compound mixed with hydrogen cyanide and other ingredients were employed.[4] The following relative toxicities have been given:[5] Cl_2 1, $AsCl_3$ 1·5, $COCl_2$ 5·5, but there is considerable divergence of opinion as to the relative values of chlorine and phosgene, Haber and others [6] putting the lethal value of the latter at 17 to 19 times that of the former.

A series of epidemics among fisherfolk on the shores of the Gulf of Dantzig in 1924–25, known as "Haff sickness," was supposed to be due to poisoning resulting from the presence in the atmosphere of arsenious chloride. The possible source of the latter was the waste liquors from cellulose factories in the neighbourhood, being derived either from the sulphurous acid prepared from arsenical pyrites containing sodium chloride [7] or from the action of algæ on the arsenical trade waste.[8] The findings of the Government Laboratory, established to investigate the problem, did not, however, confirm arsenical poisoning.[9]

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[1] Anon., *Analyst*, 1932, 57, 163.

[2] Scheringa, *Pharm. Weekblad*, 1928, 65, 677.

[3] Foulkes, "*Gas*" (Blackwood, London), 1934, p. 104.

[4] Foulkes, *ibid.*, p. 249.

[5] Chlopin, *Zeitsch. ges. Schiess. Sprengstoffw.*, 1927, 22, 127.

[6] Foulkes, *ibid.*, p. 108.

[7] Biginelli, *Giorn. Chim. Ind. Appl.*, 1925, 7, 568; Glaser, *Chem. Zeit.*, 1926, 50, 185.

[8] Juckenack and Bruning, *ibid.*, 1926, 50, 513.

[9] Lockemann, *ibid.*, 1926, 50, 701; *Zeitsch. angew. Chem.*, 1926, 39, 1446.

Application of liquid arsenious chloride to the skin also causes acute poisoning. The immediate result is necrosis ; this may be considerably retarded by washing within one minute of the application, but after five minutes washing has no effect.[1] The arsenic is rapidly absorbed by the tissues, and after a few hours, if death ensues, the element can be recovered from most of the tissues and organs of the body, especially the brain, liver and kidneys.

Arsenious chloride destroys the underground stems of some species of creeping perennials. It is very effective, even in very dilute solution, in destroying the growth of many annual weeds, including puncture vine, if applied before the seeds mature.[2] Vegetation sprayed with arsenious chloride is repulsive to grazing animals and they avoid it, whereas vegetation sprayed with arsenites is attractive and is so toxic that it may cause death (see p. 308).

Arsenious oxide, *or* **white arsenic,** is an extremely powerful poison, especially when in solution. It acts as a severe gastro-intestinal irritant. As little as 0·13 g. has proved fatal, but 0·19 g. is probably the least quantity likely to cause death. The limit of toxicity in aqueous solution is 0·2 mg. As_2O_3 per litre.

The effects when taken in powder form vary considerably with the state of division, and cases are on record [3] in which recovery has taken place after taking such large amounts as 15 to 42 g. Such large doses have generally been taken on a full stomach and have promptly been rejected with food by the brisk action of the bowels. But the toxicity of arsenious oxide depends upon its rate of solution, and this depends on the grain size. The toxic dose of potassium arsenite for man has been estimated to be [4] 0·84 g. For a dog the dangerous dose of white arsenic is 0·32 to 0·65 g., for a horse 1·94 g. and for a cow 0·65 g. The fatal dose is dependent to some extent on body weight and, expressed in g. per kg. of body weight, the fatal doses of the finely powdered oxide taken through the mouth are estimated to be : [5] for rabbits 0·2, for rats 0·1 and for chickens 0·075; while if taken in the form of a solution the quantities are respectively 0·015 to 0·020, 0·075 and 0·0667. For a sheep 0·86 g. of sodium arsenite is fatal, but half that quantity is non-toxic.[6]

It is well known that white arsenic can be taken in small quantities with apparently good effects. Thus, the arsenic eating of the Styrian peasants is said to improve the respiration and to enable them to endure fatigue better in mountain climbing ; the skin is improved and the body well developed,[7] and the arsenic eater appears to be exempt from infectious diseases. The arsenic acts as a stimulant and causes an increased flow of the gastric juice.[8] The doses taken are at first small, but are gradually increased to about 0·3 g. or more ; Knapp [9] records

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[1] Delépine, *J. Ind. Hyg.*, 1923, 4, 346, 410.

[2] Johnson, *Monthly Bull. Calif. Dept. Agr.*, 1927, 16, 354.

[3] Glaister, see Kerr, "*Forensic Medicine*" (Black, London), 1935; Guy and Ferrier, "*Principles of Forensic Medicine*," 7th Ed., revised Smith (Henry Renshaw), 1895.

[4] Marcovitch, *J. Econ. Entomol.*, 1928, 21, 108.

[5] Schwartze, *J. Pharmacol.*, 1922, 20, 181; *J. Franklin Inst.*, 1923, 195, 121.

[6] Seddon and Ramsay, *N.S.W. Dept. Agr. Vet. Research Rept.*, 1933, No. 6, Part 3, p. 113.

[7] Johnston, "*The Chemistry of Common Life*," London, 1855, 2, 201; Roscoe, *Manchester Phil. Soc.*, October 30, 1860; Maclagan, *Edin. Med. J.*, 1864, 10, 200.

[8] Frank, *Arch. exp. Path. Pharm.*, 1933, 173, 180.

[9] Knapp, *Edin. Med. J.*, 1864, 10, 669.

having witnessed the swallowing of 0·486 g. (7·5 grains). There is doubt, however, as to whether the arsenic eaten by these peasants is comparable in toxicity with ordinary white arsenic.[1] It is obtained from the flues of local smelting furnaces, being known as *hidrach*, and is probably a coarse-grained, comparatively insoluble form of arsenic. Moreover, it has not been demonstrated that habituation to arsenic is possible. The peasants can discontinue taking it only by gradually diminishing the doses ; if the doses are suddenly stopped, intense pain and sickness occur, often with fatal results.[2] In the same way the improved condition of horses, to which arsenic has been daily administered for show purposes, soon disappears when the stimulant is withdrawn. Moreover, the practice of thus feeding animals results in reduced respiratory activity and impaired reproductive functions.[3] The practice of arsenic eating also exists in parts of India.

The symptoms of acute poisoning by white arsenic usually appear in less than one hour. The victim may complain of a burning taste when taking it. He experiences a burning pain at the pit of the stomach, which is increased by pressure ; nausea, faintness and uncontrollable vomiting follows, the latter being renewed by the act of swallowing. The pain becomes more diffuse, with diarrhœa, tenesmus and dysuria. There is a sense of constriction in the throat, intense thirst, headache, restlessness and rapid but weak pulse, cramps in the legs and convulsive twitchings of the extremities. In most cases the mind remains clear until there is complete collapse or coma. Death may follow after a few hours.

Chronic poisoning, which usually results from repeated small doses as in industry or by deliberate poisoning, but may be the result of one large dose, causes chronic ill-health, which appears to be due to mild gastro-enteritis. The victim loses appetite, loathes food and suffers nausea and general malaise. There is occasional vomiting, diarrhœa and increasing prostration. The effect of the poison on the liver may cause jaundice, the mucous membranes become inflamed causing conjunctivitis, running of the eyes, coughing and bronchial catarrh. Skin eruptions and various nervous symptoms, including peripheral neuritis, may occur, and the condition becomes such that the person may die from sheer exhaustion or, if death occurs by the administration of a larger final dose, arsenical poisoning may not be suspected.

Although the symptoms enumerated above are typical, different cases may present very different and perplexing features, for whereas in one case these symptoms may be present in an aggravated form, in another they may be absent or nearly so. The pulse may be very frequent (90 to 140) or almost imperceptible (30 to 45). The taking of the poison may be followed by immediate collapse with little pain, vomiting or diarrhœa, and one case is recorded[4] where death occurred in four hours after profound sleep. The nervous symptoms, which are especially marked in chronic cases, show a similar variation and, in a consideration of 25 cases,[5] the incidence was as follows : extreme

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[1] Kesteven, *Assoc. Med. J.*, 1856, p. 811; Christison, *Edin. Med. J.*, 1856, 2, 709; Taylor, "*Medical Jurisprudence*," London, 1886.

[2] Heisch, *Chem. News*, 1860, 1, 280; *Pharm. J.*, 1860, [2], 1, 556.

[3] Roberts and Dawson, *Illinois Agric. Exp. Sta. Bull.*, 1935, No. 413, 187.

[4] Wright, *Lancet*, 1826, 12, 194.

[5] Guy and Ferrier, *loc. cit.*; Murray, *Edin. Med. Surg. J.*, 1822, 18, 167; McLeod, *ibid.*, 1819, 15, 533. Also *ibid.*, 1840, 54, 106, 262; 1841, 56, 295; 1843, 59, 250.

restlessness 5, debility 10, coma 3, delirium 3, mind unimpaired 6, cramp in legs 9 (and arms 4), convulsions 6, tetanus 2, hysteria 1, epilepsy 2, tetanus, coma and delirium, successively, 2; death in convulsions 3, in one case after horrible laughter. The nervous symptoms may persist for a considerable time; periodic epilepsy, for example, has been observed after two years.

White arsenic is not considered to be a cumulative poison, and although it is absorbed by almost every part of the body, elimination proceeds slowly and almost at once, arsenic being detectable in the urine and fæces within half an hour. The amount excreted varies directly with the dose, but the rate varies greatly with the individual.[1] It must be remembered, however, that excretion of arsenic occurs with normal persons, and the following variation has been observed in the urine of a large number of persons fed on the same diet: in 16 per cent. no arsenic present; in 43 per cent. 0·01 to 0·06 mg. As per litre; in 33 per cent. 0·07 to 0·20 mg. As per litre; and in 8 per cent. 0·21 to 0·69 mg. As per litre. The periodic variation of the arsenic content in the blood of women has been mentioned previously (p. 21). Considerable quantities of arsenic may thus appear in the excretions of individuals without discoverable cause; this is especially so in persons with jaundice, and arsenic is thought to be a contributory factor in many cases of acute yellow atrophy of the liver.[2] Also abnormal urinary arsenic accompanies many skin conditions, such as eczema, scleroderma, leucoderma, psoriasis and pemphigus, and in some cases of eczema arsenic appears to be the exciting cause.[3]

The fatal period in poisoning by white arsenic varies considerably and may be a few hours or days, or many weeks; in most fatal cases death occurs in 6 to 24 hours.

A post-mortem examination usually reveals the stomach in a state of acute inflammation and, if the arsenic was taken in solid form, small white or yellowish patches, consisting of a paste of arsenious acid and coagulable lymph, adhere to the mucous membrane forming centres of intense inflammation. The stomach may contain brown clotted matter, sometimes yellow owing to partial conversion to sulphide. The inflammation may affect the whole intestinal canal, but is most conspicuous in the lower bowel. The gullet and sometimes the throat and mouth may be inflamed. There may also be inflammation of the bladder, livid spots on the skin, and congestion of the brain. On the other hand, inflammation of the lining of the stomach may be completely absent. The arsenic is eliminated by the bowels, kidneys, and to some extent by the skin and hair. That which is absorbed is found after death mainly in the liver and, to a less extent, in the kidneys and other soft organs. Thus, in a case of suicide,[4] analysis of the viscera gave:—liver 5·6, kidneys 2·0, heart 2·5, stomach 4·0, small intestine 4·5 mg. As per kg.; while in a case of acute poisoning,[5] in which 3 to 4 times the lethal dose had been taken, the following contents were found:—liver 10, kidneys 7·5, heart 3, spleen 3, lung 7·5, blood 4, stomach 16, intestines near the duodenum 11, central portion 14, extremity 18,

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[1] Bang, *Biochem. Zeitsch.*, 1925, 165, 364, 377.

[2] Vogel, *Amer. J. Med. Sci.*, 1928, 176, 215; *Quart. J. Pharm.*, 1928, 1, 655.

[3] Thorne, van Dyck, Merples and Myers, *N.Y. State J. Med.*, 1927, 27, 757.

[4] Barral, *Ann. méd. légale criminol. police sci.*, 1928, 8, 6. See also Austen, *Pharm. Zentr.*, 1931, 72, 385.

[5] Barral, *ibid.*, p. 4.

liquid content of stomach and intestines 14·5, brain 0·5 mg. As per kg. But in chronic poisoning the arsenic permeates even to the hair and nails.[1] The normal content of arsenic in human hair is 0·01 to 0·03 mg. per 100 g., and in the nails[2] traces of this order may or may not occur, whereas the amount gradually increases after assimilation of arsenic. Nail clippings from such a person showed 2 to 13 mg. per 100 g. Moreover, characteristic nailbands appear after about 2 months when sublethal poisoning due to a few large doses has occurred.[3] The accumulation of arsenic in the hair may be made use of to determine whether one or many doses have been taken;[4] if the stomach contains large quantities of arsenic, whereas only a little is found in the hair, the case is one of acute poisoning.[5]

Absorption of arsenic by the bones also occurs to a considerable extent,[6] and their arsenic content, whether death occurs after a few hours or only after some days, may give valuable information where suspicion of poisoning exists. Thus in the case of a man who died 8 days after ingesting the poison, 110 mg. of arsenic were found in the bones, about half being present in the bones of the arms and legs and about 20 per cent. in the flat bones of the skull; but in the case of a woman who died after 12 hours, out of a total of 1907 mg. found in the body only 3·2 mg. occurred in the bones,[7] but this amount was more than was found in any other portion of the body (except the skin) not in direct contact with the alimentary canal. In experiments on dogs to which arsenic had been administered, Popp showed[8] that the amount of arsenic in the calcined bones was about one-sixth of the amount found in the bones before cremation, and less than one-thousandth of the total amount in the whole body before cremation.

Arsenic has been credited with retarding the decomposition of the body. This does not appear to be true in cases of acute poisoning, although the stomach may be preserved when the surrounding parts are in a state of advanced decay; in chronic cases, where the arsenic has pervaded the tissues, preservation may occur.

The toxic action of white arsenic has been attributed to its inhibitory action on the oxidative processes,[9] partly owing to the effect of the change of *p*H on the enzyme concerned. Small quantities of arsenious acid reduce the power of suitably prepared extracts of animal tissues to oxidise reduced phenolphthalein. The oxidation of tartaric acid at the ordinary temperature and at 37·5° C. is inhibited by arsenious acid, as also is the respiration and fermentation of yeast,[10] but the latter

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[1] See Vitte, *Bull. Trav. Soc. Pharm. Bordeaux*, 1934, 72, 357; Roberts and Dawson, *loc. cit.*

[2] van Itallie, *Pharm. Weekblad*, 1932, 69, 1134, 1145; von Vámossy, *Pharm. Monatsh.*, 1932, 13, 254.

[3] Wigand, *Deut. Z. ges. gericht. Med.*, 1933, 20, 1207.

[4] Blumenfeldt, *ibid.*, 1930, 15, 501.

[5] See also Keeser and Keeser, *Arch. exp. Path. Pharm.*, 1925, 109, 370; Oppenheim and Fantl, *Biochem. Zeitsch.*, 1934, 271, 332.

[6] Bang, *loc. cit.*; Fuchs, *Deut. Z. ges. gericht. Med.*, 1932, 19, 280; *Chem. Zentr.*, 1932, [2], 2497.

[7] Popp, *Zeitsch. angew. Chem.*, 1931, 44, 658.

[8] Popp, *ibid.*, 1928, 41, 856. For the determination of arsenic in the ash of cadavers, see also Fridli, *Ber. ungar. pharm. Ges.*, 1926, 2, 84; *Chem. Zentr.*, 1928, [1], 1561; Jesser and Schrempf, *Deut. Z. ges. gericht. Med.*, 1933, 20, 278; *Chem. Zentr.*, 1933, [1], 2728.

[9] Smorodincev and Iljin, *Biochem. Zeitsch.*, 1928, 201, 34; Wasmuth, *Arch. exp. Path. Pharm.*, 1929, 142, 17; Adova and Smorodincev, *Biochem. Zeitsch.*, 1931, 232, 459. See also Dixon, "*Manual of Pharmacology*" (Arnold, London), 1929, p. 375.

[10] Dresel, *Biochem. Zeitsch.*, 1926, 178, 70.

inhibition is minimised by the presence of sugar, the effect increasing with the sugar concentration.[1] It has been observed [2] that arsenites have a retarding effect on many oxidation-reduction systems, such as (1) acetaldehyde and colloidal platinum, (2) acetaldehyde, glycocoll and phosphate, (3) hypoxanthine-xanthine oxidase of rat or mouse skin; arsenates are comparatively inactive. In the respiration of minced heart muscle and minced liver tissue, a co-enzyme takes part which assists in the oxidation or dehydrogenation of lactic acid, and the action is poisoned by arsenious oxide, which inhibits the whole respiratory process.[3] Parfentjev found [4] that there was no disturbance of the fermentative processes in the acute poisoning of rabbits *per os*. Underhill and Dimick observed [5] that subcutaneous injection of the oxide into dogs increased the ethereal sulphate and neutral sulphur fraction of the urinary sulphur, but no consistent variations could be detected when administered by mouth. The solubility of arsenic in aqueous solutions (5 to 7 per cent.) of glucose or sucrose is very much less than in water, and Cohen [6] suggests that the variable toxicity of the oxide to animals (see p. 294) may be due to differences in the concentration of sugars in the alimentary tract. Experiments on rabbits show that there is an increase in the non-protein nitrogen of the blood due to increase in carbamide nitrogen.[7] There is also an increase in the sugar content of the blood at the expense of the glycogen of the liver, causing hyperglycæmia; some of the glycogen may also constitute the source of the lactic acid which appears in appreciable proportion in the blood in cases of arsenical poisoning.[8]

The first step in the treatment of arsenical poisoning is to wash out the stomach thoroughly, using mild emetics such as ipecacuanha, mustard or common salt, aided by copious draughts of warm milk and water. The usual antidote is freshly precipitated ferric hydroxide given moist; [9] this renders the arsenious acid insoluble (see p. 154) and is effective if administered while the poison is still in the stomach, but less so if the arsenic was taken in the solid state or if it adheres to the stomach lining. It is not a true antidote as it does not act unless it is in contact with the poison. Alternatives which may be used, though not with such good effect, are dialysed iron, magnesium hydroxide, and animal charcoal. Intravenous injections of sodium thiosulphate, in

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[1] Dresel, *Biochem. Zeitsch.*, 1926, **178**, 70; 1928, **192**, 351.

[2] Barry, Bunbury and Kennaway, *Biochem. J.*, 1928, **22**, 1102.

[3] Szent-Györgyi, *ibid.*, 1930, **24**, 1723; Banga, Schneider and Szent-Gyorgyi, *Biochem. Zeitsch.*, 1931, **240**, 462; Banga and Szent-Györgyi, *ibid.*, 1932, **246**, 303; Handovsky, *ibid.*, 1932, **249**, 195. The mechanism of arsenic action has also been studied by Korowitsky, *ibid.*, 1928, **199**, 366; Gagarina and Yankovski, *J. Exp. Biol. Med.*, 1928, **9**, 59; Bickel, *Med. Welt*, 1929, **3**, 5; *Chem. Zentr.*, 1929, [1], 2661; Rosenthal and Voegtlin, *J. Pharm. Exp. Ther.*, 1930, **39**, 347; Voegtlin, Rosenthal and Johnson, *U.S. Public Health Service Reprint*, 1931, No. 1449, 1; Wichels and Hofer, *Klin. Wochschr.*, 1933, **12**, 591.

[4] Parfentjev, *Vestn. microbiol. epidemiol.*, 1926, **5**, 269; *Chem. Zentr.*, 1927, [2], 446.

[5] Underhill and Dimick, *J. Pharm. Exp. Ther.*, 1928, **32**, 359.

[6] Cohen, *Rep. Austral. Assoc. Adv. Sci.*, 1933, **21**, 42.

[7] Pribyl, *J. Biol. Chem.*, 1927, **74**, 775. See also Nenyukov and Tarceva, *Bull. Plant Protection*, Russia, 1931, **3**, No. 1, 33; Delhougne, *Arch. exp. Path. Pharm.*, 1933, **174**, 77.

[8] van Dyke, *J. Pharm. Exp. Ther.*, 1925, **26**, 287; Paderi, *Arch. Farm. sper. Sci. aff.*, 1926, **41**, 47; Underhill and Dimick, *J. Biol. Chem.*, 1928, **76**, 163. See also Knell, *Arch. exp. Path. Pharm.*, 1936, **181**, 292.

[9] Bunsen and Berthold, *Thesis*, Gottingen, 1834.

doses of 0·6 to 1·0 g., have been recommended [1] and, although it is not an antidote,[2] this substance appears to have good effect in cases of both acute and chronic poisoning, in the latter case preventing damage to the kidneys. It diminishes the rate of arsenic excretion, and its action probably depends on the formation of an insoluble compound.[3]

The toxicity due to local or absorptive action of solid arsenious oxide is considerably decreased by boric acid, probably because the solubility of the former, which is dependent on H^+-ion concentration, is much less in the aqueous boric acid than in water; with dissolved arsenious oxide the boric acid causes a retardation but no alleviation of the toxic action.[4]

Other treatment [5] is determined by the symptoms, stimulants being necessary in cases of collapse or anodynes if the nervous condition so requires; small quantities of iced water for the intense thirst; castor oil and milk if diarrhœa is ineffectual and painful. The patient needs to be kept warm and hot blankets should be applied to the feet and abdomen.

Arsenious oxide in dilute solution is not absorbed by the unbroken skin, but absorption occurs from concentrated solution.[6] The action is not directly on the cells of the horny layer of the epithelium, but primarily on the capillaries.[7]

Arsenites, as already indicated, and **arsenates** are also poisonous, the effects resembling those of white arsenic. The employment of these compounds in England is now severely restricted, and the manufacture of such pigments as Scheele's Green and Schweinfurt or Emerald Green has practically ceased, although the latter is still produced for use as an insecticide or fungicide and for high-class decorative and artistic work; it is also employed in the manufacture of "antifouling paints" for ships' bottoms. Formerly, persons engaged in such industries as colour printing and the making of artificial flowers, fruit and leaves, in which these colours were used, frequently suffered from catarrh, sore throat and skin rashes, and the more intense symptoms were liable to occur. The modern use of arsenates as insecticides is discussed on p. 301.

The poisonous action is influenced by the solubility of the compound in water. Lethal doses of sodium arsenate for goats and rabbits are found to be approximately 0·11 and 0·05 g. per kg. body weight,[8] and the following doses which produced death of sheep not earlier than the second day have been observed,[9] the figures in brackets being non-toxic doses: sodium arsenite, 0·86 g. (0·43 g.); arsenic acid, 0·86 g. (0·43 g.); lead arsenate, 3·9 g. (2·6 g.); emerald green, 1·3 g.

An examination of the effect of arsenate on the blood glucolysis of dogs and rabbits has shown [10] that in the former case the glucolysis is

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[1] Goldstein, *J. Ark. Med. Soc.*, 1927, 23, 133; Hughes, *Med. J. Australia*, 1927, p. 543; *Quart. J. Pharm.*, 1928, 1, 145.

[2] Scaduto, *Boll. Soc. Ital. Biol. sper.*, 1931, 6, 578.

[3] Young, *J. Pharmacol. Proc.*, 1927, 31, 217; *J. Lab. Clin. Med.*, 1928, 13, 622.

[4] Taubmann and Mucke, *Arch. exp. Path. Pharm.*, 1932, 166, 545.

[5] For the influence of radium on subacute arsenical poisoning in guinea-pigs, see *Amer. Chem. Abs.*, 1931, p. 4058.

[6] Dixon, "*Manual of Pharmacology*" (Arnold, London), 1929, p. 374.

[7] Ellinger, *Arch. exp. Path. Pharm.*, 1931, 161, 562.

[8] Attia, *Ministry Agr. Egypt, Tech. and Sci. Service Bull.*, 1931, 105.

[9] Seddon and Ramsay, *N.S.W. Dept. Agr. Vet. Research Rept.*, 1933, No. 6, Part 3, p. 113.

[10] Morgulis and Pinto, *J. Biol. Chem.*, 1932, 95, 621.

diminished but in the latter it is accelerated. The inorganic phosphates of the glucolysing blood invariably increase owing to stimulation of the blood phosphatases, the effect being directly proportional to the arsenate concentration. Braunstein states [1] that the action of the arsenate is to impede the esterification of hexose with phosphate, this esterification not being a necessary condition of glucolysis but only an accompanying connected phenomenon.

The **sulphides** of arsenic are not poisonous when pure, but as they are frequently contaminated with arsenious oxide the usual symptoms may result from their ingestion. The yellow trisulphide is occasionally found adhering to the wall of the stomach after death owing to the action of hydrogen sulphide on arsenious oxide. It was observed by Ossikowsky [2] that during the decomposition of organic substances, easily oxidisable compounds, if present, become oxidised, and that under such conditions arsenious sulphide yields arsenious oxide and small quantities of arsenic pentoxide; the oxidation is facilitated by the presence of water and heat. In cases of poisoning attributed to the sulphide, the oxidation products have appeared more or less quickly, according to conditions, and have contributed to the ill-effects.

Colloidal arsenious sulphide, in whatever way it may be administered to rabbits, dogs or guinea-pigs, changes its state of dispersion, becoming granular, and poisonous effects ensue.[3]

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[1] Braunstein, *ibid.*, 1932, 98, 379; and reply by Morgulis and Pinto, *ibid.*, 1932, 98, 385.

[2] Ossikowsky, *J. prakt. Chem.*, 1880, [2], 22, 323.

[3] Meneghetti, *Biochem. Zeitsch.*, 1921, 121, 1.

CHAPTER XII.

ARSENICAL SPRAYS AND DUSTS.

Insecticides.—The use of arsenic compounds as insecticides is by far their most important application, more than 70 per cent. of the world's production being devoted to this purpose. The widespread dissemination of such compounds, in the form of dusts or spray liquids, coming into contact with edible products and with the soil, constitutes a problem which requires strict methods of control. The composition of the insecticidal mixture depends upon the nature of the pest to be eradicated and the sensitivity of the plant. It is essential that the most effective compound should be used and that amounts in excess of the desired toxicity should be avoided owing to possible injury to the foliage, arsenic being poisonous also to plant life, and because of the necessity of removing residual arsenic from fruit and vegetables before marketing. Arsenates are much less toxic, both to insects and plants, than arsenites, and are therefore generally employed, being less likely to cause damage to the crops. The two most generally effective arsenates are lead hydrogen arsenate, $PbHAsO_4$, and calcium arsenate, $Ca_3(AsO_4)_2$, but others may be employed. For the plum curculio the order of toxicity of the metallic arsenates is as follows:[1] PbH > Ba > Ca > Zn > Mn > scorodite (native iron arsenate). The dust or spray mixture generally contains, in addition to the arsenate, sulphur and slaked lime, and may contain such substances as calcium carbonate, iron oxide, aluminium sulphate or silicate, casein or starch.[2] The addition of a fish oil or a mineral oil as an emulsifier increases the adhering power. The Schweinfurt greens are frequently employed,[3] and typical spray liquids may be prepared by passing through a colloid mill suspensions of 1 to 5 g. of copper arsenite or aceto-arsenite per litre of water with 1 per cent. of starch or 10 per cent. of kaolin.[4]

The pests are destroyed by absorbing the powder either through the mouth or through the body by contact, and the sprays and dusts should contain minimum quantities of water-soluble arsenic, as this is mainly responsible for foliage injury; the fineness of division also has an effect, and injury is increased if the arsenate is too highly dispersed.[5] In the United States a legal limit (0·75 per cent. As_2O_3) is imposed as to the amount of water-soluble arsenic that may be present in lead

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[1] Snapp, *J. Econ. Entomol.*, 1928, 21, 175. *Cf.* Chapman and others, *ibid.*, 1934, 27, 421.

[2] I. G. Farbenind. A.-G., *Swiss Patent*, 120424–6 (1925); Johnson, *English Patent*, 248975 (1925); Woodman, *J. Pom. Hortic. Soc.*, 1925, 4, 78; Carpmael, *English Patent*, 287246 (1926); Goodwin and Martin, *J. Agr. Sci.*, 1926, 16, 596; Ginsburg, *J. Econ. Entomol.*, 1927, 20, 625.

[3] Deshusses, *Ann. Falsif.*, 1929, 22, 392; Brémond, *Bull. Soc. Pharm. Bordeaux*, 1928, 66, 226.

[4] Krestovnikov and Lyutringshauzen, *Min. Suir. Tzvet. Met.*, 1929, 4, 431.

[5] Carr, *Proc. Indiana Acad. Sci.*, 1927, 36, 185.

arsenate sold for agricultural purposes. It is necessary, therefore, that the insecticidal mixture should contain some substance which will inhibit the formation of soluble arsenic, but which will not itself cause injury to foliage or decrease the insecticidal value. The best results are obtained with ferric oxide or an excess of freshly slaked high-grade lime,[1] and such mixtures cause no injury to apple and only slight injury to peach foliage. Spray mixtures containing ferric oxide adhere remarkably well to the leaves, and analysis of the latter shows that more arsenic remains on them than when lime is used.

The property of adherence of dusts to the plants determines their effectiveness. It varies considerably with composition, lead hydrogen arsenate adhering to a greater extent than magnesium arsenate and this more than calcium arsenate. The presence of slaked lime reduces the adherence.[2] The air condition at the time of dusting also has an effect, the adhesion decreasing with increased wind velocity.[3]

The toxic action of arsenic on foliage is ascribed to the decomposition of glucosides to form a complex with arsenic.[4] The existence in plants of organic acids which are known to decompose arsenates led Potts [5] to examine the water (transpiration and dew) from leaves of 50 species of plants. The aqueous solutions from only three species, known to be resistant to arsenates, were alkaline; all other species gave acid solutions. Calcium arsenate and lead hydrogen arsenate are much more soluble on leaf surfaces than in distilled water, the former being the more soluble. When sprays containing the lead arsenate also contain a large quantity of calcium hydroxide, the foliage upon which they are used may give a slightly alkaline reaction, but rain removes much of the lime, carrying some of the lead arsenate with it. The leaf surface then becomes acid and dissolves calcium and lead at the expense of the arsenate, and the free arsenic acid is readily absorbed by the tissues. Much of the protection from injury which is afforded by lime is due to the removal of arsenic with the lime by rains. At the same time, the reduction of water-soluble arsenic may be due to a definite chemical reaction, as the best results are obtained [6] when the ratio As : Ca corresponds closely with that for the possible compound $2CaCO_3.Ca_3(AsO_4)_2$. Formation of complex Ca–Pb salts is improbable. Magnesium compounds give larger amounts of soluble arsenic and are therefore less suitable as correctives.

If a soap is added to a lead hydrogen arsenate-hydrated ferric oxide mixture considerable damage and leaf drop is caused, especially if the soap contains a strong base, as in the case of commercial potash fish-oil soap or potassium oleate. Laboratory tests show that more soluble arsenic is formed than with a soap of a weak base such as triethanolamine oleate.[7] The addition of cryolite to an arsenate inhibits the formation of soluble arsenic; [8] fluosilicates cause decomposition. These fluorine

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[1] Ginsburg, *N.J. Agr. Exptl. Sta. Bull.*, 1929, 468, 1; Young, *Ohio Agr. Exptl. Sta. Bull.*, 1930, 448, 3.

[2] Potts and Barnes, *J. Econ. Entomol.*, 1931, 24, 1110.

[3] Reckendorfer, *Fortschr. Landw.*, 1932, 7, 582.

[4] Parfentjev and Devrient, *J. Pharm. Exp. Ther.*, 1932, 44, 171.

[5] Potts, *J. Econ. Entomol.*, 1930, 23, 469.

[6] Streeter and Pearce, *Ind. Eng. Chem.*, 1931, 23, 1140.

[7] Ginsburg, *J. Agr. Research*, 1933, 46, 179. See also Zwolfer, *Zeitsch. angew. Entomol.*, 1930–31, 17, 188.

[8] Carter, *J. Econ. Entomol.*, 1929, 22, 814.

compounds may be employed as insecticides instead of arsenates and, in some cases, *e.g.* against the Oriental fruit moth and the plum curculio, are more effective and considerably less dangerous, since their residues are easily reduced below the limit for human consumption.[1] Manganese arsenate mixtures may be obtained with minimum quantities of soluble arsenic. The commercial salt, " Manganar," does not react with lime-sulphur mixtures to produce soluble arsenic,[2] and a product containing less than 1 per cent. of the latter results [3] by reaction of manganese dioxide and arsenious acid in aqueous medium and in the presence of lime at 100° C. and under a pressure of 80 lbs. sq. in.

The control of apple pests is best accomplished with lead hydrogen arsenate-lime-sulphur mixtures, the method of spraying being more effective than dusting for such pests as the curculio, codling moth or apple scab.[4] The addition of a mineral oil, or a fish oil such as herring oil, to the spray mixture is advantageous, giving better coverage.[5] The fruit after treatment retains varying quantities of lead and arsenic on the surface and the amount of arsenic retained may exceed the British limit of tolerance (0·01 grain As per lb. fruit) and may also cause damage to the fruit ; also the toxicity of the lead is cumulative. It is essential, therefore, that these residues be removed immediately after harvesting. The amount of residue varies very considerably with the composition of the spray, the time of spraying, the amount of rainfall between the last application and harvest, and with the variety of apple.[6] For the accurate estimation of such residues it is necessary to analyse a sample of about 50 apples picked at random.[7] The spraying should be done early in the season and, if later applications are necessary, substitutes should be used, otherwise heavy residues remain.[8] Fruit on the lower branches generally retains the largest quantities of arsenic ; [9] most of this is found on the skin, about half on the sides and half on the stem ends, very little penetrating into the pulp of the fruit.[10] Pears, which may be treated similarly, retain only slight residues, except in very dry seasons.[11]

Hand wiping or washing with water fails to remove all the arsenic ; 2 per cent. aqueous sodium hydroxide or 1 per cent. by volume of

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[1] Smyth and Smyth, jun., *Ind. Eng. Chem.*, 1932, 24, 229; Lipp, *J. Econ. Entomol.*, 1929, 22, 600; Marcovitch and others, *ibid.*, 1931, 24, 844; 1932, 25, 141.

[2] Young, *Ohio Agr. Exptl. Sta. Bull.*, 1930, 448, 3.

[3] I.C.I. Ltd., *British Patent*, 340882 (1930). See also Dearborn, *J. Econ. Entomol.*, 1930, 23, 630.

[4] Burkholder, *Purdue Agr. Exptl. Sta. Bull.*, 1932, 356, 3; Hammer, *J. Econ. Entomol.*, 1932, 25, 569; Pierstorff and Young, *Phytopath.*, 1931, 21, 131; Hough, *Va. State Hort. Soc., Proc. 38th Ann. Mtg.*, 1934, 22, [i], 65.

[5] Webster, Spuler and Marshall, *Wash. Agr. Exptl. Sta. Bull.*, 1932, 275, 32; Marshall and Groves, *Wash. State Hort. Assoc., Proc. 29th Ann. Mtg.*, 1933, p. 39.

[6] Percival and Potter, *N.H. Agr. Exptl. Sta. Tech. Bull.*, 1932, 49, 3; *N.H. Extension Circ.*, 1932, 136, 1; Ballantyne and Cayzer, *Agr. Gaz. N.S.W.*, 1932, 43, 459; Shear, *N.Y. Agr. Exptl. Sta. Bull.*, 1929, 575, 1; Andrew, *N.Z. J. Sci. Tech.*, 1927, 9, 206.

[7] Barnes, *Ind. Eng. Chem.*, 1929, 21, 172. See also Hartzell and Wilcoxon, *J. Econ. Entomol.*, 1928, 21, 125.

[8] Carter and Newcomer, *J. Econ. Entomol.*, 1933, 26, 572; Raucourt, *Ann. Falsif.*, 1933, 26, 274.

[9] McLean and Weber, *N.J. Agr. Exptl. Sta., Extension Bull.*, 1931, 87, 5; *J. Econ. Entomol.*, 1928, 21, 921.

[10] Cox, *Analyst*, 1926, 51, 131; Shutt, *ibid.*, 1926, 51, 291; Lendrich and Mayer, *Zeitsch. Unters. Lebensm.*, 1926, 52, 441; Fischler, *Wein u. Rebe*, 1931, 13, 107; *Chem. Zentr.*, 1931, [2], 1506.

[11] Blanchard, *Compt. rend. Acad. agr. France*, 1933, 19, 183.

commercial hydrochloric acid in water is more effective,[1] but calyx scald due to soluble arsenic is liable to follow, in which case the arsenic can be isolated from the injured tissues.[2] The best treatment is to wash the apples immediately after picking in 1 per cent. hydrochloric acid for 1 minute at 13° to 21° C. and rinse in water immediately.[3] The addition of sodium chloride or sodium sulphate to the hydrochloric acid increases the efficiency of the wash.[4] By such means the residual arsenic is reduced to negligible amounts, and the keeping qualities of the fruit are not affected. Even heavily sprayed tomatoes may be cleaned successfully in this way.[5] The treatment is not satisfactory, however, if oil sprays have been used or if the fruit has become waxy in storage. Accumulations of oil or wax on the skin prevent contact with the acid wash and should be first removed by dipping in a suitable solvent. Petroleum emulsion at 35° to 40° C. is a satisfactory oil remover, while methyl alcohol has been found to be an efficient wax solvent.[6]

With fruit other than apples and pears, where washing is not practicable, calcium arsenate is often a more suitable spray than lead arsenate. The latter is the best control for grape berry moth, but a practical method of residue removal is not available.[7] The problem is more difficult than with apples owing to greater fruit surface per given weight, close packing of berries, which favours clotting and retention of residues, and the highly perishable nature of the fruit. A mixture of lead arsenate and lime is safest to use for peach foliage and fruits which are extremely sensitive to arsenicals.[8] The injury is reduced to a minimum where nitrogen fertilisers are used.[9]

The application of arsenates to such trees as the orange, grape-fruit and citron is found to result in a lowering of the H^+-ion concentration of the fruit juice, and excessive amounts affect the keeping qualities of the fruit.[10] Judicious spraying, however, besides controlling harmful insects, may thus be beneficial in reducing excessive acidity of some varieties of fruit. Cherries may be treated similarly to apples.[11] A satisfactory wash, which reduces the residues to about 0·005 grain per lb., is a 0·3 per cent. hydrochloric acid solution with 3 minutes' immersion. The cherries should stand a few hours after picking, or cracking may occur during the washing operation. For the plum curculio (*cf.* p. 301) a dust containing 5 per cent. of normal lead arsenate

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[1] Cox, *loc. cit.*; Sears, *American Patent*, 1624074 (1927); Maas, *American Patent*, 1754173 (1930).

[2] Fisher and Reeves, *U.S. Dept. Agr. Tech. Bull.*, 1931, 245.

[3] Streeter and Harman, *N.Y. Agr. Exptl. Sta. Bull*, 1929, 579; Streeter, *ibid.*, 1932, 611; Shear, *ibid.*, 1929, 575; Holland, *Ohio Agr. Exptl. Sta., Bimonthly Bull.*, 1931, 151, 123; Percival and Potter, *loc. cit.*

[4] Robinson, *Ind. Eng. Chem.*, 1929, 21, 1132; Hough and others, *Va. Agr. Exptl. Sta. Bull.*, 1931, 278, 3.

[5] McLean and Weber, *N.J. State Hort. Soc. News*, 1933, 14, 490.

[6] Neller, *Ind. Eng. Chem*, 1931, 23, 323; McLean and Weber, *J. Econ. Entomol.*, 1931, 24, 1255; 1933, 26, 727; Ballantyne and Cayzer, *loc. cit.*; Snyder and Magnuson, *Idaho Agr. Exptl. Sta. Bull.*, 1932, 187, 3.

[7] Runner, *Ohio State Hort. Soc., Proc. 65th Ann. Mtg.*, 1932, p. 206; Hengl, Reckendorfer and Beran, *Wein u. Rebe*, 1931, 13, 459; Cadoret, *Prog. agr. et vit.*, 1930, 93, 241.

[8] Snapp, *J. Econ. Entomol.*, 1928, 21, 175; Swingle, *J. Agr. Res.*, 1929, 39, 393.

[9] Marcovitch and Stanley, *J. Econ. Entomol.*, 1932, 25, 213.

[10] Miller and others, *U.S. Dept. Agr. Tech. Bull.*, 1933, 350; Takahashi, *J. Okitsu Hort. Soc. (Japan)*, 1930, 25, 153.

[11] Robinson, *Oregon Agr. Exptl. Sta. Bull.*, 1932, 298, 5.

is useful as a spray, and higher concentrations give no better control.[1] Calcium arsenate and acid lead arsenate are of equal effectiveness and are superior to basic lead arsenate as determined by the time required to kill the potato and tomato looping caterpillar.[2]

The larvæ of coleoptera in sugar beet fields may be exterminated by repeated spraying with a lead arsenate spray of about 0·5 per cent. concentration during spring.[3] The larvæ in all stages of development die within 24 hours. For sugar cane pests an adherent dust containing 1 part of white arsenic or lead arsenate with 5 to 6 parts of finely powdered phosphate rock and 5 per cent. of a neutral mineral oil has been found effective in Hawaii,[4] while an effective spray mixture is also made [5] by agitation of lead hydrogen arsenate with water and fish oil in the proportions 8 : 14 : 2. In South Africa a spray mixture of calcium arsenate, lime, molasses and citronella oil has been found effective in killing locusts on sugar cane plantations.

For the larvæ of the Colorado potato beetle the established lethal dose of lead hydrogen arsenate is 0·30 mg. per gram of body weight ; [6] that of Paris green is less than one-third that amount. The quantity of arsenic remaining in potato fields after treatment is so small as to offer no danger of intoxication.[7] Calcium arsenate is most efficient and economical for the control of the potato flea beetle.[8] A study of the use of similar dusts for the control of June beetles on oak leaves showed that the death of the beetles, which occurred within 72 hours, was due to their eating the poison and not to contact with the dust.[9]

For the Mexican boll weevil a specially prepared calcium arsenate containing up to 20 per cent. of arsenic pentoxide is effective. This is prepared by heating together white arsenic and precipitated chalk in the presence of excess air at 650° C. The cotton plant is not injured by this preparation.[10] In Peru about 30,000 acres of cotton fields are dusted annually from aeroplanes with calcium arsenate. Acid arsenates of calcium appear to be more toxic to boll weevils and to locusts than the basic arsenates. This is probably because the latter must be partially hydrolysed to compounds giving more soluble arsenic before toxic results are produced.[11] The extensive application of such sprays to cotton plants is frequently followed by heavy infestations of the cotton aphis. This appears to be due in the first place to the positive phototropism of the winged females to white substances such as the arsenate, chalk or flour. Increase of the aphis population is then aided by the destruction by the spray of the hymenopterous parasites of the aphis.[12]

For the larvæ of mosquitoes, copper aceto-arsenite is more efficient

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[1] Snapp and Thompson, *J. Econ. Entomol.*, 1931, **24**, 854. See also Chapman and others, *ibid.*, 1934, **27**, 421.

[2] Cottier, *N.Z. J. Sci. Tech.*, 1933, **14**, 309.

[3] Neuwirth, *Listy Cukrovar*, 1932, **51**, 109; Neuwirth and Hula, *ibid.*, 1932, **50**, 141, 149.

[4] Pemberton, *Hawaiian Planters' Record*, 1933, **37**, 56.

[5] Porter and Sazana, *J. Econ. Entomol.*, 1928, **21**, 633.

[6] Richardson and Haas, *ibid.*, 1931, **24**, 732.

[7] Raucourt, *Ann. Falsif.*, 1933, **26**, 274.

[8] Gui, *Ohio Agr. Exptl. Sta.*, *Bimonthly Bull.*, 1932, **156**, 104.

[9] Travis and Decker, *Iowa State Coll. J. Sci.*, 1933, **7**, 493.

[10] Walker, *J. Econ. Entomol.*, 1928, **21**, 165; Bondy, *S. Car. Agr. Exptl. Sta. Ann. Rep.*, 1931, p. 28.

[11] Hendriks, Bacot and Young, *Ind. Eng. Chem.*, 1926, **18**, 50.

[12] Folsom, *J. Econ. Entomol.*, 1927, **20**, 840.

than either calcium or lead arsenate.[1] The relative toxicity of dilute acid and alkaline solutions of sodium arsenite to mosquito pupæ, which have no mouth opening, has been determined under laboratory conditions.[2] With 0·01 to 0·03 molar sodium arsenite solutions, those at *p*H 5 were about 4·5 times more rapid in toxic action than those at *p*H 11. Adsorption appears to be an important step in the process of penetration, and the greater toxicity of the acidic solutions is attributed to greater ease of penetration of the tissues by the un-ionised molecules of the weak arsenious acid contrasted with the difficulty of penetration by the ions of the alkaline solutions. In the case of the larvæ a much smaller difference was observed, probably on account of the buffering effect of the intestinal contents. The larvæ are more susceptible than pupæ to arsenic because the walls of the digestive tract are more permeable than the outer body covering.

Experiments with house flies pointed to a considerable buffering action in the intestine.[3] Solutions of arsenious acid and of the stoichiometric quantities of sodium hydroxide and arsenious oxide to form normal sodium arsenite, containing 15 g. of sucrose per 100 c.c., were fed to adult flies. The *p*H values of the former solutions were 6·58 to 6·96 and of the latter 11·3 to 11·4, but the toxicities were equal, being 0·14 mg. As per g. body weight—a large value for an insect. None of these solutions was repellent to the flies, but if the *p*H was increased beyond 11·4 repellent action was observed; house fly bait therefore should not contain more alkali than is necessary to hold the arsenic in solution. The eradication of the tsetse fly by similar means is difficult. There is not much chance of a poisonous dose being taken from the skin of a dipped animal, but a toxic dose can be taken up from an arsenic-impregnated area by means of the proboscis.[4]

A considerable demand for crude white arsenic or sodium arsenite for the destruction of grasshoppers has arisen in recent years. A good standard bait contains 5 lbs. As_2O_3 to 100 lbs. of wheat bran ;[5] this is attractive and palatable to the grasshoppers, but the amount required depends on the size and feeding capacity of the insects, so that it is economical to destroy them when young. The Mormon cricket may be controlled by dusts containing calcium or sodium arsenite with 3 to 4 parts of slaked lime, and no serious injury to the alfalfa or grain crop involved occurs.[6]

A sodium arsenate spray gives the best control of powdery mildew of cucumber, and is also effective against American mildew of gooseberry, and apple mildew.[7]

Arsenic pentoxide is found to be effective in weed eradication ; thus New Zealand hard-fern may be destroyed by midsummer spraying in dry weather with a solution containing 1 lb. of As_2O_5 in 32 gallons of water,[8] and effective control of acacia scrub or thorn bush has been obtained in South Africa by brushing the freshly cut stumps with a

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[1] Marcovitch, *J. Econ. Entomol.*, 1928, 21, 108.
[2] Hoskins, *ibid.*, 1932, 25, 1212.
[3] Pearson and Richardson, *ibid.*, 1933, 26, 486.
[4] Duke, Hall and Haddon, *Uganda Protectorate Bull. Entomol. Res.*, 1928, 19, 7.
[5] Hopper, *J. Econ. Entomol.*, 1933, 26, 292.
[6] Cowan, *ibid.*, 1928, 21, 928.
[7] Szembel, *Rev. Appl. Mycol.*, 1930, 10, 500.
[8] Levy and Madden, *N.Z. J. Agr.*, 1932, 44, 186.

solution containing 1 to 1·5 lb. As_2O_5 per gallon of water.[1] "Wild morning glory" and cactus may similarly be controlled by the use of soluble arsenicals.[2]

Vegetation in fish ponds may be controlled by treatment with white arsenic or commercial sodium arsenite if applied in concentrations of 1 to 2 parts As_2O_3 per million.[3] Several applications each year may be needed. Under these conditions the natural fish foods are uninjured and small fish are not adversely affected. Hard waters require a somewhat higher concentration of arsenic. The latter disappears rapidly from the waters, probably owing to precipitation.

It will readily be understood that the incorporation of arsenicals in the soil is a dangerous practice and may cause, as the concentration of arsenic increases, considerable injury to crops and to animals which feed on them. The total amount of arsenic present in the soil is not necessarily related to the toxicity, but the concentration of soluble arsenic is a more reliable index. Arsenious oxide, sodium and potassium arsenites, and even so-called "insoluble" arsenates, decrease the transpiration of oats, tomatoes and potted plants,[4] and 2 parts per million of calcium arsenate may provide sufficient soluble arsenic to retard definitely root and top growth of arsenic-sensitive plants.[5] An investigation of the growth and yields of cotton crops in S. Carolina, where calcium arsenate was administered for boll weevil control over a number of years, showed [6] that, on all light soils, when amounts as low as 50 lbs. per acre were applied, the yields of cotton were seriously decreased.[7] The addition of lime helped to overcome the deleterious effect of the arsenate. The growth of cow peas was similarly injured. The addition of ferric sulphate to the soil (240 lbs. per acre) in some cases greatly reduced the injury, and it was observed that less injury was shown by soils rich in iron. Laboratory experiments show that a mixture of 20 per cent. red clay soil of high iron content with top soil or grey sandy soil is generally sufficient to remove any injurious concentration of arsenic.[8] The adsorptive capacity of ferric hydroxide is discussed on p. 154. The addition of arsenic generally tends to decrease the *p*H value of the soil. The plants and fruit grown on arsenic-rich soil may absorb a considerable amount of arsenic,[9] but this depends upon the form and manner in which the arsenic has been applied. Thus, addition of 0·001 to 0·004 per cent. of As_2O_3 in the form of lead hydrogen arsenate or copper aceto-arsenite over a period of 5 years did not result in an increase of arsenic content of the grain and straw of mustard plants grown on the treated soil, nor was there any effect on the yield of the grain.[10] Single applications of 0·02 to 0·04 per cent. of As_2O_3 as the copper compound had a very deleterious effect on the germination of

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[1] Dyer, *Farming in S. Africa*, 1931, 5, 524.

[2] Johnson, *Calif. Dept. Agr., Monthly Bull.*, 1928, 17, 7.

[3] Wieber, *Trans. Amer. Fisheries Soc.*, 1930, 60, 270; Surber, *ibid.*, 1931, 61, 143, 225; *U.S. Dept. Commerce, Bur. Fisheries Investigational Rept.*, 1932, 11, 1.

[4] Morris and Swingle, *J. Agr. Res.*, 1927, 34, 159.

[5] Albert and Arndt, *S. Cal. Agr. Exptl. Sta. Ann. Rep.*, 1931, p. 47.

[6] Cooper and others, *ibid.*, 1931, p. 28.

[7] See also Rivière and Pichard, *Compt. rend.*, 1922, 174, 493; Ciferri, *Coltivatore*, 1922, Nos. 32–34.

[8] Albert, *ibid.*, 1932, p. 44.

[9] von Fellenberg, *Mitt. Lebensm. Hyg.*, 1929, 20, 338; *Biochem. Zeitsch.*, 1930, 218, 300.

[10] Reckendorfer, *Fortschr. Landw.*, 1932, 7, 437.

mustard, but single applications of 0·01 to 0·02 per cent. in the form of acid lead arsenate had no significant effect on the germination, growth, yield of seed or arsenic content of the plants. In the soil, lead hydrogen arsenate appears to be converted slowly into a basic form, but it can be applied at the rate of 1500 to 2000 lbs. per acre without affecting the growth of plants.[1] It is the least toxic of the arsenates to plants, and the danger of animal poisoning from its use as a spray arises more from its lead content than from arsenic.[2] In China, powdered white arsenic is frequently mixed with the ashes of burnt twigs or grass and added to soil in order to kill worms.[3] The mixture generally contains less than 10 per cent. of As_2O_3 and is used on soil where vegetables such as cabbage are grown.

The wholesale use of toxic sprays and dusts may be accompanied, on occasions, by considerable danger to animals. It is recorded[4] that after a stand of oak timber extending over 3500 acres had been dusted with calcium arsenate from an aeroplane, many wild animals and a great number of bees were found dead; also a number of domestic cattle which had fed on grass from the forest or from the landing field showed the characteristic symptoms of arsenical poisoning. Such dusting is particularly dangerous in bee-keeping districts, especially in wet weather. It has been found[5] that about 0·002 mg. As is a lethal dose for a bee, and the smoke from metal works may contain sufficient to cause widespread destruction. The use of arsenical sprays in closed spaces, such as greenhouses, is undesirable owing to the possibility of the formation of volatile compounds by the agency of fungi which may be present[6] (see p. 292).

The fungicidal properties of arsenic compounds may be applied to the preservation of wood. When wood is treated with arsenical solutions, the wood tannins tend to fix some of the arsenic, and if a soluble chromate or dichromate is added to the solution, chromium also is fixed in the wood fibre after drying. If a solution in which the proportions of arsenate and dichromate are $As_2O_5 : K_2Cr_2O_7 = 1 : > 1{\cdot}25$ is used, no arsenic can be leached from the treated dried wood after shaking 6 hours in 20,000 parts of water.[7] If the ratio is 1 : 1, about 1 per cent. of the arsenic is soluble and this gives the most suitable degree of toxicity; with higher proportions of arsenate the amount of soluble arsenic rapidly increases. The concentration of the solution used for impregnating the wood should be about 2 per cent. each of arsenic pentoxide and alkali dichromate; if fire-resistant properties are required, soluble phosphates may be added without affecting the applicability of the solution.

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[1] Leach, *J. Agr. Res.*, 1926, **33**, 1.
[2] von Fellenberg, *loc. cit.*
[3] Browne, *Pharm. J.*, 1928, **120**, 320.
[4] Danckwortt and Pfau, *Zeitsch. angew. Chem.*, 1926, **39**, 1486.
[5] Popp, *ibid.*, 1928, **41**, 805.

CHAPTER XIII.

THE DETECTION AND ESTIMATION OF ARSENIC.

ARSENIC is insoluble in hydrochloric acid, but readily dissolves in dilute nitric acid, yielding arsenious acid :

$$As_4 + 4HNO_3 + 4H_2O = 4H_3AsO_3 + 4NO$$

It also dissolves in concentrated nitric acid or aqua regia, and in solutions of hypochlorites, to form arsenic acid :

$$3As_4 + 20HNO_3 + 8H_2O = 12H_3AsO_4 + 20NO$$
$$As_4 + 10NaOCl + 6H_2O = 4H_3AsO_4 + 10NaCl$$

The element is generally met with in the form of its oxides or sulphides, or salts derived from these, but however it occurs it may readily be converted into a form which renders it easy of both detection and estimation. Owing to the necessity of detecting even the smallest traces of the element, the methods employed in many cases are of extreme sensitivity.

In routine analysis arsenic is precipitated from acid solution as sulphide and with antimony, molybdenum and tin is separated from the copper group by dissolution in yellow ammonium sulphide. The sulphides are reprecipitated from this solution by acidifying, and on treatment with concentrated hydrochloric acid all the sulphides, except arsenic, redissolve. The latter dissolves in aqua regia and arsenic may be identified in the solution by applying one of the tests described in the sequel.[1]

Detection of Arsenic.—*Dry Tests.* Metallic arsenic burns giving a garlic odour, which is associated with the yellow allotrope (see p. 29), and fumes of arsenious oxide. The garlic odour is noticed when any arsenic compound, mixed with sodium carbonate, is heated on charcoal. The oxygen compounds may readily be reduced to arsenic by heating in a reducing flame, and the vapours may be condensed on a cold surface and dissolved in a hypochlorite solution. Similarly, arsenious oxide or sulphide is reduced by fusion with sodium carbonate and potassium cyanide, cyanate or thiocyanate being formed. Arsenites behave similarly providing the metal yields an arsenide easily decomposed on heating. In a suitable vessel a mirror of arsenic is obtained from 0·01 mg. of arsenious acid.

When the trisulphide is ignited with sodium carbonate and nitrate, sulphate and arsenate are formed :

$$5As_2S_3 + 16Na_2CO_3 + 28NaNO_3 = 10Na_3AsO_4 + 15Na_2SO_4 + 16CO_2 + 14N_2$$

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[1] See also Grosset, *Ann. Soc. Sci. Bruxelles*, 1933, 53 B, 16; Lincoln and Olson,

When the sulphide is heated in a stream of chlorine, or when heated w ammonium chloride and ammonium nitrate (5 : 1) in a current of arsenic trichloride is volatilised.

Wet Tests. Copper sulphate gives no precipitate with solutions arsenious or arsenic acid, but if a little alkali hydroxide is added, former gives a grass-green precipitate of cupric monohydrogen ort arsenite, $CuHAsO_3$, Scheele's green, while the latter gives a pale b precipitate of the corresponding arsenate, $CuHAsO_4$. The cop arsenite is soluble in excess of alkali and the solution on boiling p cipitates cuprous oxide; the arsenate is not dissolved and is not reduc This is a sensitive reaction for distinguishing ter- and quinque-val arsenic,[1] but the presence of certain organic compounds may ca reduction of the arsenate under similar conditions.

Silver nitrate with neutral solutions of arsenites gives a pale yell precipitate of the silver salt, Ag_3AsO_3, which is soluble in both aque ammonia and in nitric acid. From acid solutions the precipitate i hydrogen arsenite, and in aqueous solutions of the mono- and di-hydro arsenites the precipitation is incomplete; the solution should theref be neutralised with ammonia. From neutral solutions of arsenat silver nitrate gives a chocolate-coloured precipitate of silver arsena Ag_3AsO_4, soluble in acids and ammonia. This test is very sensitive brown coloration being obtained with a solution containing as lit arsenic as 1 part in 150,000, whilst a distinct precipitate is obtained w 1 part in 60,000, and even in the presence of ammonium nitrate, as test is usually applied in routine analysis, it is possible to detect 1 p in 15,000.[2]

Bettendorff's Test.[3] On adding concentrated hydrochloric acid t few drops of an arsenite solution and then a little stannous chlor solution in hydrochloric acid, the solution quickly becomes brown a then black owing to the deposition of metallic arsenic:

$$2AsCl_3 + 3SnCl_2 = 3SnCl_4 + 2As$$

The reaction proceeds more readily on heating. In the absence hydrochloric acid there is no reaction, as stannous chloride does reduce arsenious acid. The test is capable of detecting 0·01 mg. As_2O_3,[4] but the sensitivity may be considerably increased by presence of a trace of mercuric chloride (0·00001M), and the rate deepening of the colour is then a function of the concentration the latter.[5] At such dilution the mercuric chloride does not produ turbidity with the stannous chloride.

To detect an *arsenite and an arsenate* in the presence of each oth the neutral solution should be treated with ammonia and magne mixture. The precipitate, treated with Bettendorff's reagent, give black precipitate of arsenic, indicating arsenate; the filtrate, acidif with hydrochloric acid and treated with hydrogen sulphide, yield precipitate of arsenious sulphide, indicating arsenite.[6]

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[1] Harting, *J. prakt. Chem.*, 1841, [1], 22, 49; Lassaigne, *J. Chim. Méd.*, 1842, [1] 584. See also Brandes and Ebeling, *Brandes' Arch. Apoth.*, 1828, 25, 269.

[2] Curtman and Daschavsky, *J. Amer. Chem. Soc.*, 1916, 38, 1280.

[3] Bettendorff, *Zeitsch. anal. Chem.*, 1870, 9, 105.

[4] Winkler, *Pharm. Zentr.*, 1921, 62, 125.

[5] King and Brown, *Ind. Eng. Chem.* (*Anal.*), 1933, 5, 168.

[6] Agostini, *Ann. Chim. Applicata*, 1929, 19, 520.

Ammonium molybdate, when added in considerable excess to a boiling solution of an arsenate in nitric acid, gives a yellow crystalline precipitate of ammonium 12-molybdo-arsenate, $(NH_4)_3H_4[As(Mo_2O_7)_6].4H_2O$ (see p. 215). Like the corresponding molybdo-phosphate, the precipitate is readily soluble in ammonia or aqueous alkali. The arsenate may be detected in the presence of phosphate by boiling the yellow precipitate with aqueous ammonium acetate until clear; a white precipitate or turbidity on cooling shows the presence of arsenate, and the filtrate may be tested for phosphate.[1]

If a drop of 0·02N aqueous sodium sulphide is added to a drop of a solution containing arsenate or phosphate on a filter paper and a drop of aqueous ammonium molybdate acidified with sulphuric acid also added, a blue colour develops;[2] ferro- and ferri-cyanides and thiocyanate should be absent. The formation of "molybdenum blue" is used in the colorimetric estimation of arsenic (see p. 321).

Sodium hypophosphite, *Thiele's* or *Bougault's reagent*,[3] affords a more sensitive test than Bettendorff's reagent.[4] It is prepared by dissolving 20 g. of sodium hypophosphite in 20 c.c. of water and adding 200 c.c. of hydrochloric acid; sodium chloride is removed by filtration and the filtrate kept until a second crop of crystals separates, when it is again filtered and is ready for use.[5] When added to a solution containing arsenic, a brown coloration or precipitate results due to separation of arsenic. This test is recommended by the Dutch and German Pharmacopœias. In the presence of ferric iron the colour of the latter interferes, and this should therefore first be reduced by means of iron powder or sodium sulphide and the test made on the filtrate.[6] Preparations containing starch or sugar may also give a dark colour with the reagents, and should therefore be ignited with sodium nitrate before the test is made.[7] The reagent cannot be used in the presence of metals whose salts it reduces, such as silver, mercury, gold, palladium and platinum, also selenium and tellurium.[8]

Calcium hypophosphite instead of the sodium salt may be used in the presence of hydrochloric acid,[9] and the reaction may be applied for the gravimetric estimation of the element, the arsenic in the residues being redissolved and determined as magnesium pyroarsenate,[10] or by titration.[11]

The Reinsch Test.[12] When a strip of polished copper foil is placed in a solution of arsenious acid a grey film is formed on the copper owing to deposition of arsenic and formation of copper arsenide, Cu_5As_2. The deposition occurs in the cold with concentrated solutions, but only on warming with dilute solutions. It is possible to detect by this means

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[1] Sheinkman and Galetzki, *Farm. Zhur.*, 1932, Nos. 3–4, 120. See also Maderna, *Atti R. Accad. Lincei*, 1910, [5], 19, ii, 68.

[2] Marrison, *Chem. and Ind.*, 1935, p. 872.

[3] Thiele, *Apoth. Ztg.*, 1890, 5, 86; Matthes, *Pharm. Ztg.*, 1926, 71, 1509.

[4] Grippa, *Ann. Chim. Appl.*, 1930, 20, 249; Wallrabe, *Pharm. Zentr.*, 1928, 69, 33.

[5] Delaville and Belin, *Bull. Soc. Chim. biol.*, 1926, 9, 91.

[6] van den Driessen Mareeuw, *Pharm. Weekblad*, 1928, 65, 70; Wallrabe, *loc. cit.*; Grippa, *loc. cit.*

[7] Joachimoglu and Zeltner, *Pharm. Ztg.*, 1928, 73, 422.

[8] Guérin, *Bull. Soc. Pharm. Bordeaux*, 1930, 65, 152.

[9] Rupp and Muschol, *Ber. Deut. pharm. Ges.*, 1923, 33, 62; Deussen, *Arch. Pharm.*, 1926, 264, 355.

[10] Pluchon, *Bull. Soc. Pharm. Bordeaux*, 1932, 70, 140.

[11] See Evans, *Analyst*, 1932, 57, 492.

[12] Reinsch, *J. prakt. Chem.*, 1841, [1], 24, 244. See Leffmann, *Analyst*, 1930, 55, 684.

1 part of As_2O_3 in 250,000 parts of water, but at great dilutions the tim required for the deposition may be from half to one hour. Arsenic aci is similarly reduced by copper, but only on warming. If much arsen is precipitated the deposit may not adhere to the copper. Oxidisin agents must be absent.

Since other metals, namely, mercury, antimony and bismuth, ar liable to be deposited on the copper, it is necessary to test for arsenic b gently heating the strip in a narrow tube,[1] when a characteristic sub limate of octahedral crystals of arsenious oxide is formed, readil distinguished from mercury, which yields mirror-like globules, o antimony, which gives a sublimate, partly needle-shaped and largel amorphous, only on prolonged heating; bismuth gives no sublimat This test is of great importance in toxicology.[2]

Other important reactions of arsenic employed for the detection o the element are also adapted for its determination either when it occu in quantity or in very small amounts. These reactions will therefor be dealt with from the point of view of their quantitative, as well as thei qualitative, application.

THE ESTIMATION OF ARSENIC.

Gravimetric Methods.—*As Sulphide.* Acidified solutions o arsenites yield with hydrogen sulphide a yellow flocculent precipitate o arsenious sulphide, As_2S_3, insoluble in dilute acids.[3] With very con centrated hydrochloric acid the sulphide is decomposed with liberatio of hydrogen sulphide and the volatile arsenic trichloride. Concentrate nitric acid also decomposes it—

$$3As_2S_3 + 28HNO_3 + 4H_2O = 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

as also does ammoniacal hydrogen peroxide—[4]

$$As_2S_3 + 14H_2O_2 + 12NH_4OH = 2(NH_4)_3AsO_4 + 3(NH_4)_2SO_4 + 20H_2O$$

The precipitate dissolves in aqueous alkali hydroxides, carbonates an sulphides with formation of arsenites and thioarsenites, thus:

$$As_2S_3 + 6KOH = K_3AsO_3 + K_3AsS_3 + 3H_2O$$

and

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$$

Little or no precipitation may occur, therefore, in solutions of norma or monohydrogen arsenites, and to ensure complete precipitation th solution must contain sufficient acid to prevent the formation of thio salts. The solution for estimation should be strongly acidified wit hydrochloric acid and hydrogen sulphide be passed in the cold. Exces of the latter is removed by passing carbon dioxide, and the precipitate after washing with hot water, is dried at 105° C. and weighed as As_2S_3.

If hydrogen sulphide is passed into a cold solution of an arsenate i

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[1] Evans, *Analyst*, 1923, 48, 357; Leffmann and Trumper, *Bull. Wagner Free Inst. Sci Philadelphia*, 1927, 2, 89.

[2] Leffmann and Trumper, *Amer. J. Pharm*, 1927, 99, 646.

[3] Bunsen, *Annalen*, 1878, 192, 320; Holthoff, *Zeitsch. anal. Chem.*, 1879, 18, 264 1884, 23, 378; Treadwell. *Ber.*, 1891, 24, 1937.

[4] Classen and Bauer, *Ber.*, 1883, 16, 1061; Classen and Ludwig, *Ber.*, 1885, 18, 1104 *Zeitsch. anal. Chem.*, 1886, 25, 106.

dilute hydrochloric acid no precipitate is formed, owing to the formation of soluble thioarsenic acids, *e.g.* H_3AsO_3S (see p. 281), until after a long time, when arsenious sulphide separates. If, however, a large excess of concentrated acid is added to the solution and the gas passed in the cold, the pentasulphide, As_2S_5, is precipitated. The precipitation is quantitative[1] if the concentration of the hydrochloric acid is at least 4N and the solution is saturated rapidly with the gas. After keeping the solution for two hours in a stoppered flask, the precipitate should be removed, washed with water and hot alcohol, dried at 105° C. and weighed as As_2S_5.

If hydrogen sulphide is passed into a hot solution of an arsenate in concentrated hydrochloric acid a mixture of the tri- and penta-sulphides is precipitated. To bring about a rapid precipitation in the form of As_2S_3, the arsenate may be reduced by boiling with sulphurous acid[2] (boiling off excess of sulphur dioxide) or by heating with ammonium iodide or potassium thiocyanate.[3] The pentasulphide, like the trisulphide, is soluble in aqueous alkali hydroxides, carbonates and sulphides, forming thioarsenates, while fuming nitric acid or ammoniacal hydrogen peroxide converts it to arsenic acid.

The sensitivity of hydrogen sulphide as a reagent for detecting tervalent arsenic by the yellow colour produced in the presence of hydrochloric acid has been stated in widely different terms;[4] the smallest amount thus detected is given as 1 part of As_2O_3 in 1,024,000 parts of water.[5]

Arsenious sulphide is completely precipitated from a hot acid solution of an arsenite, and arsenic pentasulphide from one of an arsenate, by the addition of sodium thiosulphate, whilst both arsenites and arsenates are precipitated quantitatively as arsenious sulphide by ammonium thioacetate.[6]

A solution of normal sodium arsenate in aqueous ammonia and methyl or ethyl alcohol yields with lithium salts a pale pink precipitate which is quantitative and may be dried, ignited and weighed. An arsenite does not precipitate lithium. A mixture of the two acids may thus be quantitatively separated, the arsenate first by lithium in the presence of aqueous ammonia and alcohol, and the arsenite in the filtrate by precipitation with magnesium chloride solution.[7]

As Magnesium Pyroarsenate. The arsenic must be present as arsenate, so that any arsenite must first be oxidised, for example by

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[1] Bunsen, *Annalen*, 1878, 192, 305; Neher, *Zeitsch. anal. Chem.*, 1893, 32, 45. See also Brauner and Tomíček, *Monatsh.*, 1887, 8, 607; McCay, *Zeitsch. anal. Chem.*, 1887, 26, 635; Thiele, *Annalen*, 1891, 265, 65; Piloty and Stock, *Ber.*, 1897, 30, 1649.

[2] Brauner and Tomíček, *loc. cit.*; McCay, *Chem. Zeit.*, 1885, 9, 469.

[3] Winkler, *Zeitsch. angew. Chem.*, 1919, 32, I, 122.

[4] Pfaff, "*Handbuch der analytischen Chemie*," Altona, 1822, 1, 112; Brandes and Ebeling, *Brandes' Arch. Apoth.*, 1828, 25, 269; Reinsch, *J. prakt. Chem.*, 1838, [1], 13, 133, 1840, [1], 21, 244; 1841, [1], 24, 244; Lassaigne, *J. Chim. Méd.*, 1842, [1], 8, 584; Wormley, "*Microchemistry of Poisons*," New York, 1867; von Fellenberg, *Mitt. Lebensm. Hyg.*, 1934, 25, 318.

[5] Jackson, *J. Amer. Chem. Soc.*, 1903, 25, 992.

[6] Schiff and Tarugi, *Ber.*, 1894, 27, 3437.

[7] Gaspar, *Anal. Fís. Quím.*, 1932, 30, 406; Arnal, *Ann. Chim. anal.*, 1933, [2], 15, 193. For the separation of arsenites, arsenates and phosphates, see Tananaev and Potschinok, *Zeitsch. anal. Chem.*, 1932, 88, 271. For the separation of arsenites, arsenates, sulphites and sulphates, see Malinovski and Lopatina, *J. Appl. Chem. (U.S.S.R.)*, 1935, 8, 944; and of arsenites, arsenates, selenites and selenates, see Milbauer and Vodrážka, *Chem. Listy*, 1937, 31, 177.

means of chlorine or bromine in the presence of aqueous alkali, or bromine water in the presence of hydrochloric acid.[1] The addition of magnesia mixture, *i.e.* a solution of magnesium and ammonium chlorides, in the presence of aqueous ammonia, then precipitates white crystalline magnesium ammonium arsenate, $MgNH_4AsO_4.6H_2O$.[2] This, after 12 hours, is washed with ammonia, and is usually heated to about 500° C. until no more ammonia is expelled, then being ignited at 800° to 900° C. and so converted to magnesium pyroarsenate, $Mg_2As_2O_7$, and weighed. Accurate results have been obtained[3] for potassium dihydrogen arsenate, with which the precipitation is complete in half an hour, by ignition to constant weight at 500° to 600° C. The long standing does not appear to be necessary for complete precipitation.

The magnesium ammonium arsenate may also be weighed as such with accurate results. The precipitated mixture should be filtered after cooling for about 2 hours at 0° to 5° C., washed with alcohol and ether, dried in a vacuum at room temperature, and weighed as $MgNH_4AsO_4.6H_2O$. This process is suitable for semimicro-determinations.[4]

Volumetric Methods.—*Iodometrically.* A hot solution of arsenious oxide or an arsenite in concentrated hydrochloric or sulphuric acid when treated with potassium iodide gives a red precipitate of arsenic triiodide.

When potassium iodide is added to a strongly acid solution of an arsenate, reduction to arsenite occurs with liberation of iodine:

$$Na_3AsO_4 + 2HI = Na_3AsO_3 + I_2 + H_2O$$

This reaction is quantitative if the iodine is removed by titration with thiosulphate.[5] It is necessary to allow the solution to stand for 10 to 15 minutes, preferably in the dark, before completing titration, to ensure completion of the reaction. During titration the high acid concentration may cause decomposition of the thiosulphate; the solution is therefore diluted. The above reaction, however, is reversible, and considerable dilution will cause reversal, leading to low results; satisfactory results are obtained[6] when the solution is about 4N with respect to hydrochloric acid and contains about 1 per cent. of potassium iodide. The titration should be made at the ordinary temperature and starch indicator may or may not be used. The addition of sodium chloride to the arsenate solution has been advocated.[7] When only very small quantities of arsenic are being determined, an atmosphere of carbon dioxide is essential for accurate results, as iodine is liberated by the action of air on strongly acid iodide solutions.[8]

An alternative method of employing the reaction is to expel the iodine by heating, or by a current of carbon monoxide and dioxide generated

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[1] Backstrom, *Zeitsch. anal. Chem.*, 1892, **31**, 663; Friedheim and others, *ibid.*, 1905, **44**, 684

[2] Levol, *Ann. Chim. Phys.*, 1846, [3], **17**, 501. Virgili, *Zeitsch. anal. Chem.*, 1905, **44**, 192.

[3] McNabb, *J. Amer. Chem. Soc.*, 1927, **49**, 1451.

[4] Dick, *Zeitsch. anal. Chem.*, 1933, **93**, 429; Fridli. *Pharm. Zentr.*, 1926, **67**, 241.

[5] Rosenthaler, *Zeitsch. anal. Chem.*, 1906, **45**, 596 See also Gooch and Browning, *Amer. J. Sci.*, 1890, **40**, 66; Gooch and Morris, *Zeitsch. anorg. Chem.*, 1900, **25**, 227; Williamson, *J. Soc. Dyers and Color.*, 1896, p. 86.

[6] Pedersen-Bjergaard, *Dansk. Tidsskr. Farm.*, 1928, **2**, 1.

[7] Stale, *Mitt. Lebensm. Hyg.*, 1932, **23**, 72.

[8] Bottger and Bottger, *Zeitsch. anal. Chem.*, 1927, **70**, 97; Winkler, *loc. cit.*

by the action of sulphuric acid on oxalic acid,[1] and after adding excess of sodium bicarbonate estimate the equivalent quantity of arsenite remaining in the solution by titration with iodine as described below.

If iodine solution is added to a neutral or alkaline solution of an arsenite, the former is decolorised and oxidation occurs :

$$Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI$$

This is the reverse of the reaction discussed above, and for the reaction to run completely in this direction the hydrogen iodide must be neutralised as fast as it is formed. An alkali cannot be added as it would react with the iodine, but the hydrogen iodide may be safely neutralised with sodium bicarbonate :

$$NaHCO_3 + HI = NaI + H_2O + CO_2$$

The reaction is then quantitative and important use of it is made in volumetric analysis, not only as a method for estimating arsenic, but a standard solution of pure arsenious oxide containing sodium bicarbonate is used as a standard in iodimetry.

To estimate *arsenite and arsenate* when present together, the former may first be determined in a portion of the solution by titration with iodine in the presence of sodium bicarbonate. Another portion is acidified strongly with hydrochloric acid, some ferrous sulphate and potassium bromide are added and the whole of the arsenic is distilled off as chloride and collected in water.[2] The reduction may also be accomplished by cuprous chloride.[3] The arsenious acid in the aqueous distillate is determined as above and the arsenic acid found by difference.

Small amounts of arsenic (as little as 0·00002 g.) may be determined by converting to arsine and absorbing the latter in standard iodine, the residual iodine being titrated.[4]

Many modifications of the iodometric method have been applied.[5]

With Potassium Bromate. When a hydrochloric acid solution of an arsenite reacts with potassium bromate, the arsenic is completely oxidised to arsenic acid and the end of the reaction is indicated by the liberation of bromine :

$$3Na_2HAsO_3 + KBrO_3 + 6HCl = 6NaCl + KBr + 3H_3AsO_4$$
$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3H_2O + 3Br_2$$

If methyl orange is present, an acid reaction is indicated as long as arsenite is present, but the appearance of free bromine renders it colourless.[6] Instead of methyl orange, colloidal red selenium may be used

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[1] Ormont, *Zeitsch. anal. Chem.*, 1926, 67, 417; 1927, 70, 310. But see Rosenthaler, *ibid.*, 1926, 68, 232; 1927, 71, 190. See also Taboury and Audidier, *Bull. Soc. chim.*, 1934, [5], 1, 1570; Winkler, *Bull. Soc. chim. Belg.*, 1927, 36, 491.

[2] Pedersen-Bjergaard, *Dansk. Tidsskr. Farm.*, 1928, 2, 1; Terényi and Páskuj, *Zeitsch. anal. Chem.*, 1931, 84, 416.

[3] Roark and MacDonnell, *J. Ind. Eng. Chem.*, 1916, 8, 327.

[4] Wiley, Bewley and Irey, *Ind. Eng. Chem.* (*Anal.*), 1932, 4, 396; Křepelka and Rakušan, *Lékárn.*, 1934, 14, 290; *Chem. Zentr.*, 1935, [1], 757.

[5] See, for example, *Ann. Chim. anal.*, 1921, 3, 85. Nikolai, *Zeitsch. anal. Chem.*, 1922, 61, 257; Bang, *Biochem. Zeitsch.*, 1925, 161, 195; Fitz-Gibbon, *Analyst*, 1933, 58, 469; Strock, *Zeitsch. anal. Chem.*, 1934, 99, 321; Deshusses, *Helv. Chim. Acta*, 1927, 10, 517.

[6] For applications of this method, see de Bacho, *Annali Chim. Appl.*, 1919, 12, 153; von Villecz, *Ber. Ungar. pharm. Ges.*, 1928, 4, 313; *Chem. Zentr.*, 1928, [2], 2173; Schulek and von Villecz, *Zeitsch. anal. Chem.*, 1929, 76, 81; Pieters and Mannens, *Chem. Weekblad*, 1929, 26, 559; Pásky, *Magyar Chem. Fol.*, 1930, 36, 76, 95; *Chem. Zentr.*, 1930, [2], 1905.

as a reversible reduction-oxidation indicator.[1] This method may be used for determining arsenic in the presence of antimony and tin.[2]

Other Oxidation Methods. Satisfactory titrimetric methods are based on the oxidation of arsenious acid to arsenic acid by means of potassium iodate,[3] potassium dichromate,[4] potassium permanganate[5] and ceric sulphate.[6] The last two methods are of importance.

Potassium permanganate oxidises arsenious acid rapidly and quantitatively in the presence of a trace of potassium iodide, which acts catalytically.[7] The reaction takes place in the presence of mineral acid and the use of an indicator or of sodium bicarbonate is unnecessary. The titration may be carried out at any temperature up to 95° C. A slight correction is necessary for the oxidation of the iodide; other iodides are less effective than the potassium salt. This method is comparable in accuracy with the iodometric method.

Ceric sulphate similarly causes quantitative oxidation. The reaction should take place in the presence of 4N hydrochloric acid, with bivalent manganese present as catalyst and iodine monochloride as indicator. The iodine of the latter is first liberated and then oxidised—[8]

$$I_2 + 2HCl + O = 2ICl + H_2O$$

and the end-point is determined by disappearance of the iodine. The end-point may also be determined electrometrically.

Some of the volumetric methods described above may also be adapted to the electrometric determination of arsenic. Such methods have been described for titration of arsenites with ceric sulphate,[9] iodine in the presence of sodium bicarbonate,[10] "chloramine" (*p*-toluenesulphone chloramide),[11] alkaline potassium ferricyanide solution,[12] potassium bromate[13] or potassium iodate[14] in the presence of hydrochloric acid, silver nitrate[15] (by applying a secondary titration with 0·1N alkali to maintain the desired low $H^{\cdot}$-ion concentration), and with

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[1] Szebellédy and Schick, *Zeitsch. anal. Chem.*, 1934, 97, 186; *Chem. Zentr.*, 1934, [I], 1082.

[2] Biltz, *Zeitsch. anal. Chem.*, 1930, 81, 82.

[3] Andrews, *J. Amer. Chem. Soc.*, 1903, 25, 756; Lure, *Min. Syr.*, 1932, 6, 731; *Brit. Chem. Abs.*, 1932, B, 1083; Schoonover and Furman, *J. Amer. Chem. Soc.*, 1933, 55, 3123.

[4] Bunsen, *Annalen*, 1853, 86, 290; Vohl, *ibid.*, 1855, 94, 219; Kessler, *Pogg. Annalen*, 1855, 95, 204; 1861, 113, 134; 1863, 118, 17.

[5] Waitz, *Zeitsch. anal. Chem.*, 1871, 10, 188, Vanino, *ibid.*, 1895, 34, 426; Kuhling, *Ber.*, 1901, 34, 404; Jolles, *Zeitsch. angew. Chem.*, 1888, 1, 160, Cantoni, *Annali Chim. Appl.*, 1926, 16, 439; Kanô, *Sci. Rep. Tôhoku*, 1927, 16, 873; Reinitzer, *Zeitsch. anal. Chem.*, 1929, 77, 407, Katô, *J. Chem. Soc. Japan*, 1933, 54, 642.

[6] Willard and Young, *J. Amer. Chem. Soc.*, 1928, 50, 1322, 1372; Lang and Zwerina, *Zeitsch. anal. Chem.*, 1932, 91, 95.

[7] Pročke and Švéda, *Chem. Zentr.*, 1926, [I], 1859, Germuth, *Amer. J. Pharm.*, 1927, 99, 751; Kanô, *Sci. Rep. Tôhoku*, 1927, 16, 873, Lang, *Zeitsch. anal. Chem.*, 1931, 85, 176.

[8] Swift and Gregory, *J. Amer. Chem. Soc.*, 1930, 52, 901, Furman, *ibid.*, 1932, 54, 4335.

[9] Willard and Young, *ibid.*, 1928, 50, 1372

[10] Robinson and Winter, *J. Ind. Eng. Chem.*, 1920, 12, 775; Jander and Harms, *Zeitsch. angew. Chem.*, 1935, 48, 267.

[11] Tomíček and Sucharda, *Lékárn.*, 1931, 11, 285, 309.

[12] del Fresno and Valdés, *Zeitsch. anorg. Chem.*, 1929, 183, 258; *Anal. Fís. Quím.*, 1929, 27, 595.

[13] Nakasono and Inoko, *J. Chem. Soc. Japan*, 1926, 47, 20; Zintl and Betz, *Zeitsch. anal. Chem.*, 1928, 74, 330.

[14] Schoonover and Furman, *J. Amer. Chem. Soc.*, 1933, 55, 3123.

[15] Hume Bedford, Lamb and Spicer, *ibid.*, 1930, 52, 583.

titanium trichloride;[1] and for titration of arsenates with sodium iodide[2] in the presence of sulphuric acid at 95° C., with mercurous nitrate[3] (in 24 per cent. aqueous ethyl alcohol solution), and with silver nitrate.[4]

Methods Depending upon the Production of Arsine.

The Marsh Test.[5]—The necessity for determining with accuracy very small quantities of arsenic has led to the perfecting of several methods which require definitely standardised conditions. Compounds of arsenic may be reduced in acid solution by means of nascent hydrogen to form arsine, which by thermal decomposition yields free arsenic (see p. 89). If the hydrogen, with the entrained arsine, is passed through a heated glass or silica tube, the arsenic condenses on the walls of the tube beyond the heated place as a brownish-black mirror. The arsenic may be determined by comparison of the deposit with a series of standard deposits obtained in the same way with known amounts of arsenic. The appearance of the deposit varies with the rate of formation and comparison is satisfactory only when conditions are definite and uniform. The reagents used must be free from arsenic, and this applies also to the materials of the vessels used, for which silica is preferable to glass.[6] Zinc and sulphuric acid are usually employed to generate the hydrogen, but the reaction is more rapid with copper-coated zinc, or a copper or platinum salt may be added as an accelerator.[7] Hydrochloric acid should not be used, as the reaction

$$Zn + 2HCl = ZnCl_2 + H_2$$

is reversible and deposition of a zinc mirror may occur.[8] Aluminium may be used with hydrochloric acid.[9] Nitric acid should not be present in the test solution, as nitric oxide is liberated and may cause an explosion.[10] Many modifications of the method, both as regards reagents and apparatus, have been recommended.[11]

The *Electrolytic Method* is one of the most satisfactory adaptations of the Marsh process. Instead of generating arsine by the action of zinc on acid, it is produced by cathodic reduction.[12] The amount of *nascent* hydrogen produced during electrolysis is connected with the

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[1] Oliverio, *Annali Chim. Appl.*, 1931, 21, 211. See Francis, *J. Amer. Chem. Soc.*, 1926, 48, 655.

[2] Robinson and Winter, *loc. cit.*

[3] Spacu, *Zeitsch. anal. Chem.*, 1935, 100, 187.

[4] Hume Bedford, Lamb and Spicer, *loc. cit.* See also Hanson, Sweetser and Feldman, *J. Amer. Chem. Soc.*, 1934, 56, 577. For the simultaneous determination of iron, copper and arsenic, see Zintl and Schloffer, *Zeitsch. angew. Chem.*, 1928, 41, 956.

[5] Marsh, *Edin. Phil. J.*, 1836, 21, 229; Sanger, *Amer. Chem. J.*, 1891, 13, 431; *Zeitsch. anal. Chem.*, 1899, 38, 137, 377; Lockemann, *Zeitsch. angew. Chem.*, 1905, 18, 429, 491.

[6] Lockemann, *ibid.*, 1935, 48, 199; 1936, 49, 252; *Zeitsch. anal. Chem.*, 1935, 100, 20; 101, 340; Deckert, *ibid.*, 1935, 101, 338.

[7] de Vámossy, *Bull. Soc. chim.*, 1906, [3], 35, 24; Gautier, *ibid.*, 1906, [3], 35, 207; Bishop, *J. Amer. Chem. Soc.*, 1906, 28, 178.

[8] Arbuckle and Thies, *J. Elisha Mitchell Sci. Soc.*, 1927, 43, 50; Colley and Lockwood, *J. Soc. Chem. Ind.*, 1929, 48, 226T.

[9] Svenson, *Chemist-Analyst*, 1929, 18, 5.

[10] Schoofs, *Bull. Soc. chim. Belg.*, 1926, 35, 121.

[11] See, for example, Gadamer, *Lehrb. d. Chem. Tox.*, 1924, p. 166; Gnessin, *Pharm. J. Russia*, 1928, 89, 442; *Chem. Zentr.*, 1929, [2], 2269; Gangl and Sánchez, *Zeitsch. anal. Chem.*, 1934, 98, 81; Gangl, *Oesterr. Chem. Ztg.*, 1935, 38, 64; Davis and Malt, *Analyst*, 1936, 61, 96.

[12] Bloxam, *Zeitsch. anal. Chem.*, 1862, 1, 483; Thorpe, *Proc. Chem. Soc.*, 1903, 19, 183; Thomson, *Manchester Mem.*, 1904, 48, No. 17; Tootmann, *Chem. Zentr.*, 1904, [1], 1295; Sand and Hackford, *ibid.*, 1904, [2], 259.

phenomenon of cathodic overvoltage, which is influenced by the surface condition of the metallic cathode[1] and depends on the current density. The metal best suited to give constancy of surface and high cathodic overvoltage is mercury,[2] and this metal is employed in the apparatus designed by Aumonier for use in the Government laboratories in London.[3] The apparatus, shown in fig. 13, is suitable for determining quantities of arsenic equivalent to 0·001 to 0·010 mg. As_2O_3, which covers the limits most often to be determined in food examination.

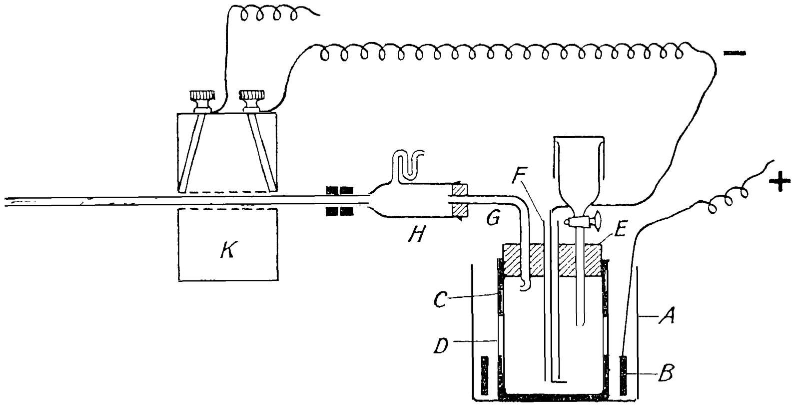

Fig. 13.—Aumonier's Electrolytic Marsh Apparatus.

The glass vessel A, maintained at an even temperature by a jacket of running water, contains a platinum foil anode B loosely fitting outside the cathode cell C, which is a porous pot, the upper and lower parts of which are made impervious by means of wax, the annulus D being left porous. The rubber stopper E carries a delivery funnel fused to a capillary stem through which dilute sulphuric acid (1 vol. pure conc. H_2SO_4 : 7 vols. H_2O) is passed at a definite rate, and which is protected from dust by a loose cover. The current is conducted from the mercury cathode by a platinum wire through a tube open at both ends, F. The voltage applied is 4 to 5 volts. The hydrogen and arsine escape through the delivery tube G, passing through a drying tube H containing neutral calcium chloride, and into an electric furnace K consisting of a silica tube, 4 cm. long and 0·5 cm. diam., wound with nichrome wire. The mirrors are formed in tapering tubes drawn out from combustion tubing and containing two gauge marks between which the deposit forms. The deposit tubes are sealed when full of hydrogen, and compared with standards prepared under the same conditions.

If larger quantities of arsenic are present, arsenic may be deposited on the cathode, but at high electric potentials and low temperature, arsine is evolved quantitatively and may be absorbed in a solution of iodine in potassium iodide and the excess of iodine titrated. Suitable forms of apparatus have been described.[4]

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[1] Pring and Curzon, *Trans. Faraday Soc.*, 1912, 7, 237.

[2] Ramberg, *Lunds Univ. Arskrift*, *N.F.*, 11, 14, No. 21.

[3] Aumonier, *J. Soc. Chem. Ind.*, 1927, 46, 341T.

[4] Hefti, *Inaug. Dissert.*, Zürich, 1907; W. D. Treadwell, "*Elektroanalytische Methoden*," 1915. See F. P. Treadwell and Hall, "*Analytical Chemistry*" (Wiley), 1924, [2], 205.

Several other types of electrolytic apparatus have been successfully employed, the most satisfactory using either the mercury cathode[1] or a cathode of arsenic-free lead.[2]

The Gutzeit Test.[3]—This test is as accurate as the Marsh test and the apparatus necessary is comparatively simple. It consists in allowing the arsine to react with strips or discs of dry filter paper impregnated with silver nitrate or, in the more recent modifications of the method, mercuric chloride or bromide. A yellow to brown or black stain is produced,[4] which is compared with a set of standard strips prepared under similar conditions. The chief difficulty encountered is to obtain a reliable and permanent set of standards; especially is this the case with silver nitrate, the stains of which do not keep. The most satisfactory method[5] of preparing such stains is to soak the filter paper in gum tragacanth, dry it, soak it in silver nitrate solution, again dry it, expose to arsine under the requisite conditions and fix the stain by repeated soaking in very dilute ammonia and coating with paraffin. By the use of 66 per cent. silver nitrate solution, $0{\cdot}1 \times 10^{-6}$ g. of As may be detected.[6]

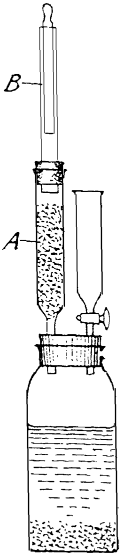

Fig. 14.
Gutzeit Test.

The use of mercuric chloride is much more convenient and almost as accurate, and this compound is now generally employed.[7] The test may be conducted in the simple apparatus shown in fig. 14; the same precautions as to the purity of all reagents are as necessary as in the Marsh test. The hydrogen is best generated from pure stick zinc and 20 per cent. sulphuric acid or from granular arsenic-free aluminium and 5 per cent. hydrochloric acid,[8] a little stannous chloride being added to ensure a uniform rate of evolution of the gas.[9] The tube A contains glass wool moistened with lead acetate solution to remove traces of hydrogen sulphide which may be formed; if filter paper or cotton wool is employed, the acid vapours cause the cellulose to retain arsenic.[10] The tube B contains a dry strip of mercuric chloride paper prepared by allowing strips of thick drawing paper to remain for an hour in alcoholic mercuric

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[1] Sensi, *Annali Chim. Appl.*, 1926, 16, 491; Callan and Parry Jones, *Analyst*, 1930, 55, 90; Callan and Clifford, *ibid.*, 1930, 55, 102.

[2] Monier-Williams, *Analyst*, 1923, 48, 112; Evers, *Pharm. J.*, 1926, 117, 183, 212; Scheermesser, *Pharm. Ztg.*, 1932, 77, 112; Damany, *Chim. et Ind.*, 1932, Mar., Spec. No., p. 167. See also Fink, *J. Biol. Chem.*, 1927, 72, 737; Osterberg, *ibid.*, 1928, 76, 19; Moerk, *Trans. Electrochem. Soc.*, 1933, 64, 173; Veinberg and James-Levi, *Reports Inst. Metals, Leningrad*, 1933, 13, 136

[3] Gutzeit, *Pharm. Ztg.*, 1879, 24, 263; Dowsart, *J. Chem. Soc*, 1901, 79, 715; Gotthelf, *J. Soc. Chem. Ind.*, 1903, 22, 191. Priority for the introduction of this test is assigned to Mayençon and Bergeret (*Compt. rend.*, 1874, 79, 118) See Crossley, *J. Soc. Chem. Ind.*, 1936, 55, 272T; Arnaud and Dyer, *Analyst*, 1936, 61, 757.

[4] The reactions incurred are described on pp. 93, 94.

[5] Martin and Pien, *Bull. Soc. chim*, 1930, [4], 47, 646.

[6] Lockemann and von Bulow, *Zeitsch. anal. Chem.*, 1933, 94, 322.

[7] Hefti, *Inaug. Dissertation*, Zurich, 1907; Sanger and Black, *J. Soc. Chem. Ind.*, 1907, 26, 1115; *Proc. Amer. Acad. Arts and Sci.*, 1907, No. 8; Cribier, *J. Pharm. Chim.*, 1921, [7], 24, 241.

[8] Mayrand, *J. Amer. Pharm. Assoc.*, 1931, 20, 637; Gross, *J. Assoc. Off. Agric. Chem.*, 1933, 16, 398.

[9] Sanger and Black, *loc. cit.*; Mayrand, *loc. cit.*; Allen and Palmer (*8th Intern. Cong. Appl. Chem.*, 1912, 1, 9) added also a ferrous salt.

[10] Ward, *Analyst*, 1926, 51, 457; 1930, 55, 630.

chloride solution and allowing them to dry in the air. The strip is exposed to the arsine-bearing gas for a definite time, sufficient for a maximum depth of colour to be obtained.

Many modifications of the apparatus and method have been recommended.[1] Discs of paper may be fixed across the mouth of the tube B in various ways and the stain, thus localised, is uniform in colour and sharp in outline and therefore more readily compared with standards.[2] Mercuric bromide papers are satisfactory in use,[3] but should be freshly prepared; the stains may be developed in aqueous potassium or cadmium iodide and compared with a colour standard.[4]

Many efforts have been made to render the stains permanent. The length of an arsenic stain is affected by changes in temperature, and by immersing the whole apparatus in a constant temperature bath, say at 30° C., stains of uniform length and intensity are obtainable [5] for any definite quantity of arsenic. The lengths vary from one set of tests to another, but the ratios between the lengths for different weights of arsenic remain constant, and a set of tables can therefore be prepared from which the values from any series of tests may be derived.[6] The use of painted colour strips as permanent standards has been suggested.[7]

The sensitivity of the Gutzeit test varies with the conditions. Variation in the humidity of the gas should be avoided.[8] Under ordinary laboratory conditions 10^{-6} g. of As may be detected, but amounts of 1, 2 and 3×10^{-6} g. are not easily differentiated.[9] If the quantity of arsenic in the aliquot test portion is as much as 0·04 mg. the comparison of the stains is not satisfactory.[10] It has been observed that arsenic stains which are invisible to the naked eye become strikingly visible under ultraviolet rays.[11]

Fleitmann's Test,[12] which consists in treating the substance with sodium hydroxide and aluminium foil and testing the gases evolved for arsine, is confined to the qualitative detection of arsenic. The liberated gas was formerly allowed to come into contact with silver nitrate paper, but as aluminium foil almost always contains sufficient silicon to cause

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[1] See, for example, Cribb, *Analyst*, 1927, 52, 701; Green, *Ind. Eng. Chem.*, 1927, 19, 424; Comrie and Ward, *J. Inst. Brew.*, 1928, 34, 530; Heidenhain, *J. Assoc. Off. Agric. Chem.*, 1928, 11, 107; Lerrigo, *Analyst*, 1928, 53, 90; Martin and Pien, *Bull. Soc. chim.*, 1930, [4], 47, 646; Davis, *Food Technology*, 1931, 1, 145; Pointing, *ibid.*, 1931, 1, 146; Gnessin, *Pharm. Zentr.*, 1934, 75, 719; Steinbruck, *ibid.*, 1935, 76, 5; Crossley, *J. Soc. Chem. Ind.*, 1936, 55, 272T.

[2] White, *Analyst*, 1927, 52, 700; Stubbs, *ibid.*, 1927, 52, 700; Dodd, *ibid.*, 1928, 53, 152; Manley, *ibid.*, 1929, 54, 30; Lindsey, *ibid.*, 1930, 55, 503; Ward, *ibid.*, 1930, 55, 630; Davis, *ibid.*, 1931, 56, 30; Thomas, *Ind. Eng. Chem.*, 1934, 26, 356.

[3] Kemmerer and Schrenk, *Ind. Eng. Chem.*, 1926, 18, 707; Neller, *J. Assoc. Off. Agric. Chem.*, 1929, 12, 332; Deckert, *Zeitsch. anal. Chem.*, 1932, 88, 7; Schroder and Lühr, *Z. Unters. Lebensm.*, 1933, 65, 168.

[4] Lachele, *Ind. Eng. Chem.* (*Anal.*), 1934, 6, 256; Snijders and van der Drift, *Chem. Weekblad*, 1935, 32, 275.

[5] Heidenhain, *loc. cit.*

[6] Thomas, *loc. cit.*

[7] Henley, *J. Inst. Brew.*, 1928, 34, 608.

[8] Mühlsteph, *Zeitsch. anal. Chem.*, 1936, 104, 333.

[9] Steinbruck, *loc. cit.*

[10] Barnes and Murray, *Ind. Eng. Chem.* (*Anal.*), 1930, 2, 29. See also Clarke, *J. Assoc. Off. Agric. Chem.*, 1928, 11, 438; Neller, *ibid.*, 1929, 12, 332; Green and Schoetzow, *J. Amer. Pharm. Assoc.*, 1930, 19, 1310; Martin and Pien, *Bull. Soc. chim.*, 1930, [4], 47, 646; Youden, *Contrib. Boyce Thompson Inst.*, 1931, 3, 363.

[11] King, *Chem. and Ind.*, 1928, 47, 301.

[12] Fleitmann, *Annalen*, 1850, 77, 127.

blackening of the paper by silicane, mercuric chloride papers, similar to those already described above, and which are unaffected by the silicon hydride, should be used.[1]

Colorimetric Methods.—*Denigès' Molybdenum Blue Test.*[2] A sensitive method for the colorimetric estimation of arsenates (or phosphates) consists in the formation of blue-coloured compounds of composition $(4MoO_3.MoO_2).XO_4H_3$, where X = As or P. The reagents are (*a*) an acid solution of ammonium molybdate, and (*b*) a reducing agent. Denigès made the former by mixing a 10 per cent. solution of ammonium molybdate with an equal volume of concentrated sulphuric acid, and this, after dilution with three volumes of water, was reduced by means of copper turnings; the decanted solution, containing quadrivalent molybdenum, could be kept for one week. The following reagents are more satisfactory:[3] (*a*) 10N-sulphuric acid containing 2·5 g. ammonium molybdate per 100 c.c., (*b*) a solution of 25 g. of pure stannous chloride crystals in 1 litre of 10 volume-per cent. hydrochloric acid. In making the test, 100 c.c. of the arsenate solution are treated with 4 c.c. of (*a*) and 6 drops of (*b*). A blue colour develops immediately. Hydrazine sulphate may also be used as the reducing agent.[4] The test is particularly applicable for the detection of arsenate or phosphate in minute quantity, the sensitivity being[5] about 1 in 1,000,000. The intensity of the colour is proportional to the amount of arsenic (or phosphorus) present and to apply the test quantitatively the blue colour is compared after 10 minutes, when it reaches a maximum, with standards generated under the same conditions. When the quantity of arsenic is very small, the blue colour is liable to fade or to be masked by the brown reduction products of molybdenum; the blue compound should therefore be extracted with methyl or amyl alcohol and compared with standards similarly obtained.[6]

If arsenate and phosphate are present together, the total arsenic and phosphorus is first determined, the arsenic is then removed with hydrogen sulphide and the phosphorus determined alone.[7]

This method for determining arsenic is particularly useful in biological and toxicological studies.[8] The material under test is oxidised with a mixture of sulphuric and nitric acids and perhydrol, the arsenic is precipitated as sulphide, which is then oxidised and the arsenic determined colorimetrically after addition of sodium molybdate and stannous chloride. The formation of the molybdenum blue compound is also applied to the micro-determination of arsenic in soil extracts.[9]

A reagent, prepared by mixing equal volumes of a 1 per cent. solution of potassium molybdate and a 2 per cent. solution of cocaine

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[1] Dauvé, *Ann. Chim. anal.*, 1928, [2], 10, 320; Sauvé, *Bull. Biol. Pharm.*, 1932, p. 280.

[2] Denigès, *Compt. rend.*, 1927, 185, 777; *Mikrochem.*, 1929, *Pregl Fest.*, p. 27.

[3] Truog and Meyer, *Ind. Eng. Chem.* (*Anal.*), 1929, 1, 136.

[4] Maechling and Flinn, *J. Lab. Clin. Med.*, 1930, 15, 779.

[5] Polyakov and Kolokolov, *Biochem. Zeitsch.*, 1929, 213, 375.

[6] Polyakov and Kolokolov, *loc. cit.*; Escolar, *Anal. Fís. Quím.*, 1930, 28, 167.

[7] Truog and Meyer, *loc. cit.*

[8] Youngburg and Farber, *J. Lab. Clin. Med.*, 1932, 17, 363.

[9] Zinzadze, *Z. Pflanz. Dung.*, 1930, 16 A, 129; 1932, 23 A, 447; *Ann. Agron.*, 1931, No. 3, 321; *Proc. Intern. Soc. Soil Sci.*, 1931, 6, 95. See also Deemer and Schricker, *J. Assoc. Off. Agric. Chem.*, 1933, 16, 226; Burkard and Wullhorst, *Z. Unters. Lebensm.*, 1935, 70, 308.

with two volumes of N-hydrochloric acid, exhibits turbidity with minute traces of arsenates.[1] The presence of neutral salts up to N concentration does not affect the test, but phosphoric acid must be absent. As little as 1×10^{-6} mg. As may be determined nephelometrically by this means.

Other methods for the colorimetric determination of arsenic have been described. Thus, for example, sodium sulphide is added to an acid solution of the sample and the precipitated arsenious sulphide washed and dissolved in 2 per cent. aqueous ammonia; on adding aqueous silver nitrate a brown colour forms, which may be compared with standards prepared under the same conditions.[2] This test may be applied in the presence of organic substances to the determination of arsenic in concentrations of not less than 0·0001 per cent.

A *drop reaction* for tervalent arsenic consists in treating a drop of the sample on filter paper with hydrochloric acid and a 0·5 per cent. aqueous solution of kairin (N-ethyl-8-hydroxytetrahydroquinoline hydrochloride); on adding a drop of aqueous ferric chloride and warming the test paper, a reddish-brown colour appears.[3] The test is sensitive to 6×10^{-10} g. Mercury, lead and copper interfere.

Many of the processes already described have been adapted for **microchemical methods,** especially in connection with organic materials. The organic matter is usually destroyed by digesting with sulphuric acid and hydrogen peroxide or nitric acid, and the arsenic may then be determined iodometrically,[4] as magnesium pyroarsenate [5] or, after removing arsenic as chloride and precipitating as sulphide, the latter may be titrated in alkaline solution with 0·01N-potassium permanganate [6] or determined colorimetrically.[7]

Applied as a microchemical test, Bettendorff's test is ten times as sensitive as the Marsh test.[8]

A **biological test** for arsenic employs *Penicillium brevicaule* (grown on sterilised bread at 37° C.), by which means 0·001 mg. As_2O_3 may be detected, a garlic odour being developed in about 24 hours [9] (see also p. 292).

Arsenic may be detected **spectroscopically,** either an intermittent arc (broken 5 to 10 times per second) or a flame arc being suitable.[10] The electrodes should be metallic, the metal chosen having bands distinct from those of arsenic, and the solid or liquid to be examined should be placed in a small depression in the face of one of the electrodes.

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[1] Kleinmann and Pangritz, *Biochem. Zeitsch.*, 1927, 185, 14, 44; Kleinmann, *Deut. Z. ges. gerichtl. Med.*, 1927, 11, 61; *Chem. Zentr.*, 1928, [1], 945.

[2] Jochelson, *Ukrain. Chem. J.*, 1934, 9, 344.

[3] Reppmann, *Zeitsch. anal. Chem.*, 1934, 99, 180. For other colorimetric methods, see Delaville and Behn, *Bull. Soc. Chim. biol.*, 1927, 9, 91; Denigès, *ibid.*, 1927, 9, 343; Reith, *Pharm. Weekblad*, 1933, 70, 369, Quincke and Schnetka, *Z. Unters. Lebensm.*, 1933, 66, 581; Taubmann, *Arch. exp. Path. Pharm.*, 1934, 176, 751.

[4] Szendro and Fleischer, *Mikrochem.*, 1929, *Pregl Fest.*, p. 323.

[5] Heller, *ibid.*, 1929, 7, 208.

[6] Morner, *Zeitsch. anal. Chem.*, 1902, 41, 397; von Fellenberg, *Mitt. Lebensm. Hyg.*, 1929, 20, 321; *Chem. Zentr.*, 1930, [1], 1239; *Biochem. Zeitsch.*, 1930, 218, 283.

[7] Reith, *Pharm. Weekblad*, 1932, 69, 1358.

[8] Schencher, *Monatsh.*, 1921, 42, 411.

[9] For a résumé of the literature dealing with the liberation of volatile arsenic compounds by the agency of micro-organisms and enzymes, see Lerrigo, *Analyst*, 1932, 57, 155. Also see Remenec, *Chem. Listy*, 1936, 30, 96.

[10] Viterbi, *Annali Chim. Appl.*, 1929, 19, 329; Riedl, *Zeitsch. anorg. Chem.*, 1932, 209, 356; van Someren, *J. Soc. Chem. Ind.*, 1936, 55, 136T.

In a solid, 2×10^{-8} g. As can be detected; in a liquid the limit is 0·01 per cent. As from 2 c.c. The method has been applied to the quantitative determination of arsenic in lead alloys, an error of 10 per cent. being sufficiently accurate for ordinary production control.[1]

Determination of Arsenic in Gases.—To estimate the number of particles of arsenical dust in a sample of air, counts of the number of particles in a dust sample are made before and after heating at 250° C.; at this temperature arsenious oxide is removed but other constituents are unaltered.[2]

In cases of arsenical poisoning, the expired air contains traces of arsenic which may be detected by absorption with bromine and ammonia and treatment with a solution of *Penicillium brevicaule* (see p. 322).[3]

To remove arsine from hydrogen gas, the mixture should be washed with 6 per cent. potassium permanganate and then passed up a tower containing absorption charcoal.[4] It is probable that the latter absorbs elementary arsenic rather than undecomposed arsine, and it may readily be recovered by digesting with normal sodium hydroxide and normal sulphuric acid. Charcoal is not a satisfactory absorbent for arsine in illuminating gas, however, only a small fraction of that present being removed; the best absorbent in this case is arsenic-free bromine, from which the arsenic is recovered by evaporation on a water bath and determined in the residue.

In determining the constituents of a gaseous mixture containing arsine, Wilmet[5] separated them by using the following absorbents in the order given: for hydrogen sulphide, a neutral solution of zinc acetate; for carbon dioxide, potassium hydroxide solution; for arsine, a neutral or slightly acid solution of cadmium acetate; for phosphine, 30 per cent. selenium dioxide solution; for acetylene, an alkaline solution of potassium mercuri-iodide. An 80 per cent. cadmium acetate solution will absorb 40 times its volume of arsine, but the absorption is somewhat slow.

Kubina[6] recommends the following method for estimating arsine volumetrically. The absorbing medium is an acid solution of iodine monochloride, the iodine being liberated according to the equation

$$AsH_3 + 8ICl + 4H_2O = H_3AsO_4 + 4I_2 + 8HCl$$

and titrated with a solution of potassium iodate in the presence of a cyanide, with a drop of carbon tetrachloride as indicator, the reaction being:

$$HIO_3 + 2I_2 + 5HCN = 5ICN + 3H_2O$$

To determine arsenic in a *volatile liquid*, this may be poured into a Marsh apparatus and burned at the jet, partly as vapour and partly as reduction products, the products of combustion being aspirated through

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[1] Eddy, *Chem. Eng. Mining Rev.*, 1932, 24, 239.

[2] Faber, *Zentr. Gewerbehyg. Unfallverh.*, 1931, 19, 211; *Chem. Zentr.*, 1934, [I], 3888.

[3] Pleschtizer and Preobrajensky, *Arch. Gewerbepath. Gewerbehyg.*, 1935, 6, 80.

[4] Lockemann, *Zeitsch. angew. Chem.*, 1926, 39, 1125.

[5] Wilmet, *Compt. rend.*, 1927, 185, 1136.

[6] Kubina, *Zeitsch. anal. Chem.*, 1929, 76, 39. *Cf.* Reckleben and Lockemann, *Zeitsch. anal. Chem.*, 1908, 47, 126. For method of determining arsenic in gas from sulphuric acid contact process, see Vinogradov and Tikhvinskaya, *J. Chem. Ind.* (*Moscow*), 1932, No. 4, 51. For a colorimetric method of estimating small quantities of arsine in air, see Raschkovan, *J. Gen. Chem.* (*U.S.S.R.*), 1935, 5, 675.

a solution of sodium hydroxide.[1] This is then oxidised with hydrogen peroxide, acidified with sulphuric acid, and examined for arsenic in the usual Marsh or Gutzeit apparatus.

The application of the foregoing analytical methods to the detection, separation and estimation of arsenic in a great variety of materials is the subject of an extensive literature, and a list of references to some useful papers of recent date is appended.[2]

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[1] Faust and Fischer, *Zeitsch. anorg. Chem.*, 1926, 158, 181.

[2] For the determination of arsenic in metals and ores, see Rosendahl, *Chem. Zeit.*, 1926, 50, 73; Evans, *Analyst*, 1929, 54, 523; Fester, *Zeitsch. angew. Chem.*, 1929, 42, 1040; in copper, Heath, *J. Ind. Eng. Chem.*, 1911, 3, 74; Meurice, *Ingénieur chimiste*, 1927, 10, 117; Furman, *Ind. Eng. Chem.* (*Anal.*), 1931, 3, 217; in iron and steel, MacPherran and others, *Amer. Soc. Testing Matls.*, 1927, No. 10 (preprint); Misson, *Chim. et Ind.*, 1931, Spec. No. 194; Stadeler, *Arch. Eisenhüttenw.*, 1935–6, 9, 423; in presence of Cu, Hg and Fe, Foerster, *Ann. Chim. anal.*, 1931, [2], 13, 225; in presence of Sb, Zintl and Wattenberg, *Ber.*, 1923, 56 B, 472; McCay, *J. Amer. Chem. Soc.*, 1928, 50, 368; Rathsburg, *Ber.*, 1928, 61 B, 1663; Sirois, *Chemist-Analyst*, 1929, 18, 14; Clennell, *Mining Mag.*, 1931, 45, 151, 211; Furman, *J. Amer. Chem. Soc.*, 1932, 54, 4235; Tananaev and Ponomarjev, *Zeitsch. anal. Chem.*, 1935, 101, 183; separation of As and Sn, Muschter, *Chem. Weekblad*, 1927, 24, 115; Harris, *Canadian Patent*, 271497 (1927); Little, *American Patent*, 1670307 (1928); separation of As, Sb and Sn, Thürmer, *Zeitsch. anal. Chem.*, 1928, 73, 196; Biltz, *ibid.*, 1930, 81, 82; Donath, *Chem. Zeit.*, 1932, 56, 483; separation from Ge, Müller, *J. Amer. Chem. Soc.*, 1921, 43, 2549; Abrahams and Muller, *ibid.*, 1932, 54, 86; from Tl, Moser and Brukl, *Monatsh.*, 1927, 47, 709; from Se, Fridli, *Pharm. Zentr.*, 1926, 67, 369; from W, Moser and Ehrlich, *Ber.*, 1922, 55 B, 430; Lukas and Jílek, *Chem. Listy*, 1930, 24, 320; separation of arsenate and phosphate, Banga and Braun, *Biochem. Zeitsch.*, 1933, 265, 148; Pett, *Biochem. J.*, 1933, 27, 1672; Bălănescu and Ionescu, *Bull. Soc. Chim. Románia*, 1935, 17, 93; separation of arsenate, vanadate and phosphate, Jochem, *German Patent*, 521191 (1929); Travers and Lu, *Compt. rend.*, 1933, 196, 703.

For the detection and estimation of arsenic in glass, see Geilmann, *Glasstech. Ber.*, 1926, 4, 92; Heinrichs and Salaquarda, *ibid.*, 1926, 4, 130; Heinrichs, *J. Soc. Glass Tech.*, 1926, 11, No. 41, 63; Lockemann, *ibid.*, 1926, 11, No. 41, 62; *Keram. Rundschau*, 1926, 34, 815; in commercial Schweinfurt green, Deshusses and Deshusses, *Helv. Chim. Acta*, 1927, 10, 517; in organic materials, Ter Meulen, *Rec. Trav. chim.*, 1926, 45, 364; Wintersteiner and Hannel, *Mikrochem.*, 1926, 4, 155; Berat, *J. Pharm. Chim.*, 1929, [8], 10, 49; Cislak and Hamilton, *J. Amer. Chem. Soc.*, 1930, 52, 638; Das-Gupta, *J. Indian Chem. Soc.*, 1932, 9, 203; Reith, *Pharm. Weekblad*, 1932, 69, 1358; Kahane, *Compt. rend.*, 1932, 195, 48; Gross, *Ind. Eng. Chem.* (*Anal.*), 1933, 5, 58; Garelli and Carli, *Annali Chim. Appl.*, 1933, 23, 129; Garelli, *Chim. et Ind.*, 1933, 29, Spec. No. 262; Tseng, *J. Chinese Chem. Soc.*, 1935, 3, 122.

For Reports on the determination of arsenic in foods, see Taber, *J. Assoc. Off. Agric. Chem.*, 1930, 13, 417; 1931, 14, 436; in food colouring materials, Callan and Clifford, *Analyst*, 1930, 55, 102; for the determination of arsenic in cocoa, Luhrig, *Pharm. Zentr.*, 1926, 67, 1; in wines and fruit beverages, Berg and Schmechel, *Chem. Zeit.*, 1933, 57, 262; von der Heide and Hennig, *Zeitsch. Unters. Lebensm.*, 1933, 66, 341; in molasses, Rogai, *Boll. ist. super. agrar. Pisa*, 1931, 7, 531; in medicinal compounds, Escolar, *Anales Soc. Españ. Fis. Quim.*, 1930, 28, 167; Weissmann and Babitsch, *Pharm. Zentr.*, 1930, 71, 721; Binova and Raihorodska, *Farm. Zhur*, 1932, 11–12, 335; in insecticides, François and Séguin, *Ann. Falsif.*, 1927, 20, 217; Fester, *Zeitsch. angew. Chem.*, 1929, 42, 1040; Wessel, *Chem. Zeit.*, 1930, 54, 97; Terényi and Páskuj, *Zeitsch. anal. Chem.*, 1931, 84, 416; Selaw, *Chemist-Analyst*, 1931, 20, No. 5, 6; in soils, Greaves, *Soil Sci.*, 1934, 38, 355; Zinzadze, *Z. Pflanz. Dung. u. Bodenk.*, 1932, A 23, 447; in preservative-treated timbers, Cohen, *J. Coun. Sci. Ind. Res. Australia*, 1936, 9, 1; *Adaptations of Soc. of Pub. Anal.*, 1930, B, p. 638.

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