A TEXT-BOOK OF
INORGANIC CHEMISTRY.
VOLUME II.

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THE PERIODIC TABLE.*

PERIODS.	GROUP O.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.		
First short period	*2* He 4·00	*1* H 1·008 *3* Li 6·94	*4* Gl 9·1	*5* B 11·0	*6* C 12·005	*7* N 14·01	*8* O 16·00	*9* F 19·0			
Second short period	*10* Ne 20·2	*11* Na 23·00	*12* Mg 24·32	*13* Al 27·1	*14* Si 28·3	*15* P 31·04	*16* S 32·06	*17* Cl 35·46			
First long period Even series	*18* A 39·88	*19* K 39·10	*20* Ca 40·09	*21* Sc 44·1	*22* Ti 48·1	*23* V 51·0	*24* Cr 52·0	*25* Mn 54·93	*26* Fe 55·85	*27* Co 58·97	*28* Ni 58·68
Odd ,,		*29* Cu 63·57	*30* Zn 65·37	*31* Ga 69 9	*32* Ge 72·5	*33* As 74·96	*34* Se 79·2	*35* Br 79·92			
Second long period Even series	*36* Kr 82·9	*37* Rb 85·45	*38* Sr 87·63	*39* Y 89·0	*40* Zr 90·6	*41* Cb 93·5	*42* Mo 96·0	*43* ...	*44* Ru 101·7	*45* Rh 102·9	*46* Pd 106·7
Odd ,,		*47* Ag 107·88	*48* Cd 112·4	*49* In 114·8	*50* Sn 119·0	*51* Sb 120·2	*52* Te 127·6	*53* I 126·92			
Third long period Even series	*54* X 130·2	*55* Cs 132·81	*56* Ba 137·37	*57–71* THE RARE EARTH METALS.	*72* ...	*73* Ta 181·5	*74* W 184·0	*75* ...	*76* Os 190·9	*77* Ir 193·1	*78* Pt 195·2
Odd ,,		*79* Au 197·2	*80* Hg 200 6	*81* Tl 204·0	*82* Pb 207·20	*83* Bi 208·0	*84* Po	*85* ...			
Fourth long period	*86* Nt 222·4	*87* ...	*88* Ra 226·0	*89* Ac	*90* Th 232·4	*91* Pa	*92* U 238·2	...	...	...	...
Formulæ of oxides Formulæ of hydrides	... ...	R_2O RH	RO RH_2	R_2O_3 RH_3	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	RO_4 ...		
Volume in this series of text-books.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		

* The International Atomic Weights for 1918 are adopted in this Table. Atomic numbers are in italics.

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With Frontispiece and Illustrations.

LONDON:
CHARLES GRIFFIN & COMPANY, LIMITED,
EXETER STREET, STRAND, W.C. 2.
1924.

Printed in Great Britain by
NEILL & Co., LTD., EDINBURGH.

GENERAL INTRODUCTION TO THE SERIES.

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

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

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

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

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

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

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

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

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid 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 in the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

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

Hydrogen = 1·00762.
Sodium = 22·996.
Potassium = 39·100.
Silver = 107·880.
Carbon = 12·003.
Nitrogen = 14·008.
Oxygen = 16·000.
Sulphur = 32·065.
Fluorine = 19·015.
Chlorine = 35·457.
Bromine = 79·916.
Iodine = 126·920.

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

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

The addition of the *Table of Dates of Issue of Journals* (pp. xix-xxvi) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr F. W. Clifford and his staff. To these gentlemen, the editor and the author 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 and Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

February, 1924.

PREFACE.

This volume is concerned with the first group of the Periodic System, and gives an account of the elements hydrogen, lithium, sodium, potassium, rubidium, cæsium, copper, silver, gold, and their compounds. It deals also with the radical ammonium and its principal derivatives. The reasons for the inclusion of hydrogen among the elements of Group I. are considered in the Introduction. So far as the limitations of space have permitted, an attempt has been made to summarize the main work done in this field of inorganic chemistry, and by means of numerous references it is hoped to give the reader easy access to the literature of those subjects of interest to him. Many of the original papers mentioned have been consulted. In addition, valuable information has been afforded by Abegg and Auerbach's *Handbuch der anorganischen Chemie*, by Thorpe's *Dictionary of Applied Chemistry*, by the *Abstracts* and *Annual Reports* of the Chemical Society, and by the *Chemisches Zentralblatt.*

The author desires to express his hearty thanks to Dr F. Challenger, F.I.C., for reading the proofs twice, and for making many valuable criticisms and suggestions; to Mr F. W. Clifford and his staff at the library of the Chemical Society for their kindness in checking the accuracy of many of the references; to Dr J. Newton Friend, F.I.C., for numerous helpful suggestions respecting the text, and for preparing the section on the atomic weight of lithium, and also the subject index and the table of contents; to Mr H. F. V. Little, B.Sc., D.I.C., for writing the sections on the other atomic weights, and for making the drawing of Morley's apparatus; to Dr O. E. Mott, O.B.E., F.I.C., for drawing the solubility-curves; to Dr A. E. H. Tutton, F.R.S., for contributing the section on the isomorphism of the sulphates and selenates of the alkali-metals; and to the publishers for the care bestowed by them on the production of the volume.

Although every effort to eliminate error from the text and from the references has been made, mistakes are inevitable, and the author would be glad if readers would notify to the publishers such errors as they may observe.

A. J. W.

February, 1924

CONTENTS.

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914 +).
Ann. Chim. anal	Annales de Chimie analytique appliquée à l'Industrie, a l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. Phys	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Mines	Annales des Mines.
Ann. Pharm.	Annalen der Pharmacie (1832–1839).
Ann. Phys. Chem.	Annalen der Physik und Chemie (1819–1899).
Ann. Physik	Annalen der Physik (1799–1818, and 1900 +).
Ann. Physik, Beibl.	Annalen der Physik, Beiblätter.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torinò	Atti della Reale Accademia delle Scienze di Torinò.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B.A. Reports	British Association Reports.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bot. Zeit.	Botanische Zeitung.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. de Belg.	Bulletin de la Société chimique Belgique.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
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 für Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Drude's Annalen	Annalen der Physik (1900–1906).
Electrochem. Met. Ind.	Electrochemical and Metallurgical Industry.

Abbreviated Title.	Journal.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Geol. Mag.	Geological Magazine.
Int. Zeitsch. Metallographie	Internationale Zeitschrift für Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch für Mineralogie.
Jahresber.	Jahresbericht über die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift für Naturwissenschaft.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal für Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
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. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Mém. Paris Acad.	Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France.
Mon. scient.	Moniteur scientifique.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Münch. Med. Wochenschr.	Münchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Öfvers. K. Vet.-Akad. Forh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Pharm. Post	Pharmazeutische Post.
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. Chem. Soc.	Proceedings of the Chemical Society.
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.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal für Chemie und Physik.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.

ABBREVIATED TITLE.	JOURNAL.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu Wien.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
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. 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.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedermann's Annalen der Physik und Chemie (1877–1899).
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.
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 as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
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.*

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1830	17, 18	...	43–45	7–8	31–34	...	...	35–38	16	...	...	7, 8	120	18–20	...	...	
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1860	...	29, 30	...	113–116	...	58–60	17, 18	101–104	...	2	1, 2	...	...
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1860	50, 51	155–158	...	...	...	37, 38	79–81	...	...	...	4	...	19, 20
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1860	150	109–111	...	10, 11	13	...	39–42	...	...	...	...	...	...
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1865	155	124–126	...	14	...	...	51, 52	...	...	4	...	...	...
66	156	127–129	...	15	...	...	53, 54	...	...	5	...	...	...
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69	159	136–138	...	17, 18	...	...	59, 60	...	...	8	...	...	...
1870	160	139–141	...	18, 19	...	...	61, 62	...	...	9	...	...	...
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1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
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98	307–310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311–314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
01	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
02	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
03	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
04	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
06	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
07	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
08	323	38	30	93, 94		27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
09	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89, 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102–104	37, 38

* See footnote, p. xx.

Year.	Phil. Trans.	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, 48, 49	9	99	10	39–41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	...	11	57, 58, 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, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	15	64, 65, 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	Continued as Annalen der Physik.	39	13	22–25	6, 7	32–34	32–35
01	196, 197	2	17	68, 69	20	110	21		40	14	26–29	7	34–36	36–38
02	198, 199	3	18	69, 70	21	111	22		41	15	29–33	8	36, 37	39–42
03	200–202	4	19	71, 72	22	112	23		42	16	33–37	9	37–39	43–46
04	203	5	20	72, 73, 74	23	113	24		43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
06	206	7	22	A. 77. 78	25	115	26		45	19	48–52	12	42, 43	54–57
07	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
08	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
09	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 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	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
1915	215, 216	16	Publication of matter of scientific interest now abandoned.	...	34	...	35		54	28	90–93	21	55	89, 90
16	216, 217	17		...	35	...	36		55	29	94–98	22	.	91, 92
17	217	18		...	36, 37	...	37		56	30	99–101	23	...	92
18	217	...		...	37	...	38		57	31	102–104	24	No	92
19	...	...		...	38	...	39		58	32	105–109	25	issue*	...

* Remainder of vol. 55 appeared in 1920.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. II.

THE ALKALI-METALS AND THEIR CONGENERS.

CHAPTER I.

INTRODUCTION.

THE first group of the periodic system[1] includes *hydrogen* ($H=1\cdot008$); the alkali-metals *lithium* ($Li=6\cdot94$), *sodium* ($Na=23\cdot00$), *potassium* ($K=39\cdot10$), *rubidium* ($Rb=85\cdot45$), and *cæsium* ($Cs=132\cdot81$); and the metals *copper* ($Cu=63\cdot57$), *silver* ($Ag=107\cdot88$), and *gold* ($Au=197\cdot2$). The inclusion of hydrogen in Group I. was suggested by Mendeléeff,[2] but the arrangement has been subjected to much adverse criticism, many chemists preferring to class it with the halogens as the first member of Group VII. An account of the arguments advanced by both schools of thought is given on pp. 6 to 8. The close resemblance of the compounds formed by the interaction of ammonia[3] and acids to the metallic salts, and especially to the salts of potassium, makes it desirable to include these compounds in a description of the derivatives of the elements of Group I. They contain the univalent radical *ammonium*, NH_4 (p. 8).

The Alkali-Metals.

The name *alkali* is derived from the Arabic *Al kaljun*, meaning the ashes of sea-plants and land-plants. Prior to the French Revolution the carbonates of sodium and potassium were manufactured by lixiviation of these ashes; and, on the isolation of sodium and potassium (pp. 82 and 152), the name was employed to denote the group of which they are typical.

The inclusion of iron, cobalt, nickel, and certain other metals in Group VIII.[4] enables the alkali-metals lithium, sodium, potassium, rubidium, and cæsium to be placed in their natural position as a sub-group of Group I. of the periodic system, in juxtaposition to the related sub-group containing copper, silver, and gold (p. 3). This arrangement

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[1] See Frontispiece.

[2] Mendeléeff, *Annalen*, 1872, Suppl. 8, 133.

[3] This series, Vol. VI.

[4] This series, Vol. IX.

of the alkali-metals, based on the values of their atomic weights, is fully justified by the physical and chemical properties of the elements. The subjoined tabular summary indicates the gradual change in physical properties which accompanies increase in atomic weight.

	Li.	Na.	K.	Rb.	Cs.
Atomic weight .	6·94	23·00	39·10	85·45	132·81
Density at 0° C.	0·534	0·972[1]	0·859[1]	1·525[1]	1·903[1]
Atomic volume .	13	23·7	45·35	55·8	71·0
Melting-point, °C.	186[1]	97·5[2]	62·5[2]	38·5[3]	28·25[4]
Boiling-point, °C.	Red heat	742	667	696	670
Critical temperature, °C.	. .	2025[5]	1965[5]	1857[5]	1627[5]
Colour . .	White	White	White	White with yellow tinge	Pale yellow
Ionic conductivity at 18° C.	33·4	43·4	64·5	67·5	68·0

The *atomic volume* is the quotient obtained by dividing the atomic weight of an element by its density :

$$\text{Atomic volume} = \frac{\text{Atomic weight}}{\text{Density}} = \frac{A}{d}.$$

The atomic volumes express the relative volumes of the atoms in the solid or liquid state. Both the densities[6] and atomic volumes increase with the atomic weights, and since the relative increase of the atomic weights is much greater than that of the densities, the increase of the atomic volumes is also relatively greater. The fusibility and volatility of the metals increase with the atomic weights, corresponding with a fall in the melting-points. There is also a fall in the boiling-points from lithium to potassium, and from rubidium to cæsium. In contrast with these properties is the fall in volatility of the oxides of lithium, sodium, and potassium with increase in the value of the atomic weight of the metal.[7] The alkali-metals are characterized by their white (or yellowish) colour, silvery lustre, and wax-like softness at the ordinary temperature.

In their chemical reactions the alkali-metals exhibit univalency. With hydrogen they form hydrides of the type M·H, the symbol M indicating the alkali-metal. They combine very readily with oxygen, yielding oxides M_2O. They decompose water with great energy, each gram-atom of the metal liberating one gram-atom of hydrogen, with

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[1] Kahlbaum, *Zeitsch. anorg. Chem.*, 1900, 23, 220.
[2] Kurnakoff and Pushin, *ibid.*, 1902, 30, 109.
[3] Erdmann and Köthner, *Annalen*, 1897, 294, 55.
[4] Rengade, *Bull. Soc. chim.*, 1909, [4], 5, 994.
[5] Hackspill, *Ann. Chim. Phys.*, 1913, [8], 28, 613.
[6] The density of potassium is out of accord with this rule.
[7] Mott, *Trans. Amer. Electrochem. Soc.*, 1918, 34, 255.

production of strongly basic hydroxides of the formula M·OH, distinguished by their great solubility in water, their very caustic nature, and their complete stability at high temperatures. According to Hackspill,[1] no action on ice can be detected for sodium at —98° C., for potassium at —105° C., for rubidium at —108° C., and for cæsium at —116° C. These results indicate that rise in the atomic weight of the metals is accompanied by a development in the electropositive character. They neutralize all acids, forming salts of the type M·X in which the metal is univalent. The chemical activity of the members of the series increases with their atomic weights in the order lithium, sodium, potassium, rubidium, and cæsium.

Despite the close resemblance between the members of the alkali-group, important differences in character must be noted. The properties of certain salts of lithium and sodium present a marked contrast to those of the corresponding salts of potassium, rubidium, and cæsium. While the normal carbonates and phosphates of all other metals are insoluble in water, those of the alkali-metals dissolve, but the carbonate and phosphate of lithium are characterized by their comparatively slight solubility (pp. 74 and 76). In this respect lithium displays more analogy to the alkaline-earth-metals than to its companions in Group I. A similar difference in character between the first member of a group and the succeeding members is displayed in other instances.[2] Potassium, rubidium, and cæsium differ from lithium and sodium in forming comparatively insoluble chloroplatinates and primary tartrates, and deliquescent carbonates. Lithium and sodium, members of the two short periods, possess the general group-character, whereas potassium, rubidium, and cæsium, belonging to long periods, display almost complete homology.

Copper, Silver, and Gold.

The metals copper, silver, and gold occupy corresponding positions in the three long periods of the periodic system, and furnish a connecting link between the high-melting and non-volatile metals nickel, palladium, and platinum of Group VIII.[3] and the readily fused volatile metals zinc, cadmium, and mercury of Group II.[4] Their relationship to the alkali-metals, especially to sodium, is analogous to that of zinc, cadmium, and mercury to magnesium. These analogies are illustrated by the subjoined table of atomic weights:

	Na=23·00	Mg=24·32
Ni= 58·68	Cu= 63·57	Zn= 65·37
Pd=106·7	Ag=107·88	Cd=112·40
Pt=195·2	Au=197·2	Hg=200·6

The atomic volumes and coefficients of expansion display a similar relationship.

Some of the physical constants of the copper group are cited in the appended table :

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[1] Hackspill, *Ann. Chim. Phys.*, 1913, [8], 28, 613.

[2] Compare carbon (this series, Vol. V.), glucinum (this series, Vol. III.), and fluorine (this series, Vol. VIII.).

[3] This series, Vol. IX., Part I.

[4] *Ibid.*, Vol. III.

	Cu.	Ag.	Au.
Atomic weight . .	63·57	107·88	197·2
Density	8·96	10·5	19·33
Atomic volume . .	7·1	10·3	10·2
Melting-point, °C. . .	1084 [1]	960 [2]	1062·4 [3]
Boiling-point, °C. . .	2310 [4]	1955 [4]	. .
Specific heat . . .	0·0951 [5]	0·0590 [5]	0·0316
Ionic conductivity at 18° C.	45·9	54·0	. .
Colour	Red	White	Yellow

Both densities and atomic volumes increase with the atomic weights; but, owing to the rapid increase in density, silver and gold have practically identical atomic volumes. The regular fall of melting-point with increase in atomic weight, characteristic of the alkali-metals, is lacking for the copper group.

In their *ous* compounds, with the formula M·X, these metals are univalent, and thus resemble the alkali-metals. The sulphates of sodium and silver are isomorphous, and the chlorides of sodium and silver and cuprous chloride also display isomorphism.

The compounds of these elements also exhibit some analogies in solubility. The carbonate and hydroxide of copper are insoluble in water, while the carbonate and hydroxide of silver dissolve to some extent; the corresponding compounds of lithium are less soluble than those of sodium. The usual crystalline form of sodium sulphate has the formula $Na_2SO_4,10H_2O$, that of copper sulphate $CuSO_4,5H_2O$, while that of silver is anhydrous.

Although in certain respects the metals of the copper group resemble sodium and the other alkali-metals, the analogy must not be too much strained. The heavy metals zinc, cadmium, and mercury, belonging to Group II.,[6] have properties reminiscent of those of the light metal magnesium, a co-member of the same group, but in many respects their behaviour is in marked contrast with that of magnesium. A similar antithesis is observed between the heavy metals copper, silver, and gold and the light metal sodium, an example being the insolubility of the oxides, sulphides, and many of the salts of the three heavy metals. Other points of dissimilarity are the lack of resemblance of the higher oxides of these metals to those of the alkali-metals, the bivalency of copper in the cupric compounds, CuX_2, and the tervalency of gold in the auric compounds, AuX_3.

The stability of the oxides is much inferior to that of the corresponding alkali-metal oxides. The monoxides of lithium and sodium

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[1] Holborn and Wien, *Wied. Annalen*, 1892, 47, 107; 1895, 56, 360; Holborn and Day, *Ann. Physik*, 1900, [4], 2, 523; 1901, [4], 4, 99; Glaser, *Metallurgie*, 1904, 1, 103, 121.

[2] Day and Sosman, *Amer. J. Sci.*, 1910, [4], 29, 93. Berthelot gives 962° C. (*Ann. Chim. Phys.*, 1902, [7], 26, 58).

[3] Day and Sosman, *loc. cit.* Holborn and Day give 1064° C. (*Ann. Physik*, 1901, [4], 4, 99).

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

[5] Magnus, *Ann. Physik*, 1910, [4], 31, 597.

[6] This series, Vol. III.

are not decomposed by heat, but cupric oxide is converted into cuprous oxide, and the elimination of the oxygen from the oxides of silver and gold can be effected without the application of excessive heat.

The cupric compounds, CuX_2, show a marked resemblance to those of the metals of Group II. and to those of other metals characterized by their bivalency, an example being the similarity of constitution and isomorphism of cupric sulphate with the sulphates of magnesium and zinc, and with the *ous* sulphates of iron, nickel, cobalt, and manganese. All these sulphates combine with those of the alkali-metals to form double salts analogous in constitution and crystal form. Isomorphism is also a feature of the corresponding carbonates, $\overset{\text{II}}{M}CO_3$; chlorates, $\overset{\text{II}}{M}(ClO_3)_2,6H_2O$; and bromates, $\overset{\text{II}}{M}(BrO_3)_2,6H_2O$.

The auric compounds, $\overset{\text{III}}{Au}X_3$, are related to the corresponding derivatives of such tervalent metals as aluminium, $\overset{\text{III}}{Al}X_3$, and indium, $\overset{\text{III}}{In}X_3$, another instance of the close connexion subsisting between the valency of a metal and the typical characteristics of the compounds derived from it. Three series of oxides are given below, the compounds formed from each member being similar in character to the corresponding compounds of the same series:

Na_2O	Ag_2O	Cu_2O	Au_2O	Tl_2O
Sodium	Silver	Cuprous	Aurous	Thallous
MgO	ZnO	CuO	FeO	HgO
Magnesium	Zinc	Cupric	Ferrous	Mercuric
Al_2O_3	Fe_2O_3	Au_2O_3	Tl_2O_3	
Aluminium	Ferric	Auric	Thallic	

Chromium,[1] manganese,[2] and iron[3] also exemplify the alteration in the character of compounds occasioned by a change of valency. In the first series even the heavy metals have a very positive and basic character, silver oxide and thallous oxide being strong bases, and cuprous oxide and aurous oxide having a more pronounced basic character than the corresponding higher oxides. The oxides of the third series are slightly acidic, a characteristic associated with the somewhat metalloidic character of the tervalent metals from which they are derived. The hydrogen of aluminium hydroxide, $Al(OH)_3$, and of auric hydroxide, $Au(OH)_3$, resembles that of boric acid, $B(OH)_3$, in being replaceable by alkali-metals with formation of compounds of the type $Al(ONa)_3$. Indium oxide, In_2O_3, is also soluble in alkalis, but does not appear to form a definite compound.

The alkali-metals are distinguished from the heavy metals of the copper group by the formation of very stable hydroxides and carbonates. Copper hydroxide, $Cu(OH)_2$, is very easily decomposed into the oxide and water, and the hydroxides of silver and gold have not been isolated. The behaviour of the carbonates is similar; thus, silver carbonate is rapidly decomposed at 200° C., with evolution of carbon dioxide.[4]

The compounds of the alkali-metals with weak anions, such as O'' or

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[1] This series, Vol. VII.
[2] *Ibid.*, Vol. VIII.
[3] *Ibid.*, Vol. IX.
[4] Joulin, *Ann. Chim. Phys.*, 1873, [4], 30, 260.

OH', S'', CO_3'', and PO_4''', or with anions of medium strength, such as the halogens, are characterized by their ready solubility, with the exception of the carbonate and phosphate of lithium (pp. 74 and 76). The corresponding salts of the metals of the copper group are insoluble, with the exception of the cupric and auric halides (pp. 273 and 342).

On the other hand, Abegg and Bodländer have pointed out that the solubility of the salts of the strongest anions diminishes with increase in the strength of the constituent cation. The following table[1] gives the solubilities in gram-equivalents per litre of the chlorates, perchlorates, nitrates, chloroplatinates, and alums of cæsium, rubidium, and potassium, the electroaffinity of the metals diminishing in the order given.

	ClO_3' (about 20° C.).	ClO_4' (about 20° C.).	NO_3' (20° C.).	$PtCl_6''$ (15° C.).	$Al(SO_4)_2'$ (about 18° C.).
Cs	..	..	1·1	0·002	0·01
Rb	0·3	0·06	3·1	0·006	0·04
K	0·57	0·14	2·8	0·045	0·3

In aqueous solution the salts of the metals of Group I. must be classed as strong electrolytes, a statement also applicable to the hydroxides of the univalent cations, except aurous hydroxide, AuOH. This hydroxide shares with cupric hydroxide and auric hydroxide a weak basic character, solutions of their salts having an acidic reaction, due to hydrolytic dissociation.

Position of Hydrogen in the Periodic System.

As stated on p. 1, there has been much controversy as to the right position of hydrogen in the periodic system.[2] On account of its chemical properties, it was placed by Mendeléeff[3] above lithium in Group I., but others have advocated associating it with the halogens as the first member of Group VII.[4] Since hydrogen is the only known element besides helium capable of occupying a position in the first horizontal row of the periodic system, its atomic weight affords no indication of the group to which it should be assigned.

The most important argument in favour of placing hydrogen in the first group rests on its electrochemical character. It is a constituent of all acids, and these substances may be regarded as salts of hydrogen. Abegg[5] has pointed out that the gradation of the polarity is in opposite directions for the two sub-groups, cæsium, the heaviest member of the alkali group, and copper, the lightest member of the copper group, being the most positive of their respective groups. This gradation of polarity supports the inclusion of hydrogen in Group I., and affords a

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[1] Abegg and Auerbach, *Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i., 3.

[2] Compare Friend, *Theory of Valency* (Longmans, 1909), chap. iv.

[3] Mendeléeff, *Ber.*, 1870, 3, 990; *J. Russ. Phys. Chem. Soc.*, 1871, 3, [7], 25; *J. Chem. Soc.*, 1871, 24, 483.

[4] This series, Vol. VIII.

[5] Abegg and Auerbach, *Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i., 1.

strong reason for not placing it in Group VII., since it indicates that the first member of the halogen group must be more electronegative than fluorine, the most electronegative of all the elements. So convinced was Mendeléeff as to the antithesis between hydrogen and the halogens, that in his last speculations [1] as to the possibility of the existence of still undiscovered elements he discusses a hypothetical member of the seventh group with an atomic weight of about 3.

In 1872 Newlands [2] associated hydrogen with chlorine, because chlorine can replace hydrogen in organic compounds without material alteration in the character of the substances, and because he considered that its atomic weight shows it to be the lowest member of the halogen group.

Masson [3] has given a number of reasons for including hydrogen in Group VII. A summary of his views is appended:

1. Hydrogen is univalent.[4]
2. The molecule of hydrogen, like that of a halogen, is diatomic, but the molecule of an alkali-metal is monatomic.
3. The gaseous character and very low boiling-point of hydrogen. The alkali-metals are solid at ordinary temperatures, and increasing atomic weight is accompanied by a fall in boiling-point.
4. The average difference between the atomic weights of the adjacent members of a horizontal series is 3, so that by placing hydrogen at the head of Group VII. it is brought next to helium with the atomic weight 4, the first member of the zero group.[5] Since the mean difference between the atomic weights of successive members of the same group is 16, this arrangement brings hydrogen into line with fluorine, the difference of their atomic weights being 18, and that of hydrogen and lithium 6.
5. Both the liquid and solid forms of hydrogen lack metallic properties; [6] thus, the liquid is a non-conductor of electricity.
6. The mutual replaceability of hydrogen and chlorine in organic compounds, first noticed by Dumas. It should be observed that in substitution in inorganic compounds hydrogen displays a much closer analogy to the alkali-metals than to the halogens, as is illustrated by the acids and the corresponding salts (p. 6).

Moissan [7] found that the hydrides of lithium, sodium, potassium, rubidium, and cæsium are non-conductors of electricity, and therefore cannot be regarded as alloys. He considered that in these compounds hydrogen has a metalloidic character, and that it is not comparable with the metals, an argument against its inclusion in Group I.[8]

Both the electrochemical character of the element (p. 6) and its behaviour as an inorganic substituent (*ut supra*) seem to indicate the desirability of including it in Group I., the arrangement adopted in

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[1] Mendeléeff, *Prometheus*, 1903, 15, 145–151; *Chem. Centr.*, 1904, i., 138.

[2] Newlands, *Chem. News*, 1896, 72, 305.

[3] Masson, *ibid.*, 283.

[4] The univalency of hydrogen cannot be regarded as an argument for preferring Group VII. to Group I. A more cogent reason is the non-variant character of its valency, in which it is akin to the alkali-metals.

[5] This series, Vol. I.

[6] It should be noted that hydrogen resembles the metals in crystallizing in the cubic system (p. 20). It also has the power of displacing certain metals from solutions of their salts (p. 26).

[7] Moissan, *Compt. rend.*, 1903, 136, 591.

[8] Compare Brauner, *Chem. News*, 1901, 84, 233; and lithium hydride (p. 59).

this series of text-books. In the table of the elements suggested by Werner,[1] hydrogen is also classed as the first member of the alkali-metal group.[2]

A new form of the periodic table containing the elements arranged in seventeen vertical groups has been devised by A. C. and A. E. Jessup.[3] They base their views on astrospectroscopic observations, and consider that matter in the nebulous stage consists of only four elements. Two of them are unknown, and the other two are hydrogen and helium. These original elements are called *protons*, and are regarded as derived from primary corpuscles by aggregation into stable integral systems, such corpuscles at one time representing the only form of matter. Other atoms are supposed to be evolved by condensation of the corpuscles round the proton groups, the various elements representing groupings of maximum stability in a gradual and continuous process. The first proton, hydrogen, gives rise to the alkali-metals; the second, "proto-glucinum," to the alkaline-earth-metals; and the fourth, helium, to the zero group. By "direct" evolution the third proton, "protoboron," yields the elements of Group III., and by "indirect" evolution along the horizontal series it produces carbon, which gives rise directly to silicon, and indirectly to nitrogen, oxygen, and fluorine. By similar indirect processes silicon produces all the elements between titanium and arsenic; and they, with the exception of manganese, yield by direct evolution products of the same valency.[4]

A "cubic" periodic system has been described by van den Broek.[5]

The unique character of hydrogen, and its relation to the other univalent elements as interpreted by the aid of Lewis's electronic theory of valency, have been the subject of an interesting communication by Lowry.[6]

The Ammonium Compounds.

As mentioned on p. 1, ammonia combines with acids to form salts analogous to the metallic salts, most of them being isomorphous with the corresponding salts of potassium, and very similar to them. In these salts the univalent radical *ammonium*, NH_4, functions as a metal. It has never been isolated, but its metallic character is displayed in the formation of an ammonium-amalgam (p. 211) resembling the amalgams of sodium and potassium.

The presence of the ions $NH_4^{\cdot}$ and OH' in the aqueous solution of ammonia is proved by its alkaline reaction and electrical conductivity. The presence of these ions necessitates the existence in the solution of some undissociated ammonium hydroxide, $NH_4{\cdot}OH$, to establish the equilibrium

$$NH_4{\cdot}OH \rightleftharpoons NH_4^{\cdot}+OH'.$$

The monohydrate, NH_3,H_2O, has been isolated (p. 220); on heating in solution it decomposes into ammonia and water. The electric conductivity of its solution is much less than that of the corresponding

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[1] Werner, *Ber.*, 1905, 38, 914.

[2] Compare Loring, *Chem. News*, 1920, 121, 315; Oddo, *Gazzetta*, 1920, 50, ii., 213.

[3] Jessup, *Phil. Mag.*, 1907, [6], 15, 21.

[4] Compare p. 31.

[5] van den Broek, *Physikal. Zeitsch.*, 1911, 12, 490.

[6] Lowry, *Chemistry and Industry*, 1923, 42, 43.

solution of sodium or potassium hydroxide, 5 per cent. of ionized ammonium hydroxide molecules being present in a tenth-normal solution, as against 91 per cent. of ionized potassium hydroxide molecules in a solution of similar concentration. The quaternary ammonium bases or tetra-alkylammonium hydroxides are organic derivatives of ammonium hydroxide formed by replacement of the four hydrogen atoms of the ammonium radical by alkyl-groups. An example of these compounds is tetramethylammonium hydroxide, $N(CH_3)_4{\cdot}OH$. Their degree of ionization in aqueous solution is proved by the electric conductivity, which is comparable with that of the hydroxides of sodium and potassium. They are thick liquids of strongly alkaline reaction, and in chemical character closely resemble these bases. It is reasonable to assume that if ammonium hydroxide could attain the same concentration in solution as a quaternary ammonium base, it would exhibit similar electric conductivity. The dissimilarity of ammonium hydroxide in this respect is due to its decomposition, mainly into ammonia and water.

The comparatively feeble basic reaction of an aqueous solution of ammonia is traceable to this tendency to decomposition, and not to lack of ionization of the ammonium hydroxide.[1] In the neutral reaction of its salts with strong acids, such as the chloride and nitrate, and in the alkaline reaction of those with weak acids, exemplified by the carbonate and cyanide, the radical ammonium displays complete analogy with the metals potassium and sodium. This fact constitutes a strong argument in favour of the view that ammonium hydroxide, so far as it is present in an aqueous solution of ammonia, is to a great extent ionized.

The formation of an ammonium-amalgam, the general character of the ammonium salts, the existence of the monohydrate, the electrochemical properties of aqueous solutions of ammonia, and the similarity of the quaternary ammonium bases to the hydroxides of sodium and potassium, justify the consideration of the ammonium compounds in conjunction with those of the alkali-metals.

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[1] Compare Schlubach and Ballauf, *Ber.*, 1921, 54, [B], 2825.

CHAPTER II.

HYDROGEN.

Symbol, H. Atomic weight, 1·008 (O = 16).

Occurrence.—Hydrogen is very widely distributed, being found terrestrially to a small extent in the free state, as well as in enormous quantities in combination with oxygen as water. Spectroscopic analysis has revealed it as a constituent of most celestial bodies.

The proportion of free hydrogen in the earth's atmosphere is very minute, a fact accounted for by the great affinity of the element for oxygen. There is much discrepancy between the analytical results of different investigators. Gautier [1] found 0·02 per cent. by volume, but Rayleigh's value [2] is only 0·003 per cent. Dewar [3] detected only 0·001 per cent. Claude [4] found less than 0·0001 per cent., and Ramsay [5] gives an equally low value.

The decomposition of organic matter by specific organisms, and the exhalations of volcanoes, are the two main sources of atmospheric hydrogen. In the absence of air, certain anaërobic bacteria induce fermentation of cellulose and proteins, with production of free hydrogen, most of the hydrogen of the atmosphere having this origin. According to Bunsen,[6] the volcanic gases of Iceland contain 25 per cent. of hydrogen, and Moissan [7] found 22·3 per cent. in the gases evolved from Mont Pelée in Martinique during the eruption of 1902. Its presence in these gases is probably the result of the interaction of metals with water-vapour at a high temperature.

Hydrogen was also found by Gautier [8] in many large rocks, and by Reichardt [9] in the occluded gases of the coloured salt-deposits at Stassfurt. Pollacci [10] has observed it in the gases given out by green plants.

Hinrichs [11] has calculated that at a height of 100 kilomètres the earth's atmosphere contains 95 per cent. of hydrogen, the high proportion being due to the low density of the gas, and to the fact that the lower the

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[1] Armand Gautier, *Ann. Chim. Phys.*, 1901, [7], 22, 5; *Compt. rend.*, 1902, 131, 86, 535, 647, 1276.

[2] Rayleigh, *Phil. Mag.*, 1901, [6], 1, 100; 1902, [6], 3, 416.

[3] Dewar, *Proc. Roy. Soc.*, 1901, [A], 68, 360.

[4] Claude, *Compt. rend.*, 1909, 148, 1454.

[5] Ramsay, *Proc. Roy. Soc.*, 1905, [A], 76, 111.

[6] Bunsen, *Pogg. Annalen*, 1851, 83, 197.

[7] Moissan, *Compt. rend.*, 1902, 135, 1085.

[8] Armand Gautier, *loc. cit.*

[9] Reichardt, *Pogg. Annalen*, 1858, 103, 347.

[10] Pollacci, *Atti R. Inst. Botan. Univ. Pavia*, 1901, June.

[11] Hinrichs, *Compt. rend.*, 1900, 131, 442.

density of an atmospheric gas the less rapidly does the amount of it present diminish with increase in the height of the atmosphere.

History.—Hydrogen was known to the alchemists as a product of the interaction of acids and metals, and was called "inflammable air."

The suggestion first made by John Joachim Becher (1635–1682), that combustion is essential to chemical change, was further developed by Georg Ernst Stahl[1] (1660–1734). Stahl's theory involved a number of assumptions, which admit of the following summary :

1. All combustible substances are compounds.
2. Burning eliminates from these substances a constituent common to them all, "phlogiston" (φλογιστός, burnt).
3. The degree of combustibility increases with the proportion of phlogiston present.
4. Substances like phosphorus, carbon, sulphur, and many organic bodies contain a large proportion of phlogiston.
5. Metals also contain phlogiston in varying proportions. They are to be regarded as compounds of this substance with the calx left after their combustion.
6. The reconversion of metallic calxes into the metal by heating with carbon, gases, and other substances—in modern parlance the reduction of the oxide—is the result of a combination of the phlogiston of the reagent with the calx.

The phlogiston theory remained unrefuted for about fifty years. In 1772 Rutherford discovered nitrogen, and in 1774 Priestley isolated oxygen ("dephlogisticated air"). Between the years 1772 and 1788 Lavoisier made numerous investigations into the nature of combustion, his results leading him to the conclusion that there is no essential difference between respiration, combustion, and calcination.

In 1781 Cavendish and Watt proved water to be produced by the combustion of hydrogen. A repetition of their experiments in 1783 by Lavoisier and Laplace indicated that water contains 1 volume of oxygen and 1·91 volume of hydrogen. The interaction of red-hot iron and steam, with liberation of free hydrogen and production of a calx of iron, was also observed by Lavoisier.

The discovery of the compound nature of water by Cavendish and Watt, and the results obtained by Lavoisier and his coadjutors in their investigations of the quantitative composition of this substance, rendered the phlogiston theory untenable. It had played a useful part as the first step to placing the science of chemistry on a rational basis, and it is interesting to note that both Priestley and Cavendish remained phlogistians to the end.

Preparation.—The choice of a method for the preparation of hydrogen in the laboratory is decided by the degree of purity required in the gas, but by suitable means the product obtained by the interaction of a metal and an acid can be sufficiently purified for ordinary use.

1. One of the best methods for the preparation of pure hydrogen is the electrolysis of water containing sulphuric acid or potassium hydroxide to augment the conductivity. The acid or alkali plays an important part in the process, as indicated in the schemes

$$(a)\ H_2SO_4=2H^{\cdot}+SO_4'' ;\ H_2O+SO_4''=H_2SO_4+O.$$
$$(b)\ KOH=K^{\cdot}+OH' ;\ K^{\cdot}+H_2O=KOH+H ;\ 2OH'=H_2O+O.$$

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[1] Stahl, *Fundamenta Chymiae*, Norimbergae, 1723.

When sulphuric acid is employed, the SO_4'' ions liberated at the anode interact with the water to regenerate the sulphuric acid and liberate oxygen, while hydrogen is evolved at the cathode; with potassium hydroxide, the potassium ions at the cathode act on the water with formation of potassium hydroxide and evolution of hydrogen, the hydroxyl ions uniting at the anode with production of water and oxygen. The regeneration of the acid and alkali respectively enables the electrolysis to proceed without further addition of either. Platinum electrodes should be employed in the electrolytic cell. Morley[1] has shown that hydrogen evolved from alkali solutions is always contaminated by organic substances. The exclusion of air is attained by making all the joints of the apparatus air-tight, avoiding the use of long pieces of rubber tubing, and allowing the electrolysis to proceed for some time before collecting the gas. When diffusion of oxygen from the anode to the cathode is prevented, the evolved hydrogen contains only from 0·001 to 0·0005 per cent. of nitrogen. von der Pfordten[2] recommends the removal of oxygen by passing the gas through a solution of chromous chloride in hydrochloric acid, another method being to lead it through a heated tube containing palladized asbestos.

2. Several experimenters[3] advocate preparing pure hydrogen by the interaction of aluminium-amalgam or magnesium-amalgam and water, and consider the method very convenient:

$$2Al+3H_2O=3H_2+Al_2O_3;$$
$$Mg+H_2O=H_2+MgO.$$

3. Mauricheau-Beaupré[4] has shown that treatment of aluminium filings with a small proportion of mercuric chloride and potassium cyanide yields a powder stable in dry air. He called this substance "hydrogenite," and found that one kilogram of it treated with water yields 1300 litres of pure hydrogen, measured at 15° C. and 760 mm.

4. The ordinary laboratory method for the preparation of hydrogen consists in the decomposition of dilute sulphuric acid or hydrochloric acid by zinc:

$$Zn+H_2SO_4=H_2+ZnSO_4;$$
$$Zn+2HCl=H_2+ZnCl_2.$$

Since the crude materials employed often contain arsenic, phosphorus, sulphur, and carbon, such impurities as arsine, phosphine, hydrogen sulphide, and hydrocarbons are frequently present in the hydrogen evolved. Morley[5] found that zinc occludes carbon dioxide, which contaminates the hydrogen. If the sulphuric acid employed is too concentrated, the hydrogen contains hydrogen sulphide and sulphur dioxide, formed by partial reduction of the acid by the nascent gas:

$$H_2SO_4+8H=H_2S+4H_2O;$$
$$H_2SO_4+2H=SO_2+2H_2O.$$

To remove these impurities, the hydrogen can be washed with caustic

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[1] Morley, *Amer. J. Sci.*, 1891, [3], 41, 220.
[2] von der Pfordten, *Annalen*, 1885, 228, 112.
[3] Baille and Féry, *Ann. Chim. Phys.*, 1889, [6], 17, 248; Wislicenus and Kaufmann, *Ber.*, 1895, 28, 1323; Fleck and Basset, *J. Amer. Chem. Soc.*, 1895, 17, 789.
[4] Mauricheau-Beaupré, *Compt. rend.*, 1908, 147, 310.
[5] Morley, *Amer. Chem. J.*, 1890, 12, 460.

alkali and with an oxidizing-solution such as acidified potassium permanganate. To remove arsenic, Reckleben and Lockemann[1] recommend passing the gas through a saturated solution of potassium permanganate or a 5–10 per cent. solution of silver nitrate, or over cupric oxide; for use on the manufacturing scale they advise employing a solution of bleaching-powder.

It is noteworthy that pure zinc decomposes dilute acids very slowly, but that addition of a few drops of a solution of cupric sulphate or platinum chloride greatly augments the velocity of the reaction. A similar effect is produced by amalgamating the metal. In both instances the acceleration is due to electrolytic action, the copper and platinum being deposited on the zinc (compare method 2, p. 12).

For any metal the power of decomposing water and acids is determined by two factors: the potential of the metal must be more negative, and its solution-pressure must be higher, than the corresponding constants of the hydrogen evolved from the water or dilute acid.

Victor Meyer and von Recklinghausen[2] have pointed out that contact with hydrogen materially increases the tendency of potassium permanganate to evolve oxygen, so that in washing with this reagent there is risk of introducing oxygen as an impurity. They explain the slow absorption of hydrogen by potassium permanganate by assuming oxidation to hydrogen peroxide, which is then decomposed by the permanganate with evolution of oxygen.

An improved type of generator for producing hydrogen from zinc and an acid has been described by Edwards.[3] It is said to be superior to the ordinary Kipp apparatus in rapidity of furnishing a supply of hydrogen free from air.

5. Solution of zinc, aluminium, and tin in concentrated caustic alkalis evolves hydrogen, with formation of the zincate, aluminate, and stannate of the alkali-metal:

$$Zn+2KOH=H_2+ZnO,K_2O;$$
$$2Al+6KOH=3H_2+Al_2O_3,3K_2O;$$
$$Sn+4KOH=2H_2+SnO_2,2K_2O.$$

6. Hydrogen is evolved from aqueous solutions of strong reducing-agents, such as chromous salts,[4] potassium cobaltocyanide,[5] chloromolybdenum chloride[6] (Mo_3Cl_6), and from all reducing-agents with a reduction-potential higher than that of hydrogen. The velocity of the gaseous evolution is considerably accelerated by addition of finely divided platinum or palladium, especially from chromous chloride.[7]

7. Bruno[8] has prepared hydrogen by agitating iron filings with water saturated with carbon dioxide, the operation lasting 20–40 hours:

$$Fe+H_2O+CO_2=H_2+FeCO_3.$$

Manufacture of Hydrogen.—Several methods are employed in the preparation of hydrogen on the large scale.

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[1] Reckleben and Lockemann, *Zeitsch. angew. Chem.*, 1908, 21, 433.
[2] Victor Meyer and von Recklinghausen, *Ber.*, 1896, 29, 2549, 2828.
[3] Edwards, *J. Ind. Eng. Chem.*, 1919, 11, 961.
[4] Berthelot, *Compt. rend.*, 1898, 127, 24.
[5] Peters, *Pharm. Centralhalle*, 1898, 39, 695; Manchot and Herzog, *Ber.*, 1900, 33, 1742.
[6] Muthmann and Nagel, *Ber.*, 1898, 31, 2012.
[7] Peters, *Zeitsch. physikal. Chem.*, 1898, 26, 193.
[8] Bruno, *Bull. Soc. chim.*, 1907, [4], 1, 661.

1. When steam is passed over carbon, in the form of coke[1] or coal, the so-called "water-gas" is formed. Two strongly endothermic reactions are involved:

$$[C]+2(H_2O)=2(H_2)+(CO_2)-21{\cdot}700 \text{ Cal.};$$
$$[C]+(H_2O)=(H_2)+(CO)-31{\cdot}700 \text{ Cal.}$$

As indicated by the equations, heat is absorbed and increase in volume accompanies both reactions, so that they are promoted by rise in temperature and reduction of pressure. Lang[2] found that the higher the temperature the greater is the proportion of carbon monoxide: at 600° C. the product consists almost wholly of hydrogen and carbon dioxide, but at 1000° C. the composition of the equilibrium mixture expressed in atmospheres is

$$CO_2=0{\cdot}012,\ CO=0{\cdot}296,\ H_2=0{\cdot}303,\ H_2O=0{\cdot}031.$$

Bay[3] gives a summary of methods described in certain French patents for removing the oxides of carbon from water-gas. In one process these gases are eliminated by treatment with calcium carbide:

$$2CaC_2+2CO+CO_2=CaO+CaCO_3+6C.$$

In another method the poisonous carbon monoxide is oxidized by ferric oxide to innocuous carbon dioxide, the product containing 85 per cent. of hydrogen, and having a lower density and higher calorific value than ordinary water-gas:

$$Fe_2O_3+4CO+H_2O=H_2+4CO_2+2Fe.$$

Carbon monoxide can also be removed by passing the water-gas three times over powdered calcium oxide or hydroxide, or a mixture of these substances, at 400° C. The carbon monoxide is replaced by hydrogen, methane, and ethylene, the reaction proceeding in three stages:[4]

(i.) $CO+Ca(OH)_2=CaCO_3+H_2$;
(ii.) $4CO+2Ca(OH)_2+CaO=3CaCO_3+CH_4$;
(iii.) $8CO+4Ca(OH)_2+2CaO=6CaCO_3+C_2H_4+2H_2$.

By Claude's[5] method hydrogen containing not more than 1·5 per cent. of carbon monoxide, and suitable for the production of synthetic ammonia,[6] can be prepared from water-gas. Part of the carbon monoxide is removed by preliminary cooling, and the residual gas is allowed to expand whilst doing external work.

2. Calcium hydride,[7] CaH_2, known as "hydrolite," is decomposed by water, with evolution of hydrogen:

$$CaH_2+2H_2O=2H_2+Ca(OH)_2.$$

Jaubert[8] considers this method well adapted for preparing hydrogen to fill balloons in the field. It was employed with very satisfactory

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[1] Compare Näher and Müller, *German Patent*, 1911, No. 237283.
[2] Lang, *Zeitsch. physikal. Chem.*, 1888, 2, 181.
[3] Bay, *Mon. Scient.*, 1908, [4], 22, ii., 727.
[4] Vignon, *Bull. Soc. chim.*, 1911, [4], 9, 18.
[5] Claude, *Compt. rend.*, 1921, 173, 653.
[6] This series, Vol. VI.
[7] *Ibid.*, Vol. III.
[8] Jaubert, *Rev. gén. Chim.*, 1907, 10, 266.

results by Dr George C. Simpson in Captain Scott's last Antarctic expedition (1910–1912). In a modified form [1] of this process, the hydride is mixed with sodium hydrogen carbonate, boric acid, or soda-lime, and heated at 80° C. Namias [2] has pointed out that the use for balloons of hydrogen evolved from sulphuric acid and cast iron involves damage to the envelopes, the arsine and phosphine present becoming oxidized to arsenic acid and phosphoric acid respectively, and these acids exert a corrosive action on the material of the gas-bag. Jorissen [3] has given a useful summary of the methods employed in the preparation of gas for balloons.

3. Jaubert [4] described a process involving the use of "hydrogenite," a mixture of silicon, calcium hydroxide, and sodium hydroxide. At red heat it reacts in accordance with the equation

$$Si+Ca(OH)_2+2NaOH=SiO_4Na_2Ca+2H_2.$$

This method is also employed for balloon-gas.

4. At red heat calcium carbide reacts with water-vapour, liberating hydrogen and carbon dioxide: [5]

$$CaC_2+5H_2O=CaO+2CO_2+5H_2.$$

The carbon dioxide is absorbed by lime. The yield is excellent; the hydrogen produced is very pure, and is well adapted for heating and lighting, and for filling balloons.

5. Lavoisier's work on the composition of water showed that steam reacts with iron at 150° C., liberating hydrogen and forming ferroso-ferric oxide, Fe_3O_4:

$$3Fe+4H_2O \rightleftharpoons 4H_2+Fe_3O_4.$$

Deville [6] investigated the reaction, and proved it to be reversible. The proportion of hydrogen in the equilibrium mixture is greatest at 800° C.,[7] a higher temperature shifting the equilibrium to the left, and causing reduction of the iron oxide. Deville believed the composition of the solid phase to correspond with the formula Fe_4O_5, but later work by Preuner [8] leaves it still undecided between Fe,FeO; FeO,Fe_3O_4; and Fe,Fe_3O_4.

The interaction of steam and iron takes place in three stages: [9]

(1) Dissociation of steam:

$$H_2O \rightleftharpoons 2H+O.$$

(2) Combination of the nascent oxygen with the iron to form ferrous oxide:

$$Fe+O \rightleftharpoons FeO.$$

After one hour at 350° C. this reaction becomes perceptible.

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[1] Bamberger, Böck, and Wanz, *German Patent*, 1910, No. 218257.

[2] Namias, *L'Industria Chimica*, 1907, 7, 257.

[3] Jorissen, *Chem. Weekblad*, 1911, 8, 625.

[4] Jaubert, *Rev. gén. Chim.*, 1910, 13, 341, 357.

[5] Siemens and Halske, *German Patent*, 1910, No. 220486.

[6] Deville, *Compt. rend.*, 1870, 70, 1105, 1201; 71, 30; *Annalen*, 1871, 157, 71.

[7] Lettermann, *J. Gasbeleuchtung*, 1896, 39, 187, 204.

[8] Preuner, *Zeitsch. physikal. Chem.*, 1904, 47, 385.

[9] Friend, *J. West of Scotland Iron and Steel Inst.*, 1910, 17, 66; *J. Iron and Steel Inst.*, 1909, ii., 172; Friend, Hull, and Brown, *Trans. Chem. Soc.*, 1911, 99, 969; Chaudron, *Compt. rend.*, 1914, 154, 237; Friend, *The Corrosion of Iron and Steel* (Longmans, 1911), chap. iii. Further details are given in this series, Vol. IX., Part II.

(3) The further oxidation to ferroso-ferric oxide :

$$3FeO+O=Fe_3O_4.$$

6. A mixture of aluminium with small proportions of mercuric oxide and sodium hydroxide reacts with water instantaneously, and yields 1500 times its volume of hydrogen.[1]

Physical Properties.—At ordinary temperatures hydrogen is a gas, without colour, odour, or taste, and very slightly soluble in water. For temperatures between 0° C. and 25° C., Timoféeff[2] found that the volume of hydrogen dissolved in one volume of water at 760 mm., or the absorption-coefficient (α) is given by the equation

$$\alpha=0{\cdot}021528-0{\cdot}00010216t+0{\cdot}000001728t^2,$$

where t stands for the temperature. For alcohol he gives the value of α at 0° C. as 0·0676, at 6° C. as 0·0693, at 13·4° C. as 0·0705, and at 18·8° C. as 0·0740, indicating that rise of temperature is attended by increase of solubility. The same phenomenon was noted by Just[3] with a number of other organic solvents. Its solubility in liquid air is considerable, Dewar[4] having observed that this solvent dissolves one-fifth of its volume of gaseous hydrogen at temperatures between −200° C. and −210° C.

Morley[5] gives the weight of one litre of hydrogen at normal temperature and pressure as 0·089873±0·0000027 gram, the density compared with air being therefore 0·0694. Guye[6] gives for this constant the value 0·08987, the error not exceeding one ten-thousandth of this number. Victor Meyer's[7] investigations of the density of hydrogen at higher temperatures furnished no evidence of dissociation.

Regnault's value for the coefficient of expansion of hydrogen[8] at 760 mm. between 0° C. and 100° C. is 0·0036613. His experiments demonstrated that on subjection to pressures between 1 and 27 atmospheres[9] the compressibility of the gas is less than that indicated by Boyle's law. The remarkable nature of this phenomenon was accentuated by his further observation that nitrogen, air, and carbon dioxide are more compressible than they would be if they obeyed this law.

Two series of experiments carried out by Amagat[10] confirmed Regnault's results for hydrogen, and proved methane to resemble nitrogen in being more compressible than theory demands. In one set of observations he employed pressures up to 400 atmospheres, measured directly by means of a manometer ; in the other the gas was submitted to pressures up to 3000 atmospheres. Amagat's work was confirmed by the researches of Wroblewsky.[11]

[1] Chemische Fabrik Griesheim-Elektron, *German Patent*, 1910, No. 229162.

[2] Timoféeff, *Zeitsch. physikal. Chem.*, 1890, 6, 14 ; Winkler, *Ber.*, 1891, 24, 89.

[3] Just, *Zeitsch. physikal. Chem.*, 1901, 37, 359.

[4] Dewar, *Proc. Chem. Soc.*, 1897, 13, 186.

[5] Morley, *Zeitsch. physikal. Chem.*, 1896, 20, 242 ; compare p. 47.

[6] Guye, *Compt. rend.*, 1907, 144, 976.

[7] Victor Meyer, *Ber.*, 1880, 13, 2019 ; Nernst, *Zeitsch. Elektrochem.*, 1903, 9, 626

[8] Regnault, *Pogg. Annalen*, 1842, 57, 118.

[9] Regnault, *Relation des Expériences*, Paris, 1847 ; *Mém. de l'Acad.*, 1847, 21, 329.

[10] Amagat, *Compt. rend.*, 1872, 75, 479 ; 1880, 90, 995 ; 1882, 95, 281 ; *Ann. Chim. Phys.*, 1880, [5], 19, 345 ; 1881, [5], 22, 353 ; 1883, [5], 28, 456, 464 ; 1893, [5], 29, 68.

[11] Wroblewsky, *Monatsh.*, 1888, 9, 1067.

The behaviour of hydrogen at very low pressures has been investigated by Rayleigh.[1] At about 1·5 mm. it obeys Boyle's law, and continues to do so within very narrow limits up to 150 mm.

Holborn[2] has studied the isothermals of hydrogen at 0° C., 50° C., and 100° C., the pressure limits being 20 and 100 atmospheres. As unit of pressure he selected that of a column of mercury having a height of one mètre at 0° C. under the normal gravity, $g=980{\cdot}665$ cm.-sec.^{2}; and the unit of volume was the volume of the gas under this pressure. Within the limits of experimental error, amounting to a few parts in ten thousand, the isotherms for 50° C. and 100° C. were linear; whilst the deviation of that for 0° C. did not exceed one part per thousand. The results obtained can be expressed in the following formulæ:

$$\begin{aligned} 0^\circ\text{ C.}: &\ pv=0{\cdot}99918+0{\cdot}00082094p+0{\cdot}0000003745p^2; \\ 50^\circ\text{ C.}: &\ pv=1{\cdot}18212+0{\cdot}00089000p; \\ 100^\circ\text{ C.}: &\ pv=1{\cdot}36506+0{\cdot}00091400p. \end{aligned}$$

Expressed as functions of $\frac{1}{v}$, the formulæ are:

$$\begin{aligned} 0^\circ\text{ C.}: &\ pv=0{\cdot}99918+(0{\cdot}00081613)/v+(0{\cdot}000001220)/v^2; \\ 50^\circ\text{ C.}: &\ pv=1{\cdot}18112+(0{\cdot}0010505)/v+(0{\cdot}000001015)/v^2; \\ 100^\circ\text{ C.}: &\ pv=1{\cdot}36506+(0{\cdot}0012450)/v+(0{\cdot}000001240)/v^2. \end{aligned}$$

The effect of pressure on hydrogen is represented graphically in fig. 1 (p. 18), the product pv being plotted[3] against the pressure p. Neon and helium resemble hydrogen in being less compressible than Boyle's law demands.[4]

Travers[5] observed that at ordinary temperature the expansion of hydrogen without doing work is attended by rise of temperature, indicating that under these conditions it behaves as an "ultra-perfect" gas; at −80° C. and 200 atmospheres its effusion without doing work is unaccompanied by calorific effect, a property characteristic of a perfect gas. Dewar[6] found that at −200° C. hydrogen begins to assume the character of an imperfect gas, expansion without external work being attended by a fall in temperature. Landolt[7] gives the diffusion-coefficient of hydrogen with respect to oxygen as 0·677 sq. cm.-sec. at 0° C. and 760 mm.

Hydrogen is absorbed by wood-charcoal, and Kasper[8] has shown that 1 c.c. of this substance at 0° C. and 430 mm. absorbs 1·5 c.c.; at the same temperature and 1800 mm. it absorbs 11·7 c.c.

Lehfeldt[9] gives for the electrochemical equivalent of hydrogen 96,590 coulombs, or 0·17394±0·00001 c.c. of gas per coulomb. The

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[1] Rayleigh, *Phil. Trans.*, 1901, 196, 205; 1902, 198, 417; 1905, 204, 351; *Proc. Roy. Soc.*, 1905, [A], 74, 446.

[2] Holborn, *Ann. Physik*, 1920, [4], 63, 674.

[3] Fig. 1 is taken from this series, Vol. I., 29. In that volume comparative details of the behaviour of other gases under pressure are given.

[4] Compare this series, Vol. I., Part II.

[5] Travers, *Phil. Mag.*, 1901, [6], 1, 411.

[6] Dewar, *Chem. News*, 1896, 73, 40.

[7] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 375.

[8] Kasper, *Wied. Annalen*, 1881, 12, 526.

[9] Lehfeldt, *Phil. Mag.*, 1908, [6], 15, 614.

thermal conductivity of hydrogen is stated by Stefan[1] to be seven times that of air.

At 16° C. the specific heat of hydrogen at constant volume is 4·875.[2] The mean value of the specific heat between 0° C. and 2350° C. has been proved by Pier[3] to be given by the expression $4{\cdot}700+4{\cdot}5\times10^{-4}t$. For the specific heat at constant pressure Lewis and Randall[4] give the expression $C_p=4{\cdot}50+0{\cdot}0009T$.

Regnault's[5] value for the molecular heat of hydrogen at constant pressure and the ordinary temperature is 6·81 cal., and at constant volume 4·81 cal. For the specific heat at constant pressure, Escher[6] gives 3·4219, and for the molecular heat at constant volume 4·913. The mean value of the molecular heat at constant volume between 1300° C. and 1700° C. is given by Langen[7] as $4{\cdot}8+0{\cdot}00061t$, where t expresses degrees centigrade. According to Mallard and Le Chatelier,[8] the mean molecular heat at constant pressure is given by $6{\cdot}5+0{\cdot}0006T$, where T denotes absolute temperature. Röntgen[9] found for the ratio of the two specific heats (γ) at ordinary temperature $C_p/C_v=1{\cdot}41$. Grüneisen and Merkel[10] give the velocity of sound in hydrogen as 1260·6 m.-sec.; and the value of γ at 0° C. and 760 mm. as $C_p/C_v=1{\cdot}408$.

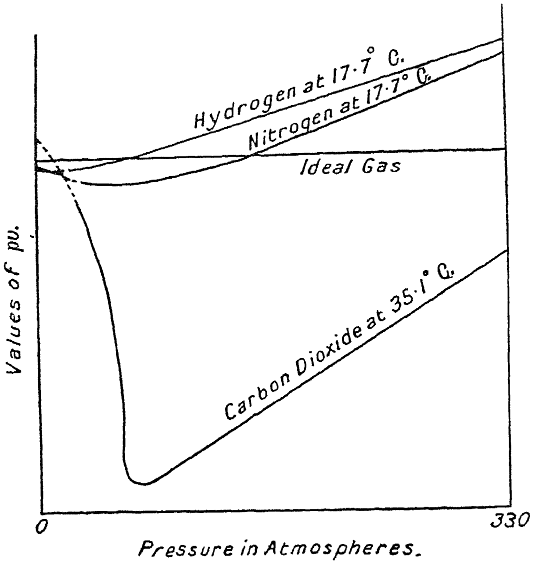

Fig. 1.—Effect of pressure on hydrogen.

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[1] Stefan, *Sitzungsber. K. Akad. Wiss. Wien*, 1872, 65, ii., 45.
[2] Scheel and Heuse, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 44.
[3] Pier, *Zeitsch. Elektrochem.*, 1909, 15, 536.
[4] Lewis and Randall, *J. Amer. Chem. Soc.*, 1912, 34, 1128.
[5] Regnault, *Mém. de l'Acad.*, 1862, 26, 1.
[6] Escher, *Ann. Physik*, 1913, [4], 42, 761.
[7] Langen, *Mitteil. über Forschungsarb. auf dem Gebiete des Ingenieurwesens*, Berlin, 1903, Part 8, 1.
[8] Mallard and Le Chatelier, *Wied. Annalen Beibl.*, 1890, 14, 364; *Zeitsch. physikal. Chem.*, 1887, 1, 456; *Compt. rend.*, 1887, 104, 1780.
[9] Röntgen, *Pogg. Annalen*, 1873, 148, 580.
[10] Grüneisen and Merkel, *Ann. Physik*, 1921, [4], 66, 344.

Croullebois[1] has determined the refractive indices at ordinary temperature and pressure for the C, E, and G lines of the solar spectrum. Merton and Barratt[2] have studied the spectrum of hydrogen.

Liquefaction.—The fact that hydrogen cannot be liquefied solely by pressure engendered a belief in the impossibility of its liquefaction. In 1877 Cailletet[3] allowed hydrogen at a pressure of 280 atmospheres to expand adiabatically to the pressure of the atmosphere, whereupon the temperature dropped below −200° C., and a fine, transient mist of hydrogen appeared. Olszewski[4] confirmed Cailletet's results, and by the aid of liquid air as a cooling-agent Dewar[5] effected complete liquefaction. He cooled the gas to −205° C. at a pressure of 180 atmospheres, and then allowed it to expand to atmospheric pressure, collecting the condensed hydrogen in a double-walled vacuum-flask, silvered to retard absorption of heat. On the initiative of Travers[6] and of Olszewski,[7] the principle of Linde's air-liquefier has been utilized in the construction of a machine for the liquefaction of hydrogen on the large scale, the gas being first cooled to −200° C.

In the liquid state hydrogen is colourless and transparent, and a non-conductor of electricity. Although its surface-tension is low, being $\frac{1}{35}$ that of water and $\frac{1}{5}$ that of liquid air, it has a distinct meniscus and drops well. It obeys the law of Dulong and Petit, its specific heat[8] being about 6. Its atomic volume at the boiling-point is 14·3, and its density is 0·07, or $\frac{1}{14}$ of that of water.[9] Its density at −252·83° C. and 745·52 mm. is 0·07105.[10] The latent heat of evaporation at the boiling-point is 123·1 cal.[11] Dewar[12] gives the boiling-point at atmospheric pressure as −252·5° C., or 20·5° abs. Olszewski[13] gives −252·6° C., and for the critical temperature −240·8° C., and for the critical pressure 13·4–15 atmospheres. The value calculated by Goldhammer[14] for the critical density is 0·02743. Travers and Jacquerod[15] have tabulated the values obtained by them for the vapour-pressure :

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[1] Croullebois, *Ann. Chim. Phys.*, 1870, [4], 20, 136.

[2] Merton and Barratt, *Phil. Trans.*, 1922, [A], 222, 369.

[3] Cailletet, *Compt. rend.*, 1877, 85, 851; *Ann. Chim. Phys.*, 1878, [5], 15, 132.

[4] Olszewski, *Compt. rend.*, 1885, 101, 238.

[5] Dewar, *Trans. Chem. Soc.*, 1898, 73, 528; *Chem. News*, 1900, 81, 136. For a general account of the liquefaction of gases, see this series, Vol. I., 39 to 42.

[6] Travers, *Phil. Mag.*, 1901, [6], 1, 411; *Zeitsch. physikal. Chem.*, 1901, 37, 100; *The Study of Gases* (Macmillan, 1901).

[7] Olszewski, *Ann. Chim. Phys.*, 1903, [7], 29, 289; *Bull. Acad. Sci. Cracow*, 1902, 619; 1903, 241.

[8] Dewar, *Proc. Roy. Soc.*, 1901, [A], 68, 360.

[9] Dewar, *Trans. Chem. Soc.*, 1898, 73, 528.

[10] Augustin, *Ann. Physik*, 1915, [4], 46, 419.

[11] Dewar, *Proc. Roy. Soc.*, 1905, [A], 76, 325.

[12] Dewar, *ibid.*, 1901, [A], 68, 44, 360.

[13] Olszewski, *Drude's Annalen*, 1905, 17, 986; *Bull. Acad. Sci. Cracow*, 1908, 375.

[14] Goldhammer, *Zeitsch. physikal. Chem.*, 1910, 71, 577.

[15] Travers and Jacquerod, *Chem. News*, 1902, 86, 61.

Pressure in mm. of Mercury.	Absolute Temperature.	
	On the Hydrogen Scale.	On the Helium Scale.
800	20°·41	20°·60
760	20·22	20·41
700	19·93	20·12
600	19·41	19·61
500	18·82	19·03
400	18·15	18·35
300	17·36	17·57
200	16·37	16·58
100	14·93	15·13
50	..	14·11

Solidification.—By rapidly evaporating liquid hydrogen on the pump, Dewar [1] cooled the residual liquid so much that it solidified to an ice-like mass, frothy on the surface, at −258° C., or 15° abs. This is the triple point of hydrogen at 55 mm., and further evacuation on the pump lowered the temperature to −260° C., or 13° abs. The heat of fusion of the solid is 16 cal.[2] It crystallizes in the cubic system,[3] thus resembling the metals. The most probable temperature of melting is regarded by Dewar [4] as −257° C., and by Guertler and Pirani [5] as −259° C.

Occlusion by Metals, and Diffusion [6] *through them.*—Hydrogen has the property of diffusing through certain metals, such as platinum, palladium, iron, copper, and nickel, but at ordinary temperatures the velocity of occlusion and of diffusion are so slow as to preclude the possibility of measuring the volume of gas which has penetrated the metal within a reasonable time. At low red heat, however, the rate of diffusion is measurable, as is proved by the work of several investigators.[7] When an evacuated vessel or tube fitted with a plate of platinum, palladium, or iron is heated to redness in an atmosphere of hydrogen, the vacuum is destroyed owing to diffusion of the hydrogen through the heated plate. The converse phenomenon, the production of a vacuum owing to diffusion of hydrogen out of a tube, can be demonstrated by filling with hydrogen a tube similar to that just described, and heating it in air. Since the hydrogen diffuses outwards, and the air cannot diffuse inwards to replace it, a vacuum is produced in the tube. A

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[1] Dewar, *Proc. Chem. Soc.*, 1897, 13, 196; *Chem. News*, 1901, 84, 49, 293; *Ann. Chim. Phys.*, 1901, [7], 23, 417.

[2] Dewar, *Proc. Roy. Soc.*, 1901, [A], 68, 360.

[3] Wahl, *ibid.*, 1913, [A], 88, 61.

[4] Dewar, *ibid.*, 1901, [A], 68, 360; compare Dewar, *Trans. Chem. Soc.*, 1898, 73, 534.

[5] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

[6] The diffusion of hydrogen through balloon fabrics and soap films has been studied by McLennan and Shaver, *Phil. Mag.*, 1920, [6], 40, 272.

[7] Ramsay, *Phil. Mag.*, 1894, [5], 38, 206; Deville and Troost, *Compt. rend.*, 1864, 59, 102; Graham, *Bull. Soc. chim.*, 1867, [2], 8, 87; Cailletet, *Compt. rend.*, 1868, 66, 847.

variation of the experiment is to fill the tube with nitrogen, which is superior to air because of its inertness towards hydrogen; on heating it in an atmosphere of hydrogen, diffusion inwards causes a rise in the pressure of the gas within the tube.

Sieverts[1] observed that at high temperatures copper-wire, iron-wire, nickel, cobalt, and platinum[2] occlude hydrogen, but that silver does not (p. 294). He found that diffusion through copper begins at 640° C., through iron[3] at 300° C., and slowly through nickel at 450° C., but that there is no diffusion through silver at 640° C. Sieverts's[4] results also indicate the insolubility of the gas in cadmium, thallium, zinc, lead, bismuth, tin, antimony, aluminium, gold, tantalum, and tungsten, but Heald[5] states that most freshly precipitated metals absorb hydrogen.

Metals permitting the passage of hydrogen at a red heat, but not of other gases, may be regarded as having the character of a semi-permeable membrane. Palladium is the most permeable of these metals, Graham[6] having found that a sheet with a thickness of 1 mm. allows 327 c.c. to pass per sq. cm. in one minute at 265° C., and 3992 c.c. at 1062° C. The fact that the velocity of diffusion, although dependent on the pressure, does not decrease proportionally with it, is cited by Winkelmann[7] as an argument in support of his theory of the atomic condition of hydrogen occluded by palladium.[8]

Many metals occlude hydrogen, and there is a close connexion between their power of occlusion and their magnetic properties.[9] At the ordinary temperature, elements with a specific magnetic susceptibility exceeding $0{\cdot}9 \times 10^{-6}$ occlude hydrogen readily; but, as a general rule, other elements lack this capacity.

The amount of hydrogen occluded by metals depends on the pressure, and diminishes with rise of temperature. It is also affected by the physical condition and previous history of the metal. Mond, Ramsay, and Shields[10] found that at ordinary temperature and 1 to 4·6 atm. the absorption of hydrogen by palladium-black is 873 vols., and between these limits is independent of the pressure. For spongy palladium the absorption is 852 vols.; and for palladium-foil previously heated to redness, 846 vols. Most of the occluded gas is evolved in vacuum at the ordinary temperature, and the residual 2–8 per cent. at that of boiling sulphur. At different stages of the occlusion the heat evolved is the same, being 4·370 cal. for each gram of hydrogen. At ordinary temperatures spongy platinum absorbs 110 vols. of hydrogen, variations of pressure between 0·5 and 4·5 atm. producing little effect on the amount occluded.

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[1] Sieverts, *Zeitsch. physikal. Chem.*, 1907, 60, 129. With respect to nickel, compare Mayer and Altmayer, *Ber.*, 1908, 41, 3062; Sieverts and Hagenacker, *Ber.*, 1909, 42, 338; *Zeitsch. physikal. Chem.*, 1909, 68, 115.

[2] Compare Nernst and Lessing, *Göttinger Nachrichten*, 1902, 146; Gutbier and Maisch, *Ber.*, 1919, 52, [B], 1368; Schmidt and Lücke, *Zeitsch. Physik*, 1921, 8, 152.

[3] Compare Nernst and Lessing, *loc. cit.*; Schmidt and Lücke, *loc. cit.*

[4] Sieverts and Krumbhaar, *Ber.*, 1910, 43, 893; *Zeitsch. physikal. Chem.*, 1910, 74, 277; Sieverts, *Zeitsch. Elektrochem.*, 1910, 16, 707; Sieverts and Bergner, *Ber.*, 1911, 44, 2394.

[5] Heald, *Physikal. Zeitsch.*, 1907, 8, 659.

[6] Graham, *Proc. Roy. Soc.*, 1867, 15, 227; 1868, 16, 422; 1869, 17, 212, 500.

[7] Winkelmann, *Drude's Annalen*, 1901, 6, 104; Ramsay, *Phil. Mag.*, 1894, 38, 206.

[8] See this series, Vol. IX., Part I., 176.

[9] D. P. Smith, *J. Physical Chem.*, 1919, 23, 186.

[10] Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1897, 62, 290; *Zeitsch. anorg. Chem.*, 1898, 16, 325; *Zeitsch. physikal. Chem.*, 1898, 25, 657.

In vacuum a part of the gas is evolved, but the bulk comes off at 250° to 300° C., and the residue at red heat. Like that of palladium, the heat of occlusion is the same at different stages of the process, and amounts to 6·880 Cal. per gram absorbed.

Hoitsema[1] has demonstrated the reversibility of the occlusion of hydrogen by palladium, and examined the influence exerted by pressure. He found that at low pressures the concentration of the hydrogen in the metal is proportional to the square root of the pressure. The results of his experiments, carried out at 100° C., can be tabulated thus :

Pressure in mm. (p).	Vol. in c.c. of 2 mg. of Occluded Hydrogen $\left(\frac{1}{c}\right)$.	$\frac{\sqrt{p}}{c}$
26·2	3·084	15·8
82·8	1·827	16·6
165·4	1·299	16·6
393·7	0·771	15·3

From these values Hoitsema postulated the monatomicity of hydrogen occluded by palladium at low pressures. For higher pressures the concentration of the occluded gas is approximately proportional to the pressure, indicating that in these circumstances the molecular formula of the occluded gas is H_2. The occlusion by palladium can be represented by the equilibrium

$$H_2 \rightleftharpoons 2H,$$

increase of pressure altering the equilibrium to the left, and decrease to the right.[2]

Fall of temperature is accompanied by an increase in the volume of hydrogen occluded by palladium, a phenomenon observed by Schmidt[3] for the range 140° to 300° C.; by Paal and Amberger[4] down to —10° C.; and by Gutbier, Gebhardt, and Ottenstein[5] down to —50° C.

The influence of temperature on the occlusion by palladium has also been investigated by Firth.[6] He employs the term "adsorption" to denote the surface phenomenon of rapid occlusion of hydrogen, diffusion not being a determinable factor; limits "absorption" to slow occlusion in which the rate of diffusion or solution is a determinable factor; and uses the collective term "sorption" to include both adsorption and absorption.[7] Firth observed adsorption only below 0° C.; between 0° and 150° C. he also observed absorption; but above 150° C. found absorption only.

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[1] Hoitsema, *Zeitsch. physikal. Chem.*, 1895, 17, 1.

[2] Holt, Edgar, and Firth, *Zeitsch. physikal. Chem.*, 1913, 82, 513; 83, 507; Gutbier, Gebhardt, and Ottenstein, *Ber.*, 1913, 46, 1453; Andrew and Holt, *Proc. Roy. Soc.*, 1913, [A], 89, 170.

[3] Schmidt, *Ann. Physik*, 1904, [4], 13, 747.

[4] Paal and Amberger, *Ber.*, 1905, 38, 1394.

[5] Gutbier, Gebhardt, and Ottenstein, *Ber.*, 1913, 46, 1453.

[6] Firth, *Trans. Chem. Soc.*, 1920, 117, 171; compare Troost and Hautefeuille, *Compt. rend.*, 1874, 78, 686; Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1897, 62, 290; Andrew and Holt, *ibid.*, 1913, [A], 89, 170; Halla, *Zeitsch. physikal. Chem.*, 1914, 86, 496; Holt, *Proc. Roy. Soc.*, 1914, [A], 90, 226; Partington, *Trans. Faraday Soc.*, 1919, 14, 259.

[7] Compare McBain, *Phil. Mag.*, 1909, [6], 18, 916.

Palladium-black contains both amorphous and crystalline palladium, and the proportion of each constituent and the sorptive capacity of the substance vary with the conditions of preparation. At low temperatures the sorptive capacity of palladium-black depends on the temperature at which sorption begins. When a sample saturated with hydrogen at 100° C. is cooled in the gas, it sorbs more hydrogen. From 100° to 20° C. the sorptive capacity decreases slightly, and increases continuously from 20° to −190° C. By heating palladium-black it is possible to increase the proportion of the crystalline variety.[1] The relationship between the occlusive power of palladium for hydrogen and the activity of the metal for catalytic hydrogenation has been investigated by Maxted.[2]

The occlusion of hydrogen by palladium decreases very rapidly with rise of temperature from 100° to 600° C., more slowly up to 800° C., and only very slightly between 800° and 1500° C.[3]

The effect of " poisons " on the occlusion of hydrogen by palladium has been studied by Maxted.[4] Hydrogen sulphide diminishes the occluding power of the metal, each atom of sulphur rendering almost exactly four atoms of palladium incapable of occluding the gas, while the remaining palladium occludes normally. de Hemptinne[5] found that carbon monoxide deprives palladium of its sorptive power for hydrogen at low temperatures. Paal and Hartmann[6] proved that carbon monoxide inhibits the activity of palladium for the catalytic reduction of sodium picrate, and observed[7] mercury to exert a similar effect on palladium hydrosols.

A volumetric method for the estimation of hydrogen, either alone or in gaseous mixtures, is based by Paal and Hartmann[8] on sorption by colloidal palladium, a simple gas-pipette being employed.

The occlusion of hydrogen by various metals has been investigated by Graham,[9] and also by Neumann and Streintz.[10] Their results are appended in tabular form, and give the volume of hydrogen under normal conditions sorbed by one volume of the metal. It is noteworthy that their observation regarding silver is not confirmed by the more recent work of Sieverts :

Silver (wire)	0·21	Iron (reduced)	0·4–19·2
Silver (powder)	0·91–0·95	Magnesium	1·4
Aluminium (foil)	1·1–2·7	Nickel (reduced)	17–18
Cobalt (reduced)	59–153	Gold (leaf)	0·48
Copper (wire)	0·3	Gold (precipitated)	37–46
Copper (reduced)	0·6–4·8	Lead (fused)	0·11–0·15
Iron (wire)	0·46	Zinc	Traces
Iron (malleable)	0·57–0·8		

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[1] Firth, *Trans. Chem. Soc.*, 1921, 119, 1120.

[2] Maxted, *ibid.*, 225, 1280.

[3] Sieverts, *Zeitsch. physikal. Chem.*, 1914, 88, 103, 451.

[4] Maxted, *Trans. Chem. Soc.*, 1919, 115, 1050 ; 1920, 117, 1280.

[5] de Hemptinne, *Zeitsch. physikal. Chem.*, 1898, 27, 249.

[6] Paal and Hartmann, *Ber.*, 1910, 43, 243.

[7] Paal and Hartmann, *Ber.*, 1918, 51, 711 ; Paal and Steyer, *ibid.*, 1743.

[8] Paal and Hartmann, *Ber.*, 1910, 43, 243 ; compare Brunck, *Chem. Zeit.*, 1910, 34, 1313.

[9] Graham, *Phil. Mag.*, 1866, [4], 32, 401, 505 ; 1874, [4], 47, 324.

[10] Neumann and Streintz, *Pogg. Annalen*, 1839, 46, 431.

Chemical Properties.—Although a very reactive substance under certain conditions, hydrogen is characterized by its inertness at ordinary temperatures. An exception to this rule was observed by Moissan and Dewar,[1] who found that even at −210° C. it ignites spontaneously when brought into contact with solid or liquid fluorine, forming hydrogen fluoride. With chlorine it combines slowly at the ordinary temperature, with production of hydrogen chloride: direct sunlight so accelerates the reaction as to cause an explosion. This photochemical reaction has been investigated by Baly and Barker.[2] By employing activating light of varying intensity, they found that with a given light-intensity the proportion of hydrogen chloride formed in unit time is small at first, and then rapidly increases up to a constant maximum. Reference is also made to an unpublished observation by Campbell that the constant maximum rate of formation of hydrogen chloride is not proportional to the intensity of the light.

Combination with the other halogens and with the elements of the oxygen group has a measurable velocity only at elevated temperature. Dixon and Coward[3] have determined the ignition-temperature[4] of hydrogen in oxygen and air, the mean result for both gases being 585° C. They define the ignition-temperature as "the temperature to which the gases must be heated separately so as to cause them to inflame immediately when brought into contact." Within 10° C. the ignition-temperature determined by Dixon's apparatus for hydrogen in oxygen or air is independent of the velocity of the gases within wide limits. It is unaffected by the material and surface-character of the apparatus, and also by the velocity of heating.[5] The results of later work[6] on electrolytic gas gave the ignition-temperature 526° C.[7] Fiesel[8] found the minimum ignition-temperature for the mixture $3H_2+2O_2$ to be 397·5° C., that for equal volumes of the dry gases to be 407° C., and that for the mixture $4H_2+O_2$ to be 433° C. An interesting account of the subject was given by Dixon[9] in his presidential address to the Chemical Society of London.

For the lower dilution-limit of inflammability of hydrogen in air, Somermeier[10] gives 5·9 per cent., and Coward and Brinsley[11] give 4·1 per cent. of hydrogen. Terres[12] gives the limits of inflammability in air as between 9·5 and 65·2 per cent., and in oxygen as between 9·2 and 91·6 per cent.

One of the lessons taught by the Great European War was the extreme vulnerability of airships and balloons filled with hydrogen, due

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[1] Moissan and Dewar, *Bull. Soc. chim.*, 1897, [3], 17, 932.

[2] Baly and Barker, *Trans. Chem. Soc.*, 1921, 119, 653; compare this series, Vol. VIII.

[3] Dixon and Coward, *Trans. Chem. Soc.*, 1909, 95, 514.

[4] See this series, Vol. VII.

[5] Compare Mitscherlich, *Zeitsch. anorg. Chem.*, 1921, 121, 53.

[6] Dixon and Crofts, *Trans. Chem. Soc.*, 1914, 105, 2036. Their result is not strictly comparable with the others, being derived from experiments involving adiabatic compression.

[7] Older values are 853° (Helier, *Ann. Chim. Phys.*, 1897, [7], 10, 521), 660°–700° (Bodenstein, *Zeitsch. physikal. Chem.*, 1899, 29, 665), 589° (Emich, *Monatsh.*, 1900, 21, 1061), 550° (Mallard and Le Chatelier, *Compt. rend.*, 1880, 91, 825), and 540° C. (Falk, *J. Amer. Chem. Soc.*, 1906, 28, 1517; 1907, 29, 1536).

[8] Fiesel, *Zeitsch. physikal. Chem.*, 1921, 97, 158.

[9] Dixon, *Trans. Chem. Soc.*, 1910, 97, 661; compare Carter, *J. Gasbeleuchtung*, 1913, 56, 545.

[10] Somermeier, *J. Ind. Eng. Chem.*, 1914, 6, 191.

[11] Coward and Brinsley, *Trans. Chem. Soc.*, 1914, 105, 1859.

[12] Terres, *J. Gasbeleuchtung*, 1920, 63, 785, 805, 820, 836.

to the ready inflammability of mixtures of the gas and air. During the war it was found possible to develop the production of helium within the British Empire on a commercial basis, and to employ this gas as a safe substitute for hydrogen in connexion with warfare in the air.[1] Within certain limits it has been found practicable to utilize non-inflammable mixtures of helium and hydrogen for this purpose. Such mixtures have the advantage of possessing a greater lifting power than pure helium. Ledig[2] found that a jet of helium with more than 14 per cent. of hydrogen can be ignited in air, but that in balloon practice from 18 to 20 per cent. of hydrogen can be employed, as the mixture does not burn with a persistent flame. With a proportion of hydrogen exceeding 20 per cent., the mixture is unsafe for use in war aeronautics.

von Wartenberg and Sieg[3] found that the union of hydrogen and oxygen between 600° and 1000° C. is attended by the formation of a considerable proportion of hydrogen peroxide, this product rapidly decomposing into water and oxygen. Ozone is formed by condensation of a part of the oxygen. The velocity of decomposition of the ozone being less than that of the hydrogen peroxide, a greater proportion of ozone is found in the mixture. Fiesel[4] states that with moist hydrogen and oxygen the reaction is bimolecular, and that hydrogen peroxide may be an intermediate product; with the absolutely dry gases the reaction is termolecular.

The combination of hydrogen and nitrogen under pressure was effected by Le Chatelier[5] in 1901, but owing to an explosion the method was not worked commercially. In 1905 the subject was further studied by Haber and van Oordt,[6] who found that at red heat the velocity of combination is too slow to admit of measurement, and that at higher temperatures the amount of ammonia formed is small, either on account of rapid dissociation or because the reaction-affinity is small.

In 1910 Haber[7] found that in presence of metallic osmium 1 volume of nitrogen unites with 3 volumes of hydrogen at 550° C. and 200 atmospheres, the yield being 8 per cent. of the mixed gases. On the manufacturing scale, osmium can be replaced by the less costly uranium, and a continuous circulation method is employed, with a temperature about 500° C.[8] Any carbon monoxide present in the hydrogen should be removed.[9]

Methods for producing ammonia from its elements under the influence of the silent discharge and of the electric spark have not proved commercially successful.[10]

The other members of the nitrogen group do not form hydrides by

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[1] Compare McLennan, *Trans. Chem. Soc.*, 1920, 117, 923.

[2] Ledig, *J. Ind. Eng. Chem.*, 1920, 12, 1098.

[3] von Wartenberg and Sieg, *Ber.*, 1920, 53, [B], 2192.

[4] Fiesel, *Zeitsch. physikal. Chem.*, 1921, 97, 158.

[5] Le Chatelier, *French Patent*, 1901, No. 313950; *Compt. rend.*, 1917, 164, 588.

[6] Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1905, 44, 341.

[7] Haber, *Zeitsch. Elektrochem.*, 1910, 16, 244.

[8] Compare Claude, *Compt. rend.*, 1922, 174, 681.

[9] Lamb, Scalioni, and Edgar, *J. Amer. Chem. Soc.*, 1922, 44, 738.

[10] Compare Müller and Geisenberger, *British Patents*, 1879, No. 1481; 1879, No. 1592; Young, *British Patent*, 1880, No. 1700; Société d'Azote, *German Patent*, No. 17070; Nithack, *German Patent*, No. 95532; West-Deutsche Thomasphosphatwerke, *German Patents*, Nos. 157287 and 179300; Gorianoff, *French Patent*, No. 368585; Hooper, *U.S. Patent*, No. 791194; Cassel, *German Patent*, No. 175480; Briner and Mettler, *Compt. rend.*, 1907, 144, 694; Davies, *Zeitsch. physikal. Chem.*, 1908, 64, 657.

direct heating in hydrogen, the cause of this phenomenon with phosphorus being the rapid increase in the dissociation of the hydride with rise of temperature.

The nature of the products obtained by the interaction of hydrogen and carbon depends on the experimental conditions. Bone and Coward [1] found that hydrogen unites with very pure carbon at 1100° to 1200° C., producing 75 per cent. of the theoretical yield of methane. By means of an arc-discharge between carbon poles in an atmosphere of hydrogen at a temperature of about 4000° C., Berthelot [2] synthesized acetylene, an endothermic substance.

Gautier [3] has studied the interaction of carbon monoxide and hydrogen at 300° to 1250° C. A mixture of 3 volumes of hydrogen and 1 volume of the monoxide passed through a porcelain tube begins to react at 400° C., water, carbon dioxide, and a small proportion of methane being formed. The action attains its maximum at 1000° C.

Under the influence of ultraviolet rays, carbon dioxide and nascent hydrogen yield formaldehyde,[4] a reaction with an important bearing on the formation of carbohydrates in the plant.

The behaviour of hydrogen with metals is discussed on pp. 27 and 28, and also under the individual metals described in this volume and the other volumes of the series.

Reduction.—According to theory, hydrogen should precipitate from their salts all metals below it in the potential series. When it is passed into a solution of silver nitrate, silver is slowly deposited : with palladous chloride there is a rapid, quantitative precipitation of the metal. Although at ordinary temperatures the rate of deposition of the metal from solutions of cupric sulphate, platinum chloride, and auric chloride is too slow to be measured, the reduction of these and other salts is greatly accelerated by introducing the hydrogen occluded in palladium. In some instances reduction by hydrogen is facilitated by increase of pressure, examples being afforded by solutions of mercuric chloride and mercurous nitrate, which are reduced at 100 atmospheres, but not at the ordinary pressure.[5]

Similar conditions govern the interaction of hydrogen and oxidizers. Although the number of observed instances of direct reduction of oxidizing-agents by gaseous hydrogen is small in comparison with those theoretically possible, such reactions are often induced by the presence of finely divided platinum or palladium, and especially by palladium-occluded hydrogen. Gladstone and Tribe [6] cite examples such as the reduction of chlorates to chlorides, nitrates to ammonia, sulphurous acid to hydrogen sulphide, ferricyanides to ferrocyanides, arsenic acid to arsenious acid, nitrobenzene to aniline, and indigo to indigo-white. Further instances of reduction by hydrogen and colloidal palladium are given by other investigators.[7]

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[1] Bone and Coward, *Trans. Chem. Soc.*, 1908, 93, 1975; compare Bone and Jerdan, *ibid.*, 1897, 72, 41; Pring and Hutton, *ibid.*, 1906, 89, 1591; Mayer and Altmayer, *Ber.*, 1907, 40, 2134.

[2] Berthelot, *Compt. rend.*, 1862, 54, 646.

[3] Armand Gautier, *ibid.*, 1910, 150, 1383, 1564.

[4] Stoklasa and Zdobnický, *Chem. Zeit.*, 1910, 34, 945.

[5] Compare Ipatieff and Werchowsky, *Ber.*, 1909, 42, 2079 ; 1911, 44, 1755.

[6] Gladstone and Tribe, *Chem. News*, 1878, 37, 68.

[7] Paal and Roth, *Ber.*, 1908, 41, 2282; Skita, *Ber.*, 1909, 42, 1627; Wallach, *Annalen*, 1911, 381, 51. A description of the experimental details of the reduction is given by Tinkler and Challenger, *Chemistry of Petroleum* (Crosby Lockwood & Son, 1920), 247.

Gaseous substances also react with hydrogen occluded by metals, the increased activity being probably due to the existence of the hydrogen partly in the atomic state and partly as hydride. The combination of hydrogen with the halogens and oxygen is promoted by the catalytic action of platinum and palladium, the same effect being noted by Kuhlmann[1] for the interaction of hydrogen and nitric oxide to form ammonia. The direct combination of nitrogen and hydrogen is not induced by these catalysts. It is noteworthy that hydrogenation cannot be induced by either the spongy or colloidal form of platinum or palladium completely freed from oxygen,[2] and that hydrogen desorbed from these metals retains activity for some time.[3]

A most important method for the application of hydrogen as a reducing agent has been discovered and elucidated by the researches of Sabatier and Senderens.[4] A very succinct summary of their work and that of other investigators has been given by Sabatier.[5] The method is simple, and consists in passing a mixture of the gaseous substance and hydrogen through a tube containing the finely divided metallic catalyst, obtained by previous reduction of the oxide in the same tube. For each reaction there is a suitable temperature, sometimes that of the atmosphere, but more usually 150° to 200° C. The neighbourhood of 180° C. has been found well adapted for many reactions. The metals employed have been platinum-black, nickel, cobalt, iron, and copper. Of these catalysts nickel is the most active,[6] and shares with cobalt the power of inducing reactions not promoted by the other metals. Copper is the least useful of the five, platinum and iron occupying an intermediate position.

The preparation of the catalyst can be exemplified by a description of the operations involved in the case of nickel. Unglazed biscuit-ware, broken to the size of peas, and freed from iron by boiling for several days with dilute hydrochloric acid, is rendered more porous by heating to redness for half an hour. After immersion in a concentrated solution of nickel nitrate, and evaporation of the liquid, the material is dried at 100° C., and subsequently heated until evolution of oxides of nitrogen ceases :

$$2Ni(NO_3)_2 = 2NiO + 4NO_2 + O_2.$$

The reduction to metal is effected in the hydrogenation apparatus, the oxide being placed in a hard-glass tube 1 mètre long, and with a bore of 2 cm., supported in a slanting position, and surrounded by an iron tube having holes drilled in it for the insertion of thermometers. The hydrogen employed is washed successively with an acid solution of potassium permanganate, concentrated sodium hydroxide, and concentrated sulphuric acid, and finally passed over heated, palladized asbestos. During the operation the temperature of the reduction tube is maintained at 300° C., the end of the reaction being indicated by cessation in the production of water.

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[1] Kuhlmann, *Annalen*, 1839, 29, 272.

[2] Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, 54, [B], 113.

[3] Anderson, *Trans. Chem. Soc.*, 1922, 121, 1153; compare Chattock and Tyndall, *Phil. Mag.*, 1908, [6], 16, 24; Usher, *Trans. Chem. Soc.*, 1910, 97, 400; Collie and Patterson, *Proc. Chem. Soc.*, 1913, 29, 22, 117; Lind, *J. Amer. Chem. Soc.*, 1919, 41, 545; Wendt, *ibid.*, 1920, 42, 930.

[4] Sabatier and Senderens, *Compt. rend.*, 1897, 124, 1358; 1899, 128, 1173; 1900, 130, 1761, 131, 40; 1901, 132, 1254, 133, 321; 1902, 134, 514, 135, 225.

[5] Sabatier, *Ber.*, 1911, 44, 1984.

[6] See this series, Vol. IX., Part I., 95.

The reduction processes effected by this method can be classed in four groups :

1. Simple reduction, without addition of hydrogen, exemplified by the conversion of nitrous oxide into water and nitrogen.

2. Reductions accompanied by addition of hydrogen, such as the formation of methane from the oxides of carbon, effected by nickel or cobalt only, or of benzene from halogen-benzenes. In these reactions the hydrogen replaces oxygen or halogen. The reduction of nitric oxide and nitrogen peroxide to ammonia, and of nitrobenzene to aniline, belong to the same group.

3. Addition of hydrogen to compounds with multiple bonds, such as the formation of ethane from ethylene or acetylene. Rideal[1] found 137° C. to be the optimum temperature for the hydrogenation of ethylene, and considers the mechanism of the process to be explicable on the hypothesis of Langmuir[2] that the reaction proceeds in a unimolecular film on the surface of the nickel catalyst.

4. Sometimes the metallic catalyst exerts a more or less powerful tendency to break down the molecule, hydrogen being added not only to the initial substance, but also to its fission-products. Examples are the conversion of benzene at 300° C. into methane ; of acetylene at 200° C. into a liquid resembling American petroleum, above red heat into one like Caucasian petroleum, and at red heat into a product similar to a mixture of the two varieties.

The two factors essential to success in the application of the method are purity of material and a suitable temperature.

Orloff[3] found that in presence of coke coated with nickel or palladium hydrogen reacts at 95° to 100° C. with carbon monoxide, yielding ethylene and water. The reaction can be assumed to take place in two stages :

$$CO+2H_2=CH_2+H_2O\ ;\ 2CH_2=C_2H_4.$$

Gauthier[4] prepares the finely divided nickel by depositing nickel oxide on glass beads of 2 mm. diameter, and reducing at 330° C.

Nascent Hydrogen.—At the moment of liberation from its compounds, hydrogen displays much greater chemical activity than it does in its ordinary condition, and is able to effect reductions beyond the power of gaseous hydrogen at atmospheric temperature, the method being specially suited to the reduction of organic compounds. When in this state, hydrogen is termed *nascent*. The method employed for preparing nascent hydrogen depends in each instance on the nature of the reduction contemplated. The action of an amalgam of sodium, magnesium, or aluminium on water serves for the reduction of aldehydes and ketones to alcohols ; that of metals such as zinc, tin, and iron on acids is employed to convert nitro-compounds into amines ; the decomposition of a concentrated solution of hydrogen iodide in a sealed tube at 150° to 275° C. is applied to the hydrogenation of unsaturated hydrocarbons. Ostwald[5] attributes the reducing power of nascent hydrogen to an increase in free energy, just as in electrolytic reductions the chemical

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[1] Rideal, *Trans. Chem. Soc.*, 1922, 121, 309 ; compare Sabatier, *Compt. rend.*, 1897, 124, 1360 ; Dorothy M. Palmer and William G. Palmer, *Proc. Roy. Soc.*, 1921, [A], 99, 402.

[2] Langmuir, *J. Amer. Chem. Soc.*, 1915, 37, 1162 ; *Trans. Faraday Soc.*, 1921, 16.

[3] Orloff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1588, 1590 ; *Ber.*, 1909, 42, 895.

[4] D. Gauthier, *Ann. Chim. Phys.*, 1909, [8], 16, 289.

[5] Ostwald, *Lehrbuch der allgemeinen Chemie*, Leipsic, 1893, 2, ii., 585.

activity of the evolved hydrogen depends on the pressure at which it is discharged at the cathode.

Zenghelis[1] proved the chemical activity of hydrogen to be much increased by bringing the gas in very minute bubbles into contact with solutions. His process consisted in forcing the gas into paper cartridges under such conditions as to inhibit bubbling through the paper, but so as to facilitate reaction with the dissolved substance in the pores of the cartridge. At 90° C. an appreciable reduction of mercuric chloride to mercurous chloride was observed, and between 80° and 85° C. a similar reduction of potassium chlorate to potassium chloride. Contact for three days at the ordinary temperature, and more rapidly at 65° C., yielded evidence of the conversion of carbon dioxide into formaldehyde and substances with characteristic sugar properties. At ordinary temperature, potassium nitrate was reduced to potassium nitrite; and under similar conditions of temperature an experiment lasting half an hour transformed sufficient nitrogen into ammonia to give the Nessler test.

The energy characteristic of the nascent state is attributed by Zenghelis to the very fine state of division of the reacting gas.

Reduction of Metallic Oxides.—Hydrogen can displace many metals from their oxides, the reduction taking place at the ordinary temperature, as with silver and palladium oxides, or on heating, as with the oxides of copper, cadmium, lead, antimony, nickel, cobalt, and iron. Sometimes these reductions are incomplete, an equilibrium being attained. Such equilibria depend on the experimental conditions, an example being the action of steam on heated iron (p. 15).

Raschig[2] observed that a mixture of hydrogen and nitrogen peroxide passed through a heated tube reacts with such violence as to cause explosion.

The influence of the silent electric discharge on mixtures of hydrogen and other gases has been studied by Losanitch.[3] Sulphur dioxide is rapidly reduced, with liberation of sulphur:

$$SO_2+2H_2=2H_2O+S.$$

Nitric oxide reacts fairly rapidly, forming ammonium nitrite. Two stages may be assumed:

$$2NO+2H_2=2H_2O+N_2; \quad N_2+2H_2O=NH_4NO_2.$$

At ordinary temperature, pure hydrogen slowly reduces concentrated sulphuric acid to sulphur dioxide and water.[4] Carbon disulphide forms a brown, insoluble solid of the formula $3CS_2,H_2$. Acetylene produces a light yellow mass containing two substances: one is a thick liquid with the formula $(C_2H_2,2C_2H_4)_2$, is soluble in ether, and has a pleasant odour; the other is an insoluble solid, $(2C_2H_2,C_2H_4)_x$, of pungent odour and high molecular weight.

Triatomic Hydrogen.—Papers on the reactivity of hydrogen prepared by the electrolysis of dilute sulphuric acid have been published by Osann.[5] The special reactivity of the gas was proved by Löwenthal[6] to be due to the presence of sulphur dioxide derived from the sulphuric acid.

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[1] Zenghelis, *Compt. rend.*, 1920, 170, 883.

[2] Raschig, *Zeitsch. angew. Chem.*, 1907, 20, 694.

[3] Losanitch, *Ber.*, 1907, 40, 4656.

[4] Jones, *Mem. Manchester Phil. Soc.*, 1917, 61, No. 3, 1.

[5] Osann, *J. prakt. Chem.*, 1853, 58, 385; 1854, 61, 500; 1855, 56, 102; 1856, 69, 1; 1857, 71, 355; 1859, 78, 93; 1860, 81, 20; 1864, 92, 210.

[6] Löwenthal, *J. prakt. Chem.*, 1858, 73, 116.

An active form of hydrogen ("hyzone") has been prepared by Wendt and Landauer[1] by the action of an electrical discharge on dry hydrogen at reduced pressure. The product reduces sulphur to hydrogen sulphide; it also reduces nitrogen, phosphorus, arsenic, and both acidic and neutral solutions of potassium permanganate. It is unstable, its reconversion into the ordinary form being complete in the space of about a minute. The formula H_3 is suggested for this variety of hydrogen. It has not been possible to convert more than 0·02 per cent. of the hydrogen into the active form. The contraction in volume of the hydrogen during the transformation indicates the polyatomic nature of the product. It liquefies when cooled with liquid oxygen.

The Hydrogen Ion.—The *acids* are compounds of hydrogen characterized by an acid taste, the power to turn blue litmus red, and the capacity for evolving hydrogen when in contact with metals such as zinc. These acids are electrolytes, and have one constituent common to all, the *hydrogen ion,* which has the same composition as hydrogen. The hydrogen ion in acids is to be regarded as positively charged hydrogen, since during electrolysis of an acid it moves towards the cathode, there giving up its charge and evolving as hydrogen.[2] Solutions of different acids of equimolecular strength do not contain the same number of hydrogen ions, as is indicated by variation in their acid taste, in their velocity of reaction with metals, in their electrical resistance, and in their power of inducing catalysis. Such acid solutions contain three constituents in equilibrium, the cation $H^{\cdot}$, the anion A', and the non-ionized acid HA :

$$H^{\cdot}+A' \rightleftharpoons HA.$$

The *strength* of an acid is proportional to the extent of its electrolytic dissociation ; that is, to the number of hydrogen ions present.

According to Kendall,[3] the conductivity of the hydrogen ion at 18° C. is $313{\cdot}9 \pm 0\ 4$, and at 25° C. is $347{\cdot}2 \pm 0{\cdot}4$.

Many reactions can be induced by the presence of hydrogen ions as a catalyst, among them the saponification of esters, and the inversion and mutarotation of sugar. The opposite effect of retardation has sometimes been observed: Lapworth and Hann[4] noticed it in connexion with the establishment of equilibrium between ketonic and enolic substances; and Kerp and Baur[5] noted the same phenomenon in regard to the formation of primary sulphite derivatives of arabinose, dextrose, and other substances.

The velocity of inversion of sucrose and that of the saponification of methyl acetate under the catalytic influence of hydrogen ions are proportional to the concentration of these ions in the solution, so that measurement of these velocities affords a means of estimating the ionic concentration.[6] The velocity of inversion of sucrose is conveniently determined by the aid of the polarimeter, and that of the saponification

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[1] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1920, 42, 930; 1922, 44, 510.

[2] An example of the liberation of hydrogen at the anode is mentioned in connexion with lithium hydride (p. 59).

[3] Kendall, *Trans. Chem. Soc.*, 1912, 101, 1275 ; compare this series, Vol. I., 206.

[4] Lapworth and Hann, *Trans. Chem. Soc.*, 1902, 81, 1508.

[5] Kerp, *Arbeiten kaiserl. Gesundheitsamt,* 1904, 21, 180 ; Kerp and Baur, *ibid.*, 1907, 26, 249, 278.

[6] Compare Palmaer, *Zeitsch. physikal. Chem.*, 1897, 22, 504; Sand, *Ber.*, 1906, 39, 2038.

of methyl acetate by a volumetric method. Bredig and Fraenkel[1] have based an accurate volumetric method of determining the concentration of hydrogen ions on the catalytic decomposition of ethyl diazoacetate.

Tolman[2] found for the transport-number of the hydrogen ion the value 0·184.

A characteristic of the hydrogen ion is its tendency to form complex ions, yielding with ammonia the radical ammonium, NH_4,[3] and with the amines substituted ammonium radicals. The cation of the oxonium salts may be regarded as a complex ion formed by union of a neutral compound, such as ethyl ether, with the hydrogen ion. Dimethylpyrone[4] also yields complex hydrogen ions, other examples being the anions of the primary salts HSO_4', HF_2', HCO_3', HC_2O_4', and others.[5]

References to the work of other investigators of the hydrogen ion are appended.[6]

THE STRUCTURE OF ATOMIC NUCLEI.

The problem of the constitution of atomic nuclei has been attacked from two opposite points of view. One method has consisted in attempting to synthesize nuclei heavier than the parent; the other has been concerned with the disruption of atomic nuclei.

The synthetic process is exemplified by the work of Collie and his coadjutors[7] on the effect produced by exposing hydrogen at low pressure to the action of cathode rays. Many experiments under different conditions were made. In some of them the residual gas was found to contain varying proportions of helium and neon; in others the results were negative. It has been suggested that the presence of these gases might be due to contamination from the material of the apparatus or from the atmosphere, but the elaborate experimental precautions adopted make such an explanation untenable. Earlier work by Ramsay and by Collie[8] had proved the presence of both helium and neon in the residual gases of old X-ray bulbs.

Sir J. J. Thomson[9] tried the effect of cathode rays in experiments similar to those of Collie and Patterson, and obtained not only helium and neon, but also a considerable proportion of a gas denoted by him as X_3. Thomson believed the helium and neon to have been evolved from the materials of the apparatus under the influence of the electric discharge; Collie and Patterson regarded these gases as having been

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[1] Bredig and Fraenkel, *Zeitsch. Elektrochem.*, 1905, 11, 525; *Zeitsch. physikal. Chem.*, 1907, 60, 202.

[2] Tolman, *J. Amer. Chem. Soc.*, 1911, 33, 121.

[3] Werner and Miolati, *Zeitsch. physikal. Chem.*, 1893, 12, 35.

[4] Walden, *Ber.*, 1901, 34, 4185.

[5] Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1898, 20, 475.

[6] Ostwald, *Lehrbuch der allgemeinen Chemie*, Leipsic, 1893, 2, i., 904 and 952; *Zeitsch. physikal. Chem.*, 1900, 35, 333; Wilsmore, *ibid.*, 291, 302; Bose, *ibid.*, 1900, 34, 702; Wulf, *ibid.*, 1904, 48, 87; Ostwald and Luther, *Hand- und Hilfs-buch*, 3rd ed., Leipsic, 1910, 437; Nernst, *Ber.*, 1897, 30, 1557; Lapworth, *Trans. Chem. Soc.*, 1908, 93, 2187; Baly, Burke, and Marsden, *ibid.*, 1909, 95, 1096. Cathcart (*J. Ind. Eng. Chem.*, 1922, 14, 278) has described a simple hydrogen generator for use in making hydrogen-ion determinations.

[7] Collie and Patterson, *Trans. Chem. Soc.*, 1913, 103, 419; *Proc. Chem. Soc.*, 1913, 29, 217; Collie, *Proc. Roy. Soc.*, 1914, [A], 90, 554; Collie, Patterson, and Masson, *ibid.*, 91, 30; compare Masson, *Proc. Chem. Soc.*, 1913, 29, 233.

[8] Ramsay and Collie, *Nature*, 1912, 89, 502; Ramsay, *Trans. Chem. Soc.*, 1913, 103, 264.

[9] Thomson, *Nature*, 1913, 90, 645.

formed from hydrogen by a synthetic process. Thomson's gas X_3 has since been prepared by Wendt and Landauer (p. 30) from hydrogen by activation, and found to have the formula H_3.[1]

Working on the lines indicated by Collie, negative results were obtained by Strutt,[2] by Merton,[3] and by Piutti and Cardoso[4]; but with Merton's actual apparatus Collie was able to demonstrate the formation of both helium and neon. Baly[5] attributes the divergence in results obtained, not only by different observers but by the same individuals, to the necessity of the discharge being tuned to the particular tube employed.

An example of the disruptive method of investigating the structure of atomic nuclei is Sir Ernest Rutherford's[6] work on the effect of passing swiftly moving particles of radium-C through nitrogen. A few of the atomic nuclei are disrupted, with production of hydrogen atoms. From oxygen no hydrogen is formed.

Whatever may be the final decision as to the interpretation of these remarkable phenomena of the synthesis and disruption of atomic nuclei, it is obvious that the old view as to the immutability of the atom can no longer be regarded as axiomatic.[7]

An important theory as to the structure of atomic nuclei has been developed by Harkins.[8] He assumes the elements to belong to one of two classes, those of even atomic number, or those of odd atomic number. The atomic nuclei of the even series are supposed to be composed of helium nuclei only, or of helium nuclei with cementing electrons; those of the odd series are assumed to consist of helium and hydrogen nuclei with cementing electrons. Harkins further postulates that the helium nucleus consists of four hydrogen nuclei with two cementing electrons, the reduction in mass being attributed to the packing effect. The helium nucleus is supposed to have the greatest stability, that of the atoms of even atomic number coming next. Apart from nitrogen, the lighter elements of odd atomic number are assumed always to have three hydrogen nuclei associated with the helium nuclei, indicating the possibility of this group of three hydrogen nuclei having the atomic weight 3, and being an "isotope"[9] (p. 33) of hydrogen. It is possible that this form of hydrogen is identical with the hypothetical "nebulium," believed to have an atomic weight approximating to 3.[10]

Modern astrophysical views incline to the belief that in the stars there is going on a synthetic formation of the chemical elements from hydrogen and helium. Possibly the starting-point in these syntheses is nebulium, the first step being its conversion into hydrogen, and the second the association of the hydrogen to form helium. Further association of the helium to elements of even atomic numbers would constitute the next

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[1] Compare F. W. Aston, *Phil. Mag.*, 1920, [6], 39, 611.

[2] Strutt, *Proc. Roy. Soc.*, 1914, [A], 89, 499.

[3] Merton, *ibid.*, [A], 90, 549.

[4] Piutti and Cardoso, *Gazzetta*, 1920, 50, i., 5.

[5] Baly, *Ann. Rep. Chem. Soc.*, 1914, 11, 45; 1920, 17, 29.

[6] Rutherford, *Proc. Roy. Soc.*, 1920, [A], 97, 374.

[7] Compare Faraday's statement, quoted on p. 55.

[8] Harkins, *J. Amer. Chem. Soc.*, 1917, 39, 856; *Physical Rev.*, 1920, 15, 73; compare Harkins and Wilson, *J. Amer. Chem. Soc.*, 1915, 37, 1367, 1383, 1396; Harkins and Hall, *ibid.*, 1916, 38, 169; Harkins, *ibid.*, 1921, 43, 1038; *Phil. Mag.*, 1921, [6], 42, 305; *Nature*, 1921, 107, 202; Harkins and Madorsky, *Physical Rev.*, 1922, 19, 135.

[9] Compare Soddy, *Ann. Rep. Chem. Soc.*, 1913, 10, 263; *Trans. Chem. Soc.*, 1919, 115, 14.

[10] Fabry and Buisson, *Astrophys. J.*, 1914, 40, 256.

step. If this conception be correct, a marked tendency towards the formation of elements with even atomic numbers would be anticipated. Harkins has pointed out that there is actually a great predominance of elements of this type.

Through his work on the mass spectra of the elements, Aston[1] is convinced that, with the exception of H_2 and H_3, all masses measured by him are whole numbers. The conclusion is subject to the limits of experimental error, but is equally true of atomic, molecular, elementary, and compound masses. Aston has obtained evidence of the existence of isotopes, believed by Harkins to account for the divergence of atomic weights from whole numbers. Indications of the separation of chlorine into two isotopes have also been described by Harkins.[2]

In Rutherford's earlier experiments on the disruption of nitrogen and oxygen by the particles of radium-C,[3] he thought that both gases were capable of disintegration with expulsion of an atom of mass 3. His later investigations proved the method employed to fix the source of the radiation to be untrustworthy on account of the considerable variation in the thickness of films of metal foil. The results obtained by a more direct and simple method indicated, at least for oxygen, that the particles originate in the radioactive source, and not in the volume of the surrounding gas. In his view much experiment will be required to fix definitely the nature of the radiation, but the general evidence indicates it to consist of particles of mass 4 projected from the source, and to constitute a new mode of transformation of radium-C.[4]

As a result of the insight respecting the inner constitution of atoms gained during the last twenty years, modern thought regards the atoms of all the different elements as having the same general type of structure. The greater part of the mass of the atom is due to the presence at the centre of the atom of a positively charged nucleus of minute dimensions. Around the nucleus is a region with a diameter of the order of 2×10^{-8} cm. occupied by electrons maintained in equilibrium by the forces from the nucleus. According to the law of Moseley, the resultant nuclear charge of an atom is equal to the atomic or ordinal number of that atom, varying from one " atom " of electricity for hydrogen to ninety-two " atoms " for uranium, the ordinal numbers also representing the number of " planetary " electrons surrounding the atomic nucleus. Except for mass, the ordinary physical and chemical properties of the atom depend entirely on the number and arrangement of the external electrons; that is, on the nuclear charge. The mass of the atom is a property of the nucleus, its effect on the ordinary properties of the atom and on the distribution of the electrons being much less pronounced. The production of atoms with the same nuclear charge but of different nuclear masses, known as *isotopes*, is explicable on this assumption.

The removal of one or more of the external planetary electrons from the atom under the influence of electrical discharges or of light, or the elimination of one of the more strongly bound electrons by means of X-rays or β-rays, would effect a transformation of the atom of a temporary nature only, for its restoration to its original condition would

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[1] F. W. Aston, *Phil. Mag.*, 1920, [6], 39, 611.

[2] Harkins, *Science*, 1920, 51, 289; *Physical Review*, 1920, 15, 74; Harkins and Hayes, *J. Amer. Chem. Soc.*, 1921, 43, 1803.

[3] Rutherford, *Proc. Roy. Soc.*, 1920, [A], 97, 374.

[4] Rutherford, *Trans. Chem. Soc.*, 1922, 121, 400.

soon result from the acquirement of a new electron from outside. Disruption of the nucleus itself appears to be essential to a permanent change in the atom, and this disintegration can be effected by the elimination of a charged unit of the nuclear structure causing a permanent alteration in the nuclear charge, for there is no evidence indicating the process to be reversible. The probability of the forces holding together the components of the nucleus being very powerful, induced Rutherford to experiment with the swift α-particles of radium and thorium, as mentioned on p. 32. This method of attack has been extended to a number of elements, and a very interesting account of the work was given by Sir Ernest Rutherford in a lecture before the Chemical Society of London on 9th February, 1922.[1] The results of the work done in this field hitherto indicate a high degree of stability to be characteristic of most atoms, and point to the existence of such powerful forces holding the nucleus together as are only likely to yield to the attack of a concentrated source of energy like the α-particle. Up to the present, when disintegration has been accomplished by its aid, the rupture of the atom has only been effected to a very minute extent.

DETECTION AND ESTIMATION OF HYDROGEN.

The qualitative detection and quantitative estimation of hydrogen in compounds are effected by methods described in text-books of organic chemistry. A quantitative volumetric method described by Lidoff[2] is applicable to both inorganic and organic substances. The material is heated to redness in a test-tube with magnesium powder, the evolved hydrogen being collected in a Lunge nitrometer.

ATOMIC WEIGHT OF HYDROGEN.

In the history of chemistry there is no more interesting chapter than that recounting the controversy waged regarding the choice of the best standard of atomic weight. The various determinations of the atomic weight of hydrogen are of special interest and importance, because for many years this element was the arbitrary standard. In the early years of the nineteenth century, it was first selected for this purpose by John Dalton, its atomic weight being taken as unity[3] and the atomic weights of the other elements being expressed relatively to this value. Dalton's choice was determined by the fact that hydrogen is the lightest of the elements, but the weak point in selecting it as standard lies in the fact that the atomic weights of most of the other elements cannot be determined directly with reference to hydrogen. This defect was noted by Berzelius and by Wollaston, who adopted oxygen as the basis of their atomic weight systems. Since most of the elements combine with oxygen, it furnishes a useful standard of atomic weight, and any revision of the ratio hydrogen : oxygen does not necessitate recalculation of the whole of the atomic weight table. Wollaston chose for his fundamental atomic weight $O=10$, and was followed by later chemists, such as Despretz in 1826, Kühn in 1837, and Cauchy in 1838. Berzelius objected to Wollaston's value for oxygen on the ground that it necessitated

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[1] Rutherford, *Trans. Chem. Soc.*, 1922, 121, 400; see also Allen, *Chemistry and Industry*, 1923, 42, 338.

[2] Lidoff, *J. Russ. Phys. Chem. Soc.*, 1907, 39, 195.

[3] Compare this series, Vol. I., 16 and 230.

expressing the atomic weight of hydrogen by a fraction, and founded his table on the basis O = 100. The standard O = 1 was adopted by Meinecke in 1817, by Bischof in 1819, and also by Thomson.

Dalton formulated water as HO, but Berzelius considered that its formula should be H_2O, since it can be produced from two volumes of gaseous hydrogen and one volume of gaseous oxygen. Convinced of the impossibility of determining atomic weights accurately, Gmelin and his adherents in 1826 and later years advocated the adoption of a set of equivalents, that of hydrogen being taken as unity, and that of oxygen as 8 on the basis of Dalton's formula for water. According to Berzelius's view, the atomic weight of hydrogen compared with oxygen as 100 was 6·24, but in deference to the views of Gmelin he introduced the conception of double atoms, denoted by a horizontal line through the symbol of the element, the corresponding numbers being known as "Berzelius's atomic weights." In the table based on this compromise the ratio H : O was 12·48 : 100 in Berzelius's notation, or in round numbers 1 : 8 in that of Gmelin.

Experiments by Dumas and by Erdmann and Marchand in 1842 fixed the ratio H : O as 12·5 : 100 = 1 : 8·00, and it remained unaltered until 1860. In 1858–1860 Cannizzaro proposed adopting for oxygen the atomic weight O = 16, and, in accordance with his suggestion, the atomic weights of a number of the elements were taken as double their equivalents. In 1860 Stas determined the atomic weight of hydrogen to be 1·005 (O = 8), in terms of Berzelius's system; and in 1865 he gave the value as 1·0025 compared with O = 16, in accordance with modern conceptions.

Although neither of these numbers agrees with the present accepted value, it is noteworthy that Stas was among the first to suggest employing O = 16 as the standard, a system adopted by him almost exclusively in his published work. He did not utilize the standard H = 1, beyond stating that in comparison with it the value for oxygen could not exceed 15·96, and giving a number of atomic weights calculated on this basis; but the atomic weight of hydrogen as unity proved very attractive, and was always employed by many chemists, although some adhered to Stas's table, calculated from O = 16. In his book on atomic weights, published in 1882, Clarke employed chiefly the values H = 1 and O = 15·96 as the basis of calculation, although he also used O = 16 as standard. In a treatise on atomic weights, published in 1883, Lothar Meyer and Seubert adopted the ratio H : O = 1 : 15·96 : but they also tried to introduce a system based on the value O = 1.

In 1882 Stas announced a new value for the atomic weight of hydrogen, 1·01 (O = 16), and in the following year Marignac[1] urged without success the adoption of Stas's original value O = 16 as the standard. In 1885 Ostwald[2] criticized Stas's conclusion that the value O = 16 necessitates for hydrogen a value higher than unity, and employed the ratio H : O = 1 : 16 as the basis of his atomic weights.

Such was the condition of the subject in 1887, when the publication of results obtained by Cooke and Richards, and by Keiser, shed a new light on the matter. Their work, confirmed by that of Rayleigh and of Crafts, proved the ratio H : O = 1 : 15·96 to be inaccurate, and indicated

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[1] Marignac, *Arch. Sci. phys. nat.*, 1883, **10**, 5–27; *Œuvres Complètes*, Geneva, 1902, **2**, 714.

[2] Ostwald, *Lehrbuch der allgemeinen Chemie*, Leipsic, 1885, **1**, 44.

15·87 as the atomic weight of oxygen. Lothar Meyer and Seubert still held out for the old ratio, and advocated the employment of H=1 as standard.

In 1888 papers were published almost simultaneously by Brauner,[1] Ostwald,[2] and Venable[3] advocating the adoption of the standard O=16, in accordance with Marignac's suggestion made in 1883. In 1889 the German Atomic Weight Committee was appointed at the instance of Brauner,[4] and in 1906 the International Committee on Atomic Weights, constituted in 1900, took the decisive step of adopting O=16 as the sole standard.[5] The atomic weight of hydrogen given in the current table is 1·008.

A summary of the literature of the dispute has been given in a paper by Küster,[6] and in another by Brauner.[7]

Methods of determining the Atomic Weight.

From the historical standpoint it will be most interesting to consider the various determinations of atomic weight in chronological order, giving the values according to both the oxygen standard and the hydrogen standard, the values for the older determinations being expressed in the notation of the period. For convenience in treatment, the methods described will be classified in two divisions :

1. Gravimetric methods involving the synthesis of water by various processes.
2. Physical, physico-chemical, and volumetric methods employing gaseous hydrogen and oxygen.

I. Gravimetric Methods.

In 1819 Berzelius and Dulong[8] reduced a weighed quantity of cupric oxide at red heat in a current of hydrogen, and weighed the water produced. The loss in weight of the cupric oxide gave the weight of oxygen in the water formed, whilst the difference between the weight of the water and that of the oxygen gave the weight of the hydrogen. In three experiments the ratio H : O was found to be 1 : 16·124, 15·863, and 16·106 respectively, the mean being 1 : 16·031. In Berzelius's system the corresponding value for the ratio H : O is 6·2379 : 100, the atomic weight for hydrogen employed by Berzelius being 6·24. Dulong and Berzelius determined the densities of the two gases, the ratio being $D_H : D_O = 0·0688 : 1·1026$, and the corresponding atomic weight of oxygen 6·2398, which agrees well with that calculated by the gravimetric method. The ratio is

$$\mathbf{H : O = 1 : 16{\cdot}031 = 0{\cdot}99804 : 16.}$$

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[1] Brauner, *Chem. News*, 1888, 58, 307.
[2] Ostwald, *Zeitsch. physikal. Chem.*, 1888, 2, 765.
[3] Venable, *J. Anal. Chem.*, 1888, 3, I., 1.
[4] Brauner, *Ber.*, 1889, 22, 1186.
[5] Report of the International Committee on Atomic Weights, *Proc. Chem. Soc.*, 1906, 22, 2.
[6] Küster, *Zeitsch. anorg. Chem.*, 1897, 14, 251, 256.
[7] Brauner, *ibid.*, 1901, 26, 186.
[8] Berzelius and Dulong, *Ann. Chim. Phys.*, 1820, [3], 15, 386.

To correct the error caused by weighing in air, this value has been recalculated,[1] introducing a correction for vacuum, and the value H=6·2915 obtained. The corresponding ratio is

$$\mathrm{H : O = 1 : 15{\cdot}894 = 1{\cdot}0067 : 16},$$

a close approximation to the value accepted at the present day.

In 1842, in co-operation with Stas, Dumas[2] repeated the work of Berzelius and Dulong, employing many precautions to ensure the purity of the materials. Without applying any corrections, the value of the ratio found was

$$\mathrm{H : O = 1 : 15{\cdot}958 = 1{\cdot}0026 : 16}.$$

Subtracting the weight of the water formed from the air dissolved in the dilute sulphuric acid employed to generate the hydrogen,[3] Dumas obtained the ratio

$$\mathrm{H : O = 1 : 15{\cdot}988 = 1{\cdot}00012 : 16}.$$

The ratio of the two equivalents is 1 : 8, from which the ratio of the atomic weights in accordance with modern views is

$$\mathrm{H : O = 1 : 16}.$$

This value was for many years adopted as the atomic weight. Dumas's method has been subjected to searching criticism at various times. Berzelius[4] objected to it on the ground that the air employed to displace the hydrogen at the end of the experiment dissolved in the water formed, thus augmenting the value for the atomic weight of hydrogen, and diminishing that for oxygen. Melsens[5] pointed out that a similar error resulted from occlusion of hydrogen by the reduced copper, the weight of the oxygen being consequently too low. The chief source of error in Dumas's method was the presence of occluded gases in the cupric oxide employed, a point noted by Richards and Rogers.[6] During reduction these gases were given up by the oxide, the consequent loss of weight being reckoned as oxygen, whereas part of it was due to other occluded gas. The result, 15·96 to 15·99 (H=1), indicates too low a value for the atomic weight of hydrogen and too high for oxygen.

In 1842 Erdmann and Marchand[7] followed closely the lines marked out by the earlier work of Berzelius and Dulong, and especially that of Dumas. The precautions taken and the sources of error overlooked were similar to those characteristic of Dumas's work. In some of their experiments the copper oxide was prepared from metallic copper, and in others by heating copper nitrate. From one set of four experi-

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[1] Compare Clarke, *A Recalculation of the Atomic Weights*, 3rd ed. (Smithsonian Miscellaneous Collections, Washington, 1910, 54, No. 3).

[2] Dumas, *Ann. Chim. Phys.*, 1843, [3], 8, 189.

[3] Compare Sebelien, *Beiträge zur Geschichte der Atomgewichte*, Brunswick, 1884, 119.

[4] Berzelius, *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 3, 1183; compare Sebelien, *Beiträge zur Geschichte der Atomgewichte*, Brunswick, 1884, 120.

[5] Melsens, compare Sebelien, *ibid.*, 119.

[6] Richards and Rogers, *Amer. Chem. J.*, 1893, 15, 567.

[7] Erdmann and Marchand, *J. prakt. Chem.*, 1842, 26, 461.

ments the mean value obtained was 6·2742 (O=100), from which follows the ratio

$$\mathrm{H : O = 1 : 15{\cdot}938 = 1{\cdot}0039 : 16.}$$

In another set of experiments efforts were made to determine the amount of air occluded on the surface of the copper oxide and the metallic copper, but the results obtained varied between wide limits. Four experiments were then made, each tube and its contents being weighed in vacuum before and after the experiment. The mean of the four results obtained was 6·2459 (O=100), corresponding with the ratio

$$\mathrm{H : O = 1 : 16{\cdot}015 = 0{\cdot}9993 : 16,}$$

or, in round numbers, **1 : 16**, a value regarded by Erdmann and Marchand as fully supporting the work of Dumas.

From his examination of the relation of silver to silver nitrate and ammonium chloride, Stas[1] in 1860 found the value 1·005, the "atomic weight" (according to the nomenclature of the period) of oxygen being taken as 8. The corresponding ratio is

$$\mathrm{H : O = 1 : 15{\cdot}924 = 1{\cdot}005 : 16.}$$

Five years later, Stas[2] stated that, although there was no certainty as to the exact value of the ratio of the atomic weights of hydrogen and oxygen, he was convinced by the results of the various researches on the composition of water, on the density of hydrogen and of oxygen, and on the ratio of ammonium chloride and silver, that if the atomic weight of hydrogen were taken as unity, that of oxygen could not exceed 15·96, so that

$$\mathrm{H : O = 1 : 15{\cdot}96 = 1{\cdot}0025 : 16.}$$

This number differs from the accepted atomic weight more than the first result of Stas.

In the experiments of Thomsen,[3] published in 1870, the weight of water formed by the interaction of a known volume of hydrogen with cupric oxide and with oxygen was determined, the ratio calculated being

$$\mathrm{H : O = 1 : 15{\cdot}9605 = 1{\cdot}00247 : 16.}$$

Thomsen's result was vitiated by his employment of an inaccurate value given by Regnault for the weight of a litre of hydrogen, 0·08954 gram. Clarke[4] recalculated the ratio, employing the modern value for the weight of a litre of hydrogen (p. 47), his result being

$$\mathrm{H : O = 1 : 15{\cdot}91 = 1{\cdot}0057 : 16.}$$

The application of a new combined gravimetric and volumetric method to the determination of the ratio of silver to ammonium chloride and also to ammonium bromide furnished Stas[5] in 1882 with another

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[1] Stas, *Œuvres Complètes*, Brussels, 1894, 1, 417.

[2] Stas, *ibid.*, 442.

[3] Thomsen, *Ber.*, 1870, 3, 928.

[4] Clarke, *A Recalculation of the Atomic Weights*, 3rd ed. (Smithsonian Miscellaneous Collections, Washington, 1910, 54, No. 3).

[5] Stas, *Œuvres Complètes*, Brussels, 1894, 1, 812.

basis for ascertaining the atomic weight of hydrogen. His mean result, recalculated with the atomic weights Ag=107·880, Cl=35·457, Br=79·916, and N=14·010, gives the ratio

$$\mathbf{H : O = 1 : 15{\cdot}793 = 1{\cdot}0131 : 16.}$$

The value for hydrogen thus obtained was too high, in contrast with the low ratios previously published by Stas.

By oxidation of a known volume of hydrogen, van der Plaats[1] in 1886 obtained a mean value corresponding with the ratio

$$\mathbf{H : O = 1 : 15{\cdot}95 = 1{\cdot}003 : 16.}$$

The investigation of Cooke and Richards,[2] begun in 1882, marks the opening of a new era in the history of the determination of the atomic weight of hydrogen, and after the application of necessary corrections the results yield a value identical with that obtained by Morley (p. 41) in 1895. The hydrogen employed was prepared from zinc and hydrochloric acid, by electrolysis of dilute hydrochloric acid with a zinc-amalgam anode, or by the action of aluminium on potassium hydroxide; and so purified by contact with potassium hydroxide, calcium chloride, sulphuric acid, and phosphorus pentoxide that spectroscopic tests failed to reveal the presence of any extraneous substance. The hydrogen was weighed directly, and oxidized by copper oxide prepared from pure electrolytic copper, the water formed being absorbed by phosphorus pentoxide and weighed, all weighings being reduced to vacuum. It was noted by Mendeléeff,[3] and later by Agamennone,[4] that the volume of an evacuated glass globe is diminished by atmospheric pressure, and at the suggestion of Lord Rayleigh[5] a correction for this diminution was introduced by Cooke and Richards[6] into their calculation, the hydrogen having been weighed in an elongated, cylindrical glass flask. The ratio obtained was

$$\mathbf{H : O = 1 : 15{\cdot}869 = 1{\cdot}00826 : 16.}$$

An observation of Mendeléeff[7] that a change of pressure of one atmosphere produces a corresponding change in the volume of water, suggested to Brauner[8] the necessity for applying a further correction to the calculation of Cooke and Richards, to eliminate an error introduced by their method of determining the capacity of their glass vessel. The ratio as recalculated by Brauner is

$$\mathbf{H : O = 1 : 15{\cdot}879 = 1{\cdot}00762 : 16.}$$

The method employed by Keiser[9] in 1887 involved weighing hydro-

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[1] van der Plaats, *Ann. Phys. Chim.*, 1886, [6], 7, 529.

[2] Cooke and Richards, *Proc. Amer. Acad.*, 1887, 23, 149; *Amer. Chem. J.*, 1888, 10, 81.

[3] Mendeléeff, *The Elasticity of Gases* (Russian ed.), 1875, 1, §§ 85 and 86, p. 218.

[4] Agamennone and Bonetti, *Atti R. Accad. Lincei*, 1885, [4], 1, 665, 699.

[5] Rayleigh, *Proc. Roy. Soc.*, 1888, 43, 356.

[6] Cooke and Richards, *Proc. Amer. Acad.*, 1888, 23, 182; *Amer. Chem. J.*, 1888, 10, 191.

[7] Mendeléeff, *The Weight of a Litre of Air* (Russian ed.), 1894, 1, 57.

[8] Brauner, *Abegg and Auerbach's Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i., 20.

[9] Keiser, *Ber.*, 1887, 20, 2323.

gen after occlusion by palladium, and weighing the water produced by its combustion. The mean of three experiments gave the ratio

$$H : O = 1 : 15{\cdot}864 = 1{\cdot}0086 : 16.$$

In a later paper[1] Keiser published a new value for the ratio, based on the mean of ten experiments :

$$H : O = 1 : 15{\cdot}9514 = 1{\cdot}00307 : 16.$$

The process employed by Rayleigh[2] was an improved modification of that of Fourcroy, Vauquelin, and Séguin, weighed quantities of pure hydrogen and oxygen being mixed together, the mixture introduced into a eudiometer in successive steps, exploded electrically, and the residual gas analysed. By applying Rayleigh's correction for the diminution in volume of the evacuated glass flask, and consequent change in weight, the ratio obtained was

$$H : O = 1 : 15{\cdot}89 = 1{\cdot}0069 : 16.$$

Almost simultaneously with Rayleigh's paper appeared one by Noyes.[3] The noteworthy feature of Noyes's investigation was the simple form of apparatus employed, the interaction of the hydrogen and copper oxide and the weighing of the resulting water being carried out in the same vessel. In the experimental work minute care was taken to eliminate sources of error, but the results were adversely criticized by Johnson [4] as being too low. His objection was based on observations made during his own earlier work,[5] in which he noted the occlusion of hydrogen by reduced copper, a fact previously mentioned by Melsens (p. 37). Noyes considered that the precautions taken eliminated this source of error, and calculated from the mean of twenty-four experiments the ratio

$$H : O = 1 : 15{\cdot}897 = 1{\cdot}0065 : 16.$$

The principle of the method employed by Dittmar and Henderson [6] is similar to that of Berzelius and Dulong's method (p. 36), the weight of the hydrogen oxidized by the cupric oxide not being determined directly, but calculated indirectly from the quantity of water produced. Two series of experiments were made, and after completion of the first series the authors observed a source of error in their method, due to the contamination of the hydrogen by sulphur dioxide in consequence of reduction of the sulphuric acid used for drying. Dumas (p. 37) also noticed the same difficulty, and tried to prevent the reduction to sulphur dioxide by cooling the sulphuric-acid drier with ice. In their second series of experiments Dittmar and Henderson removed the sulphur dioxide by passing the dried hydrogen over fused potassium hydroxide. The ratio calculated from the mean result of both series of experiments was

$$H : O = 1 : 15{\cdot}865 = 1{\cdot}0085 : 16,$$

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[1] Keiser, *Amer. Chem. J.*, 1888, 10, 249.

[2] Rayleigh, *Proc. Roy. Soc.*, 1889, 45, 425.

[3] Noyes, *Amer. Chem. J.*, 1889, 11, 155; 1890, 12, 441.

[4] Johnson, *Chem. News*, 1889, 59, 272.

[5] Johnson, *Trans. Chem. Soc.*, 1879, 35, 232.

[6] Dittmar and Henderson, *Proc. Phil. Soc. Glasgow*, 1892, 22, 33; *Chem. News*, 1893, 67, 54, 68, 77, 90, 104, 115, 126, 139, 151, 164.

the mean value for the atomic weight in the first series being 1·00850, and in the second 1·00848.

Leduc,[1] in 1892, also synthesized water by oxidizing hydrogen with cupric oxide, the mean of two experiments giving the ratio

$$\mathbf{H:O=1:15{\cdot}88=1{\cdot}0075:16.}$$

The classical research of Morley,[2] a masterpiece of skill, ingenuity, and patience, carried out by a master of experimental method, consisted of four parts. In the first he determined the weight of a normal litre of oxygen; in the second the value of the same constant for hydrogen; in the third the relative proportions by volume in which, under normal conditions, hydrogen and oxygen unite to form water; and in the fourth the amount of water formed by the union of weighed quantities of oxygen and hydrogen. The methods of the first three parts are considered on pp. 47 to 49, since they are of a physico-chemical nature; the fourth part involves a gravimetric process, and is accordingly described here.

In Morley's experiments the weight of oxygen contained in two globes was determined, and a quantity of hydrogen was weighed while absorbed in palladium. The two gases were combined, and the weight of water produced was ascertained. The gases were brought into contact at two platinum jets enclosed in a small glass apparatus (fig. 2) previously exhausted and weighed. After the combination, the residual gas in the combustion chamber and the connecting tubes was extracted by means of a Toepler pump, measured, and analysed. The combustion chamber, the oxygen globes, and the palladium-hydrogen tube were again weighed. The difference between the original weights of oxygen and hydrogen and those of the gases analysed gave the quantities combined in the combustion chamber. The gain in weight of the combustion chamber corresponded with the amount of water produced, and should have been equal to the sum of the weights of the gases consumed. The observed difference was due to experimental errors, and indicated the degree of accuracy of the operation.

In most of the experiments the volume of hydrogen employed was between 42 and 43 litres, and the weight of water produced was about 34 grams. The proportion of uncombined gas varied between one six-hundredth and one ten-thousandth of the total amount. Each synthesis was complete in about one hour and a half.

The gases entered the combustion chamber at the jets *a*, and combination was initiated by sparking across the gap between the wires *ff*. The two tubes *bb* were filled with phosphoric anhydride kept in place by asbestos, the oxide serving to prevent the escape of any traces of water formed. The joints *cc* were ground to fit corresponding joints connecting the apparatus through other phosphoric-anhydride tubes to the sources of oxygen and hydrogen. The tubes *bb* were sealed at *d* and *e*, notches indicating the points of subsequent fracture. The hooks at the ends of the apparatus facilitated the hydrostatic weighing for determining its volume.

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[1] Leduc, *Compt. rend.*, 1892, 115, 41; *Ann. Chim. Phys.*, 1898, [7], 15, 48.

[2] Morley, *Smithsonian Contributions to Knowledge*, Washington, 1895, 29, No. 980. An account of the gravimetric work is given in *Amer. Chem. J.*, 1895, 17, 269, and a description of the density measurements in *Zeitsch. physikal. Chem.*, 1895, 17, 87. Compare also Freund, *The Study of Chemical Composition* (Cambridge University Press, 1904).

The whole vessel was exhausted to one ten-thousandth of an atmosphere, sealed off at *g*, and weighed against a similar counterpoise. The points *d* and *e* were then broken off, and the tubes *bb* connected to the oxygen and hydrogen supplies through a " manipulator " for the admission of the gases as required, and for continuous observation of their pressures and of the pressure in the combustion chamber. This device also precluded the possibility of communication between the sources of oxygen and hydrogen.

During the combustion, the apparatus was immersed in a bath of cold water. The lower part of the combustion chamber was ultimately cooled to —18° C., the uncombined gases extracted by the pump, and the apparatus closed by fusion at *hh*. It was then dried and re-weighed with the pieces detached by fusion or fracture.

The hydrogen was prepared by the electrolysis of dilute sulphuric acid, and the oxygen by heating potassium chlorate. Each gas was purified and dried carefully. The phosphoric anhydride was proved to have been without action on the oxygen, and the freedom from moisture of the hydrogen evolved from the palladium was also demonstrated. The residual gas sometimes contained traces of nitrogen, derived from the oxygen, and due allowance was made for this impurity. A similar correction was applied for traces of carbon dioxide formed by oxidation of a minute proportion of organic matter in the asbestos packing of the tubes *bb*.

For twelve experiments the ratio of the hydrogen to the oxygen employed gave the mean value

$$H : O = 1 : 15{\cdot}8792 \pm 0{\cdot}00032,$$

and for eleven experiments that of the weight of hydrogen used to the weight of water produced gave the mean value

$$H : O = 1 : 15{\cdot}8785 \pm 0{\cdot}00066.$$

Morley chose 15·8790 as the mean of these two ratios, which is also their " weighted mean." He concluded that the atomic weight of oxygen compared with hydrogen as unity approximates very closely to O = 15·8790. The value of the ratio calculated from Morley's results is therefore

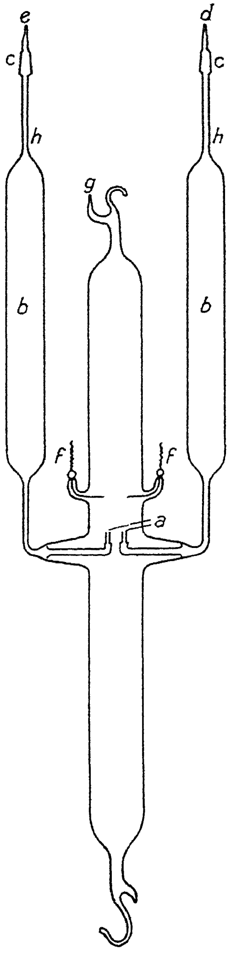

FIG. 2.—The atomic weight of hydrogen. Morley's apparatus for producing and weighing the water.

$$\mathbf{H : O = 1 : 15{\cdot}8790 = 1{\cdot}00762 : 16.}$$

In 1894 Thomsen[1] employed an indirect method for determining the atomic weight of hydrogen, involving a knowledge of the atomic weights of chlorine and nitrogen. The method was based on the direct com-

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[1] Thomsen, *Zeitsch. physikal. Chem.*, 1894, 13, 398.

bination of weighed quantities of ammonia and hydrogen chloride when passed together into water until the solution was almost neutral, the slight excess of ammonia being determined by titration. The result obtained does not accord with that of Morley.

Thomsen's second method[1] of investigation embodied a novel principle. Weighed quantities of aluminium were brought into contact with a solution of potassium hydroxide, and the evolved hydrogen dried and weighed, the results giving the value of the ratio H : Al. Another series of experiments was made, the evolved hydrogen being combined with oxygen, and the water formed weighed, the data obtained being employed to calculate the ratio O : Al. From the results of the two sets of experiments, the ratio of the atomic weights was calculated as

$$\mathbf{H : O = 1 : 15{\cdot}869 = 1{\cdot}00826 : 16.}$$

In 1897 Thomsen[2] revised the results obtained in this research, introducing a correction for the reduction of volume accompanying the solution of the aluminium in the potassium-hydroxide solution. The amended ratio is

$$\mathbf{H : O = 1 : 15{\cdot}8685 = 1{\cdot}00829 : 16.}$$

In 1898 Keiser[3] caused a known weight of hydrogen occluded in palladium to combine with oxygen, and determined the weight of the resulting water, the whole process being carried out in one apparatus. The mean of four experiments gave the ratio

$$\mathbf{H : O = 1 : 15{\cdot}880 = 1{\cdot}00756 : 16,}$$

a close approximation to Morley's value (p. 42).

The principle of the investigation carried out by Noyes[4] in 1907 was similar to that adopted by him in the research of 1889–1890 (p. 40), hydrogen being oxidized by copper oxide, and the water formed being weighed in the oxidation apparatus. Five series of experiments were made, but the results of the first were not employed in the final calculation, being vitiated by retention of water in the copper oxide. The mode of procedure was modified for each series of experiments, the mean of twenty-five observations giving the ratio

$$\mathbf{H : O = 1 : 15{\cdot}8751 = 1{\cdot}00787 : 16.}$$

For convenience in comparison, the foregoing results are grouped in the following table:

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[1] Thomsen, *Zeitsch. anorg. Chem.*, 1896, 11, 14.
[2] Thomsen, *ibid.*, 1897, 15, 447.
[3] Keiser, *Amer. Chem. J.*, 1898, 20, 733.
[4] Noyes, *J. Amer. Chem. Soc.*, 1907, 29, 1718; 1908, 30, 4.

[TABLE.

GRAVIMETRIC DETERMINATIONS OF THE ATOMIC WEIGHT OF HYDROGEN.

Investigator.	Year of Publication.	Atomic Weight of Hydrogen (Oxygen = 16).
Berzelius and Dulong	1820	0·99804
* ,, ,, ,,		1·0067
Dumas	1843	1·00012
Erdmann and Marchand	1842	1·0039
,, ,, ,,	1842	0·9993
Stas	1860	1·005
,,	1865	1·0025
Thomsen	1870	1·00247
* ,,	..	1·0057
Stas (calculated with modern atomic weights)	1882	1·0131
van der Plaats	1886	1·003
Cooke and Richards	1888	1·00826
* ,, ,, ,,	..	1·00762
Keiser	1887	1·0086
,,	1888	1·00307
Rayleigh	1889	1·0069
Noyes	1889–1890	1·0065
Dittmar and Henderson	1892	1·0085
Leduc	1892	1·0075
Morley	1895	**1·00762**
Thomsen	1896	1·00826
,,	1897	1·00829
Keiser	1898	1·00756
Noyes	1907	**1·00787**

* Recalculated.

Of those results, those of Noyes and Morley merit most confidence.

II. Physico-chemical Methods.

The physico-chemical methods consist essentially in determinations of the relative densities of hydrogen and oxygen, and of their combining volumes. From these data the weight of oxygen combining with unit weight of hydrogen can be calculated readily. Towards the close of the eighteenth century and early in the nineteenth century, several crude attempts were made to determine the atomic weight of hydrogen. In 1788 Monge, Lavoisier, and Meusnier[1] found that 12 volumes of oxygen combine with 22·924 volumes of hydrogen, or in weight proportions 1 part of hydrogen with 6·61 parts of oxygen. The corresponding ratio according to the modern system is

$$H : O = 1 : 13{\cdot}22.$$

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[1] Monge, Lavoisier, and Meusnier, *Crell's Annalen*, 1788, I, 454.

Three years later Fourcroy, Vauquelin, and Séguin[1] observed during a prolonged experiment that 12570·942 cubic inches of oxygen and 26017·968 cubic inches of hydrogen, reduced to 14° C. and 28 inches of mercury, combined to form 7249 grains of water. By direct weighing, a cubic inch of water was found to weigh 0·4925 grain, and of hydrogen 0·040452 grain. The combined weights of the two gases exceeded the weight of the water formed by 0·277 grain. It follows from the results that 1 part by weight of hydrogen combines with 6·17 parts of oxygen, giving the ratio

$$H : O = 1 : 12{\cdot}34.$$

In 1803 John Dalton fixed the atomic weight of hydrogen as unity, and gave the ratio of the atomic weights of hydrogen and oxygen acccording to the custom of the day as $H : O = 1 : 5{\cdot}5$, a value far wide of the mark. In view of the statements of Gay-Lussac and Humboldt that water was formed by the combination of 2 volumes of hydrogen with 1 volume of oxygen, and those of Cavendish and Lavoisier that oxygen was fourteen times as heavy as hydrogen, Dalton in 1808 substituted the ratio

$$H : O = 1 : 7.$$

The first calculation with any approach to accuracy was that of Wollaston[2] in 1814. From the combining volumes of hydrogen and oxygen as given by Gay-Lussac and Humboldt in 1805, coupled with Biot and Arago's determination of the densities of the two gases, Wollaston calculated the atomic weight of hydrogen to be 6·64 ($O = 100$). Expressed in modern terms the ratio is

$$H : O = 1 : 15{\cdot}09 = 1{\cdot}06 : 16.$$

Although the hypothesis of Avogadro and Ampère as to the relation between the densities and molecular weights of gases was propounded in 1811, half a century elapsed before its acceptance by the chemical world. Gay-Lussac's Law of Volumes, enunciated in 1808,[3] led Berzelius to the assumption that the densities of elementary gases are proportional to their atomic weights. Acting on this assumption, he and Dulong in 1821 determined the densities of hydrogen and oxygen, the results being referred to air as unity. For hydrogen the density was found to be 0·0688, and for oxygen 1·1026, the ratio being

$$H : O = 1 : 15{\cdot}9538 = 0{\cdot}9984 : 16.$$

This experiment gives as the atomic weight of hydrogen 0·9984 ($O = 16$), a result in good accord with that obtained by the same investigators by gravimetric methods (p. 36).

Subsequent research proved that Gay-Lussac's Law of Combining Volumes is not exact, but only an approximation,[4] so that oxygen and hydrogen do not behave as perfect gases. For an accurate calculation of the relative values for the atomic weights of hydrogen and oxygen, it is therefore essential to know not only the relative densities of the

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[1] Fourcroy, Vauquelin, and Séguin, *Ann. chim.*, 1791, [1], viii., 230; Séguin, *ibid.*, ix., 50; compare Sebelien, *Beiträge zur Geschichte der Atomgewichte*, Brunswick, 1884, 115.

[2] Wollaston, *Phil. Trans.*, 1814, 104, 20.

[3] Compare this series, Vol. I., 14.

[4] Compare *ibid.*, 15.

two gases, but also the exact ratio of their combining volumes. It will be convenient to consider each of these problems separately, and subsequently to calculate the relative atomic weights of the two elements by combining the results.

(a) *The Relative Densities of Hydrogen and Oxygen at N.T.P.*

In 1841 Dumas and Boussingault[1] gave for the density of hydrogen the mean value 0·0693, and for oxygen 1·1057 (air=1). The ratio of these densities is

$$D_H : D_O = 1 : 15{\cdot}9628 = 1{\cdot}0029 : 16.$$

In his work on the density of gases, Regnault[2] balanced the glass globe in which the gas was weighed against a second globe of similar capacity, and as nearly as possible of the same weight. The mean densities found were 0·069263 for hydrogen and 1·105633 for oxygen (air=1), the ratio of the densities being

$$D_H : D_O = 1 : 15{\cdot}9628 = 1{\cdot}0023 : 16.$$

A source of error overlooked by Regnault was first observed by Mendeléeff in 1875. When a glass globe is evacuated, the pressure of the atmosphere causes a slight contraction in volume,[3] so that, when evacuated and weighed in air, it displaces a smaller quantity of air than when weighed full of hydrogen or any other gas. The weight of hydrogen determined by difference is accordingly too low. The discrepancy is small, but not negligible, for when the two gases differ greatly in density the error introduced by omitting the correction is very considerable.

The necessary correction to Regnault's work was made by Crafts,[4] and yielded for the density of hydrogen the value 0·06949, and for oxygen 1·10562, the ratio of the densities being

$$D_H : D_O = 1 : 15{\cdot}9105 = 1{\cdot}0056 : 16.$$

In 1888 Rayleigh[5] weighed hydrogen and oxygen in the same glass globe and corrected for the reduction in the volume of the globe, the ratio of the two densities being

$$D_H : D_O = 1 : 15{\cdot}884 = 1{\cdot}0073 : 16.$$

The mean of three determinations of the density of hydrogen made by Cooke[6] is 0·06958 (air=1), and in conjunction with Crafts's value for the density of oxygen gives the ratio

$$D_H : D_O = 1 : 15{\cdot}890 = 1{\cdot}0069 : 16.$$

In 1891 Leduc[7] adopted Regnault's method, and made three determinations of the density of hydrogen, and the same number of the

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[1] Dumas and Boussingault, *Compt. rend.*, 1841, 12, 1005.

[2] Regnault, *Compt. rend.*, 1845, 20, 975; *Relation des Expériences*, Paris, 1847, 1, 136.

[3] On the influence of the shape of the vessels on the pressure exerted by equal volumes of gases, compare Noyes and Johnson, *J. Amer. Chem. Soc.*, 1916, 38, 1017.

[4] Crafts, *Compt. rend.*, 1888, 106, 1662.

[5] Rayleigh, *Proc. Roy. Soc.*, 1888, 43, 356.

[6] Cooke, *Proc. Amer. Acad.*, 1889, 24, 202.

[7] Leduc, *Compt. rend.*, 1891, 113, 186; *Ann. Chim. Phys.*, 1898, [7], 15, 29.

density of oxygen, the values obtained being 0·06948 and 1·10506. The ratio of these densities is

$$D_H : D_O = 1 : 15{\cdot}905 = 1{\cdot}0060 : 16.$$

In 1892 Rayleigh[1] employed hydrogen and oxygen prepared by electrolysis. As the mean of nineteen experiments with hydrogen and eleven with oxygen, he found the ratio of the densities to be

$$D_H : D_O = 1 : 15{\cdot}882 = 1{\cdot}00743 : 16.$$

In 1893 he determined the densities of the two gases relative to air, the ratio being

$$D_H : D_O = 1 : 15{\cdot}8818 = 1{\cdot}00744 : 16,$$

a result almost identical with that found by him in the preceding year.

In 1895 Morley[2] published an account of his researches. The gravimetric results of his investigations have already been considered on p. 41; the physico-chemical sections are briefly summarized here. The weight of a litre of oxygen at 0° C. and 760 mm., reduced to sea-level in the latitude of 45°, was determined by three series of experiments involving nine, fifteen, and seventeen observations respectively, the mean value for each series being

(1) $1{\cdot}42879 \pm 0{\cdot}000051$ grams.
(2) $1{\cdot}42887 \pm 0{\cdot}000048$ grams.
(3) $1{\cdot}42917 \pm 0{\cdot}000048$ grams.

The mean value of the three series is

$$1{\cdot}42900 \pm 0{\cdot}000034 \text{ grams.}$$

The oxygen was prepared from potassium chlorate.

The weight of a litre of hydrogen at 0° C. and 760 mm., reduced to sea-level in the latitude of 45°, was determined by five series of experiments, the number of observations being fifteen, nineteen, eight, six, and eleven respectively. The value obtained for each series was:

(1) $0{\cdot}089938 \pm 0{\cdot}000007$ gram.
(2) $0{\cdot}089970 \pm 0{\cdot}000011$ gram.
(3) $0{\cdot}089886 \pm 0{\cdot}0000049$ gram.
(4) $0{\cdot}089880 \pm 0{\cdot}0000088$ gram.
(5) $0{\cdot}089866 \pm 0{\cdot}0000034$ gram.

The mean value of all the series is 0·089897, but Morley considered the results of the first and second series to be too high, owing to the presence of mercury-vapour in the glass globe. This source of error was eliminated in the other three series, the mean value calculated from them being $0{\cdot}089873 \pm 0{\cdot}0000027$ gram.

These results give for the mean ratio of the densities of the two gases

$$D_H : D_O = 1 : 15{\cdot}9002 = 1{\cdot}00628 : 16.$$

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[1] Rayleigh, *Proc. Roy. Soc.*, 1892, **50**, 448; 1893, **53**, 144; 1900, **66**, 334.

[2] Morley, *Smithsonian Contributions to Knowledge*, Washington, 1895, **29**, No. 980, pp. 1–94 and 110–114; *Phil. Mag.*, 1904, [6], **7**, 667; compare Guye, *J. Chim. phys.*, 1907, **5**, 215.

In 1897 Thomsen[1] employed the aluminium method already cited (p. 43), and determined the weight of a normal litre of hydrogen to be 0·089947±0·000012 gram, and the corresponding weight of oxygen, prepared from potassium chlorate, to be 1·42906±0·00004 grams. The ratio of the densities is

$$D_H : D_O = 1 : 15 \cdot 8878 = 1 \cdot 00730 : 16.$$

For the sake of ready comparison, the foregoing results are grouped together in tabular form.

DETERMINATIONS OF THE RELATIVE DENSITIES OF HYDROGEN AND OXYGEN AT N.T.P.

Investigator.	Year of Publication.	Density of Oxygen (Hydrogen = 1).	Density of Hydrogen (Oxygen = 16).
Berzelius and Dulong . .	1821	15·9538	0·9984
Dumas and Boussingault .	1841	15·9628	1·0029
Regnault	1845	15·9628	1·0023
,, (corrected by Crafts)	1888	15·9105	1·0056
Rayleigh	1888	15·884	1·0073
Cooke	1889	15·890	1·0069
Leduc	1891	15·905	1·0060
Rayleigh	1892	15·882	1·00743
,, ...	1893	15·8818	1·00744
Morley	1895	15·9002	1·00628
Thomsen	1897	15·8878	1·00730

(b) *The Ratio of the Combining Volumes of Hydrogen and Oxygen at N.T.P.*

In 1892 Leduc[2] gave the ratio of the combining volumes of hydrogen and oxygen as

$$V_H : V_O = 2 \cdot 0037 : 1.$$

Morley has shown this result to be somewhat high on account of the neglect of certain errors.

In 1893 Scott[3] found the value

$$V_H : V_O = 2 \cdot 00245 : 1$$

at the temperature of the laboratory, the ratio as recalculated for N.T.P. being

$$V_H : V_O = 2 \cdot 00285 : 1.$$

In 1893 Morley determined the ratio by a eudiometric method,[4] but in 1895 he discarded the results obtained, when publishing an investigation

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[1] Thomsen, *Zeitsch. anorg. Chem.*, 1897, 12, 4.

[2] Leduc, *Compt. rend.*, 1892, 115, 311. Later, Leduc gave the value 2·0034, and criticized Morley's figures (*Ann. Chim. Phys.*, 1898, [7], 15, 49).

[3] Scott, *Proc. Roy. Soc.*, 1893, 53, 130; *Phil. Trans.*, 1893, 184, 543.

[4] Morley, *Amer. J. Sci.*, 1893, [3], 46, 220, 276.

of the ratio by another method.[1] The weight of a normal litre of detonating gas, prepared at 0° C. by electrolysis of an aqueous solution of sodium hydroxide formed by dissolving the metal in water, was determined to be 0·535510 gram. From this number, and the corresponding values for hydrogen and oxygen, the ratio of the combining volumes of hydrogen and oxygen was calculated, allowance being made for the slight excess of hydrogen always present after the explosion of detonating gas prepared at 0° C. At N.T.P. the ratio found was

$$V_H : V_O = 2{\cdot}00269 : 1.$$

Employing another method, Rayleigh[2] found the value

$$V_H : V_O = 2{\cdot}0026 : 1.$$

In 1916 a very accurate determination of the ratio was made by Burt and Edgar.[3] The hydrogen was prepared by the electrolysis of barium hydroxide, and the oxygen either by the same method or by heating potassium permanganate. The measurements were made at N.T.P., and a slight excess of hydrogen was employed. Five series of experiments gave the volume ratio

$$V_H : V_O = 2{\cdot}00288 : 1.$$

(c) *The Atomic Weight Ratio.*

Of the foregoing data, the results of Morley and of Burt and Edgar are the most trustworthy. Combining Morley's ratio for the relative densities of the gases with that for their combining volumes, the atomic weight of hydrogen (O=16) is given by the expression

$$\text{Atomic weight of hydrogen} = \frac{1{\cdot}00628 \times 2{\cdot}00269}{2}$$

$$= 1{\cdot}00763.$$

This result approximates closely to that obtained by Morley in his gravimetric researches (p. 42).

If Morley's values for the weight of 1 litre of hydrogen (0·089873 gram) and of oxygen (1·42900 gram) are employed, Burt and Edgar's ratio gives for the atomic weight of hydrogen

$$1{\cdot}00772.$$

Adopting Germann's[4] more probable value for oxygen, 1·42905, the atomic weight of hydrogen becomes

$$1{\cdot}00769,$$

which is probably the most accurate result hitherto obtained.

Other methods of calculation yield figures supporting those of Morley. They utilize the densities and other physical constants of hydrogen and oxygen, and are based on the purely physical methods

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[1] Morley, *Smithsonian Contributions to Knowledge*, 1895, 29, No. 980.

[2] Rayleigh, *Proc. Roy. Soc.*, 1904, [A], 73, 153.

[3] Burt and Edgar, *Phil. Trans.*, 1916, [A], 216, 393.

[4] Germann, *J. Chim. phys.*, 1914, 12, 66.

of "limiting densities," "critical constants," and "molecular volumes."[1] The results are given in the table, the calculations having been revised by employing throughout Morley's ratio for the densities of hydrogen and oxygen.[2]

Method.	Authority.	Year.	Atomic Weight of Hydrogen (O=16).
Density limits . .	Leduc and Sacerdote[3]	1897	1·00775
" " . .	Berthelot[4]	1898	1·00768
" " . .	Rayleigh[5]	1905	1·00775
" " . .	Jacquerod and Scheuer[6]	1905	1·00777
Critical constants .	Guye[7]	1904	1·0077
" " .	Berthelot[4]	1907	1·0076
Molecular volumes .	Leduc[8]	1909	1·00765

Conclusion.

Of the results recorded in the preceding account, the most important are:

(1) Morley's gravimetric result (p. 42): H=1·00762.
(2) Morley's physico-chemical result (p. 49): H=1·00763.
(3) Noyes's gravimetric result (p. 43): H=1·00787.
(4) Burt and Edgar's physico-chemical result (p. 49):[9] H=1·00772.

The remarkably close similarity between the two results obtained by Morley is noteworthy. The fact that Burt and Edgar's value approximates very closely to the mean of the other three, **H=1·00775**, is strong evidence in favour of its accuracy. It is also worth while to point out that, if Morley's value for the atomic weight of hydrogen is accepted, the careful syntheses of hydrogen chloride effected by Edgar,[10] and the volumetric analyses of the same compound by Gray and Burt,[11] yield values for the atomic weight of chlorine in good agreement with the

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[1] Compare this series, Vol. I., Chap. IV.; Guye, *J. Chim. phys.*, 1908, 6, 769; Little, *Science Progress*, 1913, 7, 504.

[2] For a critical discussion of these calculations, compare Jones, *J. Amer. Chem. Soc.*, 1910, 32, 513.

[3] Leduc and Sacerdote, *Compt. rend.*, 1897, 125, 297; Leduc, *Ann. Chim. Phys.*, 1898, [7], 15, 5; *J. de Physique*, 1898, [3], 7, 5.

[4] Berthelot, *Compt. rend.*, 1898, 126, 954, 1030, 1501; 1907, 144, 76, 194, 269, 352; 145, 317; *J. de Physique*, 1899, [3], 8, 263.

[5] Rayleigh, *Phil. Trans.*, 1905, [A], 204, 351.

[6] Jacquerod and Scheuer, *Compt. rend.*, 1905, 140, 1384; *Mém. Soc. phys. nat.*, 1908, 35, 659.

[7] Guye, *Compt. rend.*, 1904, 138, 1213; *J. Chim. phys.*, 1905, 3, 321.

[8] Leduc, *Compt. rend.*, 1909, 148, 407, 548; *Ann. Chim. Phys.*, 1910, [8], 19, 441.

[9] The work of Burt and Edgar is discussed in the report for 1919–20 of the International Committee on Atomic Weights, *Trans. Chem. Soc.*, 1919, 115, 880. Taking into account the researches of Morley, Noyes, and others upon the synthesis and analysis of water, the Committee considers the most probable general mean for the atomic weight of hydrogen to be 1·0078, and the approximate value 1·008 to be most suitable for ordinary use.

[10] Edgar, *Phil. Trans.*, 1908, [A], 209, 1.

[11] Gray and Burt, *Trans. Chem. Soc.*, 1909, 95, 1633.

results of modern gravimetric analysis. If Noyes's value for hydrogen is adopted in the calculations, high values for chlorine are obtained.[1]

In the opinion of Noyes, the most trustworthy value is the mean between his own and Morley's gravimetric result, H=1·00774, and this view is strongly supported by the work of Burt and Edgar, and by calculations made by the method of limiting densities.

In 1898 the German Committee on Atomic Weights selected 1·01 as the atomic weight of hydrogen.[2] In 1903 the International Committee on Atomic Weights altered[3] the number to

H=1·008,

a value still recognized at the present time. In this series of text-books the value

H=1·00762

has been selected for the calculation of atomic weights.

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[1] Sources of error in atomic-weight determinations are considered in several papers by Guye and his collaborators (*J. Chim. phys.*, 1916, 14, 25, 195, 204; 1917, 15, 60, 208, 360, 405; 1918, 16, 46).

[2] Report of the German Committee on Atomic Weights, *Ber.*, 1898, 31, 2761; compare *ibid.*, 1900, 33, 1847.

[3] Report of the International Committee on Atomic Weights, *Proc. Chem. Soc.*, 1903, 19, 2.

CHAPTER III.

LITHIUM.

Symbol, Li. Atomic weight, 6·94 (O=16).

Occurrence.—Many silicates contain traces of lithium, usually associated with large proportions of sodium and potassium. Lithium compounds are mainly derived from *lepidolite* or *lithia-mica*, a double fluosilicate of aluminium and an alkali-metal, containing 0·8–2·7 per cent. of lithium; and *petalite*, a double silicate of aluminium and lithium with an admixture of sodium, containing 2 per cent. of lithium.

Other lithium-bearing minerals are *spodumene*, a double silicate of lithium and aluminium, containing about 3·8 per cent. of lithium; *triphyllite*, a complex phosphate of lithium, iron, and manganese, with about 2·2 per cent. of lithium; and *amblygonite* and *montebrasite*, fluophosphates of lithium and aluminium, with about 2·35 per cent. of lithium, both rare minerals.

Lithium has been detected by the spectroscope in many other minerals. It is found in mineral waters, in the ashes of plants such as cocoa, tobacco, sugar-cane, and sea-weed, and traces of its sulphate have been detected in the salts of the Vesuvian fumaroles.[1] Its presence in the sun's atmosphere was established by Lockyer.[2]

History.—Lithium was identified as an independent element in 1817 by Arfvedson,[3] who noted its presence in many minerals and the similarity of its compounds to those of potassium and sodium, but failed to isolate it. Fruitless attempts to obtain the free metal were also made by Davy, Gmelin, and Kralovansky, but in 1855 Bunsen and Matthiessen[4] prepared it by electrolysis of the fused chloride. Its name is derived from the Greek λίθος, a stone.

Preparation.—Several methods[5] have been employed to isolate metallic lithium from its salts. The silicates yield lithium oxide, carbonate, or sulphate by ignition with the corresponding calcium or barium compound.[6] The solution obtained by extraction with water is freed from heavy metals by precipitation, and the lithium and other alkali-metal salts present converted into carbonates.[7] The methods employed in the separation of the mixed carbonates depend on the comparative insolubility of lithium carbonate in water, and on the

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[1] Luise, *Gazzetta*, 1919, 49, ii., 328.

[2] Lockyer, *Compt. rend.*, 1878, 86, 318.

[3] Arfvedson, *Schweigger's J.*, 1817, 22, 93; 24, 214; *Ann. Chim. Phys.*, 1819, [2], 10, 82.

[4] Bunsen, *Annalen*, 1855, 94, 107.

[5] Compare Hackspill, *Compt. rend.*, 1905, 141, 106; *Bull. Soc. chim.*, 1911, [4], 9, 446.

[6] Compare Troost, *Compt. rend.*, 1856, 43, 921.

[7] Compare Wadman, *German Patent*, 1909, No. 207845.

relatively high solubility of its chloride in alcohol or a mixture of alcohol and ether. With triphyllite fusion is unnecessary, the mineral being soluble in acids.

The method most generally applied to the isolation of lithium is based on the decomposition of the fused chloride by electrolysis, modifications in practical details having been introduced by various experimenters. Bunsen and Matthiessen[1] passed the current from six Bunsen cells through the fused chloride contained in a porcelain crucible, with a carbon rod as anode and an iron wire as cathode. Troost employed a similar method. Guntz[2] mixed lithium chloride with potassium chloride, but his product contained 1–3 per cent. of potassium. His current was 10 ampères at 20 volts, with a cathode of iron wire 3–4 mm. in diameter. Borchers[3] added chlorides of other alkali-metals and alkaline-earth-metals and a small proportion of ammonium chloride, and employed a current density of 10 ampères per 100 sq. cm. Tucker[4] electrolyzed the chloride without the addition of other material.

To avoid contamination of the lithium with alkali-metals, Ruff and Johannsen[5] employed a mixture of lithium bromide with 10–15 per cent. of lithium chloride, which melts about 520° C. The Muthmann copper electrolytic cell was used, with two iron wires of 4 mm. diameter as anode and a current of 100 ampères at 10 volts.[6]

Direct electrolytic preparation of lithium from aqueous solutions of its salts is not feasible, but can be effected when the salts are dissolved in organic solvents such as acetone and pyridine.[7] A solution of lithium chloride in pyridine was electrolyzed by Kahlenberg[8] with a cathode of sheet platinum or iron wire and a current density of 0·2–0·3 ampère per 100 sq. cm. Patten and Mott[9] found that amyl alcohol is a suitable solvent, provided the current density is sufficiently high to ensure the velocity of deposition of the metal being greater than that of its solution in the alcohol.

Winkler's[10] suggestion to reduce the hydroxide with magnesium has been proved practicable by Warren.[11] The reaction is very energetic.

Physical Properties.—Lithium is a white metal with silver-like lustre. It remains untarnished in dry air,[12] but a freshly cut surface develops a yellow tinge if moisture is present. In extremely thin layers it is translucent, the transmitted light having a dark, reddish-brown colour.[13] It is harder than cæsium, rubidium, sodium, or potassium, but softer than lead, the degree of hardness on Rydberg's[14] scale being 0·6. In ductility it resembles lead, and can be drawn into wire or rolled into thin

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[1] Bunsen, *Annalen*, 1855, 94, 107.

[2] Guntz, *Compt. rend.*, 1893, 117, 732.

[3] Borchers, *Zeitsch. Elektrochem.*, 1894, 1, 361; 1895, 2, 39.

[4] Tucker, *J. Amer. Chem. Soc.*, 1902, 24, 1024.

[5] Ruff and Johannsen, *Zeitsch. Elektrochem.*, 1906, 12, 186.

[6] Compare Guntz, *L'Industria Chimica*, 1907, 7, 284.

[7] von Laszczynski, *Ber.*, 1894, 27, 2285; *Zeitsch. Elektrochem.*, 1895, 2, 55; von Laszczynski and von Gorski, *ibid.*, 1898, 4, 290.

[8] Kahlenberg, *J. Physical Chem.*, 1899, 3, 601.

[9] Patten and Mott, *ibid.*, 1904, 8, 153.

[10] Winkler, *Ber.*, 1890, 23, 46.

[11] Warren, *Chem. News*, 1896, 74, 6.

[12] Dafert and Miklauz, *Monatsh.*, 1910, 31, 981.

[13] Dudley, *Amer. Chem. J.*, 1892, 14, 185.

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

sheets. It can be welded at the ordinary temperature. It is the lightest of the normally solid elements, Richards and Brink's[1] value for the density at 20° C. being 0·534. An earlier determination by Bunsen and Matthiessen[2] gives the value 0·59. The atomic volume, 13, is lower than those of the other alkali-metals.

According to Kahlbaum,[3] and also Guertler and Pirani,[4] the melting-point of lithium is 186° C., but Masing and Tammann,[5] and also Schukoffsky,[6] give 179° C. In vacuum it volatilizes at red heat. It has the highest specific heat of any element, Regnault's[7] value for the range 26·5° to 99·77° C. being 0·9408. The atomic heat is 6·6.

References to work on the electric conductivity and resistance of lithium are appended.[8]

Both the metal and its compounds colour the flame carmine-red. The spectrum is characterized by a bright red line and a fainter orange line.

Chemical Properties.—Although less reactive than potassium and sodium, lithium is analogous in chemical character to those metals. At ordinary temperature it is unaffected by dry oxygen or air, but the presence of moisture causes oxidation.[9] At 200° C. it ignites in air or oxygen, burning with a bright white light, and forming the monoxide and a small proportion of the peroxide. In nitrogen it is converted without application of heat into the nitride,[9] so that this substance is probably a product of its combustion in air. Its affinity for nitrogen has been applied in the isolation of argon from the atmosphere.[10] This reaction exemplifies the similarity between lithium and calcium, a resemblance also manifested in the direct combination of lithium with chlorine, bromine, iodine, and sulphur-vapour. When heated in hydrogen, lithium yields a hydride. In its compounds the metal invariably exhibits univalency.

Experiments on photographic plates with lithium and its salts produced no effect, indicating a lack of radioactivity.[11]

Lithium Ion.—The colourless univalent lithium ion, $Li^{\cdot}$, is characterized by the formation of salts of slight solubility with the anions of carbonic, hydrofluoric, and phosphoric acid, a distinction from the ions of the other alkali-metals, and an indication of the smaller electroaffinity of the lithium ion.[12] The comparatively low electroaffinity corresponds with that of strontium, and is associated with the power of the lithium salts to form complexes with ammonia in aqueous solution, and with water to yield various crystalline hydrates. In solution in

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[1] Richards and Brink, *J. Amer. Chem. Soc.*, 1907, 29, 117.

[2] Bunsen, *Annalen*, 1855, 94, 107.

[3] Kahlbaum, *Zeitsch. anorg. Chem.*, 1900, 23, 220.

[4] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

[5] Masing and Tammann, *Zeitsch. anorg. Chem.*, 1907, 67, 183.

[6] Schukoffsky, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 708; *Zeitsch. anorg. Chem.*, 1911, 71, 403.

[7] Regnault, *Ann. Chim. Phys.*, 1861, [3], 63, 11.

[8] Bernini, *Landolt, Börnstein, and Roth's Tabellen*, 4th ed., Berlin, 1912, 1073; Benoit, *ibid.*, 1082; Guntz and Broniewski, *Compt. rend.*, 1908, 147, 1474; Meissner, *Zeitsch. Physik*, 1920, 2, 373.

[9] Dafert and Miklauz, *Monatsh.*, 1910, 31, 981.

[10] Guntz, *Compt. rend.*, 1895, 120, 777.

[11] Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576; Henriot, *Le Radium*, 1910, 7, 40; *Compt. rend.*, 1911, 152, 851; Büchner, *Le Radium*, 1912, 9, 259.

[12] Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, 20, 496.

water and in various organic solvents, such as methyl and ethyl alcohol,[1] the lithium salts are highly dissociated. The electric conductivity of their dilute aqueous solutions has been investigated by Ostwald,[2] Franke,[3] and Kohlrausch and Maltby.[4] The electric conductivity of the lithium ion at 18° C. is 33·4. References to other work on the properties of lithium salt-solutions are appended.[5]

Transmutation of Copper into Lithium.—The transmutation of the baser metals into gold was one of the chief aims of the alchemists. Although their labours proved fruitless as regards their immediate object, they laid the foundation of that scientific chemistry to which the modern industrial world owes a deep debt of obligation. In 1818 Faraday contemplated as a possibility the transmutation of the metals, for he said in a lecture delivered before the City Philosophical Society: "To decompose the metals, to re-form them, and to realize the once absurd notion of transmutation—these are the problems now given to the chemist for solution."[6]

Interest in the subject was revived in 1907 by Ramsay's[7] announcement of the development of spectroscopic quantities of lithium in solutions of cupric sulphate or nitrate exposed to the radium emanation. In control experiments made without the emanation no lithium was detected. Mme. Curie and Mlle. Gleditsch[8] repeated Ramsay's experiments, employing vessels of platinum instead of glass, but failed to detect the development of even a trace of lithium. They attribute Ramsay's results to solution of lithium present in the glass of his apparatus. Mlle. Gleditsch[9] detected the presence of lithium in a sample of pitchblende from Joachimsthal, as well as in other radioactive minerals, but failed to find any simple relationship between the proportion of lithium and copper present in the minerals examined. The results[10] are summarized in the table:

Mineral.	Percentage of Copper.	Percentage of Lithium.	Ratio of Copper to Lithium.
Joachimsthal pitchblende .	1·2	0·00017	7059
Colorado pitchblende . .	0·15	0·00034	441
Carnotite	0·15	0·030	5
Chalcolite (Cornwall) . .	0·54	0·00011	491
Autunite	Nil	0·00083	..
Thorite	Trace	0·0033	..

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[1] Compare Haber and Sack, *Zeitsch. Elektrochem.*, 1902, 8, 245.

[2] Ostwald, *Zeitsch. physikal. Chem.*, 1887, 1, 83.

[3] Franke, *ibid.*, 1895, 16, 463.

[4] Kohlrausch and Maltby, *Sitzungsber. K. Akad. Wiss. Berlin*, 1899, ii., 665; Kohlrausch, *ibid.*, 1900, ii., 1002; 1901, ii., 1026; 1902, i., 572.

[5] Tolman, *J. Amer. Chem. Soc.*, 1911, 33, 121; Patten and Mott, *J. Physical Chem.*, 1904, 8, 153; Schlamp, *Zeitsch. physikal. Chem.*, 1894, 14, 273; Bredig, *ibid.*, 1894, 13, 262.

[6] Compare Hydrogen, p. 32.

[7] Ramsay, *Nature*, 1907, 76, 269; Cameron and Ramsay, *Trans. Chem. Soc.*, 1907, 91, 1593; Ramsay, *ibid.*, 1909, 95, 624.

[8] Curie and Gleditsch, *Compt. rend.*, 1908, 147, 345.

[9] Gleditsch, *ibid.*, 1907, 145, 1148.

[10] Gleditsch, *ibid.*, 1908, 146, 331; *Le Radium*, 1908, 5, 33; compare Ramsay and Cameron, *Compt. rend.*, 1908, 146, 456.

Although Ramsay's theory is not disproved by Mlle. Gleditsch's results, they afford it no support. Rutherford[1] regards the ordinary chemical methods employed as inadequate for the detection of the transformation, assuming it to have occurred.

Perman[2] exposed solid cupric nitrate and sulphate and auric chloride, contained in quartz vessels at a pressure of 0·1 mm., to the action of radium bromide for four months, but in no instance could the development of lithium be detected by the spectroscope.

Atomic Weight.—The early determinations of the atomic weight of lithium by Arfvedson,[3] Vauquelin,[4] Gmelin,[5] and Kralovansky[6] were very erroneous, owing to the presence of sodium in their calcium salts. The results obtained by Hermann,[7] Berzelius,[8] and Hagen,[9] 6·1, 6·7, and 6·6, were also incorrect, and need not be discussed.

Better determinations were made by Mallet,[10] Troost,[11] Diehl,[12] Stas,[13] and Dittmar,[14] whose results are tabulated below. The atomic-weight values are calculated from the data (p. 57).

$O = 16{\cdot}000$ $Cl = 35{\cdot}457$ $C = 12{\cdot}003$
$Ag = 107{\cdot}880$ $N = 14{\cdot}008$

Experimenter.	Year.	Ratio Measured.	Atomic Weight of Lithium.
Mallet .	1856	$AgCl : LiCl = 100 : 29{\cdot}59$	6·96
		$Ag : LiCl = 100 : 39{\cdot}274$	6·91
Diehl .	1862	$Li_2CO_3 : CO_2 = 100 : 59{\cdot}417$	7·03
Troost .	1862	$Li_2CO_3 : CO_2 = 100 : 59{\cdot}456$	7·00
		$AgCl : LiCl = 100 : 29{\cdot}5925$	6·96
Stas .	1865	$Ag : LiCl = 100 : 39{\cdot}358$	7·002
		$LiCl : LiNO_3 = 100 : 162{\cdot}5953$	6·960
Dittmar .	1889	$Li_2CO_3 : CO_2 = 100 : 59{\cdot}638$	6·89

The manipulation of Stas was much superior to that of the other investigators, and his ratio $LiCl : LiNO_3$ is very nearly correct. His analysis of lithium chloride is very erroneous, as was shown by Richards and Willard[15] in their classic researches on the atomic weight of lithium.

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[1] Rutherford, *Trans. Chem. Soc.*, 1922, 121, 400.
[2] Perman, *ibid.*, 1908, 93, 1775.
[3] Arfvedson, *Schweigger's J.*, 1817, 22, 93.
[4] Vauquelin, *Ann. Chim. Phys.*, 1818, 7, 284.
[5] Gmelin, *Gilbert's Annalen*, 1822, 72, 399.
[6] Kralovansky, *Schweigger's J.*, 1827, 54, 231.
[7] Hermann, *Pogg. Annalen*, 1829, 15, 480.
[8] Berzelius, *ibid.*, 1829, 17, 379.
[9] Hagen, *ibid.*, 1839, 48, 361.
[10] Mallet, *Amer. J. Sci.*, 1856, [2], 22, 349; 1859, [2], 28, 349.
[11] Troost, *Compt. rend.*, 1862, 54, 366; compare *Ann. Chim. Phys.*, 1857, [3], 51, 108.
[12] Diehl, *Annalen*, 1862, 121, 93.
[13] Stas, *Œuvres Complètes*, Brussels, 1894, 1, 710, 717.
[14] Dittmar, *Trans. Roy. Soc. Edin.*, 1889, 35, ii., 429.
[15] Richards and Willard, *Carnegie Institute of Washington Publications*, 1910, No. 125; *J. Amer. Chem. Soc.*, 1910, 32, 4; compare Richards and Cox, *Chem. News*, 1913, 107, 267; *J. Amer. Chem. Soc.*, 1914, 36, 819.

The results of their analyses of lithium chloride are

$$\text{AgCl} : \text{LiCl} = 100 : 29{\cdot}5786, \text{ whence } \mathbf{Li = 6{\cdot}940};$$
$$\text{Ag} : \text{LiCl} = 100 : 39{\cdot}2992, \text{ whence } \mathbf{Li = 6{\cdot}939}.$$

A description of the determination of the first of these ratios is given in Volume I. of this series of text-books, as an example of the refinements employed in modern atomic-weight research.

Further evidence concerning the atomic weight of lithium was furnished by Richards and Willard in their synthesis of lithium perchlorate by evaporating lithium chloride with perchloric acid. The result obtained was

$$\text{LiCl} : 4\text{O} = 100 : 150{\cdot}968, \text{ whence } \mathbf{Li = 6{\cdot}936}.$$

In the foregoing calculations the modern values for the atomic weights of silver and chlorine have been employed, but the following calculation indicates the assumption to be unnecessary. Taking the composition of silver chloride to be that given by Richards and Wells,[1]

$$\text{Ag} : \text{AgCl} = 100 : 132{\cdot}867,$$

it follows that

$$\frac{\text{LiCl}}{\text{AgCl}} \times \frac{\text{AgCl}}{\text{Ag}} = \frac{\text{LiCl}}{\text{Ag}} = 0{\cdot}295786 \times 1{\cdot}32867 = 0{\cdot}393002.$$

The mean of this result and that found directly (0·392992) is 0·392997. Hence

$$\frac{4\text{O}}{\text{LiCl}} \times \frac{\text{LiCl}}{\text{Ag}} = \frac{4\text{O}}{\text{Ag}} = 1{\cdot}50968 \times 0{\cdot}392997,$$
$$= 0{\cdot}593300,$$
$$= 64 : 107{\cdot}871.$$

Accordingly, Ag=107·871, and Cl=107·871×0·32867=35·454. But

$$\text{LiCl} = 64 \div 1{\cdot}50968 = 42{\cdot}393.$$

Hence

$$\text{Li} = 42{\cdot}393 - 35{\cdot}454,$$
$$= 6{\cdot}939.$$

The current table of the International Committee on Atomic Weights gives

$$\mathbf{Li = 6{\cdot}94}.$$

Molecular Weight.—Ramsay[2] investigated the lowering of the vapour-pressure of mercury produced by dissolving lithium in that metal, and from his results calculated for the molecular weight of lithium the value 7·1, approximately the same as its atomic weight. A different result was obtained by Heycock and Neville[3] by the cryoscopic method with sodium as solvent, their value being about four times the atomic weight, the discrepancy possibly arising from the susceptibility of lithium to oxidation.

Position of Lithium in the Periodic System.—In accordance with the

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[1] Richards and Wells, *J. Amer. Chem. Soc.*, 1905, 27, 459.

[2] Ramsay, *Trans. Chem. Soc.*, 1889, 55, 521.

[3] Heycock and Neville, *ibid.*, 675.

rule that the first member of a group of the periodic system displays analogy not only to the members of its own group but also to those of the succeeding group, lithium exhibits a close relationship to the metals calcium, strontium, and barium. In the ready solubility of its halides, nitrate, and sulphate, it resembles the other alkali-metals; but in the slight solubility of its carbonate and phosphate it recalls the behaviour of the corresponding salts of the alkaline-earth-metals. The formation of a deliquescent chloride and nitrate and of a fluoride of slight solubility is a link with calcium. In its affinity for nitrogen lithium also displays analogy to the alkaline-earth-metals. A similar kinship is manifested by the heats of formation of the peroxides of lithium, calcium, strontium, and barium (p. 67).

COMPOUNDS OF LITHIUM.[1]

Lithium hydride, LiH.—At 500° C. lithium combines with hydrogen, becoming coated with a superficial layer of the hydride.[2] At bright redness the combination is complete, and is attended by incandescence.[3] The preparation of the hydride is effected by passing a current of dry hydrogen over the heated metal below 710° C., the product being a transparent, vitreous, opalescent mass, with the formula LiH. On exposure to light it acquires a blue colour, without change in composition.[4] Its melting-point is 680° C., its dissociation-pressure at this temperature being about 27 mm. The density of the hydride is 0·816, and its molecular volume 9·77.[5]

The alkali-metal and alkaline-earth-metal hydrides exhibit a slight decrease of stability with increase in the atomic weight of the metal, lithium hydride being the most stable member of the series.[6] At the ordinary temperature, in absence of moisture, atmospheric oxygen, chlorine, and hydrochloric acid have no action upon it. Both types of hydride absorb hydrogen, those of the alkaline-earth-metals to a greater extent than those of the alkali-metals. All these metals combine vigorously with hydrogen, those of the alkaline earths becoming heated to incandescence, a phenomenon probably due to the greater solubility of their hydrides in the metals.

The hydride is decomposed by water without the application of external heat, lithium hydroxide being formed and hydrogen evolved. The reaction is exothermic, and is represented by the equation

$$[\mathrm{LiH}]+\mathrm{Aq.}=(\mathrm{H_2})\ (\mathrm{dry})+\mathrm{LiOH,Aq.}+31{\cdot}6\ \mathrm{Cal.}$$

Since the heat of formation of lithium hydroxide in dilute solution from the metal and water is 53·2 Cal., the heat of formation of lithium hydride from its elements is given by the equation

$$[\mathrm{Li}]+(\mathrm{H})=[\mathrm{LiH}]+21{\cdot}6\ \mathrm{Cal.},$$

its comparatively high value according with the relative stability of

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[1] For *lithium-amalgam* see this series, Vol. III.

[2] Troost and Hautefeuille, *Annales de Chimie*, 1874, [5], 2, 279.

[3] Guntz, *Compt. rend.*, 1896, 122, 245; 123, 694.

[4] Dafert and Miklauz, *Monatsh.*, 1912, 33, 63; Moers, *Zeitsch. anorg. Chem.*, 1920, 113, 179; compare Ephraim and Michel, *Helv. Chim. Acta*, 1921, 4, 762, 900.

[5] Moers, *loc. cit.*

[6] Ephraim and Michel, *loc. cit.*

the hydride. The analogy between the physical constants and other physical properties of lithium hydride and those of the alkali-metal halides, and the liberation of lithium at the cathode and hydrogen at the anode during electrolysis, indicate the hydride to be a salt of hydrogen in its capacity as a weak acid.[1]

Lithium fluoride, LiF.—The fluoride is obtained in granular form by concentrating a hydrofluoric-acid solution of the carbonate. When crystallized from fused potassium chloride it forms regular octahedra, or leaflets with a mother-of-pearl lustre.[2] Carnelley[3] gives the melting-point as about 800° C., and Poulenc[4] as about 1000° C., but Wartenberg and Schulz[5] found 842° C. The boiling-point is 1676° C.,[6] and the vapour-pressure in atmospheres corresponds with the expression

$$\log p = -55100/4{\cdot}57T + 6{\cdot}190.$$

The density of the fluoride is about 2·6.

At 18° C. 100 parts of water dissolve 0·27 part of lithium fluoride.[7] The salt is almost insoluble in alcohol of 95 per cent. strength. de Forcrand's[8] value for the heat of solution is −1·04 Cal. Its comparatively slight solubility constitutes a link with the fluorides of the alkaline-earth-metals (p. 54), and has been put forward as an argument in favour of the double formula Li_2F_2, derived from the double molecule H_2F_2, since the salts of lithium with monobasic anions are usually readily soluble. If this view be correct, the analogy to the alkaline-earth-metallic fluorides is rendered even more striking. It is supported by the existence of *lithium hydrogen fluoride*, LiF,HF, which crystallizes from a solution of the fluoride in hydrofluoric acid.

Petersen[9] has determined the heat of formation of lithium fluoride from the hydroxide in dilute aqueous solution:

$$\mathrm{HF,Aq.} + \mathrm{LiOH,Aq.} = \mathrm{LiF,Aq.} + 16{\cdot}4\ \mathrm{Cal.}$$

The heat of neutralization of strong acids and bases is usually about 13·7 Cal., and the enhanced value for lithium fluoride may be attributed to the heat evolved during neutralization by the ionization of the weak hydrofluoric acid.

By combining the heat of neutralization given by the foregoing equation with the heats of formation of water, dissolved lithium hydroxide, and dissolved hydrogen fluoride, an equation is obtained giving the heat of formation of dissolved lithium fluoride from lithium, fluorine, and water:

$$[\mathrm{Li}] + (\mathrm{F}) + n\mathrm{H_2O} = \mathrm{LiF}\ (\mathrm{dissolved}) + 118{\cdot}4\ \mathrm{Cal.}$$

The heat of formation of the solid fluoride is unknown, since its heat of solution has not been determined.

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[1] Moers, *Zeitsch. anorg. Chem.*, 1920, 113, 179.

[2] Poulenc, *Ann. Chim. Phys.*, 1894, [7], 2, 22.

[3] Carnelley, *Landolt, Börnstein, and Roth's Tabellen*, 4th ed., Berlin, 1912, 220.

[4] Poulenc, *Ann. Chim. Phys.*, 1894, [7], 2, 22.

[5] von Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and Wartenberg, *ibid.*, 162.

[6] von Wartenberg and Schulz, *loc. cit.*

[7] Mylius and Funk, *Ber.*, 1897, 30, 1716.

[8] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[9] Petersen, *Zeitsch. physikal. Chem.*, 1889, 4, 384.

At red heat water has very slight action on lithium fluoride. With other fluorides the lithium salt yields double salts or complex compounds, such as BF_3,LiF (Berzelius); SbF_3,LiF;[1] SbF_3,LiF,HF;[1] $SiF_4,2LiF,2H_2O$;[2,3] $SnF_4,2LiF,2H_2O$.[2]

Lithium chloride, $LiCl$.—The anhydrous salt is obtained by evaporating to dryness in a current of hydrogen chloride or in presence of ammonium chloride the solution formed by dissolving the carbonate in hydrochloric acid, or decomposing the sulphate with barium chloride.[4] Bogorodsky[5] has isolated three hydrates: at very low temperatures the trihydrate, $LiCl,3H_2O$, is deposited in small needles; at −15° C. the dihydrate, $LiCl,2H_2O$, crystallizes in cubes; and at 12·5° C. octahedra of the monohydrate, $LiCl,H_2O$, are formed. At about 98° C. the anhydrous salt separates.

Various values are given for the melting-point of the chloride. Schemtschushny and Rambach[6] found 614° C., Richards and Meldrum[7] 613° C., Korreng[8] and also Schaefer[9] 609° C., Haigh[10] 607° C., Hüttner and Tammann[11] 605° to 607° C., Wartenberg and Schulz[12] 606° C., Hachmeister[13] 605° C., Carnelley[14] 602° C., Guntz[15] 600° C., and Ramsay[16] 491° C. The boiling-point is 1382° C.,[17] and the vapour-pressure in atmospheres corresponds with the expression

$$\log p = -37200/4{\cdot}57T + 4{\cdot}923.$$

At white heat it volatilizes completely in a current of hydrogen chloride. The specific heat of the anhydrous salt at 13° to 97° C. is 0·2821,[18] and its density[19] at 20° C. is 2·068.

Lithium chloride is a very deliquescent, white substance of saline taste, and is excessively soluble in water. Kremers[20] found that the solubility increases with rise of temperature. His values are given in the table:

Temperature, °C. . .	0	20	65	80	96	140	160
Grams LiCl in 100 g. H_2O	63·7	80·7	104·2	115	129	139	145

His results have been graphically represented by Auerbach and Brislee[21]

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[1] Stein, *Chem. Zeit.*, 1889, 13, 357.

[2] Marignac, *Ann. Mines*, 1859, [5], 15, 241.

[3] Stolba, *J. prakt. Chem.*, 1864, 91, 456; Truchot, *Compt. rend.*, 1884, 98, 1330.

[4] Simon, *J. prakt. Chem.*, 1879, [2], 20, 371.

[5] Bogorodsky, *J. Russ. Phys. Chem. Soc.*, 1893, 25, 316; 1894, 26, 209.

[6] Schemtschushny and Rambach, *ibid.*, 1909, 41, 1785.

[7] Richards and Meldrum, *J. Amer. Chem. Soc.*, 1917, 39, 1816.

[8] Korreng, *Jahrb. Min. Beil.-Bd.*, 1914, 37, 51.

[9] Schaefer, *ibid.*, 1919, 43, 132.

[10] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[11] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 224.

[12] von Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and von Wartenberg, *ibid.*, 162.

[13] Hachmeister, *Zeitsch. anorg. Chem.*, 1919, 109, 145.

[14] Carnelley, *Landolt, Börnstein, and Roth's Tabellen*, 4th ed., Berlin, 1912, 220.

[15] Guntz, *Compt. rend.*, 1893, 117, 732.

[16] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[17] von Wartenberg and Schulz, *loc. cit.*

[18] Landolt, Börnstein, and Roth, *Tabellen*, 4th ed., Berlin, 1912, 756.

[19] Haigh, *loc. cit.*

[20] Kremers, *Pogg. Annalen*, 1857, 99, 47, 443.

[21] Auerbach and Brislee, *Abegg and Auerbach's Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i., 122.

(fig. 3), the two breaks in the curve near 20° C. and 100° C. corresponding with the transition-temperatures of the individual hydrates. The three portions of the curve correspond with the solid phases $LiCl,2H_2O$, $LiCl,H_2O$, and LiCl. The break on the dotted portion of the curve at —15° C. represents the transition-point of the trihydrate, $LiCl,3H_2O$. A saturated solution of the chloride in contact with the solid phase boils at 168° C.[1]

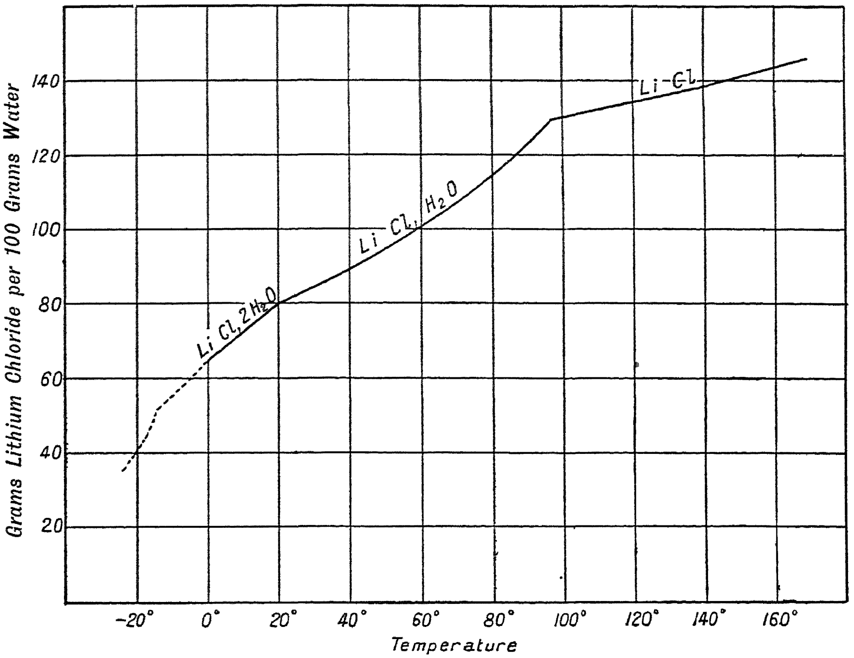

FIG. 3.—Solubility-curve of lithium chloride.

The solubility of lithium chloride has also been investigated by Gerlach,[1] whose results are given in the table :

Temperature, °C. . . .	0	10	20	30	40	50	60	80	100
Grams LiCl in 100 g. H_2O .	67	72	78·5	84·5	90·5	97·0	103·0	115·0	127·5

References to work on the physical properties of aqueous solutions of lithium chloride are appended.[2]

Solutions of lithium chloride resemble water in their power of absorbing ammonia, complex ammonia compounds being formed.[3] The anhydrous lithium halides also absorb ammonia, Bonnefoi[4] having

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[1] Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 281.

[2] Lemoine, *Compt. rend.*, 1897, 125, 603; Hosking, *Phil. Mag.*, 1904, [6], 7, 469; Jones and Getman, *Zeitsch. physikal. Chem.*, 1903, 46, 269; Jahn, *ibid.*, 1901, 37, 673; 1905, 50, 129; Biltz, *ibid.*, 1902, 40, 184; Arrhenius, *ibid.*, 1887, 1, 295; Wagner, *ibid.*, 1890, 5, 31; Abegg, *ibid.*, 1893, 11, 251; Öholm, *ibid.*, 1905, 50, 309.

[3] Abegg and Riesenfeld, *Zeitsch. physikal. Chem.*, 1902, 40, 84; Dawson and McCrae, *Trans. Chem. Soc.*, 1901, 79, 493.

[4] Bonnefoi, *Ann. Chim. Phys.*, 1901, [7], 23, 317.

prepared a series of compounds such as $LiCl,NH_3$, $LiCl,2NH_3$, $LiCl,3NH_3$, and $LiCl,4NH_3$. On heating, the ammonia is expelled, leaving the lithium chloride in a very porous condition, in which it combines readily with organic amines to form a series of analogous derivatives of complex type.

Lithium chloride is soluble in many organic solvents :[1] among them are alcohols, such as methyl alcohol, ethyl alcohol, higher alcohols, and glycerol ; aldehydes and ketones, such as acetaldehyde, paraldehyde, and acetone ; fatty acids, such as formic acid and acetic acid ; nitriles, such as acetonitrile and propionitrile ; phenol ; and bases, such as pyridine. Solution is sometimes accompanied by evolution of heat and formation of compounds, examples of those isolated[2] being

$$LiCl,3CH_3OH, \quad LiCl,4C_2H_5OH, \quad LiCl,(CH_3)_2CO, \quad LiCl,2C_5H_5N.$$

Kahlenberg and Krauskopf[3] have utilized the solubility of lithium chloride in anhydrous pyridine in separating it from the chlorides of the other alkali-metals and barium, these salts being insoluble.

The degree of dissociation in acetone and pyridine is very small,[4] but in formic acid it is of the same order as in water.[5] For the alcohols and acetaldehyde it is considerable, and somewhat less for paraldehyde and acetonitrile.[6] Acetic acid causes association to double molecules,[7] which become partially dissociated with rise of temperature.[8]

The electrolysis of solutions of lithium chloride in various solvents, such as water, alcohols, glycerol, and phenol, has been investigated by Patten and Mott.[9]

The latent heat of fusion of lithium chloride per gram is 0·086 Cal.[10]

The heat of formation of dilute aqueous solutions is given by the equation

$$LiOH,Aq.+HCl,Aq.=LiCl,Aq.+13{\cdot}85 \text{ Cal.}$$

Since the heat of solution of hydrochloric acid is 39·3 Cal., and that of lithium in water is given by the equation[11]

$$[Li]+Aq.=LiOH,Aq.+(H)+53{\cdot}2 \text{ Cal.},$$

the heat of formation of lithium chloride in dilute solution is given by the equation

$$[Li]+Cl+Aq.=LiCl,Aq.+106{\cdot}35 \text{ Cal.}$$

Since the heat of solution of the anhydrous salt is 8·44 Cal., the heat

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[1] Compare Marden and Dover, *J. Amer. Chem. Soc.*, 1917, 39, 1.

[2] von Laszczynski, *Ber.*, 1894, 27, 2285 ; *Zeitsch. Elektrochem.*, 1895, 2, 55 ; von Laszczynski and von Gorski, *ibid.*, 1898, 4, 290 ; Simon, *J. prakt. Chem.*, 1879, [2], 20, 371 ; Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1904.

[3] Kahlenberg and Krauskopf, *J. Amer. Chem. Soc.*, 1908, 30, 1104.

[4] von Laszczynski, *loc. cit.* ; von Laszczynski and von Gorski, *loc. cit.*

[5] Zanninovich-Tessarin, *Zeitsch. physikal. Chem.*, 1896, 19, 251.

[6] Schlamp, *ibid.*, 1894, 14, 273 ; Völlmer, *Wied. Annalen*, 1894, 52, 328 ; Coffetti, *Gazzetta*, 1903, 33, i., 53 ; Andrews and Ende, *Zeitsch. physikal. Chem.*, 1895, 17, 136 ; Dutoit and Friderich, *Bull. Soc. chim.*, 1898, [3], 19, 321.

[7] Zanninovich-Tessarin, *Zeitsch. physikal. Chem.*, 1896, 19, 251.

[8] Ley, *ibid.*, 1897, 22, 77.

[9] Patten and Mott, *J. Physical Chem.*, 1904, 8, 153.

[10] Schemtschushny and Rambach, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1785.

[11] Guntz, *Compt. rend.*, 1896, 122, 245 ; 123, 694.

of formation of lithium chloride from its elements is expressed by the equation

$$[Li]+(Cl)=[LiCl]+97{\cdot}9 \text{ Cal.}$$

The heat of solution in ethyl alcohol is 11·74 Cal.,[1] in methyl alcohol 10·9 Cal.[2] The formation of compounds with alcohols has been investigated[3] (see p. 62). At 25° C. 100 grams of ethyl alcohol dissolve 25·83 grams of the salt.[4]

Lithium chloride forms double salts with the chlorides of other metals, such as copper,[5] manganese,[6] iron,[6] cobalt,[6] nickel,[6] and uranium.[7] With sodium chloride it forms a series of mixed crystals, but not with potassium chloride.[8]

Lithium subchloride, Li_2Cl.—According to Guntz,[9] lithium chloride is converted by lithium into a hard, greyish substance of the formula Li_2Cl. It decomposes water readily:

$$2Li_2Cl+2H_2O=2LiCl+2LiOH+H_2.$$

Lithium bromide, LiBr.—The anhydrous bromide is obtained by dissolving the carbonate in aqueous hydrobromic acid, and evaporating the solution to dryness in a current of gaseous hydrogen bromide. Bogorodsky[10] has isolated three hydrates from the aqueous solution, each forming very deliquescent crystals. At very low temperatures the trihydrate, $LiBr,3H_2O$, is deposited; at 4° C. it is changed to the dihydrate, $LiBr,2H_2O$; at 44° C. this substance yields the monohydrate, $LiBr,H_2O$; above 159° C. the anhydrous salt is deposited. A crystalline form is also described[11] containing $1\text{–}1\tfrac{1}{2}H_2O$. For the melting-point of anhydrous lithium bromide Carnelley[12] gives 547° C., and Wartenberg and Schulz[13] give 549° C.; but Ramsay and Eumorfopoulos[14] found the much lower value 442° C. At its melting-point it evolves bromine freely.[15] The boiling-point is 1310° C.,[16] and the vapour-pressure in atmospheres corresponds with the expression

$$\log p = -35600/4{\cdot}57T + 5{\cdot}109.$$

The values obtained by Kremers[17] for the solubility in water are given in the table:

Temperature, °C. . . .	0	10	20	30	40	50	60	80	100
Grams LiBr in 100 g. H_2O .	143	161	177	190	202	214	224	245	266

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[1] Pickering, *Trans. Chem. Soc.*, 1888, 53, 865.

[2] Lemoine, *Compt. rend.*, 1897, 125, 603.

[3] Turner and Bissett, *Trans. Chem. Soc.*, 1914, 105, 1777.

[4] Turner and Bissett, *ibid.*, 1913, 103, 1904.

[5] Chassevant, *Compt. rend.*, 1891, 113, 646; Cambi, *Gazzetta*, 1909, 39, i., 361.

[6] Chassevant, *Compt. rend.*, 1892, 115, 113.

[7] Aloy, *Bull. Soc. chim.*, 1899, [3], 21, 264; compare Liebisch and Korreng, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 192.

[8] Schaefer, *Jahrb. Min. Beil.-Bd.*, 1919, 43, 132.

[9] Guntz, *Compt. rend.*, 1895, 121, 945.

[10] Bogorodsky, *J. Russ. Phys. Chem. Soc.*, 1893, 25, 316; 1894, 26, 209.

[11] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.

[12] Carnelley, *Landolt, Börnstein, and Roth's Tabellen*, 4th ed., Berlin, 1912, 220.

[13] von Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and von Wartenberg, *ibid.*, 162.

[14] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[15] Guareschi, *loc. cit.*

[16] von Wartenberg and Schulz, *loc. cit.*

[17] Kremers, *Pogg. Annalen*, 1858, 103, 57; 104, 133; 105, 360.

Other investigations of the properties of aqueous solutions have been made by various experimenters.[1] Bonnefoi[2] has prepared complex compounds of lithium bromide and ammonia analogous to those formed by the chloride (p. 62).

Although the heat of formation of lithium bromide in aqueous solution has not been determined, analogy with the corresponding sodium compounds indicates that it should be similar to that of lithium chloride (p. 62) :—

$$\mathrm{LiOH,Aq.+HBr,Aq.=LiBr,Aq.+13{\cdot}85\ Cal.}$$

By combining this value with the heat of solution of lithium in water (53·2 Cal.) and with the heat of formation of hydrobromic acid in dilute solution (28·38 Cal.), there results the equation

$$\mathrm{[Li]+Br+Aq.=LiBr,Aq.+95{\cdot}43\ Cal.}$$

Subtraction of the heat of solution of the anhydrous bromide (11·35 Cal.)[3] gives the heat of formation of the salt from its elements in accordance with the equation

$$\mathrm{[Li]+Br=[LiBr]+84{\cdot}1\ Cal.}$$

Like the chloride, lithium bromide yields double compounds with alcohols.[4]

Lithium bromide forms double salts with other metallic bromides, such as those of copper[5] and tin.[6]

Lithium iodide, LiI.—On evaporation of the solution obtained by the interaction of lithium carbonate and hydriodic acid, or barium or calcium iodide, lithium iodide crystallizes in the form of hydrates,[7] a trihydrate, dihydrate, and monohydrate having been isolated. Above 300° C. the anhydrous salt is formed, but its action on glass and porcelain at high temperatures has prevented its preparation in the pure state. The boiling-point of the iodide is 1170° C.,[8] and the vapour-pressure in atmospheres corresponds with the expression

$$\log p = -40300/4{\cdot}57T + 6{\cdot}105.$$

The excessive solubility of the iodide is shown by the table :[9]

Temperature, °C.	0	10	20	30	40	50	60	70	80	99	120
Grams LiI in 100 g. H_2O	151	157	165	171	179	187	202	230	433	476	588

Other properties of dilute aqueous solutions have been studied by several investigators.[10]

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[1] Wegner, *Dissertation*, Berlin, 1889; Biltz, *Zeitsch. physikal. Chem.*, 1902, 40, 184; Tammann, *Landolt, Börnstein, and Roth's Tabellen*, 4th ed., Berlin, 1912, 273.

[2] Bonnefoi, *Ann. Chim. Phys.*, 1901, [7], 23, 317.

[3] Bodisko, *J. Russ. Phys. Chem. Soc.*, 1888, 20, 500; 1889, 21, 7.

[4] Turner and Bissett, *Trans. Chem. Soc.*, 1914, 105, 1777.

[5] Kurnakoff and Sementschenko, *J. Russ. Phys. Chem. Soc.*, 1898, 30, 701.

[6] Leteur, *Compt. rend.*, 1891, 113, 540.

[7] Firstoff, *J. Russ. Phys. Chem. Soc.*, 1893, 25, 467; Bogorodsky, *ibid.*, 1897, 29, 179.

[8] von Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and von Wartenberg, *ibid.*, 162.

[9] Kremers, *Pogg. Annalen*, 1858, 104, 133; 1860, 111, 60.

[10] Biltz, *Zeitsch. physikal. Chem.*, 1902, 40, 185; Bein, *Landolt, Börnstein, and Roth's Tabellen*, 4th ed., Berlin, 1912, 274; Ostwald, *Zeitsch. physikal. Chem.*, 1887, 1, 83; Franke, *ibid.*, 1895, 16, 463.

The heat of formation in aqueous solution can be calculated like that of the chloride or bromide, and is given by the expression

$$[Li]+[I]+Aq.=LiI,Aq.+80{\cdot}1 \text{ Cal.};$$

and, since the heat of solution is 14·9 Cal.,[1] the heat of formation of the anhydrous iodide from lithium and iodine is expressed by

$$[Li]+[I]=[LiI]+65{\cdot}2 \text{ Cal.}$$

Lithium iodide resembles the chloride and bromide in the formation of double compounds with alcohols.[2] At 25° C., 250·8 grams of the salt dissolve in 100 grams of ethyl alcohol.[3] With propyl alcohol it yields a complex of the formula

$$LiI,4C_3H_7{\cdot}OH.^4$$

Like the other halides, lithium iodide forms double salts with other metallic iodides, such as those of mercury[5] and lead.[6]

Lithium iodide tetrachloride,[7] $LiICl_4,4H_2O$, forms yellow, deliquescent needles, melting at 70° to 80° C., and is prepared by the action of chlorine and iodine on a saturated solution of lithium chloride in hydrochloric acid.

Lithium hypochlorite, $LiOCl$.—The hypochlorite is very unstable, and has not been isolated. It is formed in solution by the action of chlorine on a solution of lithium hydroxide,

$$2LiOH+Cl_2=LiOCl+LiCl+H_2O,$$

but is rapidly decomposed with formation of chlorate:

$$3LiOCl=2LiCl+LiClO_3.$$

It is probably also present in the product formed by the action of chlorine on dry lithium hydroxide.[8]

Lithium chlorate, $LiClO_3$.—On evaporation of the solution obtained by mixing aqueous solutions of lithium sulphate and barium chlorate, or by neutralizing chloric acid with lithium carbonate, lithium chlorate separates in needles. According to Potilitzin,[9] the crystals thus obtained have the formula $2LiClO_3,H_2O$, but other investigators[10] state that they consist of the anhydrous salt. Above 270° C. the chlorate decomposes into chloride, perchlorate, and oxygen, in accordance with the equations

$$2LiClO_3=2LiCl+3O_2;$$
$$4LiClO_3=LiCl+3LiClO_4.$$

Lithium chlorate is more soluble in water than any other inorganic

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[1] Bodisko, *J. Russ. Phys. Chem. Soc.*, 1888, 20, 500; 1889, 21, 7.

[2] Turner and Bissett, *Trans. Chem. Soc.*, 1914, 105, 1777.

[3] Turner and Bissett, *ibid.*, 1913, 103, 1904.

[4] Turner and Bissett, *ibid.*, 1906.

[5] Dobrosserdow, *J. Russ. Phys. Chem. Soc.*, 1901, 32, 774.

[6] Bogorodsky, *ibid.*, 1893, 25, 316; 1894, 26, 209.

[7] Wells and Wheeler, *Zeitsch. anorg. Chem.*, 1892, 2, 55.

[8] Kraut, *Annalen*, 1882, 214, 354; Lunge and Naef, *Ber.*, 1883, 16, 840.

[9] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1888, 20, 541.

[10] Mylius and Funk, *Ber.*, 1897, 30, 1716; Retgers, *Zeitsch. physikal. Chem.*, 1890, 5, 449.

salt, 313·5 grams dissolving in 100 grams of water at 18° C. It is readily soluble in alcohol. Its density[1] at 25° C. is 2·428.

Lithium perchlorate, $LiClO_4$.—The perchlorate is prepared by neutralizing perchloric acid with lithium carbonate, evaporating to dryness, extracting with alcohol, and concentrating the alcoholic solution. From aqueous solution the trihydrate, $LiClO_4,3H_2O$, crystallizes. It melts at 95° C., passes into the monohydrate at 98° to 100° C., and into the anhydrous salt at 130° to 150° C. The anhydrous salt melts at 236° C., and is converted with evolution of oxygen into the chlorate and chloride above 380° C.[2] Between 410° C. and 430° C. the decomposition is slow, but it becomes rapid at 450° C.[3]

Lithium bromate, $LiBrO_3$.—The preparation of the bromate is analogous to that of the chlorate, the salt crystallizing from aqueous solution either in the anhydrous form or as monohydrate,[4] $LiBrO_3,H_2O$. At 18° C., 100 grams of water dissolve 153·7 grams of the anhydrous salt.[5]

Lithium iodate, $LiIO_3$.—The iodate is obtained by neutralizing iodic acid with lithium carbonate or hydroxide, the salt crystallizing from aqueous solution in very deliquescent crystals of pearl-like lustre. It is doubtful whether they consist of the anhydrous salt or have the formula $LiIO_3,\frac{1}{2}H_2O$.[5] At 18° C., 100 grams of water dissolve 80·3 grams of the anhydrous salt.

Lithium periodates.—Three periodates can be obtained by the action of lithium carbonate on periodic acid in aqueous solution. According to Rammelsberg,[6] when sufficient carbonate to neutralize the acid is employed, crystals are deposited, probably the *ortho-salt*, Li_5IO_6; but with a smaller proportion of carbonate a salt, $Li_4I_2O_9,3H_2O$, is formed, which at 200° C. loses water, yielding a salt, probably $Li_2H_3IO_6$. Addition of periodic acid to the aqueous solution of the complex tetralithium salt produces the *meta-periodate*, $LiIO_4$.

In more recent work by Rosenheim and Loewenthal,[7] it was not found possible to prepare Rammelsberg's ortho-salt or his meta-salt. One molecule of periodic acid reacts with two molecules of lithium hydroxide, precipitating colourless, microscopic spherules of the salt $Li_3H_2IO_6$. On standing, the mother-liquor gradually deposits colourless, small, six-sided bipyramids of the formula $Li_2H_3IO_6$.

Lithium monoxide, Li_2O.—The monoxide prepared by heating the metal in oxygen at 200° C. always contains the peroxide, but it can be obtained pure by heating the carbonate at 780° to 800° C. in a current of hydrogen,[8] or by heating the hydroxide[9] at 780° C. or the nitrate to fusion under similar conditions. The volatility of the monoxide necessitates careful regulation of the temperature.[10]

Lithium monoxide forms a white, amorphous, more or less porous mass. Its melting-point is unknown, owing to its volatility at high

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[1] Richards and Willard, *J. Amer. Chem. Soc.*, 1910, 32, 4.

[2] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1888, 20, 541.

[3] Richards and Cox, *J. Amer. Chem. Soc.*, 1914, 36, 819.

[4] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1891, 22, 391.

[5] Mylius and Funk, *Ber.*, 1897, 30, 1716.

[6] Rammelsberg, *Pogg. Annalen*, 1868, 134, 363; compare Barker, *Trans. Chem. Soc.*, 1908, 93, 15.

[7] Rosenheim and Loewenthal, *Kolloid. Zeitsch.*, 1919, 25, 53.

[8] de Forcrand, *Compt. rend.*, 1907, 144, 1402; compare Lebeau, *ibid.*, 1903, 136, 1256.

[9] de Forcrand, *ibid.*, 1907, 144, 1321; Dittmar, *J. Soc. Chem. Ind.*, 1888, 7, 730.

[10] Lebeau, *Compt. rend.*, 1903, 136, 1256.

temperatures.[1] For the density of an impure specimen, Brauner and Watts [2] found at 15° C. the value 2·102. At a high temperature it attacks platinum,[3] but its great stability is exemplified by its indifference towards hydrogen, carbon, and carbon monoxide.

Lithium monoxide is slowly attacked by water, with formation of the intensely alkaline solution of the hydroxide. The heat evolved is given by the equation [4]

$$[Li_2O]+Aq.=2LiOH,Aq.+31{\cdot}20 \text{ Cal.}$$

Since the heat evolved by solution of 2 gram-atoms of lithium in water is 106·4 Cal. (p. 62), and the heat of formation of water is 68·3 Cal., the heat of formation of the oxide from its elements is given by the equation

$$2[Li]+(O)=[Li_2O]+143{\cdot}5 \text{ Cal.}$$

Lithium peroxide, Li_2O_2.—Addition of alcohol to the aqueous solution obtained by the interaction of hydrogen peroxide and lithium hydroxide precipitates the crystalline product $Li_2O_2,H_2O_2,3H_2O$, a substance converted by drying over phosphoric anhydride into the anhydrous peroxide, Li_2O_2. The method resembles that employed in the preparation of the peroxides of the alkaline-earth-metals.[5] The combustion of lithium in oxygen yields only a small proportion of peroxide, a distinction from sodium. The peroxide boils [6] at 258° C.

The heat of formation of the peroxide from the monoxide and oxygen is given by the equation [6]

$$[Li_2O]+(O)=[Li_2O_2]+7{\cdot}97 \text{ Cal.},$$

the corresponding equations for the peroxides of calcium, strontium, and barium being

$$[CaO]+(O)=[CaO_2]+4{\cdot}11 \text{ Cal.},$$
$$[SrO]+(O)=[SrO_2]+13{\cdot}07 \text{ Cal.},$$
$$[BaO]+(O)=[BaO_2]+18{\cdot}36 \text{ Cal.}$$

In this respect lithium displays close analogy to the alkaline-earth-metals, occupying a position between calcium and strontium. Further analogy is shown by the heat of formation of lithium peroxide from its elements,[6]

$$2[Li]+(O_2)=[Li_2O_2]+151{\cdot}29 \text{ Cal.},$$

a value closely approximating to that of calcium peroxide,

$$[Ca]+(O_2)=[CaO_2]+150{\cdot}43 \text{ Cal.}$$

Divergence from the other alkali-metals is made evident by the fact that sodium peroxide has a considerably lower heat of formation : [7]

$$2[Na]+(O_2)=[Na_2O_2]+117{\cdot}69 \text{ Cal.}$$

Lithium hydroxide, LiOH.—The hydroxide can be prepared from the

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[1] Rieke and Endell, *Sprechsaal*, 1910, 43, 683.
[2] Brauner and Watts, *Phil. Mag.*, 1881, [5], 11, 60.
[3] Rieke and Endell, *loc. cit.*
[4] de Forcrand, *Compt. rend.*, 1907, 145, 702.
[5] de Forcrand, *ibid.*, 1900, 130, 1465.
[6] de Forcrand, *Ann. Chim. Phys.*, 1908, [8], 15, 433.
[7] de Forcrand, *Compt. rend.*, 1900, 130, 1465.

metal or monoxide by the action of water, or by the interaction of aqueous solutions of barium hydroxide and lithium sulphate. It crystallizes from solution as the hydrate $LiOH,H_2O$, which is converted into the anhydrous substance by heat. The monohydrate boils at 181° C. de Forcrand[1] has described several other hydrates.

Lithium hydroxide is a white, crystalline substance, melting unchanged at 445° C.[2] At 780° C. it is converted into the monoxide (p. 66). Its dissociation-pressure has been investigated by Johnston.[3] The hydroxide is strongly basic, in this and other respects resembling the corresponding derivatives of sodium and potassium. It dissolves in water with evolution of heat, and is somewhat hygroscopic. Its heat of neutralization in dilute solution by hydrochloric acid is given by Thomsen[4] as 13·85 Cal.

Various investigators[5] have studied the properties of lithium hydroxide in dilute solution.

The heat of formation of the hydroxide in dilute aqueous solution from the metal and water is 53·2 Cal. (p. 62); that from its elements and water is given by the equation[6]

$$[Li]+(O)+(H)+Aq.=LiOH,Aq.+121{\cdot}5\text{ Cal.}$$

Since the heat of solution of the hydroxide is 4·5 Cal., the expression for the heat of formation becomes

$$[Li]+(O)+(H)=[LiOH]+117{\cdot}0\text{ Cal.}$$

For the action of water on the monoxide the heat of formation of the solid hydroxide is given by the equation

$$[Li_2O]+H_2O=2[LiOH]+22{\cdot}2\text{ Cal.}$$

The heat of neutralization of the hydroxide by mineral acids has been investigated by Richards and Rowe.[7]

Lithium monosulphide, Li_2S.—The monosulphide can be prepared by direct synthesis or by reduction of the sulphate with charcoal. The yellow product is amorphous, but heating in the electric furnace transforms it into transparent cubes[8] of specific gravity 1·63 to 1·7. Evaporation of its aqueous solution yields hygroscopic crystals of the *hydrosulphide*, LiSH:

$$Li_2S+H_2O \rightleftharpoons LiSH+LiOH.$$

This decomposition is similar to that undergone by other alkali-metal sulphides. The heat of formation of the hydrosulphide in dilute solution is given by the equation

$$[Li]+[S](\text{rhombic})+(H)+Aq.=LiSH,Aq.+68{\cdot}3\text{ Cal.}$$

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[1] de Forcrand, *Compt. rend.*, 1908, 146, 802.

[2] de Forcrand, *ibid.*, 1906, 142, 1255; Dittmar, *J. Soc. Chem. Ind.*, 1888, 7, 730.

[3] Johnston, *Zeitsch. physikal. Chem.*, 1908, 62, 330.

[4] Thomsen, *Thermochemistry* (Longmans, 1908), 115.

[5] Pickering, *Trans. Chem. Soc.*, 1893, 63, 909; Raoult, *Compt. rend.*, 1883, 97, 941; *Zeitsch. physikal. Chem.*, 1888, 2, 489; Arrhenius, *ibid.*, 495; Ostwald, *J. prakt. Chem.*, 1887, [2], 35, 112.

[6] Guntz, *Compt. rend.*, 1896, 122, 245; 123, 694; de Forcrand, *ibid.*, 1907, 145, 702; *Ann. Chim. Phys.*, 1908, [8], 15, 433.

[7] Richards and Rowe, *J. Amer. Chem. Soc.*, 1922, 44, 684.

[8] Mourlot, *ibid.*, 1899, [7], 17, 512.

Lithium polysulphides.—Fusion of lithium hydroxide with sulphur yields a yellow mass like "liver of sulphur," probably consisting of polysulphides of lithium. Berzelius isolated a hydrated disulphide, Li_2S_2,nH_2O, by concentrating an aqueous solution of the monosulphide.

Lithium sulphite, Li_2SO_3.—Evaporation of the solution obtained by the action of sulphur dioxide on lithium carbonate suspended in water yields the monohydrate, Li_2SO_3,H_2O; addition of alcohol or ether precipitates the dihydrate, $Li_2SO_3,2H_2O$. The sulphite is readily soluble in water, and is susceptible to atmospheric oxidation. Heat expels the water of crystallization, and causes partial decomposition into sulphate and sulphide. Double sulphites of lithium with potassium and sodium have been prepared.[1]

Lithium sulphate, Li_2SO_4.—The hydrated sulphate, Li_2SO_4,H_2O, is obtained in monoclinic plates[2] by evaporating a solution of sulphuric acid neutralized with lithium carbonate. Its density is 2·02 to 2·06. The anhydrous salt is said to have been prepared by Retgers,[3] its melting-point being given by Hüttner and Tammann[4] as 859° C., by Ramsay and Eumorfopoulos[5] as 853° C., and by Müller[6] as 843° C. Its density is 2·21.

Lithium sulphate is readily soluble in water. The heat of formation in dilute aqueous solution from lithium hydroxide and sulphuric acid is given by the equation[7]

$$2LiOH,Aq.+H_2SO_4,Aq.=Li_2SO_4,Aq.+31{\cdot}29\text{ Cal.}$$

Since the heat evolved by solution of 2 gram-atoms of lithium in water is 106·4 Cal. (p. 62), and the heat of formation of sulphuric acid from its elements[8] is 192·92 Cal., and its heat of solution in water[9] is 17·85 Cal., the heat of formation of the sulphate in dilute solution from the elements is given by the expression

$$2[Li]+[S]+2(O_2)+Aq.=Li_2SO_4,Aq.+348{\cdot}46\text{ Cal.}$$

Taking 6·05 Cal. as the heat of solution of anhydrous lithium sulphate, the value given by Thomsen,[10] the equation for the heat of formation of the anhydrous sulphate becomes

$$2[Li]+[S]+4(O)=[Li_2SO_4]+342{\cdot}41\text{ Cal.}$$

For the heat of solution of the hydrate, Li_2SO_4,H_2O, Thomsen[10] gives the value 3·41 Cal., and for its heat of hydration[11] the equation is

$$[Li_2SO_4]+H_2O=Li_2SO_4,H_2O+2{\cdot}64\text{ Cal.}$$

References are appended to investigations on double sulphates

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[1] Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 217.
[2] Traube, *Jahrb. Min.*, 1892, ii., 58.
[3] Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 33.
[4] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 224.
[5] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.
[6] Müller, *N. Jahrb. Mineral Beil.-Bd.*, 1914, 30, 1; *Zeitsch Kryst. Min.*, 1914, 53, 511.
[7] Thomsen, *Thermochemistry* (Longmans, 1908), 115.
[8] Thomsen, *ibid.*, 212.
[9] Thomsen, *ibid.*, 47.
[10] Thomsen, *ibid.*, 49.
[11] Thomsen, *ibid.*, 62.

with sodium, potassium, ammonium, and copper.[1] Müller[2] has prepared a double sulphate with rubidium, Li_2SO_4,Rb_2SO_4, melting at 730° C., and one with cæsium, Li_2SO_4,Cs_2SO_4, melting at 729° C. Bergius[3] has described a crystalline acid sulphate, $Li_2SO_4,7H_2SO_4$, which melts about 12° C. Lescœur[4] mentions *lithium hydrogen sulphate*, $LiHSO_4$, which forms deliquescent crystals, melting at 120° C. Other double sulphates of lithium and hydrogen[5] are $Li_2SO_4,7H_2SO_4$, melting at 13·6° C.; $Li_2SO_4,2H_2SO_4$, unstable at its melting-point; and Li_2SO_4,H_2SO_4, unstable at its melting-point, 170·5° C. (by extrapolation).

Lithium persulphate.—When a solution of lithium sulphate in sulphuric acid is electrolyzed, a solution of lithium persulphate is formed, but the salt has not been obtained crystalline.[6]

Lithium thiosulphate, $Li_2S_2O_3$.—The trihydrate, $Li_2S_2O_3,3H_2O$, is prepared by the interaction of barium thiosulphate and lithium sulphate in aqueous solution.[7] Heating eliminates the water of crystallization, and then decomposes the anhydrous substance into sulphur, sulphate, and sulphide. The salt is very deliquescent.

Lithium dithionate, $Li_2S_2O_6$.—The dithionate is obtained as trihydrate from the corresponding barium salt and lithium sulphate. It forms deliquescent crystals of density 2·158.

Lithium selenide, Li_2Se.—The anhydrous selenide is a very unstable compound obtained by the action of hydrogen on lithium selenate.[8] A hydrated form, $Li_2Se,9H_2O$, was obtained by Fabre[9] in colourless crystals by passing hydrogen selenide through a concentrated aqueous solution of lithium hydroxide in absence of air. It retains its water of crystallization tenaciously. The heat of formation of the anhydrous compound from its elements is given by the equation

$$2[Li]+[Se](cryst.)=[Li_2Se]+88{\cdot}1\ Cal.$$

Lithium selenite, Li_2SeO_3.—Nilson[10] has described the monohydrate, Li_2SeO_3,H_2O, silky needles of slight solubility; and has also prepared two acid salts, $LiHSeO_3$ and $LiH_3(SeO_3)_2$.

Lithium selenate, Li_2SeO_4.—Neutralization of selenic acid with lithium carbonate and concentration of the solution yields, according to the temperature, either the monoclinic hydrate, Li_2SeO_4,H_2O, or the rhombic anhydrous salt.[11]

Lithium chromate,[12] Li_2CrO_4.—The dihydrate, $Li_2CrO_4,2H_2O$, is obtained by dissolving lithium carbonate in chromic acid. It forms rhombic plates, with high polarizing power; and is converted at 150° C.

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[1] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 85; Retgers, *ibid.*, 1891, 8, 33; Schreinemakers, *ibid.*, 1909, 66, 687; Traube, *Jahrb. Min.*, 1892, ii., 58; Rammelsberg. *Pogg. Annalen*, 1845, 66, 79; Spielrein, *Compt. rend.*, 1912, 155, 346; 1913, 157, 46.

[2] Müller, *N. Jahrb. Mineral Beil.-Bd.*, 1914, 30, 1; *Zeitsch. Kryst. Min.*, 1914, 53, 511.

[3] Bergius, *Zeitsch. physikal. Chem.*, 1910, 72, 338.

[4] Lescœur, *Bull. Soc. chim.*, 1875, [2], 24, 516; *Ann. Chim. Phys.*, 1893, [6], 28, 248.

[5] Kendall and Landon, *J. Amer. Chem. Soc.*, 1920, 42, 2131.

[6] Otin, *Zeitsch. Elektrochem.*, 1911, 17, 919.

[7] Fock and Klüss, *Ber.*, 1889, 22, 3099.

[8] Fonzes-Diacon, *Dissertation*, Montpellier, 1901.

[9] Fabre, *Ann. Chim. Phys.*, 1887, [6], 10, 498.

[10] Nilson, *Bull. Soc. chim.*, 1874, [2], 21, 253.

[11] Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 33; compare Pettersson, *Ber.*, 1876, 9, 1678.

[12] See also this series, Vol. VII., Part III.

into needles, probably the anhydrous salt[1] and isomorphous with the corresponding sulphate and selenate. It yields a double salt with potassium, $LiKCrO_4$. At 18° C., 100 grams of water dissolve 110·9 grams of the dihydrate.[2]

A *lithium dichromate* has also been prepared.[3]

Lithium permanganate, $LiMnO_4$.—The trihydrate, $LiMnO_4,3H_2O$, forms dark-violet crystals, isomorphous with the perchlorate.[4] The manganate has not been isolated.

Lithium molybdates.[5]—By varying the experimental conditions, Ephraim and Brand[6] have prepared six different molybdates by the interaction of lithium carbonate and molybdic acid: Li_2O,MoO_3; $2Li_2O,3MoO_3$; $Li_2O,2MoO_3,5H_2O$; $3Li_2O,7MoO_3,28H_2O$; $Li_2O,3MoO_3,7H_2O$; and $Li_2O,4MoO_3,7H_2O$. They failed to obtain a salt with a higher proportion of MoO_3.

Ephraim and Brand have also described a number of *phosphomolybdates* of lithium.[7]

Lithium nitride, Li_3N.—The nitride is best prepared by the action of nitrogen on the metal at ordinary temperatures,[8] the product being a grey, amorphous, hygroscopic substance, unaffected by dry hydrogen or air, but rapidly decomposed by moisture. It absorbs both nitrogen and oxygen from the air. A ruby-red, crystalline modification is formed by the action of lithium on nitrogen at 450° to 460° C. It is less hygroscopic than the amorphous form, and does not absorb gases in the cold. At 840° to 845° C. in a current of nitrogen the amorphous nitride becomes crystalline.

Water decomposes the nitride according to the equation

$$Li_3N+3H_2O=3LiOH+NH_3.$$

Guntz recommends the formation of the nitride as a convenient means of isolating argon,[9] and its interaction with metallic chlorides as a method for preparing other nitrides.[10] For the heat of formation he found 49·5 Cal.[11] It is formed by the action of light on lithium imide, Li_2NH (p. 72):[12]

$$2Li_2NH \rightleftharpoons Li_3N+LiNH_2.$$

Lithium hydrazoate, LiN_3.—Neutralization of hydrazoic acid with lithium hydroxide and concentration of the solution yields colourless needles of the monohydrate, LiN_3,H_2O. It is hygroscopic and explosive, and is decomposed by heat.[13]

Lithamide, $LiNH_2$.—The amide can be prepared by the action of

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[1] Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 33.

[2] Mylius and Funk, *Ber.*, 1897, 30, 1716.

[3] Rammelsberg, *Pogg. Annalen*, 1866, 128, 311.

[4] Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 33.

[5] See also this series, Vol. VII., Part III.

[6] Ephraim and Brand, *Zeitsch. anorg. Chem.*, 1909, 64, 258.

[7] Ephraim and Brand, *ibid.*, 1910, 65, 233.

[8] Dafert and Miklauz, *Monatsh.*, 1910, 31, 981; compare Lenz, *Ber. Deut. pharm. Ges.*, 1910, 20, 227; Guntz, *Compt. rend.*, 1895, 121, 946.

[9] Guntz, *Compt. rend.*, 1895, 120, 777.

[10] Guntz, *ibid.*, 1902, 135, 738.

[11] Guntz, *ibid.*, 1896, 123, 995.

[12] Dafert and Miklauz, *Monatsh.*, 1912, 33, 63.

[13] Dennis and Benedict, *J. Amer. Chem. Soc.*, 1898, 20, 225.

lithium on liquefied ammonia,[1] or by passing dry ammonia over the metal at 400° C.[2] It is a white, crystalline substance of density 1·178 at 17·5° C., and melts without decomposition at 373° to 375° C. It is more stable than the amides of sodium and potassium. On heating, it partially sublimes, but in vacuum at 620° to 640° C. it is transformed into lithium imide. It is converted by water into the hydroxide and ammonia.[3]

Several investigators have described products formed by the interaction of lithium and liquefied ammonia, but there seems to be a considerable measure of uncertainty as to the true nature of the reaction.[4]

The mechanism of the action of hydrogen on lithium nitride is also a matter of dispute, *trilithium amide*, Li_3NH_2, and *trilithium ammonium*, Li_3NH_4, being products mentioned in the literature.[5] *Lithium imide*, Li_2NH, is a yellowish-white solid formed by the decomposition in sunlight of trilithium amide : [6]

$$Li_3NH_2 = Li_2NH + LiH.$$

Lithium nitrite, $LiNO_2$.—The monohydrate, $LiNO_2,H_2O$, is obtained by the interaction of lithium chloride and silver nitrite,[7] and also by that of lithium sulphate and barium nitrite.[8] It forms colourless, deliquescent needles, very soluble in water. At 0° C. its density is 1·615,[9] and between 21° C. and 31° C. 1·671. Its molecular volume is 63·44.[10] Under the influence of sunlight it decomposes, with formation of the red nitride. Oswald[11] also prepared a colourless, deliquescent semihydrate, and proved that the colourless anhydrous salt becomes hydrated through the action of the moisture of the atmosphere.

Lithium nitrate, $LiNO_3$.—Evaporation of an aqueous solution of nitric acid neutralized by lithium carbonate yields at ordinary temperatures deliquescent needles of the trihydrate, $LiNO_3,3H_2O$; at 30° C. the semihydrate, $2LiNO_3,H_2O$; and at 90° C. the very deliquescent anhydrous salt, $LiNO_3$,[12] melting-point 253° C.,[13] $D^{20}_4 = 2·366$.[14] Lithium nitrate is very soluble in water, readily yielding supersaturated solutions. At 19·05° C. 100 grams of saturated solution contain 40·4 grams, and at 70·9° C. 66·1 grams. Donnan and Burt[12] have plotted a solubility-curve (fig. 4), which indicates the transition-temperature of the trihydrate into the semihydrate to be about 29·9° C. (*C*), and that of the semihydrate into the anhydrous salt to be about 61° C. (*D*). The boiling-point of a saturated aqueous solution in contact with the solid is above 200° C.

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[1] Ruff and Goerges, *Ber.*, 1911, 44, 502.

[2] Dafert and Miklauz, *Monatsh.*, 1912, 33, 63.

[3] Titherley, *Trans. Chem. Soc.*, 1894, 65, 504.

[4] Moissan, *Bull. Soc. chim.*, 1899, [3], 21, 904, 911, 917 ; Ruff and Hecht, *Zeitsch. anorg. Chem.*, 1911, 70, 49 ; Ruff and Goerges, *Ber.*, 1911, 44, 502.

[5] Dafert and Miklauz, *Monatsh.*, 1909, 30, 649 ; *Ber.*, 1911, 44, 809 ; Ruff and Goerges, *ibid.*, 502.

[6] Dafert and Miklauz, *Monatsh.*, 1909, 30, 649.

[7] Oswald, *Ann. Chim. Phys.*, 1914, [9], 1, 32.

[8] Ball and Abram, *Trans. Chem. Soc.*, 1914, 103, 2130.

[9] Oswald, *loc. cit.*

[10] Rây, *Trans. Chem. Soc.*, 1908, 93, 997.

[11] Oswald, *loc. cit.*

[12] Donnan and Burt, *Trans. Chem. Soc.*, 1903, 83, 335.

[13] Carveth, *J. Physical Chem.*, 1898, 2, 209 ; Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[14] Haigh, *loc. cit.*

References to other investigations of the properties of dilute solutions of the nitrate are appended.[1]

The heat of formation of lithium nitrate in dilute solution is given by the equation

$$[Li]+(N)+3(O)+Aq.=LiNO_3,Aq.+116{\cdot}1 \text{ Cal.}$$

Its heat of solution is only 0·3 Cal., a phenomenon probably due to the formation of hydrates. It follows that the heat of formation of the anhydrous salt from its elements is given by

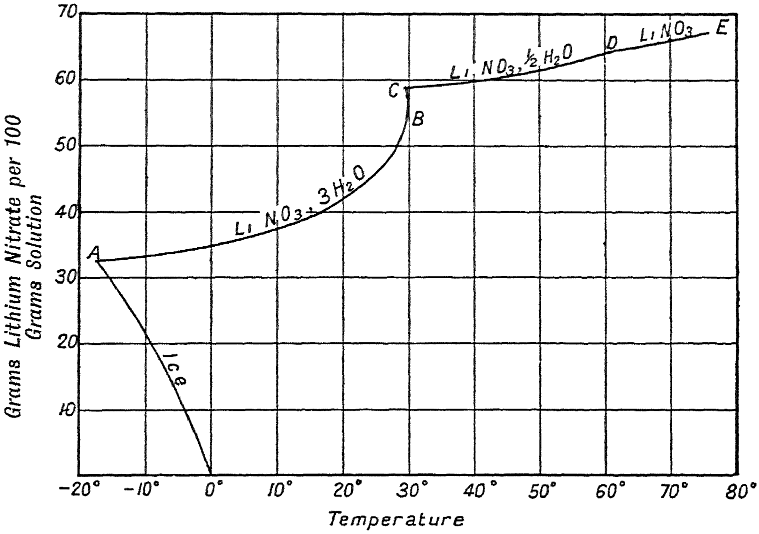

FIG. 4.—Solubility-curve of lithium nitrate.

$$[Li]+(N)+3(O)=[LiNO_3]+115{\cdot}8 \text{ Cal.}$$

The heat of solution in alcohol is 4·66 Cal.[2]

With ammonia in absence of water lithium nitrate forms a liquid characterized by its lack of action on machine-steel, iron-wire, or nichrome-wire after contact for several months. It has been suggested that the addition of a small percentage of water would render the liquid a good absorbent for the removal of ammonia from mixtures of the gas with nitrogen and with hydrogen.[3]

The molecular electric conductivity of lithium nitrate between 272° and 440·6° C. is given by the formula [4]

$$\mu_t=41{\cdot}14-0{\cdot}238(t-300).$$

Lithium nitrate resembles the chloride in the non-formation of isomorphous mixed crystals with the corresponding sodium salt.[5]

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[1] Jones and Getman, *Zeitsch. physikal. Chem.*, 1903, 46, 269; Jones and Lindsay, *Amer. Chem. J.*, 1902, 28, 329; Lincoln and Klein, *J. Physical Chem.*, 1907, 11, 318; Hartley, Thomas, and Applebey, *Trans. Chem. Soc.*, 1908, 93, 538.

[2] Pickering, *Trans. Chem. Soc.*, 1888, 53, 865.

[3] Davis, Olmstead, and Lundstrum, *J. Amer. Chem. Soc.*, 1921, 43, 1575.

[4] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.

[5] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 85.

Lithium phosphide.—The interaction of phosphorus and lithium yields a substance with which water produces spontaneously inflammable phosphine. Its constitution is unknown.

Lithium salts of the lower oxy-acids of phosphorus.—Salts of hypophosphorous, phosphorous, pyrophosphorous, and hypophosphoric acids have been described.[1]

Lithium orthophosphate, Li_3PO_4.—The orthophosphate is precipitated by addition of a soluble phosphate to a boiling solution of a lithium salt, the formula of the product according to Mayer[2] being $2Li_3PO_4,H_2O$. The dihydrate, $Li_3PO_4,2H_2O$, is also known, and at 60° C. is slowly transformed into the semihydrate.[3] Crystallization of the semihydrate from fused lithium chloride yields the anhydrous salt in crystals[4] melting about 857° C., and with the density 2·41 at 15° C. The crystalline anhydrous salt is also obtained by fusing lithium carbonate with potassium phosphate.[5] At 25° C. one litre of water dissolves 0·297 gram of Li_3PO_4.[3]

Dilithium hydrogen phosphate has not been isolated, but Rammelsberg[6] prepared *lithium dihydrogen phosphate*, LiH_2PO_4, by concentration of an acid solution containing lithium and phosphoric acid. The hygroscopic salt dissolves readily in water, and is converted at 200° to 250° C. into the glass-like metaphosphate, $LiPO_3$. On slow evaporation, phosphoric-acid solutions of the dihydrogen phosphate yield deliquescent crystals of the *acid phosphate*, LiH_2PO_4,H_3PO_4,H_2O.

Lithium pyrophosphate, $Li_4P_2O_7$.—The dihydrate, $Li_4P_2O_7,2H_2O$, is obtained as a bulky, crystalline precipitate by adding sodium pyrophosphate to lithium chloride in aqueous solution, dissolving the impure salt in acetic acid, and reprecipitating by means of alcohol.[7] The water of crystallization is expelled by heating to 200° C.[8]

Lithium metaphosphate, $LiPO_3$.—Rapid dehydration of lithium dihydrogen phosphate yields the metaphosphate as a glass-like solid, readily soluble in water, and of density 2·226, this form being probably a mixture of several modifications.[9] Slow dehydration of the dihydrogen salt, or slow cooling of the fused glass-like variety, produces a crystalline modification of slight solubility, and with the density 2·461. It melts at low redness, and on slow cooling the vitreous form is produced.[10] The crystalline modification yields double phosphates with ammonium, potassium, and sodium.[11]

Lithium arsenide, Li_3As.—At the temperature of the electric furnace lithium arsenate is reduced by charcoal to the arsenide, a dark brown crystalline substance of great reactivity.[12]

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[1] Rammelsberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1872, 416; Amat, *Ann. Chim. Phys.*, 1891, [6], 24, 309, 352; Salzer, *Annalen*, 1878, 194, 32; Rosenheim and Reglin, *Zeitsch. anorg. Chem.*, 1921, 120, 103.

[2] Mayer, *Annalen*, 1856, 98, 193.

[3] Rosenheim and Reglin, *loc. cit.*

[4] de Schulten, *Bull. Soc. chim.*, 1889, [3], 1, 479.

[5] Ouvrard, *Compt. rend.*, 1890, 110, 1333; compare Quartaroli, *Gazzetta*, 1907, 37, i., 598.

[6] Rammelsberg, *Wied. Annalen*, 1882, 16, 705; 1883, 20, 946; *Sitzungsber. K. Akad. Wiss. Berlin*, 1883, 21.

[7] Merling, *Zeitsch. anal. Chem.*, 1879, 18, 565.

[8] Rammelsberg, *loc. cit.*

[9] Rammelsberg, *loc. cit.*; Merling, *loc. cit.*; Tammann, *J. prakt. Chem.*, 1892, [2], 45, 417.

[10] Merling, *loc. cit.*; Tammann, *loc. cit.*

[11] Tammann, *loc. cit.*

[12] Lebeau, *Compt. rend.*, 1899, 129, 49.

Lithium meta-arsenite, $LiAsO_2$.—At 25° C. the ternary system *lithium oxide—arsenious oxide—water* indicates the existence of a meta-arsenite soluble in water without decomposition.[1]

Lithium arsenate, Li_3AsO_4.—The semihydrate, $2Li_3AsO_4.H_2O$, is obtained by the action of lithium carbonate on arsenic acid.[2] The anhydrous salt is prepared by recrystallizing this hydrate from fused lithium chloride,[3] its density at 15° C. being 3·07. With excess of arsenic acid the normal salt yields deliquescent prisms of the *dihydrogen arsenate,* $2LiH_2AsO_4,3H_2O$, from which water regenerates the trilithium salt.[4]

Lithium antimonide, Li_3Sb.—Since the direct combination of lithium and antimony is very violent, Lebeau[5] recommends preparing the antimonide by the electrolysis of a fused mixture of lithium and potassium chloride with an iron cathode covered with antimony. It is a dark-grey, crystalline substance of a very reactive nature. Its density at 17° C. is 3·2, and its melting-point is 950° C. The compound is also formed by the action of antimony on a solution of lithium in liquefied ammonia.[6]

Lithium antimonate, $LiSbO_3,3H_2O$.—The antimonate is precipitated in crystalline form on addition of potassium antimonate to a lithium salt in solution.[7] Like the sodium salt, it is only slightly soluble in water.

Lithium carbide, Li_2C_2.—The carbide was first prepared by Moissan[8] by the reduction of lithium carbonate with charcoal in the electric furnace :

$$Li_2CO_3+4C=Li_2C_2+3CO.$$

Tucker and Moody[9] were unable to prepare the almost pure carbide described by Moissan, and attributed their failure to the very small temperature-interval between the formation and the decomposition of the substance. The carbide is also formed by the interaction of lithium and any of the allotropic modifications of carbon in vacuum at dull red heat ; and by the combination of the metal with carbon monoxide or dioxide, or with ethylene or acetylene, an impure product is obtained.[10]

Lithium carbide is a white or grey crystalline substance, its density at 18° C. being 1·65. At bright red heat it is decomposed, and Tucker and Moody found that at 925° C. and a pressure of fifty pounds to the square inch it absorbs nitrogen freely with formation of cyanamide, dicyanamide, and cyanide. It is a powerful reducer, decomposing water energetically at ordinary temperatures with formation of acetylene :

$$C_2Li_2+2H_2O=C_2H_2+2LiOH.$$

It ignites in fluorine and chlorine without the application of heat, and on gentle warming in the vapour of bromine, iodine, or phosphorus. It combines with oxygen, sulphur, and selenium at dull redness.

Guntz[10] gives the heat evolved in its action on water as 37·1 Cal.,

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[1] Schreinemakers and de Baat, *Rec. trav. chim.*, 1920, 39, 423.

[2] Rammelsberg, *Pogg. Annalen*, 1866, 128, 311.

[3] de Schulten, *Bull. Soc. chim.*, 1889, [3], 1, 479.

[4] Rammelsberg, *loc. cit.*

[5] Lebeau, *Bull. Soc. chim.*, 1902, [3], 27, 254.

[6] Lebeau, *ibid.*, 256.

[7] Beilstein and von Blaese, *Melanges phys. et chim. de Bull. St. Pétersbourg*, 1889, 13, 1.

[8] Moissan, *Compt. rend.*, 1896, 122, 362.

[9] Tucker and Moody, *J. Amer. Chem. Soc.*, 1911, 33, 1478.

[10] Guntz, *Compt. rend.*, 1896, 123, 1273 ; 1898, 126, 1866.

and calculates the heat of formation of the carbide from its elements to be that given by the equation

$$2[C](\text{diamond})+2[Li]=[Li_2C_2]+11{\cdot}3\text{ Cal.}$$

Moissan[1] has prepared an ammonia addition-product of primary lithium acetylide, $LiHC_2$, although the free primary compound has not been isolated.

Lithium carbonate, Li_2CO_3.—The carbonate is prepared by boiling a solution of a lithium salt with ammonium, sodium, or potassium carbonate, its slight solubility inducing crystallization and facilitating purification. A process for its manufacture from lepidolite has also been devised.[2]

The melting-point of the carbonate is given as 618° C. (Ramsay and Eumorfopoulos), 695° to 699° C. (Carnelley), and 710° C. (Le Chatelier). Its boiling-point is 1200° C.,[3] and its density is 2·111. The number of grams of lithium carbonate which dissolve in 100 grams of water at various temperatures is given in the following table, after Bewad[4]:

Temperature, °C.	0	10	20	30	40	50	60	80	100
Grams Li_2CO_3 in 100 g. H_2O . .	1·54	1·43	1·33	1·25	1·17	1·08	1·01	0·85	0·72

Rothmund[5] gives the solubility at 25° C. as 0·1687 gram-molecules per litre. According to Tschugajev and Chlopin,[6] 100 grams of the saturated solution at 75° C. contain 0·833 gram of the salt, and at 95° C. 0·723 gram. With the exception of the phosphate and fluoride, the carbonate is the most insoluble salt of lithium. The solubility is considerably increased by the presence of carbon dioxide, a solution of lithium hydrogen carbonate being formed. On evaporation of the solution the carbon dioxide is expelled, so that the primary carbonate is decomposed and has not been isolated. Geffcken[7] has studied the influence of other salts on the solubility of the normal carbonate. According to Bewad,[8] the density of the saturated solution at 0° C. is 1·017, and at 15° C. it is 1·014.

When heated below 1000° C. lithium carbonate undergoes partial decomposition into the oxide and carbon dioxide, a resemblance to calcium, but a distinction from sodium and potassium :[9]

$$Li_2CO_3=Li_2O+CO_2.$$

The dissociation-pressure has been investigated by Johnston.[10] Heating

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[1] Moissan, *Compt. rend.*, 1898, 127, 911.

[2] Schiefelin and Cappon, *J. Soc. Chem. Ind.*, 1908, 27, 549.

[3] de Forcrand, *Compt. rend.*, 1908, 146, 511.

[4] Bewad, *J. Russ. Phys. Chem. Soc.*, 1884, 16, 591; *Bull. Soc. chim.*, 1885, [2], 43, 123. Rosenheim and Reglin (*Zeitsch. anorg. Chem.*, 1921, 120, 103), observed elimination of carbon dioxide from the aqueous solution of the carbonate at its boiling-point, the solution finally containing approximately equimolecular proportions of hydroxide and carbonate. In view of this decomposition, Bewad's solubility values at higher temperatures are untrustworthy.

[5] Rothmund, *Zeitsch. physikal. Chem.*, 1909, 69, 523.

[6] Tschugajev and Chlopin, *Zeitsch. anorg. Chem.*, 1914, 86, 154.

[7] Geffcken, *ibid.*, 1905, 43, 197.

[8] Bewad, *loc. cit.*

[9] de Forcrand, *Ann. Chim. Phys.*, 1908, [8], 15, 433; compare Lebeau, *Compt. rend.*, 1903, 136, 1256.

[10] Johnston, *Zeitsch. physikal. Chem.*, 1908, 62, 330.

with charcoal yields the monoxide, sodium carbonate being reduced to the metal by similar treatment. At the temperature of the electric furnace excess of charcoal produces the carbide (p. 75), an example of the relationship between lithium and calcium.

The heat of formation of the normal carbonate and that of the primary carbonate have been calculated by Muller :[1]

$$2\mathrm{LiOH,Aq.}+\mathrm{CO_2,Aq.}=\mathrm{Li_2CO_3,Aq.}+20{\cdot}4\ \mathrm{Cal.};$$
$$2\mathrm{LiOH,Aq.}+2\mathrm{CO_2,Aq.}=2\mathrm{LiHCO_3,Aq.}+22{\cdot}1\ \mathrm{Cal.}$$

For the heat of formation of the solid normal carbonate de Forcrand[2] gives the equations

$$\mathrm{Li_2O,Aq.}+(\mathrm{CO_2})=[\mathrm{Li_2CO_3}]+54{\cdot}23\ \mathrm{Cal.};$$
$$2[\mathrm{Li}]+(\mathrm{O})+(\mathrm{CO_2})=[\mathrm{Li_2CO_3}]+44{\cdot}20\ \mathrm{Cal.}$$

Basic carbonates have been described by Flückiger,[3] and a double salt with potassium by Le Chatelier.[4]

Lithium percarbonate, $Li_2C_2O_6$.—Electrolysis of a solution of lithium carbonate at —30° to —40° C. yields a solution of the percarbonate, which liberates iodine from potassium iodide instantaneously. The crystalline salt has not been isolated.[5]

Lithium cyanide has not been isolated, but Varet[6] has determined its heat of formation from the hydroxide and hydrocyanic acid :

$$\mathrm{LiOH,Aq.}+\mathrm{HCN,Aq.}=\mathrm{LiCN,Aq.}+2{\cdot}925\ \mathrm{Cal.}$$

The low value is due to the heat absorbed during the ionization of the weak acid.

Lithium thiocyanate, LiCNS.—The thiocyanate is obtained by neutralizing an aqueous solution of thiocyanic acid with lithium carbonate, and evaporating.[7] It forms very deliquescent plates, readily soluble in alcohol.

Lithium silicide, Li_6Si_2.—By heating excess of lithium with silicon, and expelling the uncombined metal at 400° to 500° C., the silicide is obtained as a very hygroscopic, dark-violet, crystalline substance[8] of density 1·12. It is a very reactive product and a powerful reducer. With concentrated hydrochloric acid it yields spontaneously inflammable silicoethane, Si_2H_6, of which it may be considered a derivative.

Lithium silicates.—Fusion of sand with lithium chloride yields the *orthosilicate*, Li_4SiO_4, the *metasilicate*, Li_2SiO_3, and an *acid silicate*, $Li_2O,5SiO_2$.[9] When the chloride is replaced by the carbonate, the same substances are formed,[10] also another *acid silicate*,[10] $Li_2O,2SiO_2$, and a *subsilicate*, Li_8SiO_6.[11] A study by Niggli[11] has proved the system

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[1] Muller, *Ann. Chim. Phys.*, 1888, [6], 15, 517.
[2] de Forcrand, *Compt. rend.*, 1908, 146, 511.
[3] Flückiger, *Arch. Pharm.*, 1887, [3], 25, 509.
[4] Le Chatelier, *Zeitsch. physikal. Chem.*, 1896, 21, 557.
[5] Riesenfeld and Reinhold, *Ber.*, 1909, 42, 4377.
[6] Varet, *Compt. rend.*, 1895, 121, 598.
[7] Hermes, *J. prakt. Chem.*, 1866, 97, 465.
[8] Moissan, *Compt. rend.*, 1902, 134, 1083 ; 135, 1284.
[9] Hautefeuille and Margottet, *ibid.*, 1881, 93, 686.
[10] Rieke and Endell, *Sprechsaal*, 1912, 44, 97.
[11] Niggli, *J. Amer. Chem. Soc.*, 1913, 35, 1693.

lithium carbonate–silica to have the equilibrium indicated by the scheme

$$2Li_2CO_3+Li_4SiO_4 \rightleftharpoons Li_8SiO_6+2CO_2.$$

The monohydrate of the metasilicate, Li_2SiO_3,H_2O, is obtained as an almost insoluble, white, granular precipitate by the interaction at 80° to 90° C. of a solution of sodium metasilicate and the equivalent amount of lithium chloride in presence of normal lithium hydroxide. It is also produced by dissolving silicic acid dried below 100° C. in twice the theoretical proportion of twice-normal lithium hydroxide at the ordinary temperature, and subsequently heating the solution to 80° C. A readily soluble modification has also been prepared.[1]

Several investigators have studied the properties of the silicates of lithium, but there is considerable divergence between the results obtained. Wallace[2] has described the orthosilicate as forming strongly double-refracting crystals, melting-point 1168° C., and $D^{18}=2{\cdot}61$. van Klooster[3] mentions slight double refraction, and gives the melting-point as 1243° C., the density at 15° C. as 2·346, that of water at 15° C. being taken as unity, and the hardness (Mohs's scale) as 3–4. Rieke and Endell[4] found for the melting-point 1215° C., and observed that water causes complete decomposition. More recent work by Jaeger and van Klooster[5] gives the melting-point as 1256° C., and the density at 25° C. as 2·392. Dana and Foote[6] found the melting-point to be 1255° C. Schwarz and Haacke[7] regard the melting-point as being 1249° C., and the density as 2·28. The heat of fusion is 62 Cal.[8]

The metasilicate melts at 1180° C. (Rieke and Endell), or 1188° C. (van Klooster), or 1201·8° C.,[9] or 1202° C.,[10] or 1209° C.[11] For the density at 24·9° C., Jaeger[12] gives 2·5203; and for the heat of fusion Schwarz and Sturm[13] give 80·2 Cal. In an earlier paper van Klooster[14] gave its density at 15° C. as 2·258, water at 15° C. being taken as unity, and its hardness (Mohs's scale) as 3. Friedel[15] describes it as forming crystals of density 2·529 at 15° C., and as being decomposed by boiling water or dilute hydrochloric acid.[16]

In aqueous solution the silicates of lithium undergo extensive hydrolytic dissociation.[17]

Double silicates of lithium and other metals have been described by Wallace.[18]

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[1] Vesterberg, *Medd. K. Vetenskapsakad. Nobel Inst.*, 1919, 5, No. 30, 1.
[2] Wallace, *Zeitsch. anorg. Chem.*, 1909, 63, 1.
[3] van Klooster, *ibid.*, 1910, 69, 135.
[4] Rieke and Endell, *Sprechsaal*, 1910, 43, 683.
[5] Jaeger and van Klooster, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 857.
[6] Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186.
[7] Schwarz and Haacke, *Zeitsch. anorg. Chem.*, 1921, 115, 87.
[8] Schwarz and Sturm, *Ber.*, 1914, 47, 1730.
[9] Jaeger, *J. Washington Acad. Sci.*, 1914, 1, 49.
[10] Dana and Foote, *loc. cit.*
[11] Schwarz and Sturm, *loc. cit.*
[12] Jaeger, *loc. cit.*
[13] Schwarz and Sturm, *loc. cit.*
[14] van Klooster, *loc. cit.*
[15] Friedel, *Bull. Soc. franç. Min.*, 1901, 24, 141.
[16] On the composition of lithium silicates, compare Ordway, *Amer. Chem. J.*, 1907, [4], 24, 473; and on their dissociation, compare Derome, *Compt. rend.*, 1907, 144, 1321.
[17] Kahlenberg and Lincoln, *J. Physical Chem.*, 1898, 2, 77.
[18] Wallace, *loc. cit.*

Lithium borates.—A borate of the formula $LiBO_2,8H_2O$ crystallizes from mixed solutions of lithium hydroxide and boric acid. At 47° C. it melts in its water of crystallization, loses seven molecules of water at 110° C., and the eighth at 160° C. The tenacity with which the final molecule of water is retained points to the possibility of the salt being an orthoborate, $LiH_2BO_3,7H_2O$.[1] At 14·7° C. its density is 1·397.

The anhydrous *metaborate*, $LiBO_2$, is precipitated by the interaction of alcoholic solutions of a lithium salt and boric acid,[2] and can also be obtained by fusing lithium carbonate with boric acid.[3] It forms triclinic leaflets of pearl-like lustre, and melts [4] at 843° C. Boiling with water converts it into the octahydrate.

Le Chatelier's data for the solubility of the anhydrous metaborate in water are given in the following table :[5]

Solubility of Lithium Metaborate.

Temperature, °C.	0	10	20	30	40	45
Grams $LiBO_2$ in 100 grams of water	0·7	1·4	2·6	4·9	11	20

For the heat of hydration Le Chatelier found

$$[LiBO_2]+8H_2O=[LiBO_2,8H_2O]+21{\cdot}7 \text{ Cal.},$$

and for the heat absorbed by solution of the hydrate

$$[LiBO_2,8H_2O]+Aq.=LiBO_2,Aq.-14{\cdot}2 \text{ Cal.}$$

A *polyborate*, $Li_2B_8O_{13}$, is obtained in crystalline form by heating lithium carbonate with excess of boric acid at 500° to 600° C. for a long time.[6]

DETECTION AND ESTIMATION OF LITHIUM.

The flame coloration and the spectrum (p. 54) afford delicate tests for the presence of lithium. From solutions which are not too dilute it can be precipitated as phosphate, fluoride, or carbonate. Like sodium, it yields an antimonate of slight solubility, but in contradistinction to potassium its platino-chloride and hydrogen tartrate are soluble.

The quantitative estimation of lithium can be effected by conversion into the sulphate or chloride. When other alkali-metals are present, Treadwell[7] recommends Gooch's[8] method, which involves conversion into chloride, separation of this salt by solution in amyl alcohol, and transformation into lithium sulphate. A modification of Gooch's method, devised by Rammelsberg and modified by Treadwell,[9] involves the extraction of the lithium chloride with a mixture of equal

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[1] Reischle, *Zeitsch. anorg. Chem.*, 1893, 4, 169; compare Rosenheim and Reglin, *ibid.*, 1921, 120, 103.

[2] Reischle, *loc. cit.*

[3] Le Chatelier, *Compt. rend.*, 1897, 124, 1091; *Bull. Soc. chim.*, 1897, [3], 17, 585.

[4] van Klooster, *Zeitsch. anorg. Chem.*, 1910, 69, 122.

[5] Le Chatelier, *Compt. rend.*, 1897, 124, 1091.

[6] Le Chatelier, *Bull. Soc. chim.*, 1899, [3], 21, 34.

[7] Treadwell, *Analytical Chemistry*, 1st ed. (Wiley, 1904), 2, 51.

[8] Gooch, *Chem. News*, 1887, 55, 18, 29, 40, 56, 78.

[9] Treadwell, *Analytical Chemistry*, 1st ed. (Wiley, 1904), 2, 52.

proportions of alcohol and ether saturated with hydrogen chloride, the chlorides of sodium and potassium being nearly insoluble in this mixture.

In Mayer's[1] method the lithium is precipitated and weighed as phosphate, excess of sodium hydroxide being added to cause complete precipitation; but the process is condemned by Rammelsberg on account of the difficulty of eliminating the sodium. Carnot[2] separates the lithium as fluoride, and transforms it into the sulphate.

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[1] Mayer, *Annalen*, 1856, 98, 193; compare Merling, *Zeitsch. anorg. Chem.*, 1879, 18, 563.

[2] Carnot, *Zeitsch. anal. Chem.*, 1890, 29, 332.

CHAPTER IV.

SODIUM.

Symbol, Na. Atomic weight, 23·00 (O=16).

Occurrence.—Although sodium in the free state is not found in nature, it is present in combination in most minerals. *Soda-felspar* or *albite* is a double silicate of sodium and aluminium, $3Na_2O,Al_2O_3,6SiO_2$. Sea-water contains 2·6 to 2·9 per cent. of sodium chloride, NaCl, the deposits left by the evaporation of inland seas being known as *rock-salt.* Both the carbonates and the sulphate of sodium occur dissolved in the water of many mineral springs, while the sulphate is a constituent of certain double salts, such as *glauberite* or sodium calcium sulphate, and *blödite* or sodium magnesium sulphate. Great deposits of *Chile saltpetre* or sodium nitrate, $NaNO_3$, are present in Chile. *Cryolite* or sodium aluminium fluoride, $3NaF,AlF_3$, is an important mineral found in Greenland. Sodium carbonate occurs in South America and Egypt, and is also found as *gaylussite,* a double carbonate of sodium and calcium. *Tincal* or disodium tetraborate, $Na_2B_4O_7,10H_2O$, is native to Thibet, India, and California, and a double borate of sodium and calcium called *cryptomorphite* is also found.

History.—The knowledge of sodium carbonate or " soda " is of great antiquity, as indicated by two references in the Bible.[1] The word translated " nitre " in the Authorized Version means " natron " or " soda," and is correctly rendered " lye " in Jer. ii. 22 in the Revised Version. No alteration has been made in the other reference. The confusion of terms evidently originated in the resemblance between the Greek *νίτρον* employed by Dioscorides and the Latin *nitrum* used by Pliny to denote sodium carbonate, and the word " nitre," loosely employed in early English as synonymous with " natron " or " soda," but now reserved for potassium nitrate.

In the sixteenth century Biringuccio seems to have appreciated the distinction between " nitrum " or soda and " sal nitri " or saltpetre. Somewhat earlier the Arabs introduced into Europe the words " natrun," " natrum," and " natron," signifying soda, and " nitrum," meaning saltpetre. They also introduced the word " alkali " (p. 1), but drew no distinction between soda, derived from the ashes of sea-plants, and potash, obtained from the ashes of land-plants. These substances were denominated " fixed alkali " in contradistinction to the volatile ammonium carbonate.

In 1736 Duhamel de Monceau noted the difference between the " mineral alkali " or soda obtained from rock-salt and the " vegetable

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[1] Jeremiah ii. 22 ; Proverbs xxv. 20.

alkali " or potash extracted from plant-ashes. Marggraf recorded the difference in flame-coloration produced by the two substances, and in 1796 Klaproth discovered the presence of " vegetable alkali " in the mineral world as *leucite.* At an earlier date it was noticed that the so-called " mild alkali " or sodium carbonate is converted into " caustic alkali," or sodium hydroxide (in modern parlance), by the action of slaked lime, and in 1756 Black proved the presence of " fixed air " (carbon dioxide) in the " mild alkali."

In 1807 Davy isolated the alkali-metals by electrolysis of the fused hydroxides, thus proving the invalidity of Lavoisier's conception of the oxides as elementary substances.

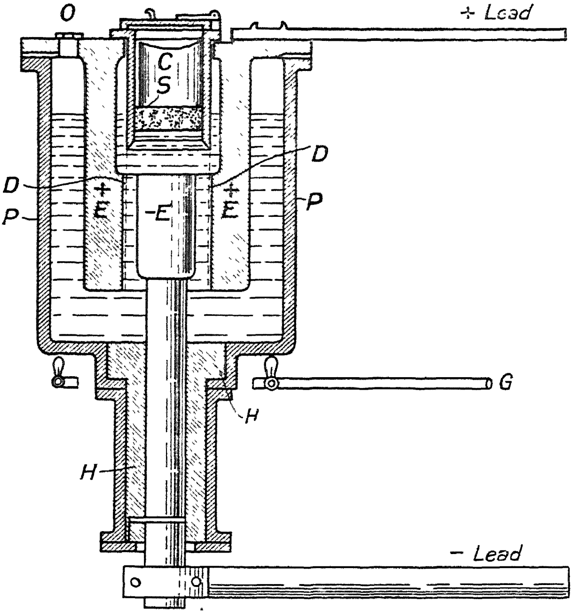

FIG. 5.—Castner's apparatus for the electrolytic production of sodium.

Preparation.[1]—Davy's original method [2] can be modified by electrolyzing a concentrated solution of the hydroxide in contact with mercury, the resulting sodium-amalgam being decomposed by volatilizing the mercury in an atmosphere of petroleum-vapour.

Several electrolytic methods have been employed in the isolation of the metal on the manufacturing scale. Castner's patent [3] is worked by the Castner Kellner Co. at Wallsend-on-Tyne. It depends on the electrolysis of fused sodium hydroxide at about 330° C. (fig. 5). The fusion is carried out in a gas-fired (*G*) iron furnace-pan (*P*), surrounded by brickwork (not shown in the figure). The metallic negative electrode (*—E*) is introduced through the bottom of the pan, and its

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[1] For a summary of modern methods of preparing alkali-metals see Herrmann, *Zeitsch. Elektrochem.*, 1913, 19, 331; 20, 2, 37.

[2] Compare Ostwald's *Klassiker*, No. 45.

[3] Castner, *British Patent*, 1890, No. 13356; *German Patent*, 1890, No. 58121; *J. Soc. Chem. Ind.*, 1891, 10, 777; compare Neumann and Giertsen, *Zeitsch. angew. Chem.*, 1914, 27, 65; Neumann, *ibid.*, 195.

lower part is surrounded by a seal of solid sodium hydroxide (H). The positive electrode ($+E$) encircles the upper part of the negative electrode, but is separated from it by a diaphragm consisting of a cylinder of wire-gauze (D) attached to the bottom of the chamber (C). Being specifically lighter than the electrolyte, the liberated sodium (S) rises to the surface. It is directed by the diaphragm (D) into the tubular iron chamber (C) placed over the negative electrode ($-E$), and is collected by means of ladles perforated to allow the molten hydroxide to drain off. The gas liberated escapes at the opening (O). The periodic addition of fresh sodium hydroxide enables the process to be carried on continuously. A current of 1000–1200 ampères at 4–5 volts is employed, and serves to maintain the temperature after fusion is complete. The yield of sodium is between 40 and 50 per cent. of the theoretical amount.

In another electrolytic method formerly worked commercially, fused sodium chloride[1] was employed as electrolyte. There are several practical difficulties to be overcome in carrying on this process, due partly to the corrosive nature of the chlorine liberated, and partly to the tendency to form the so-called subchloride of sodium. Either the formation of this subchloride must be prevented; or, if produced, it must not be permitted to regenerate sodium chloride by interaction with the chlorine evolved at the anode. The chlorine can be removed by contact at the anode with a heavy metal, such as lead, copper, or silver.[2] Lowering the temperature of fusion by admixture with chloride of potassium or of an alkaline-earth-metal,[3] or with sodium fluoride,[4] prevents the formation of the subchloride.

Electrolytic processes are gradually displacing the older chemical methods of isolating sodium dependent on the reduction of the carbonate or hydroxide with charcoal or iron.[5] On a small scale, magnesium can be employed as reducer.[6] A laboratory method is the reduction of the peroxide with wood-charcoal, coke, graphite, or calcium carbide:[7]

$$3Na_2O_2+2C=2Na_2CO_3+2Na;$$
$$7Na_2O_2+2CaC_2=2CaO+4Na_2CO_3+6Na.$$

Hydrogen is a usual impurity in metallic sodium, and is evolved when the metal reacts with mercury.[8] It can be removed by prolonged heating in vacuum.[9]

Physical Properties.—Sodium is a silver-white metal, rapidly tarnished by atmospheric oxidation, the process being attended by a greenish phosphorescence.[10] In thin layers by transmitted light the

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[1] Fischer, *Zeitsch. Elektrochem.*, 1901, 7, 349.

[2] Höpner, *German Patent*, 1884, No. 30414; Ashcroft, *ibid.*, 1903, No. 158574.

[3] Grabau, *ibid.*, 1890, No. 56230.

[4] Konsort. für elektrochem. Industr. Nürnberg, *ibid.*, 1904, No. 160540; compare Darling, *ibid.*, 1902, No. 83097; *J. Franklin Inst.*, 1902, 153, 65.

[5] Graham-Otto, *Lehrbuch der Chem.*, 3rd ed., Brunswick, 1885, 1, i., 281; Schädler, *Annalen*, 1836, 20, 2; Deville, *Ann. Chim. Phys.*, 1856, [3], 46, 415; Donny and Maresca, *Graham-Otto's Lehrbuch der Chem.*, 3rd ed., Brunswick, 1885, 1, i., 56; Warren, *Chem. News*, 1891, 64, 239; Chem. Fabrik Griesheim-Elektron, *German Patent*, 1901, No. 138368; Deville, *Ann. Chim. Phys.*, 1855, [3], 43, 5; Castner, *German Patent*, 1886, No. 40415; Thomas, *British Patent*, 1884, No. 6367; Thompson, *ibid.*, 1879, No. 2101.

[6] Winkler, *Ber.*, 1890, 23, 46.

[7] Bamberger, *Ber.*, 1898, 31, 54.

[8] Kahlenberg and Schlundt, *J. Physical Chem.*, 1905, 9, 257.

[9] Salet, *Ber.*, 1876, 9, 354.

[10] Linnemann, *J. prakt. Chem.*, 1858, 75, 128. On the preparation and preservation of untarnished specimens, compare Bornemann, *Zeitsch. angew. Chem.*, 1922, 35, 227.

metal has a brownish-yellow colour.[1] The silver-white colour can be retained by distillation in a current of hydrogen, and preservation of the distillate in a sealed tube.[2] Another method involves cleansing the surface with alcohol, and immersion of the bright metal in a saturated solution of naphthalene in light petroleum.[3] Other protectors from oxidation are vaseline-oil,[4] anhydrous ether, and petroleum freed from oxygen by distillation in hydrogen or carbon dioxide.[5]

Sodium usually crystallizes in cubes,[6] but it has also been obtained in quadratic octahedra.[7] At −20° C. it is hard, at 0° C. very ductile, at ordinary temperatures it can be moulded by the fingers, and at 50° C. it is soft.[8] For its melting-point Rengade [9] gives 97·90° C. Other values are: Regnault,[10] Hagen,[11] and Vicentini and Omodei,[12] 97·6° C.; Kurnakoff and Pushin,[13] Quercigh,[14] and Guertler and Pirani,[15] 97·5° C.; Masing and Tammann,[16] 97° C.; and Holt and Sims,[17] 92° C. The effect of pressure on the melting-point has been investigated by Tammann.[18]

Several values are recorded for the boiling-point of sodium. Carnelley and Williams [19] give values between 861° and 954° C.; Ruff and Johannsen [20] give 877·5° C.; Hansen [21] gives 742° C. at 760 mm. pressure and 418° C. at 0 mm. pressure; Perman [22] gives 742° C. at 769·6 mm. pressure; and Krafft and Bergfeld [23] give 140° C. in the vacuum of the cathode-light. In thin layers the vapour is colourless, but in thicker layers purple [24]; at red heat it is yellow.[25] The tension of the vapour [26] varies between 1·2 mm. at 380° C. and 80 mm. at 570° C.; von Rechenberg [27] found 1·94 mm. at 418° C. Its fluorescence has been studied by Dunoyer.[28]

Attempts to determine the vapour density have been made by several experimenters,[29] but the results have been unsatisfactory owing

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[1] Dudley, *Amer. Chem. J.*, 1892, 14, 185.

[2] Graham-Otto, *Lehrbuch der Chem.*, 3rd ed., Brunswick, 1885, 1, i., 284.

[3] Böttger, *Ber.*, 1874, 7, 1536.

[4] Vaubel, *Zeitsch. angew. Chem.*, 1892, 5, 200.

[5] Engler, *Ber.*, 1879, 12, 2186.

[6] Schädler, *Annalen*, 1836, 20, 2.

[7] Long, *J. Chem. Soc.*, 1860, 13, 122.

[8] Bunsen, *Annalen*, 1863, 125, 368.

[9] Rengade, *Compt. rend.*, 1913, 156, 1897; *Bull. Soc. chim.*, 1914, [4], 15, 130.

[10] Regnault, *Ann. Chim. Phys.*, 1856, [3], 46, 257.

[11] Hagen, *Wied. Annalen*, 1883, 19, 436.

[12] Vicentini and Omodei, *Wied. Annalen Beibl.*, 1888, 12, 176.

[13] Kurnakoff and Pushin, *Zeitsch. anorg. Chem.*, 1902, 30, 109.

[14] Quercigh, *ibid.*, 1910, 68, 301.

[15] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

[16] Masing and Tammann, *Zeitsch. anorg. Chem.*, 1910, 67, 183.

[17] Holt and Sims, *Trans. Chem. Soc.*, 1894, 65, 432.

[18] Tammann, *Wied. Annalen*, 1899, 68, 636.

[19] Carnelley and Williams, *Trans. Chem. Soc.*, 1879, 35, 563; 1880, 37, 125.

[20] Ruff and Johannsen, *Ber.*, 1905, 38, 3601.

[21] Hansen, *Ber.*, 1909, 42, 210; compare von Rechenberg, *J. prakt. Chem.*, 1909, [2], 79, 475.

[22] Perman, *Trans. Chem. Soc.*, 1889, 55, 326.

[23] Krafft and Bergfeld, *Ber.*, 1905, 38, 254.

[24] Graham-Otto, *Lehrbuch der Chem.*, 3rd ed., Brunswick, 1885, 1, i., 281.

[25] Dudley, *Amer. Chem. J.*, 1892, 14, 185.

[26] Gebhardt, *Verhhandl. deut. phys. Ges.*, 1905, 3, 184.

[27] von Rechenberg, *J. prakt. Chem.*, 1909, [2], 79, 475.

[28] Dunoyer, *Le Radium*, 1912, 9, 177.

[29] Dewar and Scott, *Proc. Roy. Soc.*, 1879, 28, 206, 490; *Chem. News*, 1879, 40, 293; Victor Meyer, *Ber.*, 1880, 13, 391; Ruff and Johannsen, *Ber.*, 1905, 38, 3601.

to the interaction of the vapour and the platinum, silver, iron, porcelain, or glass of the containing vessel.

The molecular weight was determined by Kraus[1] to be 23 by dissolving the metal in liquid ammonia; other investigators[2] give values for the molecular formula varying between $Na_{0\,5}$ and Na_6.

The value of the specific heat at 0° C. is given by Griffiths[3] as 0·2829. The specific heat from −185° to 20° C. is 0·2345, according to Nordmeyer and Bernoulli[4]; from −34° to 7° C. Regnault[5] gives 0·2943; from −79·5° to 17° C. Schüz[6] gives 0·2830; and from 0° to 157° C. Bernini[7] gives values varying between 0·2970 and 0·333. For the specific heat of the solid at the melting-point, Rengade[8] gives 0·3266. According to Iitaka,[9] the specific heat of the solid is 0·330, and of the liquid 0·347, the corresponding values for the atomic heat being 7·59 and 7·98.

The latent heat of fusion per gram is, according to Joannis,[10] 31·7 cal.; but Bernini[11] gives 17·75 cal., and Rengade[12] 27·23 cal.

Sodium is a good conductor of heat, and as a conductor of electricity it stands next to silver, copper, and gold. Its electric conductivity has been studied by several investigators.[13]

The mean value[14] of the density is 0·978. Gay-Lussac and Thénard[15] give the density at 15° C. as 0·972 (water at 15° C.=1); Hackspill[16] gives 0·9723 at 0° C.; Schröder[17] 0·985 compared with water at 3·9° C.; Braumhauer[18] 0·9735 at 13·5° C. and 0·9743 at 10° C. compared with water at the same temperatures; Vicentini and Omodei[19] give 0·9519 for the solid at the melting-point and 0·9287 for the liquid; Ramsay[20] 0·7414 for the liquid at the boiling-point; Dewar[21] 0·9724 at 0° C. and 1·0066 at the temperature of liquid air (water at 0° C.=1); and Richards and Brink[22] 0·9712 at 20° C.

The value last mentioned for the density gives 23·70 as the atomic

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[1] Kraus, *J. Amer. Chem. Soc.*, 1908, 30, 1197.

[2] Ramsay, *Trans. Chem. Soc.*, 1889, 55, 521; Meyer, *Zeitsch. physikal. Chem.*, 1891, 7, 477; Haber and Sack, *Zeitsch. Elektrochem.*, 1902, 8, 245; Haber, *Zeitsch. physikal. Chem.*, 1902, 41, 399; Tammann, *ibid.*, 1889, 3, 441; Heycock and Neville, *Trans. Chem. Soc.*, 1889, 55, 666; 1890, 57, 376; 1892, 61, 904; *Phil. Trans.*, 1897, 189, [A], 25; Abegg and Sackur, *Winkelmann's Handbuch der Physik*, 2nd ed., Leipsic, 1906, 3, 797.

[3] Griffiths, *Proc. Roy. Soc.*, 1914, [A], 89, 561.

[4] Nordmeyer and Bernoulli, *Ber. deut. physikal. Ges.*, 1907, 5, 175; compare Nordmeyer, *ibid.*, 1908, 6, 202.

[5] Regnault, *Pogg. Annalen*, 1856, 98, 396.

[6] Schüz, *Wied. Annalen*, 1892, 46, 177.

[7] Bernini, *Physikal. Zeitsch.*, 1906, 7, 168.

[8] Rengade, *Bull. Soc. chim.*, 1914, [4], 15, 130.

[9] Iitaka, *Sci. Rep. Tôhoku Imp. Univ.*, 1919, 8, 99.

[10] Joannis, *Ann. Chim. Phys.*, 1887, [6], 12, 381.

[11] Bernini, *Physikal. Zeitsch.*, 1906, 7, 168.

[12] Rengade, *Bull. Soc. chim.*, 1914, [4], 15, 130.

[13] Matthiessen, *Pogg. Annalen*, 1857, 100, 177; Bernini, *Cimento*, 1904, [5], 8, 262; *Physikal. Zeitsch.*, 1904, 5, 241; Guntz and Broniewski, *Compt. rend.*, 1908, 147, 1474; Müller, *Metallurgie*, 1910, 730, 755; Hackspill, *Compt. rend.*, 1910, 151, 305.

[14] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 226.

[15] Gay-Lussac and Thénard, *Gmelin, Kraut, and Friedheim's Handbuch der anorg. Chem.*, 7th ed., Heidelberg, 1910, 2, 277.

[16] Hackspill, *Compt. rend.*, 1911, 152, 259; *Ann. Chim. Phys.*, 1913, [8], 28, 613.

[17] Schröder, *Pogg. Annalen*, 1859, 106, 226; 107, 113.

[18] Braumhauer, *Ber.*, 1873, 6, 655.

[19] Vicentini and Omodei, *Wied. Annalen, Beibl.*, 1888, 12, 176.

[20] Ramsay, *Ber.*, 1880, 13, 2145.

[21] Dewar, *Chem. News*, 1902, 85, 289.

[22] Richards and Brink, *J. Amer. Chem. Soc.*, 1907, 29, 117

volume. Vanstone[1] found for the specific volume of the solid at 17° C. the value 1·0342; for the liquid at 110° C. 1·0794, and at 237° C. 1·1247.

According to Cohen and Wolff,[2] sodium exists in two allotropic forms, designated α and β. The β-modification is slightly less dense than the α-form, and is produced by cooling the molten metal rapidly. At 97·22° C. it is transformed into the α-variety, the change having a measurable velocity, and being attended by the evolution of heat.

References to investigations on the compressibility,[3] the coefficient of expansion,[4] and the surface-tension[5] are appended.

Chemical Properties.—Sodium is a very reactive substance. It decomposes water energetically, liberating hydrogen and forming sodium hydroxide, the reaction with ice beginning at $-98°$ C.:[6]

$$2Na+2H_2O=2NaOH+H_2.$$

Normally, the heat of the reaction is insufficient to ignite the hydrogen, but if the water is at a temperature of 60° C., or if the free motion of the sodium is impeded by placing it on filter-paper or by increasing the viscosity of the water by addition of gum-arabic, the evolved hydrogen ignites and burns with a characteristic yellow flame.

Ozone reacts with a solution of sodium in liquid ammonia, yielding an orange to brown precipitate. The product is readily decomposed by water or dilute acids with evolution of oxygen. It is possibly an ozonide of sodium, but owing to interaction of the ozone and ammonia[7] it has not been found possible to isolate it in the pure state. Potassium, rubidium, and cæsium react similarly.[8]

Moisture plays an important part in promoting the interaction of sodium and other substances. When quite dry, the halogens, oxygen, and hydrogen chloride do not combine with the metal, or react very slowly; but in presence of a trace of moisture these substances react vigorously with sodium, forming respectively the halide, oxide, and chloride.[9]

Neither sodium nor any of its salts exhibits radioactivity.[10]

Sodium Ion.—The strong tendency of sodium towards ionization is in accordance with the view that the ion is the more stable form, and with the fact that the heat of ionization per gram-equivalent of the metal is 57·400 Cal.[11] The ion is univalent and colourless, but with coloured anions yields substances coloured both in the solid state and in solution. For the atomic refraction Rudorff[12] gives 4·65, and for the transport-number Tolman[13] found 0·615. The conductivity of the sodium ion

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[1] Vanstone, *Chem. News*, 1911, 103, 181, 198, 207.

[2] Cohen and Wolff, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, 18, 91.

[3] Richards, *Zeitsch. physikal. Chem.*, 1907, 61, 77.

[4] Hagen, *Wied. Annalen*, 1883, 19, 436; Dewar, *Proc. Roy. Soc.*, 1902, [A], 70, 237.

[5] Hagen, *loc. cit.*; Quincke, *Pogg. Annalen*, 1868, 134, 356; 135, 621.

[6] Hackspill and Bossuet, *Compt. rend.*, 1911, 152, 874.

[7] Compare the section of this volume on ammonium nitrate.

[8] Strecker and Thienemann, *Ber.*, 1920, 53, [B], 2096; compare Traube, *Ber.*, 1912, 45, 2201; 1916, 49, 1670.

[9] Compare Cohen, *Chem. News*, 1886, 54, 305.

[10] Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576; Henriot, *Le Radium*, 1910, 7, 40; *Compt. rend.*, 1911, 152, 851; Satterly, *Proc. Camb. Phil. Soc.*, 1911, 16, 67; Büchner, *Le Radium*, 1912, 9, 259.

[11] Ostwald, *Grundriss der allgem. Chem.*, 3rd ed., Leipsic, 1899, 281.

[12] Rudorff, *Periodische System der Elemente*, Hamburg and Leipsic, 1904, 155.

[13] Tolman, *J. Amer. Chem. Soc.*, 1911, 33, 121.

at 18° C. is 43·4, and at 25° C. is 51·2. References to investigations of other properties of this ion are appended.[1]

Transmutation of Copper into Sodium.—In their account of their researches on the action of the radium emanation on solutions of copper salts, Cameron and Ramsay[2] state that sodium is probably a product of the action of the emanation on a solution of copper sulphate.[3]

Applications.—Sodium is employed in the manufacture of sodium peroxide, sodamide, and sodium cyanide, and also in organic syntheses. In the laboratory it finds application in the preparation of pure sodium hydroxide, and in presence of alcohols as a reducer.

Atomic Weight.—There is a very close association between the atomic weight of sodium and the atomic weights of potassium, silver, chlorine, bromine, and iodine, each element having been an important factor in the experimental investigation of both its own atomic weight and the atomic weights of the other five. The method of determining the ratio of the atomic weights of these elements to that of oxygen was originated by Berzelius, and was developed by Marignac and Stas. It involves three stages:

(1) The determination of the molecular weights of the chlorides, bromides, and iodides of sodium, potassium, and silver by analysis of the salts RXO_3 (R=metal, X=halogen), and induction from the ratios RX : 3O.

(2) The determination of the three ratios Ag : NaX, of the three Ag : KX, and of the three Ag : AgX, values for the atomic weight of silver being obtained from these ratios in conjunction with the previously determined molecular weights of the metallic halides NaX, KX, and AgX:

$$\frac{RX}{3O}\times\frac{Ag}{RX}=\frac{Ag}{3O}.$$

(3) The determination of the six ratios AgX : RX, and the calculation of additional values for the atomic weight of silver from the expression

$$\frac{RX}{3O}\times\frac{AgX}{RX}\times\frac{Ag}{AgX}=\frac{Ag}{3O}.$$

From the results obtained in (2) and (3) for the atomic weight of silver, a mean value is derived. Employing this figure, the molecular weights of the silver halides are calculated from the ratios Ag : AgX, compared with those obtained directly in (1), and mean values derived. Subtraction of the atomic weight of silver from these mean values gives the atomic weights of the halogens. Having thus ascertained the atomic weights of silver and the halogens, the molecular weights of the alkali-metal halides are calculated from the ratios Ag : RX, and also

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[1] Wilsmore, *Zeitsch. physikal. Chem.*, 1900, 35, 291; Haber and Sack, *Zeitsch. Elektrochem.*, 1902, 8, 246; Ostwald, *Zeitsch. physikal. Chem.*, 1888, 2, 36, 270; Rudolphi, *ibid.*, 1895, 17, 385; van 't Hoff, *ibid.*, 1895, 18, 300; Storch, *ibid.*, 1895, 19, 13; Kohlrausch, *ibid.*, 1895, 18, 662; Roloff, *Zeitsch. angew. Chem.*, 1902, 15, 525, 561, 585; Jahn, *Zeitsch. physikal. Chem.*, 1900, 35, 1; Biltz, *ibid.*, 1902, 40, 185; Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, 20, 496; Kahlenberg, *J. Physical Chem.*, 1901, 5, 375; Drucker, *Zeitsch. Elektrochem.*, 1907, 13, 81; compare Abegg, *Theorie der electrolyt. Dissoziation*, Stuttgart, 1903, 81; and Drucker, *Anomalie der starken Elektrolyte*, Stuttgart, 1905.

[2] Cameron and Ramsay, *Trans. Chem. Soc.*, 1907, 91, 1593.

[3] See p. 55.

from AgX : RX, the values compared with those obtained directly in (1), and mean values derived. Subtraction of the atomic weights of the halogens then gives the atomic weights of the alkali-metals. In practice all the ratios indicated were not determined, and the experimental work of the earlier investigators lacked some of the precision characteristic of more modern researches. The necessary calculations are complicated by the fact that some ratios appear to have been determined with more accuracy than others. If this discrepancy is due to a greater degree of concordance having been attained in successive experiments upon the ratio, suitable allowance may be made for it if the " probable errors " of all the series of experiments are calculated. If n represents the number of observations or experiments in a series, and S the sum of the squares of the variations of the individual results from the arithmetic mean, the probable error e is given by the formula

$$e = 0{\cdot}6745 \times \frac{\mathrm{S}}{n(n-1)} \cdot$$

Assuming two experimenters to have measured the same ratio, their results being R_1 and R_2, with probable errors of a and b respectively ; then, instead of adopting the arithmetic mean $(R_1+R_2)/2$, it is better to employ the " weighted mean," the results being " weighted " inversely as the squares of their probable errors. The weighted mean is then

$$\left(\frac{R_1}{a^2}+\frac{R_2}{b^2}\right)\Big/\left(\frac{1}{a^2}+\frac{1}{b^2}\right).$$

Thus, if b is three times as large as a, in taking the mean the importance attached to R_1 is ninefold that laid on R_2.

In this manner the initial ratios and their probable errors can be determined. In the calculations made from them, each result obtained by such arithmetical processes as multiplication and division has its probable error computed by known methods. Thus, when all the values for the atomic weight of silver have been calculated, each has its probable error attached ; and the weighted mean of the values is readily ascertained, and also its probable error. These data are then utilized in computing the atomic weights of the halogens and of the other elements. The method of calculation described was employed by Clarke. Like all methods of computation, it can make no allowance for chemical errors in the determination of the ratios, such as the presence of traces of impurities in the substances employed. To allow for these errors, it is necessary to examine critically the details of each determination, and form a judgement of its chemical merit. Since such a procedure cannot be made quantitative, critics must necessarily vary in their conclusions. The problem of inducing the most probable set of values for the fundamental atomic weights from the available experimental data is obviously difficult. References to the divergent methods adopted by various computers are appended.[1]

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[1] Clarke, *A Recalculation of the Atomic Weights*, Smithsonian Miscellaneous Collections, 2nd ed., Washington, 1897, 34 ; 3rd ed., 1910, 68 ; *Amer. Chem. J.*, 1902, 27, 321 ; Lothar Meyer and Seubert, *Die Atomgewichte der Elemente*, Leipsic, 1883, 50 ; Stas, *Œuvres Complètes*, Brussels, 1894, 1, 419 ; Ostwald, *Lehrbuch der allgemeinen Chemie*, Leipsic, 1885, 1, 41 ; van der Plaats, *Ann. Chim. Phys.*, 1886, [6], 7, 499 ; Thomsen, *Zeitsch. physikal. Chem.*, 1894, 13, 726. See also the various articles by Brauner in Abegg and Auerbach's *Handbuch der anorganischen Chemie.*

The earlier determinations of the ratios involving the atomic weight of sodium commence with the work of Penny[1] in 1839. Four analyses of sodium chlorate gave as the mean result

$$NaClO_3 : 3O = 100 : 45{\cdot}0705 \pm 0{\cdot}0029.$$

Several early series of analyses of sodium chloride are available, in which the silver necessary to combine with the chlorine in a known weight of sodium chloride was determined. The results of these experiments are given in the table :

Experimenter.	Date.	$Ag : NaCl = 100 : x$, where $x =$
Pelouse[2] .	1845	$54{\cdot}141 \pm 0{\cdot}0063$
Dumas[3] . .	1859	$54{\cdot}172 \pm 0{\cdot}0096$
Stas[4] . .	1860	$54{\cdot}2078 \pm 0{\cdot}0002$
Stas[5] . .	1876–1882	$54{\cdot}2047 \pm 0{\cdot}00045$

In Stas's second research allowance was made for the solubility of silver chloride in water, and for the presence of a trace of silica in the salt. Clarke has calculated the weighted mean of these four series of experiments to be

$$Ag : NaCl = 100 : 54{\cdot}2071 \pm 0{\cdot}00018.$$

The corresponding ratio for sodium bromide was also determined by Stas[6] to be

$$Ag : NaBr = 100 : 95{\cdot}4405.$$

Two series of determinations of the ratio

$$AgCl : NaCl = 100 : x$$

should be mentioned. The first was carried out by Berzelius[7] in 1811, and gave $x = 40{\cdot}885$; the second was made incidentally by Ramsay and Miss Aston[8] in their work on the atomic weight of boron, and gave $x = 40{\cdot}867$. Both these results are much too high.

The values obtained by Stas for the atomic weights of silver, chlorine, and bromine were 107·930, 35·457, and 79·952, and were employed for many years.[9] By their aid the atomic weight of sodium can be calculated from the results already cited. From Penny's experiments ($NaClO_3 : 3O$) it follows that $NaCl = 58{\cdot}500$. From the mean ratio $Ag : NaCl$ it can be calculated that $NaCl = 58{\cdot}506$. The average result is $NaCl = 58{\cdot}503$. From the ratio $Ag : NaBr$ it follows that $NaBr =$

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[1] Penny, *Phil. Trans.*, 1839, 129, 25.

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

[3] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 182.

[4] Stas, *Œuvres Complètes*, Brussels, 1894, 1, 370.

[5] Stas, *ibid.*, 768, 778.

[6] Stas, *ibid.*, 796.

[7] Berzelius, *Afhandlingar i Fysik, Kemi, etc.*, Stockholm, 1806–1816, 5, 117; Gilbert's *Annalen*, 1811, 38, 171.

[8] Ramsay and Miss Emily Aston, *Trans. Chem. Soc.*, 1893, 63, 211.

[9] A mathematical computation from all the early data leads to approximately the same values.

103·009. Hence, two values for the atomic weight of sodium can be induced:

$$\mathrm{Na} = \mathrm{NaCl} - \mathrm{Cl} = 58{\cdot}503 - 35{\cdot}457 = 23{\cdot}046\,;$$

and

$$\mathrm{Na} = \mathrm{NaBr} - \mathrm{Br} = 103{\cdot}009 - 79{\cdot}952 = 23{\cdot}057.$$

The mean value Na=**23·05** derived from the early work was adopted for many years. It was proved to be too high by Richards and Wells, whose accurate analyses of sodium chloride, computed with Ag=107·93, give Na=23·008.

Richards and his coadjutors have proved one of the fundamental errors in the work of Stas, for years regarded as a model of accuracy, to have been the employment of excessive quantities of substances. His object was to avoid errors in weighing, but his method necessitated a concentration of the solutions such as induced occlusion of extraneous material in his precipitates. This experimental defect and other sources of error have been avoided by the American school, with Richards as its leader, and a new era in the field of atomic-weight determination has been initiated.

In their analyses of sodium chloride in 1905, Richards and Wells [1] purified their materials with extreme care, an example being their application of the centrifuge to the removal of the mother-liquor from sodium chloride after crystallization. Their work involved the determination of the two ratios AgCl : NaCl and Ag : NaCl. For the experimental details of this classical investigation the original paper should be consulted. In two series of ten experiments each the results were:

$$\mathrm{AgCl} : \mathrm{NaCl} = 100 : 40{\cdot}7797, \text{ whence } \mathbf{Na = 22{\cdot}995}\,;$$

and

$$\mathrm{Ag} : \mathrm{NaCl} = 100 : 54{\cdot}185, \text{ whence } \mathbf{Na = 22{\cdot}998}.$$

The calculation is based upon the value 107·880 for the atomic weight of silver, and 36·457 for that of chlorine, these being the modern numbers obtained by Richards and his coadjutors with O=16 as primary standard.

Two analyses of sodium bromide have been made by Richards and Wells.[2] Their mean is

$$\mathrm{AgBr} : \mathrm{NaBr} = 100 : 54{\cdot}8010, \text{ whence } \mathbf{Na = 22{\cdot}998}.$$

In the calculation, the modern value for the atomic weight of bromine, 79·916, has been employed. The result calculated with Stas's values for silver and bromine is Na=23·008, a number much lower than that indicated by the work of Stas himself. This anomaly led Richards and Wells to their research on sodium chloride, and thus caused a revision of the atomic weights of sodium and chlorine.

In 1911 Goldbaum [3] employed a new method in the investigation of the atomic weight of sodium. Aqueous solutions of weighed quantities of sodium chloride and sodium bromide were electrolyzed, using a mercury cathode and a silver anode. The increase in the weight of the anode gave the amount of halogen present. Assuming Cl=35·457 and Br=79·916, the results are:

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[1] Richards and Wells, *Publications of the Carnegie Institute of Washington*, 1905, No. 28; *J. Amer. Chem. Soc.*, 1905, 27, 459; *Chem. News*, 1906, 93, 175.

[2] Richards and Wells, *Proc. Amer. Acad.*, 1906, 41, 443.

[3] Goldbaum, *J. Amer. Chem. Soc.*, 1911, 33, 35.

11 experiments. Cl : NaCl = 100 : 164·858, whence **Na = 22·997.**
8 experiments. Br : NaBr = 100 : 128·776, whence **Na = 22·997.**

In the work of Richards and Hoover [1] in 1915, pure sodium carbonate was exactly neutralized with a solution of hydrobromic acid standardized against pure silver. They found that

$$Na_2CO_3 : 2Ag = 29·4350 : 59·9168.$$

Hence, if Ag = 107·880, the molecular weight of sodium carbonate is 105·995; so that 2Na + C = 57·995. A review of the atomic weight of carbon [2] indicates that the value is probably between 12·000 and 12·005. It follows that the atomic weight of sodium must lie between **Na = 22·995** and **Na = 22·998.**

The modern work of Richards and Wells, Goldbaum, and Richards and Hoover indicates a value between 22·995 and 22·998 for the atomic weight of sodium. In the account of his work in 1915, Richards gave the preference to the lower number. In this series of text-books, the value **Na = 22·996** has been adopted for the computation of other atomic weights. The current table of the International Committee on Atomic Weights gives

Na = 23·00.

COMPOUNDS OF SODIUM.[3]

Sodium hydride, NaH.—By heating sodium contained in an iron vessel inside a sealed glass tube in an atmosphere of hydrogen, Moissan [4] obtained sodium hydride in white crystals which condensed on the cooler part of the glass tube. The temperature of reaction is about 360° C., and is a factor of importance, since for sodium hydride the interval between the temperature of formation and that of decomposition is small. Much larger quantities of the hydride can be prepared [5] by passing a rapid current of hydrogen over the surface of sodium heated to such a temperature above 350° C. as produces a yellow glow. The hydride is carried off as a white smoke, and after electrical precipitation is filtered through glass-wool. The presence of metallic calcium facilitates its formation.

The density of the hydride is 0·92,[6] and the vapour-tension for each interval of 10° between 300° C. and 410° C. is 15, 17, 21, 27, 38, 55, 87, 136, 201, 285, 396, and 540 mm. respectively.[7] Sodium hydride is the most stable of the alkali-metal hydrides, and cæsium hydride the least. The sodium derivative is unaffected by dry air, but decomposes in presence of traces of moisture. Although insoluble in organic solvents such as carbon disulphide, carbon tetrachloride, benzene, and turpentine, it dissolves in the alkali-metals and their amalgams.

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[1] Richards and Hoover, *J. Amer. Chem. Soc.*, 1915, 37, 95.

[2] This series, Vol. V., 64.

[3] For *sodium-amalgam*, see this series, Vol. III. Alloys with potassium are mentioned on p. 159.

[4] Moissan, *Compt. rend.*, 1902, 134, 71; compare Elster and Geitel, *Physikal. Zeitsch.*, 1910, 11, 257.

[5] Ephraim and Michel, *Helv. Chim. Acta*, 1921, 4, 762.

[6] Moissan, *Compt. rend.*, 1902, 134, 71.

[7] Ephraim and Michel, *Helv. Chim. Acta*, 1921, 4, 762; compare Keyes, *J. Amer. Chem. Soc.*, 1912, 34, 779.

The affinity of sodium hydride for oxygen renders it a powerful reducer. At 230° C. it ignites in oxygen, and also burns in air under the influence of heat. It is not affected by liquid oxygen, and does not combine with liquid chlorine at −35° C. Water converts it into the hydroxide, and hydrochloric acid into the chloride, both reactions being accompanied by evolution of hydrogen. Under the influence of slight heat it combines with the oxygen of carbon dioxide, depositing carbon. With oxidizers such as potassium chlorate, it unites with explosive energy.

From the heats of solution in water of the hydride and of sodium, de Forcrand[1] has calculated the heat of formation of the hydride to be in accordance with the equation

$$[\mathrm{Na}]+(\mathrm{H})=[\mathrm{NaH}]+16{\cdot}60\ \mathrm{Cal.}$$

Almost thirty years before the date of Moissan's work, a very unstable, crystalline, silver-white compound was described by Troost and Hautefeuille.[2] They obtained it by sorption of hydrogen by means of sodium above 300° C., the metal sorbing 237 times its volume of the gas. That their product was a definite chemical compound is doubtful; it was probably a solid solution of hydrogen in sodium, analogous to that formed by palladium.

Sodium fluoride, NaF.—The fluoride is precipitated on neutralizing hydrofluoric acid with the hydroxide or carbonate. It can also be prepared from cryolite,[3] $3NaF,AlF_3$, by removing the aluminium by treatment with excess of sodium hydroxide, and extracting the undissolved sodium fluoride with boiling water.

Sodium fluoride forms colourless cubes, melting at 980°,[4] 986°[5] or 988° C.,[6] and boiling at 1695° C.[7] The vapour-pressure in atmospheres corresponds with the expression[7]

$$\log p=-56600/4{\cdot}57T+6{\cdot}299.$$

The density is 2·766.[8] Sodium fluoride is the least soluble of the sodium halides, 4 parts dissolving in 100 parts of water at 15° C.,[9] and the solubility does not increase much with rise of temperature.

For the heat of neutralization of sodium hydroxide by dilute hydrofluoric acid Thomsen[10] found 16·27 Cal. Guntz[11] determined the heat of solution to be −0·6 Cal. at 12° C. For the heat of formation from the elements Thomsen gives 102·6 Cal.; Guntz gives 109·3 Cal. Between

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[1] de Forcrand, *Compt. rend.*, 1905, 140, 990.

[2] Troost and Hautefeuille, *ibid.*, 1874, 78, 809; compare Moutard, *ibid.*, 1874, 79, 1242.

[3] Schuch, *Annalen*, 1863, 126, 108; compare Jean, *Compt. rend.*, 1868, 66, 801.

[4] Ruff and Plato, *Ber.*, 1903, 36, 2363.

[5] Wolters, *Jahrb. Min. Beil.-Bd.*, 1914, 30, 55; *Zeitsch. Kryst. Min.*, 1914, 53, 514.

[6] von Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and von Wartenberg, *ibid.*, 162.

[7] von Wartenberg and Schulz, *loc. cit.*

[8] Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

[9] Frémy, *Ann. Chim. Phys.*, 1856, [3], 47, 32; Mylius and Funk, *Ber.*, 1897, 30, 1718; Ditte, *Compt. rend.*, 1896, 123, 1283.

[10] Thomsen, *Thermochemistry* (Longmans, 1908), 95.

[11] Guntz, *Compt. rend.*, 1883, 97, 1558.

15° C. and 53° C. the specific heat[1] is 0·2675. References to investigations of the properties of aqueous solutions are appended.[2]

Sodium hydrogen fluoride, NaF,HF.—A crystalline primary fluoride is obtained by the action of hydrofluoric acid on sodium fluoride. On heating, it decomposes with elimination of hydrofluoric acid. Its solubility in water increases with rise of temperature. The heat of solution is given by Guntz[3] as −6·2 Cal., and the heat of formation from solid sodium fluoride and gaseous hydrofluoric acid as 17·1 Cal.

Sodium chloride, $NaCl$.—Large quantities of sodium chloride are found in nature, the average amount present in the water of the ocean being about 2·7 per cent., while certain inland lakes contain a much higher percentage. The Great Salt Lake in Utah has up to 30 per cent. of the chloride in solution, and the Dead Sea 22 to 23 per cent. The natural product known as " rock-salt " is the residue left on evaporation of inland seas, such deposits being found in Cheshire, at Stassfurt and Berchtesgaden in Germany, at Vic in France, and at Wieliczka in Galicia. Rock-salt is usually associated with calcium sulphate, alumina, and sandstone. At Stassfurt the layer of rock-salt is covered by another layer of readily soluble salts, technically known as " Abraum " salts; that is, salts which must be removed before the rock-salt is reached.

Rock-salt can be obtained from the salt-deposits either by mining or by making borings through which the salt can be extracted by water. The colour of the mined product varies very much; it may be colourless, yellow, red, grey, or green. Iron is a frequent impurity, and other foreign substances often present are magnesium salts, calcium sulphate, alumina, silica, and so on. The presence of a small proportion of magnesium chloride renders the salt hygroscopic; it must be purified by crystallization.

When the salt is extracted from the deposits by the solution-method, two concentric copper tubes are introduced through a boring, the outer tube serving to admit the water, and the inner as a conduit for pumping off the salt-solution. The dissolved salt is obtained by evaporation.

The salt found at Droitwich is in natural solution, and is not contaminated with iron. The liquor is pumped to the surface and evaporated.

The concentration of the water of certain mineral springs and of the ocean also affords a means of isolating salt. Less soluble constituents, such as calcium sulphate, separate first. Admixture of the salt with more soluble compounds, such as magnesium chloride, is obviated by not carrying the concentration too far. Shipper[4] states that the elimination of potassium chloride can be effected by repeated crystallization of the salt from water.

For laboratory use pure sodium chloride is obtained by dissolving the commercial product in water, and reprecipitating by saturating the solution with hydrogen chloride. The pure substance can also be prepared by the action of hydrochloric acid on sodium carbonate or hydroxide.

Sodium chloride crystallizes in transparent or opaque cubes,

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[1] Baud, *J. Physique*, 1903, [4], 2, 569.

[2] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; Kohlrausch and von Steinwehr, *Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 581; Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49; Arrhenius, *ibid.*, 1892, 9, 339.

[3] Guntz, *Compt. rend.*, 1883, 97, 1558.

[4] Shipper, *Chem. News*, 1917, 116, 213.

precipitation with hydrogen chloride also yielding octahedra.[1] In deposits of rock-salt a blue variety of the compound is often found, the colour being probably an optical phenomenon and independent of the presence of any colouring matter, since in solution the blue salt is colourless, and organic solvents fail to extract any coloured substance. Wittjen and Precht [2] attribute the blue colour to reflection of the light from hollow spaces in the crystals, bounded with parallel walls and filled with gas. Their view accords with the fact that heating decolorizes the crystals, probably owing to the expulsion of the gas. Siedentopf [3] considers the probable cause of the colour to be the presence of metallic sodium in the fissures of the crystals. This phenomenon, and the development of a blue colour in sodium chloride exposed to cathode-rays or heated with sodium-vapour, have occasioned much discussion.[4]

There are remarkable discrepancies between the numerous observations recorded for the melting-point of sodium chloride, the observed temperatures lying between 733° C. and 820° C. Carnelley gives 772° C.[5] and 776° C.[6]; Victor Meyer, Riddle, and Lamb,[7] 815·4° C.; Le Chatelier,[8] 780° C.; McCrae,[9] 811° C. and 814·5° C.; Ramsay and Eumorfopoulos,[10] 733° C.; Ruff and Plato,[11] 820° C.; Hüttner and Tammann,[12] 810° C.; Arndt,[13] 805° C.; Schemtschushny and Rambach,[14] 819° C.; Schaefer,[15] 802° C.; Haigh,[16] and Foote and Dana,[17] 801° C.; Wolters,[18] 797° C.; Korreng,[19] 800° C.; and Schemtschushny,[20] 816° C. For the freezing-point Plato [21] gives 804·3° C. The latent heat of fusion per gram is 0·097 Cal.[22] Even at its melting-point sodium chloride is somewhat volatile, evolving heavy white fumes of the vapour. It has the simple molecular formula $NaCl$, as is proved by the vapour-density method,[23] by the ebullioscopic method with bismuth trichloride as solvent,[24] and by the cryoscopic method with fused mercuric chloride as solvent.[25]

The fused chloride solidifies in cubes. The question of the possibility of the formation of mixed crystals with the chlorides of potassium,

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[1] Compare Traube, *Jahrb. Min.*, 1892, 2, 163; Orloff, *Zeitsch. Kryst. Min.*, 1895, 24, 515.

[2] Wittjen and Precht, *Ber.*, 1883, 16, 1454.

[3] Siedentopf, *Physikal. Zeitsch.*, 1905, 6, 855; compare *Ann. Physik*, 1903, [4], 10, 1.

[4] Goldstein, *Wied. Annalen*, 1895, 54, 371; Wiedemann and Schmidt, *ibid.*, 1895, 54, 622; 1898, 64, 78; Elster and Geitel, *ibid.*, 1896, 59, 487; Giesel, *Ber.*, 1897, 30, 156; Kreutz, *ibid.*, 403; Abegg, *Zeitsch. Elektrochem.*, 1898, 4, 18; Wöhler and Kasarnowski, *Zeitsch. anorg. Chem.*, 1905, 47, 353; Siedentopf, *Physikal. Zeitsch.*, 1905, 6, 855; Pieszczek, *Pharm. Zeit.*, 1906, 51, 700; Doelter, *Tsch. Min. Mitt.*, 1912, [2], 30, 143.

[5] Carnelley, *J. Chem. Soc.*, 1876, 29, i., 489.

[6] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[7] Victor Meyer, Riddle, and Lamb, *Ber.*, 1893, 26, 3129.

[8] Le Chatelier, *Compt. rend.*, 1894, 118, 350.

[9] McCrae, *Ann. Physik*, 1895, [3], 55, 95.

[10] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[11] Ruff and Plato, *Ber.*, 1903, 36, 2357.

[12] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[13] Arndt, *Zeitsch. Elektrochem.*, 1906, 12, 337.

[14] Schemtschushny and Rambach, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1785.

[15] Schaefer, *Jahrb. Min. Beil.-Bd.*, 1919, 43, 132.

[16] Haigh, *J. Amer. Soc.*, 1912, 34, 1137.

[17] Foote and Dana, *Trans. Faraday Soc.*, 1920, 15, 186.

[18] Wolters, *Jahrb. Min. Beil.-Bd.*, 1914, 30, 55; *Zeitsch. Kryst. Min.*, 1914, 53, 514

[19] Korreng, *Jahrb. Min. Beil.-Bd.*, 1914, 37, 51.

[20] Schemtschushny, *J. Russ. Phys. Chem. Soc.*, 1916, 48, 203.

[21] Plato, *Zeitsch. physikal. Chem.*, 1906, 55, 721.

[22] Schemtschushny and Rambach, *loc. cit.*

[23] Nernst, *Gött. Nachr.*, 1903, 75.

[24] Rügheimer, *Ber.*, 1903, 36, 3030; *Annalen*, 1905, 339, 326.

[25] Beckmann, *Zeitsch. anorg. Chem.*, 1907, 55, 180.

lithium, and ammonium has been much debated,[1] but Schaefer[2] demonstrated that sodium chloride forms a complete series of mixed crystals with lithium chloride. It appears from the work of Kurnakoff and Schemtschushny[3] that the chlorides of sodium and potassium are completely miscible at high temperatures, although the individual crystals begin to separate about 400° C.

For the density of pure sodium chloride Clarke[4] gives 2·135; Retgers,[5] 2·167 at 17° C.; Krickmeyer,[6] 2·174 at 20° C.; and Haigh,[7] 2·170 at 20° C. Brunner[8] has investigated the density of the fused salt between its melting-point and 1000° C.

The mean value of several investigations[9] of the index of refraction of rock-salt at 18° C. for the D-line is 1·54432. For the electric conductivity of fused sodium chloride at 960° C. Braun[10] gives 0·9206 reciprocal ohms, and at 750° C. Poincaré[11] found 3·339 reciprocal ohms. For the specific heat of the fused chloride between 13° and 46° C. Kopp[12] gives 0·213, and from 15° to 98° C. Regnault[13] gives 0·2140. For rock-salt at 0° C. Weber[14] gives 0·2146, and from 13° to 45° C. Kopp[15] gives 0·219.

As indicated in the table, the solubility of sodium chloride in water is only slightly augmented by rise of temperature.

SOLUBILITY OF SODIUM CHLORIDE.

Observer.	Temperature, °C.	Grams NaCl in 100 grams Water.	Observer.	Temperature, °C.	Grams NaCl in 100 grams Water.
Andreae[16] .	0	35·63	Earl of Berkeley[17]	90	38·52
,, .	10	35·69			
,, .	20	35·82	,, ,,	100	39·12
,, .	30	36·03	Tilden and Shenstone[18]	118	39·8
,, .	40	36·32			
,, .	50	36·67	,, ,,	140	42·1
,, .	60	37·06	,, ,,	160	43·6
,, .	70	37·51	,, ,,	180	44·9
,, .	80	38·0			

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[1] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 53; Le Chatelier, *Compt. rend.*, 1894, 118, 350; Ruff and Plato, *Ber.*, 1903, 36, 2357; Ruff, *Iswiestja Polytech. Inst. St. Petersburg*, 1906, 5; *Chem. Zentr.*, 1906, i., 1728; Ostwald, *J. prakt. Chem.*, 1882, [2], 25, 8; Beketoff, *Zeitsch. anorg. Chem.*, 1904, 40, 855.

[2] Schaefer, *Jahrb. Min. Beil.-Bd.*, 1919, 43, 132.

[3] Kurnakoff and Schemtschushny, *Iswiestja Polytech. Inst. St. Petersburg*, 1905, 4, 227; *Chem. Zentr.*, 1906, i., 527.

[4] Clarke, *Constants of Nature*, Washington, 1873, 1, 30.

[5] Retgers, *Zeitsch. physikal. Chem.*, 1889, 3, 289.

[6] Krickmeyer, *ibid.*, 1896, 21, 53. [7] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[8] Brunner, *Zeitsch. anorg. Chem.*, 1904, 38, 350.

[9] Stefan, *Sitzungsber. K. Akad. Wiss. Wien*, 1871, 63, [2], 239; Langley, *Ann. Chim. Phys.*, 1886, [6], 9, 92: Borel, *Compt. rend.*, 1895, 120, 1406; Martens, *Ann. Physik*, 1902, [4], 8, 459; Dufet, *Bull. Soc. franç. Min.*, 1891, 14, 130.

[10] Braun, *Ber.*, 1874, 7, 958. [11] Poincaré, *Compt. rend.*, 1889, 109, 174.

[12] Kopp, *Annalen Suppl.*, 1864–1865, 3, i., 289.

[13] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[14] Weber, *Arch. Sci. phys. nat.*, 1895, [3], 33, 590.

[15] Kopp, *loc. cit.* [16] Andreae, *J. prakt. Chem.*, 1884, [2], 29, 467.

[17] Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 206.

[18] Tilden and Shenstone, *ibid.*, 1884, 175, 32.

According to Gerlach,[1] a saturated solution contains 40·7 grams per 100 grams of water, and in contact with the solid boils at 108·8° C. The Earl of Berkeley and Applebey [2] state the boiling-point to be 108·668° C. at 760 mm. pressure. The heat of solution is given by Thomsen [3] as —1·2 Cal.

At 25° C., 100 grams of ethyl alcohol dissolve 0·065 gram of sodium chloride.[4]

Several hydrates of sodium chloride have been described, but only the dihydrate, $NaCl,2H_2O$, seems to have been definitely isolated.[5]

For the heat of formation of sodium chloride from its elements, Thomsen [6] gives 97·69 Cal., and from the interaction of aqueous solutions of sodium hydroxide and hydrogen chloride 13·745 Cal.

Matignon [7] has determined the freezing-point of solutions of sodium chloride of various concentrations. Some of his results are given in the table:

Percentage of Sodium Chloride.	Freezing-point, °C.
11	— 6·6
15	— 9·25
20	—12·7
25	—16·66

Matignon's work indicates that a stable liquid mixture of water and sodium chloride does not exist below —21·3° C.

References are appended to investigations of the properties of dilute aqueous solutions of sodium chloride, including the molecular depression of the freezing-point [8] and elevation of the boiling-point,[9] vapour-pressure,[10] density,[11] viscosity,[12] refractive index,[13] specific heat,[14] diffu-

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[1] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.

[2] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.

[3] Thomsen, *J. prakt. Chem.*, 1877, [2], 16, 328; compare Stackelberg, *Zeitsch. physikal. Chem.*, 1896, 20, 159.

[4] Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1904.

[5] Meyerhoffer and Saunders, *Zeitsch. physikal. Chem.*, 1899, 28, 461; Meyerhoffer, *ibid.*, 1899, 31, 381; de Coppet, *Ann. Chim. Phys.*, 1872, [4], 25, 511.

[6] Thomsen, *Thermochemistry* (Longmans, 1908), 120, 259.

[7] Matignon, *Compt. rend.*, 1909, 148, 550.

[8] Roth, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 488; Hausrath, *Ann. Physik*, 1902, [4], 9, 546; Osaka, *Zeitsch. physikal. Chem.*, 1902, 41, 562; Nernst and Abegg, *ibid.*, 1894, 15, 688; Raoult, *ibid.*, 1898, 27, 658; Biltz, *ibid.*, 1902, 40, 199; Kahlenberg, *J. Physical Chem.*, 1901, 5, 353; Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, 6, 394; Jones, *ibid.*, 1893, 11, 112; Abegg, *ibid.*, 1895, 20, 220; Jahn, *ibid.*, 1904, 50, 129; 1907, 59, 31; Arrhenius, *ibid.*, 1888, 2, 496; Loomis, *Wied. Annalen*, 1894, 51, 515; 1897, 60, 527.

[9] Roth, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 499; Smits, *Zeitsch. physikal. Chem.*, 1902, 39, 385; Landsberger, *Zeitsch. anorg. Chem.*, 1898, 17, 452.

[10] Dieterici, *Wied. Annalen*, 1891, 42, 513; Tammann, *ibid.*, 1885, 24, 530; *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9.

[11] Schütt, *Zeitsch. physikal. Chem.*, 1890, 5, 349; Andreae, *J. prakt. Chem.*, 1884, 30, 305.

[12] Reyher, *Zeitsch. physikal. Chem.*, 1888, 2, 744; Arrhenius, *ibid.*, 1887, 1, 285; Hosking, *Phil. Mag.*, 1900, [5], 49, 274.

[13] Schütt, *Zeitsch. physikal. Chem.*, 1892, 9, 351; Briner, *J. Chim. phys.*, 1906, 4, 547.

[14] Thomsen, *Pogg. Annalen*, 1871, 142, 337; Winkelmann, *Wied. Annalen*, 1873, 149, 1; Teudt, *Dissertation*, Erlangen, 1900; Marignac, *Ann. Chim. Phys.*, 1876, [5], 8, 410; Demolis, *J. Chim. phys.*, 1906, 4, 526.

sion,[1] electric conductivity,[2] and the effect of other dissolved substances on the solubility[3]: also to work on the solubility in non-aqueous solvents,[4] and on the compressibility.[5]

Electrolysis.[6]—The electrolysis of sodium chloride is an important technical process, producing the hydroxide and carbonate, as well as chlorine and from it bleaching-powder. In the formation of sodium hydroxide, precautions to prevent conversion of the product into hypochlorite and chlorate are necessary.

In one process the cathodic and anodic chambers are separated by a diaphragm of porous clay,[7] the cathode being a rod of iron to resist the action of the caustic alkali, and the anode being of carbon to withstand the corrosive action of the chlorine.[8] Hargreaves and Bird[9] employ a cathode of iron-gauze.

In the mercury process the bottom of the electrolytic cell is covered with a layer of mercury into which a non-porous diaphragm dips so that the mercury forms a partition between the anodic and cathodic chamber. The anode is made of carbon, and is immersed in sodium-chloride solution; the cathode is made of iron, and is dipped into water. The mercury acts as cathode, taking up the liberated sodium to form an amalgam, which reacts with the water to produce sodium hydroxide. Various modifications of the process have been devised, one being the substitution of fused sodium chloride for the solution, and of fused lead or tin for mercury, the alloy produced being subsequently decomposed by water.[10]

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[1] Heimbrodt, *Dissertation*, Leipsic, 1903; Graham, *Zeitsch. physikal. Chem.*, 1904, 50, 257.

[2] Kohlrausch and Maltby, *Sitzungsber. K. Akad. Wiss. Berlin*, 1899, 665; Kohlrausch and Grotrian, *Pogg. Annalen*, 1875, 154, 1; Kohlrausch, Holborn, and Diesselhorst, *Wied. Annalen*, 1898, 64, 417; Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49; Arrhenius, *ibid.*, 1892, 9, 339; Krannhals, *ibid.*, 1890, 5, 250; Schaller, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 755; Déguisne, *Dissertation*, Strasbourg, 1895; Noyes and Coolidge, *Zeitsch. physikal. Chem.*, 1903, 46, 323; Jahn, *ibid.*, 1901, 37, 673; 1907, 58, 641; Schapire, *ibid.*, 1904, 49, 513; Hittorf, *Ostwald's Klassiker*, 21, 23.

[3] Karsten, *Philosophie der Chemie*, 1843; Winkelmann, *Ann. Physik*, 1873, 149, 492; Mulder, *Scheikund. Verhandel.*, 1864, 207; van 't Hoff and Reicher, *Zeitsch. physikal. Chem.*, 1889, 3, 482; Mackenzie, *Wied. Annalen*, 1877, 1, 438; Sestschenoff, *Zeitsch. physikal. Chem.*, 1889, 4, 117; Bohr, *Wied. Annalen*, 1899, 68, 500; Gordon, *Zeitsch. physikal. Chem.*, 1895, 18, 1; Roth, *ibid.*, 1897, 24, 114; Knopp, *ibid.*, 1904, 48, 97; Steiner, *Wied. Annalen*, 1894, 52, 275; Braun, *Zeitsch. physikal. Chem.*, 1900, 33, 721; McLauchlan, *ibid.*, 1903, 44, 600; Geffcken, *ibid.*, 1904, 49, 257; Rothmund, *ibid.*, 1900, 33, 401; Biltz, *ibid.*, 1903, 43, 41; Euler, *ibid.*, 1899, 31, 360; 1904, 49, 303; Levin, *ibid.*, 1906, 55, 513; Dawson, *Trans. Chem. Soc.*, 1901, 79, 493; 1906, 89, 605; Abegg and Riesenfeld, *Zeitsch. physikal. Chem.*, 1902, 40, 84; Raoult, *Ann. Chim. Phys.*, 1874, [5], 1, 262; Gaus, *Zeitsch. anorg. Chem.*, 1900, 25, 236; Riesenfeld, *Zeitsch. physikal. Chem.*, 1902, 45, 460; Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 910, 985; Joannis, *Compt. rend.*, 1891, 112, 393; Fox, *Zeitsch. physikal. Chem.*, 1902, 41, 458; Kumpf, *Wied. Beibl.*, 1882, 6, 276; Goodwin, *Ber.*, 1883, 15, 3039; Kohn and O'Brien, *J. Soc. Chem. Ind.*, 1898, 17, 1100.

[4] Schiff, *Annalen*, 1865, 118, 365; Gérardin, *Ann. Chim. Phys.*, 1865, [4], 5, 146; Lobry de Bruyn, *Rec. trav. chim.*, 1892, 11, 147; Linnebarger, *Amer. Chem. J.*, 1894, 16, 214.

[5] Richards and Jones, *J. Amer. Chem. Soc.*, 1909, 31, 158.

[6] Compare Oettel, *Elektrochem. Industrie*, Stuttgart, 1896, 112; Förster, *Elektrochemie wässriger Lösungen*, Leipsic, 1905, 385.

[7] Häussermann, *Zeitsch. angew. Chem.*, 1894, 7, 9; Kellner, *ibid.*, 1899, 12, 1080.

[8] Förster, *Zeitsch. Elektrochem.*, 1900, 7, 793.

[9] Hargreaves and Bird, *Jahrb. Elektrochem.*, 1895, 2, 224; compare Förster and Jorre, *Zeitsch. Elektrochem.*, 1903, 9, 206.

[10] Compare Haber, *Grundriss techn. Elektrochem.*, 1898, 469; *Zeitsch. Elektrochem.*, 1903, 9, 364; Förster, *Elektrochemie wässriger Lösungen*, Leipsic, 1905, 427.

The so-called "bell process" gives a better yield than the diaphragm process. The anode is contained in a bell-shaped vessel open at the bottom, the cathode being outside. The sodium-hydroxide solution formed at the cathode floats on the surface of the sodium-chloride solution, and is thus kept from contact with the chlorine evolved at the anode. The gas is removed at the top of the vessel.[1]

Reactions.—At high temperatures in presence of acids such as silicic and boric, or of alumina,[2] the chlorine of sodium chloride can be displaced by oxygen. At 400° C. under pressure the chlorine can be partially replaced by bromine.[3]

Sodium chloride is employed as a glaze for pottery, since at red heat in presence of moisture it combines with the alumina and silica to form a transparent glaze of sodium aluminium silicate. Other technical applications are the manufacture of sodium hydroxide and carbonate, and the isolation of silver and copper from their ores. It also has a dietetic value, and is employed as a preservative for meat.

Schreinemakers and de Baat[4] have described double salts of sodium chloride with cupric chloride and barium chloride.

Sodium bromide, $NaBr$.—The bromide is prepared by neutralizing sodium hydroxide or carbonate with hydrobromic acid; or by the action of bromine on sodium hydroxide, the bromate simultaneously formed being subsequently reduced by heating with charcoal:

$$6NaOH+3Br_2=5NaBr+NaBrO_3+3H_2O;$$
$$2NaBrO_3+3C=2NaBr+3CO_2.$$

Sodium bromide is a white crystalline substance belonging to the rhombic system. The values recorded for its melting-point exhibit a lack of concordance similar to that cited for the chloride (p. 94), the limits of temperature given being 733° to 765° C. Victor Meyer, Riddle, and Lamb[5] give 757·7° C.; Guareschi,[6] 760° C.; MacCrae,[7] 761·1° C.; and Ruff and Plato,[8] 765° C. Ramsay and Eumorfopoulos[9] give 733° C., and Hüttner and Tammann[10] 749° C., but their results are probably unreliable. For the density of the anhydrous salt Clarke[11] gives the mean value 3·014, and Brunner[12] has investigated the density of fused sodium bromide at temperatures up to 1000° C. The salt forms two hydrates, a dihydrate of density[13] 2·176 at 20° C., and a pentahydrate.

Sodium bromide dissolves readily in water. Some of the solubility values determined by de Coppet[14] and by Étard[15] are given in the table.

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[1] Adolph, *Zeitsch. Elektrochem.*, 1900, 7, 581.

[2] Gorgeu, *Compt. rend.*, 1886, 102, 1108, 1164.

[3] Potilitzin, *Ber.*, 1876, 9, 1025; 1879, 12, 2370.

[4] Schreinemakers and de Baat, *Zeitsch. physikal. Chem.*, 1909, 65, 586; compare Liebisch and Korreng, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 192.

[5] Victor Meyer, Riddle, and Lamb, *Ber.*, 1893, 26, 3129.

[6] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.

[7] MacCrae, *Ann. Physik*, 1895, [3], 55, 95.

[8] Ruff and Plato, *Ber.*, 1903, 36, 2357.

[9] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[10] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[11] Clarke, *Constants of Nature*, Washington, 1873, 1, 39.

[12] Brunner, *Zeitsch. anorg. Chem.*, 1904, 38, 350.

[13] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 53.

[14] de Coppet, *Ann. Chim. Phys.*, 1883, [5], 30, 411; compare Guthrie, *Phil. Mag.*, 1875, [4], 49, 210; Étard, *Ann. Chim. Phys.*, 1894, [7], 2, 539.

[15] Étard, *Compt. rend.*, 1884, 98, 1432.

SOLUBILITY OF SODIUM BROMIDE, $NaBr,2H_2O$.

Temperature, °C.	Grams NaBr in 100 grams Water.		Temperature, °C.	Grams NaBr in 100 grams Water.	
	de Coppet.	Étard.		de Coppet.	Étard.
−20	71·4	57·5	50	116	95
0	79·5	66	60	117	112
10	84·5	72	80	119	113
20	90·3	77	100	121	114
30	97·3	82·5	120	124	116
40	105·8	88	140	..	118

Meyerhoffer[1] has plotted the solubility-curve (fig. 6). The transition-temperature of the dihydrate into the anhydrous salt[2] (*D*) is 50·674° C., and that of the pentahydrate into the dihydrate (*C*) is −24° C.

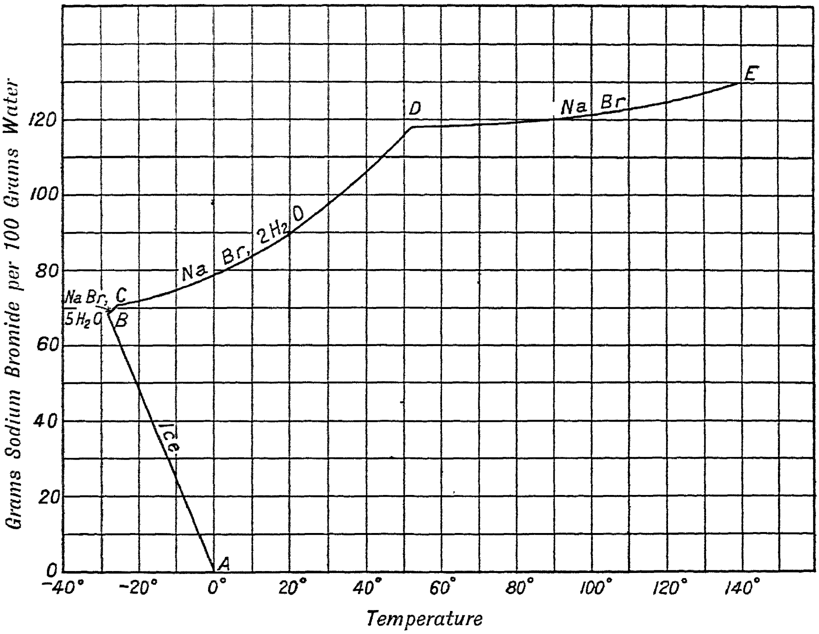

FIG. 6.—Solubility-curve of sodium bromide.

At its melting-point the salt loses only a trace of bromine, but heating with excess of iodine induces a rapid elimination of bromine.[3]

For the heat of formation of sodium bromide from its elements

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[1] Meyerhoffer, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 555.

[2] Richards and Churchill, *Zeitsch. physikal. Chem.*, 1899, 28, 314; Richards and Wells, *ibid.*, 1906, 56, 348; compare Dawson and Jackson, *Trans. Chem. Soc.*, 1908, 93, 344.

[3] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.

Thomsen[1] gives 85·77 Cal. The heat of hydration of the anhydrous salt to the dihydrate is 4·52 Cal.

References are appended to investigations of the solubility of sodium bromide in organic solvents,[2] and to others dealing with such properties of its aqueous solutions as specific heat,[3] density,[4] refractive index,[5] vapour-pressure,[6] molecular depression of the freezing-point[7] and elevation of the boiling-point,[8] electrical constants,[9] and the influence of sulphur dioxide on the solubility of the bromide.[10]

The compressibility is given by Richards and Jones[11] as $5{\cdot}1 \times 10^{-6}$.

Sodium iodide, NaI.—The iodide is prepared by neutralizing sodium hydroxide or carbonate with hydriodic acid; or by the action of iodine on sodium hydroxide, and reduction with charcoal of the iodate simultaneously formed; or from sodium hydroxide and iodine in presence of iron-filings or ferrous iodide.

The dihydrate, $NaI,2H_2O$, is a colourless, crystalline substance, readily soluble in water, and isomorphous with the corresponding hydrate of the chloride and with that of the bromide. The recorded values for the melting-point of the anhydrous salt vary between 603° C. (Ramsay and Eumorfopoulos[12]) and 694·7° C. (MacCrae,[13] who also gives 667·5° C.); Carnelley[14] gives 630° C., Victor Meyer, Riddle, and Lamb[15] 661·4° C., Hüttner and Tammann[16] 664° C., and Ruff and Plato[17] 650° C. The melting-points of the halides of sodium and of the other alkali-metals fall as the atomic weight of the halogen increases. The boiling-point of sodium iodide is 1300° C.,[18] and the vapour-pressure in atmospheres corresponds with the expression[18]

$$\log p = -37000/4{\cdot}57\mathrm{T} + 5{\cdot}130.$$

For the density of the anhydrous salt Schröder[19] gives the value 3·55, and Baxter and Brink[20] 3·665 at 25° C.; for the dihydrate Surawicz[21] gives 2·448. The specific heat between 26° and 50° C. is given by

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[1] Thomsen, *Thermochemistry* (Longmans, 1908), 318.

[2] Lobry de Bruyn, *Rec. trav. chim.*, 1892, 11, 156; Dutoit and Levier, *J. Chim. phys.*, 1905, 3, 435.

[3] Marignac, *Ann. Chim. Phys.*, 1876, [5], 8, 410.

[4] Kremers, *Pogg. Annalen*, 1855, 96, 39.

[5] Borgesius, *Wied. Annalen*, 1895, 54, 233.

[6] Tammann, *ibid.*, 1885, 24, 530.

[7] Jahn, *Zeitsch. physikal. Chem.*, 1905, 50, 129; Jones and Pearce, *Amer. Chem. J.*, 1907, 38, 683.

[8] Schlamp, *Zeitsch. physikal. Chem.*, 1894, 14, 274; Landsberger, *Zeitsch. anorg. Chem.*, 1898, 17, 452; Johnston, *Trans. Roy. Soc. Edin.*, 1906, 45, i., 193.

[9] Ostwald, *Lehrbuch der allgem. Chem.*, 2nd ed., Leipsic, 1893, 743.

[10] Fox, *Zeitsch. physikal. Chem.*, 1902, 41, 458.

[11] Richards and Jones, *J. Amer. Chem. Soc.*, 1909, 31, 158; compare Richards and Stull, *ibid.*, 1904, 26, 399; Richards, Stull, Brink, and Bonnet, *Zeitsch. physikal. Chem.*, 1907, 61, 77, 100.

[12] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[13] MacCrae, *Ann. Physik*, 1895, [3], 55, 95.

[14] Carnelley, *J. Chem. Soc.*, 1876, 29, 489.

[15] Victor Meyer, Riddle, and Lamb, *Ber.*, 1893, 26, 3129.

[16] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[17] Ruff and Plato, *Ber.*, 1903, 36, 2357.

[18] Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and Wartenberg, *ibid.*, 162.

[19] Schröder, *Annalen*, 1878, 192, 295.

[20] Baxter and Brink, *J. Amer. Chem. Soc.*, 1908, 30, 46.

[21] Surawicz, *Ber.*, 1894, 27, 1306.

Schüller[1] as 0·0881; and between 16° and 99° C. by Regnault[2] as 0·0868. Thomsen[3] gives the heat of formation from the elements as 69·08 Cal.; for the heat of solution of the anhydrous salt 1·2 Cal., and for the dihydrate —4·01 Cal.; for the heat of hydration of the anhydrous salt to the dihydrate he gives 5·23 Cal.

The table[4] indicates the solubility of sodium iodide in water at various temperatures:

Solubility of Sodium Iodide, $NaI,2H_2O$.

Solid Phase, $NaI,2H_2O$.

Temperature, °C.	—20	0	10	20	30	40	50	60	65
Grams NaI in 100 g. water	148·0	158·7	168·6	178·7	190·3	205·0	227·8	256·8	278·4

Solid Phase, NaI.

Temperature, °C.	67	70	80	100	120	140
Grams NaI in 100 grams water	293	294	296	302	310	321

The solubility-curve (fig. 7) is in conformity with the existence of a pentahydrate, the transition-point to the dihydrate[5] (*D*) being —13·5° C., that of the dihydrate to the anhydrous salt[6] (*E*) being 65° C. The boiling-point of a saturated solution[7] in contact with the solid is 141° C. At 25° C., 100 grams of ethyl alcohol dissolve 46·02 grams of sodium

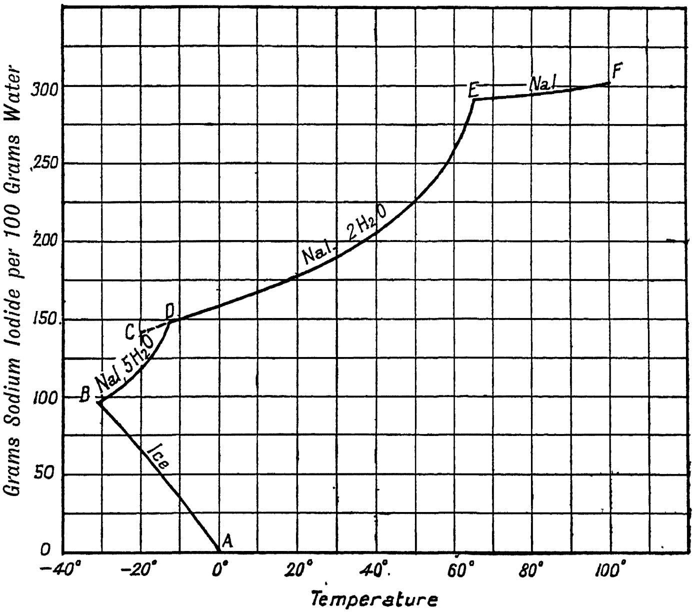

FIG. 7.—Solubility-curve of sodium iodide.

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[1] Schüller, *Pogg. Annalen*, 1869, 136, 70, 235.

[2] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129.

[3] Thomsen, *Thermochemistry* (Longmans, 1908), 49, 62, 319.

[4] See de Coppet, *Ann. Chim. Phys.*, 1883, [5], 30, 420; compare Kremers, *Pogg. Annalen*, 1856, 97, 14.

[5] Panfiloff, *J. Russ. Phys. Chem. Soc.*, 1893, 25, 262.

[6] de Coppet, *Ann. Chim. Phys.*, 1883, [5], 30, 425.

[7] Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 285.

iodide.[1] Sodium iodide dissolves in methyl alcohol, yielding at 15° to 16° C. needle-shaped crystals of the formula $NaI,3CH_3OH$.[2]

Other properties of aqueous solutions investigated are density,[3] refractive index,[4] molecular elevation of the boiling-point,[5] vapour-pressure,[6] specific heat,[7] and electric conductivity.[8] References are also appended to work on the compressibility,[9] the solubility in organic solvents[10] and sulphurous acid,[11] the molecular weight in liquid sulphur dioxide,[11] the electric conductivity in acetone[12] and dilute alcohol,[13] the non-existence of polyiodides,[14] isomorphism with potassium iodide,[15] and the formation of a double salt with silver iodide.[16]

Sodium hypochlorite,[17] $NaOCl$.—A solution of the hypochlorite in water is obtained by the action of chlorine on an aqueous solution of sodium hydroxide at a low temperature:

$$2NaOH+Cl_2=NaOCl+NaCl+H_2O.$$

Solutions containing a high percentage of sodium hydroxide yield a concentrated solution of the hypochlorite, provided additional alkali is introduced periodically to maintain the concentration of the solution.[18] Under these conditions, the sodium chloride produced by the reaction is precipitated, and a solution of hypochlorite obtained which reacts with hydrochloric acid to yield up to 49·2 grams of chlorine per 100 c.c. of solution. The temperature of the reaction should be maintained below 27° C., but the very concentrated solutions obtained lack stability, the hypochlorite changing to a mixture of chloride and chlorate, one molecule being oxidized at the expense of another. From very concentrated solution sodium hypochlorite separates as a solid hydrate,[19] its composition approximating more nearly to that of the heptahydrate than the hexahydrate.[20] It is a very unstable, hygroscopic substance, but dehydration in a current of dry air at reduced pressure converts it into the solid anhydrous hypochlorite, which melts about 45° C. It is less hygroscopic than the hydrate, and contains 40 to 60 per cent. of available chlorine.[21]

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[1] Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1904; compare *ibid.*, 1914, 105, 1777.

[2] Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1906.

[3] Kremers, *Pogg. Annalen*, 1858, 103, 57; compare Wagner, *Dissertation*, Berlin, 1889.

[4] Bender, *Wied. Annalen*, 1890, 39, 90.

[5] Schlamp, *Zeitsch. physikal. Chem.*, 1894, 14, 274; Landsberger, *Zeitsch. anorg. Chem.*, 898, 17, 452.

[6] Compare Jahn, *Zeitsch. physikal. Chem.*, 1904, 50, 129; 1907, 59, 31.

[7] Marignac, *Ann. Chim. Phys.*, 1876, [5], 8, 410.

[8] Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, Leipsic, 1898, 147; Ostwald, *Lehrbuch der allgem. Chem.*, Leipsic, 2nd ed., 1893, 743; Walden, *Ber.*, 1899, 32, 2865.

[9] Richards and Jones, *J. Amer. Chem. Soc.*, 1909, 31, 158; compare Richards and Stull, *ibid.*, 1904, 26, 399; Richards, Stull, Brink, and Bonnet, *Zeitsch. physikal. Chem.*, 1907, 61, 77, 100.

[10] Lobry de Bruyn, *Rec. trav. chim.*, 1892, 11, 156; Jakowkin, *Zeitsch. physikal. Chem.*, 1896, 20, 19; Dawson and Goodson, *Trans. Chem. Soc.*, 1904, 85, 796.

[11] Walden, *Ber.*, 1899, 32, 2865.

[12] Dutoit and Levier, *J. Chim. phys.*, 1905, 3, 435.

[13] Jones and Carroll, *Amer. Chem. J.*, 1904, 32, 521.

[14] Abegg and Hamburger, *Zeitsch. anorg. Chem.*, 1906, 50, 415.

[15] Kurnakoff and Schemtschushny, *Iswiestja Polytech. Inst. St. Petersburg*, 1905, 4, 227.

[16] Krym, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 382.

[17] For *sodium chlorite*, $NaClO_2$, see chlorous acid, this series, Vol. VIII.

[18] Muspratt and S. Smith, *J. Soc. Chem. Ind.*, 1898, 17, 1096; 1899, 18, 210.

[19] Muspratt and S. Smith, *loc. cit.*; Muspratt, *J. Soc. Chem. Ind.*, 1903, 22, 591.

[20] Applebey, *Trans. Chem. Soc.*, 1919, 115, 1106.

[21] Muspratt, *loc. ci*

When the turbid liquid formed by heating the heptahydrate at 20° C. is cooled slowly to the ordinary temperature, large greenish-yellow, very deliquescent crystals of the pentahydrate are formed. They melt at 27° C., and are stable at ordinary temperature in absence of air.[1]

Sodium hypochlorite is also manufactured by the electrolysis of sodium-chloride solution without a diaphragm (p. 97), the solution being less concentrated than that prepared by the chlorine process from sodium hydroxide, but free from the excess of alkali characteristic of that prepared by the older method.[2] The process is carried out either in the apparatus designed by Kellner,[3] or in that of Haas-Oettel,[4] sodium chlorate being a by-product (*v. infra*). It is noteworthy that electrolysis of sodium-chloride solution with an alternating current also produces sodium hypochlorite.[5]

Thomsen [6] gives for the heat of formation of sodium hypochlorite in aqueous solution from its elements the value 83·36 Cal., Berthelot [7] 84·7 Cal. For the molecular depression of the freezing-point in aqueous solution Raoult [8] found the value 3·38° C.

In aqueous solution sodium hypochlorite finds technical application in the bleaching of paper, linen, cotton, and straw. In direct sunlight, concentrated solutions rapidly lose their activity. Storage in colourless bottles accelerates the rate of decomposition, and in brown bottles retards it. The stability of the solutions is much increased by complete exclusion of light.[9]

Sodium chlorate, $NaClO_3$.—When chlorine is passed into a hot solution of sodium hydroxide, the hypochlorite primarily formed changes into a mixture of chlorate and chloride, both salts crystallizing out:

$$2NaOH+Cl_2=NaOCl+NaCl+H_2O\,;$$
$$3NaOCl=NaClO_3+2NaCl.$$

The chlorate is purified from the chloride by fractional crystallization. In Muspratt's method [10] magnesium oxide suspended in water is substituted for sodium hydroxide, the solution being concentrated after treatment with chlorine, and sodium carbonate added to precipitate the magnesium for further use. The sodium chlorate crystallizes from the mother-liquor. The salt is also formed from potassium chlorate by double decomposition with substances such as sodium hydrogen tartrate and sodium silicofluoride, as well as by the electrolytic decomposition of sodium-chloride solution under certain conditions [11] (p. 97).

Sodium chlorate is a colourless, crystalline substance, and exhibits trimorphism, forming crystals belonging to the cubic, hexagonal,[12] and

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[1] Applebey, *Trans. Chem. Soc.*, 1919, 115, 1106.

[2] Förster, *Elektrochemie wässriger Lösungen*, Leipsic, 1905, 341; Engelhardt, *Hypochlorite und elektr. Bleiche*, Halle, 1903, 63; Müller, *Zeitsch. Elektrochem.*, 1899, 5, 469; 1900, 7, 398; 1902, 8, 909; *German Patent*, 1896, No. 104442.

[3] Kellner; compare Förster, *loc. cit.*

[4] Haas-Oettel, *Zeitsch. Elektrochem.*, 1900, 7, 315; *German Patent*, 1901, No. 130345.

[5] Coppadoro, *Gazzetta*, 1906, 35, ii., 604.

[6] Thomsen, *Thermochemistry* (Longmans, 1908), 328.

[7] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 5, 338.

[8] Raoult, *Compt. rend.*, 1884, 98, 509.

[9] Bouvet, *Bull. Soc. Pharmacol.*, 1917, 24, 347.

[10] Muspratt, *Dingl. Polytechn. J.*, 1884, 254, 17.

[11] Förster, *Elektrochemie wässriger Lösungen*, Leipsic, 1905, 341; Engelhardt, *Hypochlorite und elektr. Bleiche*, Halle, 1903, 63.

[12] Retgers, *Zeitsch. Kryst. Min.*, 1894, 23, 266.

rhombic[1] systems. For its melting-point Retgers[2] gives 248° C., Foote and Levy[3] 255° C., Smits[4] 261° C., and Carnelley[5] 302° C. The density at 15° C. is given by Bödeker[6] as 2·289, by Retgers[7] as 2·490, and by Le Blanc and Rohland[8] as 2·996. The specific heat of the solid is given by Foote and Levy[9] as 0·281, and of the fused salt as 0·581, the latent heat of fusion being 48·4 cal.

At 15° C., 100 grams of water dissolve 91 grams.[10] Kremers[11] gives the solubility-table:

Solubility of Sodium Chlorate, $NaClO_3$.

Temperature, °C. . . .	0	12	20	40	60	80	100
Grams $NaClO_3$ in 100 g. water	82	98·5	99	123·5	147	175	204

The saturated solution exhibits the remarkable phenomenon of having two boiling-points, 126° C. and 255° C., a property characteristic of some other readily soluble salts, exemplified by the nitrates of sodium, potassium, silver, and thallium. It is due to an increase with rise of temperature in the vapour-pressure of the solution up to a maximum greater than the atmospheric pressure, further rise of temperature being accompanied by a diminution in the vapour-pressure of the solution as the composition of the system tends to approximate to that of the solid phase.[12]

For the heat of formation from the elements, Thomsen[13] gives 86·7 Cal., and Berthelot[14] 85·4 Cal. For the heat of solution at 10° C., Berthelot[15] gives −5·6 Cal.

References are appended to investigations of the optical properties[16] of the crystalline forms; to such properties of the aqueous solution as vapour-pressure,[17] density,[18] molecular depression of the freezing-point,[19] electric conductivity,[20] and index of refraction[21]; and to the solubility in ethyl alcohol.[22]

Sodium perchlorate, $NaClO_4$.—On heating sodium chlorate, besides

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[1] Brauns, *Jahrb. Min.*, 1898, 1, 40; compare Copaux, *Compt. rend.*, 1907, 144, 508.

[2] Retgers, *Zeitsch. Kryst. Min.*, 1895, 24, 128.

[3] Foote and Levy, *Amer. Chem. J.*, 1907, 37, 494.

[4] Roozeboom, *Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 374 (observed by Smits).

[5] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[6] Bödeker, *Beziehung zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen*, Leipsic, 1860.

[7] Retgers, *Zeitsch. physikal. Chem.*, 1890, 5, 436.

[8] Le Blanc and Rohland, *ibid.*, 1896, 19, 261.

[9] Foote and Levy, *Amer. Chem. J.*, 1907, 37, 494.

[10] Graebe, *Ber.*, 1901, 34, 648.

[11] Kremers, *Pogg. Annalen*, 1856, 97, 5.

[12] van 't Hoff, *Vorlesungen über physikal. Chemie*, 1898, 1, 32; Roozeboom, *Heterogene Gleichgewicht*, Brunswick, 1904, 2, 351; Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1905.

[13] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 1, 241.

[14] Berthelot, *Ann. Chim. Phys.*, 1877, [5], 10, 383.

[15] Berthelot, *ibid.*, 1875, [5], 4, 103.

[16] Dussaut, *Compt. rend.*, 1891, 113, 291; Kohlrausch, *Wied. Annalen*, 1878, 4, 1; Borel, *Compt. rend.*, 1895, 120, 1406; Guye, *ibid.*, 1889, 108, 348; Schucke, *Wied. Annalen*, 1878, 3, 516.

[17] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; *Wied. Annalen*, 1885, 24, 530.

[18] Kremers, *Pogg. Annalen*, 1855, 96, 39.

[19] Jahn, *Zeitsch. physikal. Chem.*, 1907, 59, 31.

[20] Ostwald, *Lehrbuch der allgem. Chem.*, 2nd ed., Leipsic, 1893, 743.

[21] Miers and Isaac. *Trans. Chem. Soc.*, 1906, 89, 413.

[22] Wittstein, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905.

the decomposition with evolution of oxygen, there is a partial conversion of the salt into perchlorate and chloride :

$$4NaClO_3=3NaClO_4+NaCl.$$

The salt can also be prepared by neutralizing perchloric acid with sodium hydroxide, but it is manufactured by the electrolytic oxidation of a 25 per cent. sodium-chlorate solution at 10° C., platinum electrodes and a high anode-potential being employed.[1] This process finds application in the manufacture of potassium perchlorate, this salt being obtained from the sodium compound by the action of potassium chloride.

At ordinary temperature, sodium perchlorate crystallizes as the very deliquescent monohydrate, but above 50° C. as the anhydrous salt.[2] Its deliquescent character hinders its technical application. The melting-point[3] of the anhydrous salt is 482° C. On heating, it is decomposed into chloride and oxygen, a proportion of chlorate being simultaneously formed.[4] From cryoscopic experiments with sodium sulphate as solvent, Löwenherz[5] inferred the molecular formula to be $NaClO_4$.

For the heat of formation[6] from its elements, Berthelot gives 100·3 Cal., and for the heat of solution[7] at 10° C., 3·5 Cal. The electric conductivity has been investigated by Ostwald[8] and by Walden.[9]

Sodium hypobromite, NaOBr.—When bromine reacts with sodium hydroxide in aqueous solution, sodium hypobromite is formed :

$$2NaOH+Br_2=NaOBr+NaBr+H_2O.$$

It is also a product of the electrolysis of sodium bromide without a diaphragm[10] (p. 103).

The salt has only been obtained in solution. In this form it is an important oxidizer in analytical operations. For the heat of formation of the dissolved compound from its elements, Berthelot[11] gives 82·1 Cal.

Sodium bromate, $NaBrO_3$.—The bromate is formed by the action of bromine on a hot solution of sodium hydroxide, but is best obtained by the electrolysis of sodium bromide under certain conditions.

Like the chlorate, sodium bromate is trimorphous, crystallizing in the cubic,[12] hexagonal, and rhombic[13] systems. Its melting-point[14] is 381° C. For the density Kremers[15] gives 3·339, and Le Blanc and Rohland[16] 3·254. At 20° C., 100 grams of water dissolve 38·3 grams, and at 100° C., 91 grams.[17] The boiling-point of the saturated solution in contact with the solid is 109° C. The compound finds application as an oxidizer.

References are appended to investigations of its optical properties[18];

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[1] Winteler, *Zeitsch. Elektrochem.*, 1898, 5, 218 ; Förster, *ibid.*, 1898, 4, 386.

[2] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1889, 1, 258.

[3] Carnelley and O'Shea, *Trans. Chem. Soc.*, 1884, 45, 409.

[4] Scobai, *Zeitsch. physikal. Chem.*, 1903, 44, 319.

[5] Löwenherz, *ibid.*, 1895, 18, 70; compare Crafts, *Trans. Chem. Soc.*, 1895, 74, 593.

[6] Berthelot, *Ann. Chim. Phys.*, 1882, [5], 27, 218.

[7] Berthelot, *ibid.*, 1875, [5], 4, 103.

[8] Ostwald, *Lehrbuch der allgem. Chem.*, 2nd ed., Leipsic, 1893, 743.

[9] Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49.

[10] Förster, *Elektrochemie wässriger Lösungen*, Leipsic, 1905, 341.

[11] Berthelot, *Ann. Chim. Phys.*, 1877, [5], 10, 19.

[12] Retgers, *Zeitsch. Kryst. Min.*, 1894, 23, 266.

[13] Brauns, *Jahrb. Min.*, 1898, 1, 40.

[14] Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 125.

[15] Kremers, *Pogg. Annalen*, 1856, 99, 443.

[16] Le Blanc and Rohland, *Zeitsch. physikal. Chem.*, 1896, 19, 261.

[17] Kremers, *Pogg. Annalen*, 1855, 97, 5.

[18] Traube, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 706.

to properties of aqueous solutions such as density,[1] molecular depression of the freezing-point,[2] and vapour-pressure[3]; and to the formation of double salts with sodium bromide.[4]

Sodium hypoiodite, $NaOI$.—The hypoiodite has never been isolated, but is formed in dilute aqueous solution by the interaction of sodium hydroxide and iodine, and to a small extent by the electrolysis of an alkaline solution of sodium iodide. The substance is extremely unstable, reduction to iodide and oxidation to iodate taking place simultaneously.[5]

Sodium iodate, $NaIO_3$.—The iodate is a constituent of Chile saltpetre or sodium nitrate, and remains in the mother-liquor after crystallization of the nitrate. It is an important source of iodine. The salt can be prepared by oxidizing sodium iodide with sodium peroxide[6] or by the electrolytic method,[7] and also by the interaction of sodium iodide and periodate.[8] It forms white crystals.

The density[9] of the iodate is 4·277. At 20° C., 100 grams of water dissolve 9·1 grams, and at 100° C., 33·9 grams.[10] Ditte[11] gives 105° C. as the boiling-point of the saturated solution in contact with the solid. It yields a pentahydrate, stable between $-2°$ and $+22°$ C.

References to work on the molecular depression of the freezing-point[12] and on the electric conductivity[13] of dilute solutions are appended.

Sodium periodates.—Several periodates of sodium have been described, derived respectively from the anhydrous acid, HIO_4, the monohydrate, H_3IO_5, and the dihydrate, H_5IO_6. The normal salt,[14] $NaIO_4$, has been prepared in the anhydrous form, and also as dihydrate, $NaIO_4,2H_2O$, and trihydrate, $NaIO_4,3H_2O$. The anhydrous salt forms quadratic crystals of density 3·865 at 16° C. They are isomorphous with the corresponding salts of ammonium, potassium, and rubidium.[15] The density of the trihydrate at 18° C. is 3·219.

Disodium periodate, $Na_2H_3IO_6$, can be prepared by the action of chlorine on a mixture of sodium iodate and hydroxide,[16] or by the oxidation of iodine with sodium peroxide.[17] It is soluble with difficulty in both cold and hot water. The table gives determinations of solubility made by Rosenheim and Loewenthal:[18]

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[1] Kremers, *Pogg. Annalen*, 1855, 96, 39.

[2] Jahn, *Zeitsch. physikal. Chem.*, 1907, 59, 31.

[3] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; *Wied. Annalen*, 1885, 24, 530.

[4] Marignac, *Jahresbericht*, 1857, 126.

[5] Péchard, *Compt. rend.*, 1899, 128, 1453; 1900, 130, 1705.

[6] Longi and Bonavia, *Gazzetta*, 1898, 28, i., 325.

[7] Förster, *Elektrochemie wässriger Lösungen*, Leipsic, 1905, 341; Engelhardt, *Hypochlorite und elektr. Bleiche*, Halle, 1903.

[8] Péchard, *Compt. rend.*, 1899, 128, 1453; 1900, 130, 1705.

[9] Kremers, *Jahresbericht*, 1857, 67.

[10] Kremers, *ibid.*; *Pogg. Annalen*, 1856, 97, 8.

[11] Ditte, *Gmelin, Kraut, and Friedheim's Handbuch der anorg. Chem.*, 7th ed., Heidelberg, 1906, 2, i., 378.

[12] Jahn, *Zeitsch. physikal. Chem.*, 1907, 59, 31.

[13] Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49; Kohlrausch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1900, 1002.

[14] Compare Rammelsberg, *Pogg. Annalen*, 1868, 134, 368, 531; Magnus and Ammermüller, *ibid.*, 1833, 28, 514; Langlois, *Ann. Chim. Phys.*, 1852, [3], 34, 257; Blomstrand, *J. prakt. Chem.*, 1850, 50, 305; Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49; Ostwald, *J. prakt. Chem.*, 1885, [2], 32, 300.

[15] Barker, *Trans. Chem. Soc.*, 1908, 93, 15.

[16] Rammelsberg, etc., *loc. cit.*

[17] Höhnel, *Arch. Pharm.*, 1894, 232, 222.

[18] Rosenheim and Loewenthal, *Kolloid. Zeitsch.*, 1919, 25, 53.

Solubility of Sodium Periodate.

Temperature, °C.	0	25	40	100
Grams of $Na_2H_3IO_6$ in 100 g. of solution	0·104	0·157	0·187	0·434

A cold, aqueous solution of sodium hydroxide converts this salt into the *periodate* of the formula $Na_3H_2IO_6$. These two substances are the only periodates of sodium known to exist in aqueous solution. The optical properties[1] and electric conductivity in aqueous solution[2] of the disodium salt have been investigated.

Other periodates have been described by Walden[2] and by Müller.[3]

Sodium manganate and permanganate.—The modes of preparation and the properties of sodium manganate and permanganate are given in Vol. VIII.

Sodium monoxide, Na_2O.—The monoxide is produced by combustion of sodium in dry air, the peroxide being formed simultaneously; or by heating the hydroxide or peroxide with sodium:[4]

$$2NaOH+2Na=2Na_2O+H_2.$$

Sodium monoxide is a white substance when cold, pale-yellow when hot, and melts at bright redness. It is very hygroscopic, combining with water to form the hydroxide, the heat evolved being 56·5 Cal.[5] For the density Beketoff[6] gives 2·314, and Rengade[7] 2·27. The heat of formation from the elements is 100·7 Cal.[8] Above 400° C. it yields equimolecular proportions of sodium and sodium peroxide. It is converted by hydrogen into an equimolecular mixture of sodium hydroxide and hydride, and it also combines with fluorine, chlorine, and iodine.

The so-called " sodium suboxide," obtained by combustion of sodium in a limited supply of oxygen, seems to be either a mixture or solid solution of sodium and sodium monoxide.

Sodium peroxide, Na_2O_2.—The peroxide is manufactured by the action of dry air, free from carbon dioxide, on sodium[9] in an iron tube at 300° C.,[10] the only process employed for its production on the large scale. The commercial article contains about 93 per cent. of sodium peroxide.

Sodium peroxide has a yellowish colour. It is not decomposed by heat, but is a very powerful chemical reagent, in many respects resembling hydrogen peroxide.

It can act as a reducer,[11] decomposing salts of silver, gold, and mercury, with evolution of oxygen. As an oxidizer, it reacts energetically with silver, tin, and lead. It converts the oxides of carbon into sodium carbonate, and nitrogen monoxide and nitric oxide into sodium nitrate. It is reduced to sodium[12] by charcoal or carbides of the alkaline-earth-

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[1] Groth, *Pogg. Annalen*, 1869, 137, 433.

[2] Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49.

[3] Müller, *Zeitsch. Elektrochem.*, 1901, 7, 509; 1904, 10, 49.

[4] Badische Anilin- und Soda-Fabrik, *German Patent*, No. 147933; Rengade, *Compt. rend.*, 1906, 143, 1152; 1907, 144, 753; *Ann. Chim. Phys.*, 1907, [8], 11, 424.

[5] Rengade, *Compt. rend.*, 1908, 146, 129; *Bull. Soc. chim.*, 1908, [4], 3, 190, 194.

[6] Beketoff, *J. Russ. Phys. Chem. Soc.*, 1887, 1, 57.

[7] Rengade, *Compt. rend.*, 1906, 143, 1152; 1907, 144, 753; *Ann. Chim. Phys.*, 1907, [8], 11, 424.

[8] Rengade, *Compt. rend.*, 1908, 146, 129; *Bull. Soc. chim.*, 1908, [4], 3, 190, 194; de Forcrand, *Compt. rend.*, 1914, 158, 991.

[9] Castner, *J. Soc. Chem. Ind.*, 1892, 11, 1005; compare Gay-Lussac and Thénard, *Recherches physico-chimiques*, Paris, 1811.

[10] Castner, *British Patent*, 1891, No. 20003.

[11] Poleck, *Ber.*, 1894, 27, 1051.

[12] Bamberger, *Ber.*, 1898, 31, 54.

metals. It reacts with ammonia, forming sodium hydroxide and evolving nitrogen :

$$2NH_3+3Na_2O_2=N_2+6NaOH.$$

It oxidizes organic substances very energetically, and finds application in organic analysis.[1]

The peroxide is not deliquescent,[2] but dissolves in water with evolution of oxygen, hydrogen peroxide being a primary product :[3]

$$Na_2O_2+2H_2O=H_2O_2+2NaOH.$$

The reaction is reversible, since sodium peroxide is formed by the interaction of hydrogen peroxide and sodium hydroxide.[4] When a mixture of aqueous hydrogen peroxide and sodium hydroxide as solid or in solution is cooled, a quantitative yield of a crystalline hydrate, $Na_2O_2,8H_2O$, with mother-of-pearl lustre is obtained.[5] This hydrate is also produced by exposing the peroxide to air in absence of carbon dioxide,[6] and forms white crystals soluble in water without evolution of oxygen,[7] this property facilitating the production of a concentrated solution of hydrogen peroxide. Decomposition of the solution begins at 30° to 40° C., and is complete at 100° C., oxygen being evolved.[8] A dihydrate is precipitated by addition of alcohol to a mixture of hydrogen peroxide and sodium hydroxide, or by keeping the octahydrate over concentrated sulphuric acid.[9] A tetrahydrate is also mentioned by Schöne.[9]

For the heat of formation of sodium peroxide from its elements, de Forcrand gives 119·8 Cal.[10] and 119·73 Cal.[11]

Sodium peroxide is employed in the laboratory and in the arts as an oxidizer. With acids it forms addition-products of the type $Na_2O_2,2HCl$, obtained by the action of dry hydrogen chloride on a suspension of the peroxide in carbon tetrachloride. The compound formulated is a white powder, and on treatment with water yields a solution containing 10 per cent. of active oxygen.[12]

Carbon monoxide converts sodium peroxide into sodium carbonate. The action of carbon dioxide is similar, but much more energetic, oxygen being evolved.[13]

For the estimation of sodium peroxide, Niemeyer[14] recommends titration with standard potassium permanganate in presence of sulphuric acid :

$$2KMnO_4+5Na_2O_2+8H_2SO_4=K_2SO_4+5Na_2SO_4+2MnSO_4+8H_2O+5O_2.$$

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[1] Pringsheim, *Ber.*, 1903, 36, 4244; 1908, 41, 4267; Pringsheim and Gibson, *Ber.*, 1905, 38, 2459; Pozzi-Escot, *Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 695.

[2] Jaubert, *Compt. rend.*, 1901, 132, 35.

[3] Schöne, *Annalen*, 1878, 193, 241; Berthelot, *Ann. Chim. Phys.*, 1880, [5], 21, 146; Schönbein, *J. prakt. Chem.*, 1859, 77, 265.

[4] Calvert, *Zeitsch. physikal. Chem.*, 1901, 38, 513.

[5] Farbenfabriken vormals Friedr. Bayer and Co., *German Patent*, 1910, No. 219790.

[6] Schöne, *Annalen*, 1878, 193, 241.

[7] Harcourt, *J. Chem. Soc.*, 1861, 14, 267.

[8] Jaubert, *Compt. rend.*, 1901, 132, 35.

[9] Schöne, *Annalen*, 1878, 193, 241.

[10] de Forcrand, *Compt. rend.*, 1898, 127, 514.

[11] de Forcrand, *ibid.*, 1914, 158, 991.

[12] Jaubert, *German Patent*, 1910, No. 229572.

[13] Zenghelis and Horsch, *Compt. rend.*, 1916, 163, 388.

[14] Niemeyer, *Chem. Zeit.*, 1907, 31, 1257.

de Forcrand[1] mentions two other *sodium peroxides*, Na_2O_3 and Na_2O_4. The heat of formation of the first from the elements is given as approximately 126·7 Cal., and of the second as approximately 130 Cal.

Sodium hydroxide, NaOH.—The pure hydroxide can be prepared in the laboratory by dissolving sodium in water and evaporating the solution,[2] or by the electrolysis of commercial sodium hydroxide in aqueous solution with a mercury cathode, the amalgam formed being decomposed by water.[3] A solution free from carbonate can be obtained in the laboratory by suspending metallic sodium in a layer of ether floating on the surface of water. The metal dissolves slowly in the water present in the ether, and the sodium hydroxide passes into the bottom aqueous layer.[4] The hydroxide is manufactured by the electrolysis of a solution of sodium chloride (p. 97); and, according to van Laer,[5] an economical yield can be obtained directly by the electrolysis with a suitable diaphragm of a solution of sodium carbonate containing nitrate or sulphate of sodium to hinder the formation of sodium hydrogen carbonate. Sodium hydroxide is also produced industrially by the much older method of decomposing sodium carbonate with slaked lime, a reversible reaction:[6]

$$Na_2CO_3+Ca(OH)_2 \rightleftharpoons 2NaOH+CaCO_3.$$

The solution of sodium hydroxide is evaporated in iron vessels, the finished product being marketed in the form of sticks or powder, or in cylindrical blocks of about 6¾ cwt. enclosed in iron drums. Slaked lime also decomposes sodium sulphate with production of sodium hydroxide, and the effect on the yield of the temperature and the dilution of the solution has been studied by Neumann and Karwat.[7]

Sodium hydroxide is a white substance of density[8] 2·130. It dissolves readily in both water and alcohol. It is very stable, melting[9] at 318·4° C. and at a higher temperature volatilizing without decomposition. Admixture with other substances lowers the melting-point.[10] The mixture containing 58·4 per cent. of potassium hydroxide melts at 167° C., that with 20·7 per cent. of a mixture of 48·5 per cent. of sodium carbonate and 51·5 per cent. of potassium carbonate at 265° C., and that with 17 per cent. of sodium carbonate at 280° C. For the latent heat of fusion per mol., Hevesy[11] gives 1·602 Cal. Its hygroscopic character causes it to liquefy on exposure to air, but it is converted into solid carbonate by the action of atmospheric carbon dioxide. The percentage of water in fused samples varies between 0·9 and 1·2, the average being 1·1.[12]

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[1] de Forcrand, *Compt. rend.*, 1914, 158, 843, 991.

[2] Compare Küster, *Zeitsch. anorg. Chem.*, 1901, 41, 474.

[3] Jorissen and Filippo, *Chem. Weekblad.*, 1909, 6, 145.

[4] Cornog, *J. Amer. Chem. Soc.*, 1921, 43, 2573.

[5] van Laer, *J. Chim. phys.*, 1917, 15, 154.

[6] Bodländer, *Zeitsch. Elektrochem.*, 1905, 12, 186; Le Blanc and Novotny, *Zeitsch. anorg. Chem.*, 1906, 51, 181; 1907, 53, 347; Wegscheider and Walter, *Annalen*, 1907, 351, 87; *Monatsh.*, 1907, 28, 543, 555, 633.

[7] Neumann and Karwat, *Zeitsch. Elektrochem.*, 1921, 27, 114.

[8] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415.

[9] Hevesy, *Zeitsch. physikal. Chem.*, 1910, 73, 667.

[10] Neumann and Bergve, *Zeitsch. Elektrochem.*, 1914, 20, 271.

[11] Hevesy, *Zeitsch. physikal. Chem.*, 1910, 73, 667.

[12] Wallace and Fleck, *Trans. Chem. Soc.*, 1921, 119, 1839.

Some of Pickering's[1] data for the solubility are given in the table, and the solubility-curve plotted from them in fig. 8.

Temperature, °C.	Grams NaOH in 100 grams Water.	Temperature, °C.	Grams NaOH in 100 grams Water.
0	42	50	145
10	51·5	60	174
20	109	80	313
30	119	110	365
40	129	192	521

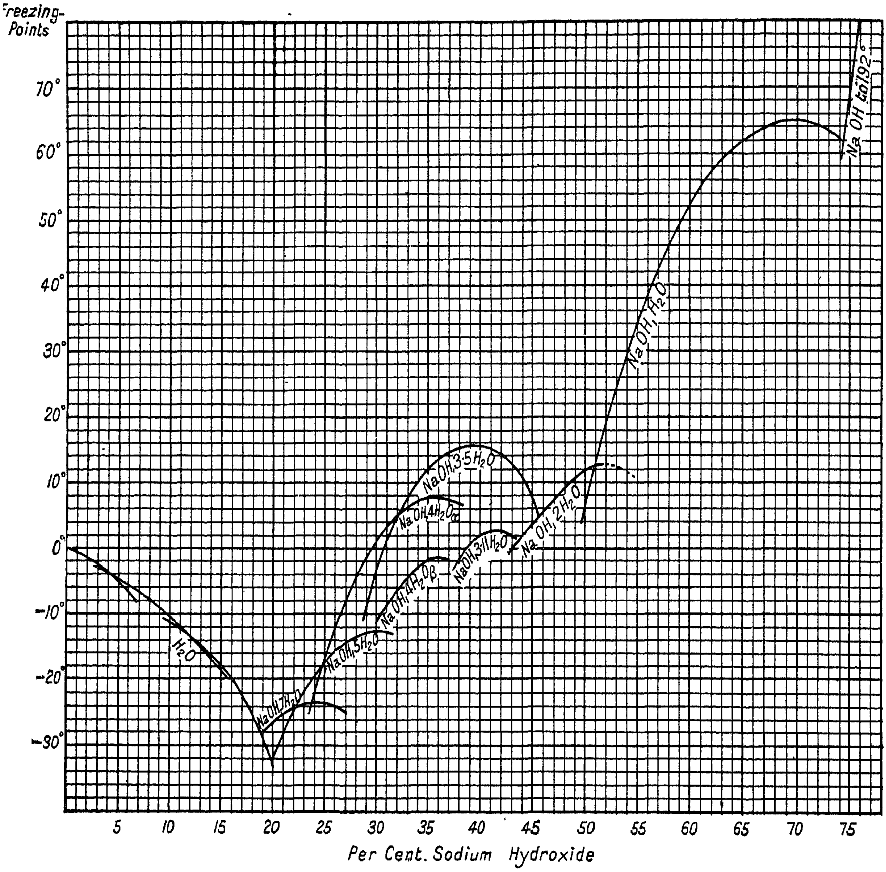

Fig. 8.—Freezing-points of solutions of sodium hydroxide.

The curve indicates the existence of several hydrates, including two tetrahydrates, α freezing at 7·57° C., and β freezing at −1·7° C. The

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[1] Pickering, *Trans. Chem. Soc.*, 1893, 63, 890.

monohydrate melts at 64·3° C. For its density Gerlach [1] gives 1·829. At 12° C. it is transformed [2] into the dihydrate, which at a concentration of 45·5 per cent. of sodium hydroxide is in equilibrium at 5° C. with a 3·5 hydrate, $2NaOH,7H_2O$, as is also the α-tetrahydrate at the same temperature and a concentration of 32 per cent. of sodium hydroxide. At −17·7° C. the α-tetrahydrate changes to the pentahydrate, and this form at −24° C. to the heptahydrate. The saturated solution in contact with the solid boils at 314° C.[3]

The specific heat of the anhydrous hydroxide is given by Blümcke [4] as 0·78 between 0° and 98° C. The mean molecular refraction of the molten hydroxide between 320° and 440° C. is 5·37.[5] The heat of formation from the elements is given by de Forcrand [6] as 103·10 Cal., and that from the solid monoxide and liquid water as 36·50 Cal. For the former, Rengade [7] gives 101·9 Cal., and in solution 111·8 Cal.; for the heat of formation in dilute solution from sodium and water he gives 44·1 Cal. The heat of solution is given by Thomsen [8] as 9·94 Cal., and by Berthelot [9] as 9·8 Cal. The heat of dilution has also been studied by both these investigators. The heat of formation of the monohydrate is given by Berthelot as 3·25 Cal. The heat of neutralization of the hydroxide by mineral acids has been investigated by Richards and Rowe.[10]

At ordinary temperatures an aqueous solution of sodium (or potassium) hydroxide dissolves sulphur, forming sulphide, polysulphides, thiosulphate, and sulphite. The reaction is very complex, but Calcagni [11] thinks that the sulphide is probably formed first, thiosulphate next, and then polysulphides. Finally, sulphite is produced by decomposition of the thiosulphate. With concentrated solutions part of the sulphur probably dissolves without entering into combination. Ammonium hydroxide of density 0·888 behaves similarly.[11]

When heated in copper vessels at temperatures between 350° and 600° C. in contact with air, sodium hydroxide has been observed to dissolve up to 0·73 per cent. of its weight of copper. The action on iron is less, and on nickel least of all.[12]

Other properties of aqueous solutions have been studied, such as the density,[13] vapour-pressure,[14] boiling-point,[15] molecular depression of the freezing-point,[16] electric conductivity,[17] electrolytic dissociation,[18]

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[1] Gerlach, *Jahresbericht*, 1886, 69.
[2] Compare Hermes, *Annalen*, 1861, 119, 170.
[3] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.
[4] Blümcke, *Wied. Annalen*, 1885, 25, 417.
[5] G. Meyer and Heck, *Zeitsch. Elektrochem.*, 1922, 28, 21.
[6] de Forcrand, *Ann. Chim. Phys.*, 1908, [8], 15, 433.
[7] Rengade, *Compt. rend.*, 1908, 146, 129; *Bull. Soc. chim.*, 1908, [4], 3, 190, 194.
[8] Thomsen, *Thermochemistry* (Longmans, 1908), 49.
[9] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 521.
[10] Richards and Rowe, *J. Amer. Chem. Soc.*, 1922, 44, 684.
[11] Calcagni, *Gazzetta*, 1920, 50, ii., 331.
[12] Wallace and Fleck, *Trans. Chem. Soc.*, 1921, 119, 1839.
[13] Pickering, *Trans. Chem. Soc.*, 1893, 63, 890; Forch, *Wied. Annalen*, 1895, 55, 100; Wegscheider and Walter, *Monatsh.*, 1906, 27, 13.
[14] Dieterici, *Wied. Annalen*, 1891, 42, 513; Tammann, *ibid.*, 1885, 24, 530; *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9.
[15] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.
[16] Loomis, *Wied. Annalen*, 1897, 60, 532.
[17] Loomis, *loc. cit.*; Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, Leipsic, 1898; Foster, *Physical Rev.*, 1899, 8, 257; Demolis, *J. Chim. phys.*, 1906, 4, 526; Kunz, *Zeitsch. physikal. Chem.*, 1903, 42, 591; Bein, *ibid.*, 1898, 27, 1; 28, 439; Kuschel, *Wied. Annalen*, 1881, 13, 289.
[18] Arrhenius, *Zeitsch. physikal. Chem.*, 1892, 9, 1339.

refractivity,[1] viscosity,[2] diffusion,[3] dissociation-pressure,[4] and power of dissolving gases.[5]

Sodium perhydroxide, $NaHO_2$.—When absolute ethyl alcohol reacts with sodium peroxide at 0° C., a perhydroxide of the formula O:Na·OH is produced, a reaction discovered by Tafel:[6]

$$C_2H_5{\cdot}OH + Na_2O_2 = O{:}Na{\cdot}OH + C_2H_5{\cdot}ONa.$$

The substance is a white powder, and undergoes explosive decomposition when heated in the dry condition, oxygen being evolved and sodium hydroxide formed. It is soluble in water, and under the influence of heat the solution decomposes without explosion, the products formed being similar to those obtained from the dry substance.[6] Another perhydroxide supposed to have the formula Na·O·OH is produced by the interaction of sodium ethoxide and hydrogen peroxide:

$$Na{\cdot}O{\cdot}C_2H_5 + HO{\cdot}OH = Na{\cdot}O{\cdot}OH + C_2H_5{\cdot}OH.$$

Like the other form, it is a powerful oxidizer, and yields an alkaline solution decomposed by heat with evolution of oxygen. Carbon dioxide converts it into sodium hydrogen percarbonate, $NaHCO_4$. It is more stable than Tafel's product.[7]

Sodium monosulphide, Na_2S.—The monosulphide is formed by the interaction of sulphur and a great excess of sodium, the superfluous metal being removed by distillation[8]; by the action of hydrogen sulphide on sodium hydroxide; and by the action of sulphur on excess of sodium dissolved in liquid ammonia, and evaporation of the solvent.[9]

A quantitative yield of sodium monosulphide is obtained by heating sodium hydrogen sulphide very gradually, the evolved hydrogen sulphide being continually removed:[10]

$$2NaSH = Na_2S + H_2S.$$

The product is a solid of faint buff colour. It dissolves readily in water and in alcohol.

Sodium monosulphide is manufactured by reducing sodium sulphate with charcoal, and can also be obtained in solution from the alkali-waste of the soda manufacturer.[11]

According to Rengade,[12] the anhydrous sulphide forms microscopic, white needles. It melts at the temperature of softening of glass, and dissolves in water with a hissing sound. It is readily oxidized, and is combustible.

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[1] Willigen, *Arch. Mus. Tayler*, 1874, 3, 15; Le Blanc, *Zeitsch. physikal. Chem.*, 1889, 4, 305; Briner, *J. Chim. phys.*, 1906, 4, 547.

[2] Kanitz, *Zeitsch. physikal. Chem.*, 1897, 22, 336.

[3] Thovert, *Compt. rend.*, 1901, 133, 1197; 1902, 134, 594; compare Arrhenius, *Zeitsch. physikal. Chem.*, 1892, 10, 51.

[4] Sacher, *Zeitsch. anorg. Chem.*, 1901, 28, 385; Johnston, *Zeitsch. physikal. Chem.*, 1908, 62, 330.

[5] Geffcken, *Zeitsch. physikal. Chem.*, 1904, 49, 257; Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 910, 985.

[6] Tafel, *Ber.*, 1894, 27, 816, 2297.

[7] Wolffenstein, *German Patent*, 1908, No. 196369.

[8] Rengade and Costeanu, *Compt. rend.*, 1913, 156, 791.

[9] Hugot, *ibid.*, 1899, 129, 388.

[10] Thomas and Rule, *Trans. Chem. Soc.*, 1913, 103, 871.

[11] Helbig, *Ber.*, 1883, 16, 95.

[12] Rengade and Costeanu, *loc. cit.*

Four hydrates have been described by Parravano and Fornaini,[1] containing respectively 9, 6, 5½, and 5 molecules of water. The pentahydrate was also prepared by Böttger[2] by adding alcohol to a solution of sodium hydroxide saturated with hydrogen sulphide. Sabatier[3] mentions a 4½-hydrate, obtained by drying the 9-hydrate over sulphuric acid.

The solution of the sulphide in water has an alkaline reaction due to hydrolytic dissociation. Atmospheric oxygen converts the dissolved sulphide into thiosulphate, and electrolytic oxidation yields the sulphate. The solution dissolves sulphur, forming polysulphides.

The melting-point of sodium monosulphide is 920° C.[4] For the anhydrous salt the density is given by Filhol[5] as 2·471, a modern determination by Rengade and Costeanu[6] being 1·856. The heat of formation from its elements is given by Sabatier[7] as 88·2 Cal., and by Rengade and Costeanu[8] as 89·7 Cal. The investigators last mentioned found the heat of solution to be 15·5 Cal. The heat of hydration of the anhydrous salt to the 9-hydrate is 31·72 Cal. For the heat of formation in aqueous solution from the elements, Thomsen[9] gives 101·99 Cal.

In aqueous solution sodium monosulphide reacts with iodine to form sodium iodide, the liberated sulphur dissolving in excess of the sulphide solution.[10] A double sulphide of the formula Na_2S,Cu_2S has been prepared.[11] It melts at 700° C.

Other investigations of solutions of sodium sulphide include the concentration of the hydroxyl-ions and the depression of the freezing-point,[12] the solubility of ammonia,[13] and the density.[14]

Sodium polysulphides.[15]—According to Thomas and Rule,[16] the whole series of polysulphides Na_2S_x exists, x being a whole number with the maximum value 5. Their results obtained by the ebullioscopic method in alcoholic solution favour the simple formula Na_2S_x as against Na_4S_x. On the other hand, Friedrich[17] claims to have prepared polysulphides with the formulæ indicated, the melting-points being given in brackets: Na_4S_3 (772° C.), Na_2S_2 (445° C.), Na_4S_5 (345° C.), Na_2S_3 (320° C.), Na_4S_7 (295° C.), Na_2S_4 (255° C.), Na_4S_9 (210° C.), and probably Na_2S_5 (185° C.).

Bloch and Höhn[18] have prepared solutions containing the *disulphide* Na_2S_2, *trisulphide* Na_2S_3, *tetrasulphide* Na_2S_4, and *pentasulphide* Na_2S_5

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[1] Parravano and Fornaini, *Atti R. Accad. Lincei*, 1907, [5], 16, ii., 464; *Gazzetta*, 1907, 37, ii., 521.

[2] Böttger, *Annalen*, 1884, 223, 335.

[3] Sabatier, *Ann. Chim. Phys.*, 1881, [5], 22, 66.

[4] Friedrich, *Metall und Erz*, 1914, 11, 79.

[5] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415.

[6] Rengade and Costeanu, *Compt. rend.*, 1914, 158, 946.

[7] Sabatier, *Ann. Chim. Phys.*, 1881, [5], 22, 15.

[8] Rengade and Costeanu, *loc. cit.*

[9] Thomsen, *Thermochemistry* (Longmans, 1908), 322.

[10] Ehrlich, *Zeitsch. anal. Chem.*, 1918, 57, 21.

[11] Friedrich, *loc. cit.*

[12] Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, 43, 53; compare Kölichen, *Zeitsch. physikal. Chem.*, 1900, 33, 173; Knox, *Zeitsch. Elektrochem.*, 1906, 12, 477.

[13] Abegg and Riesenfeld, *Zeitsch. physikal. Chem.*, 1902, 40, 84; Raoult, *Ann. Chim Phys.*, 1874, [5], 1, 262; Gaus, *Zeitsch. anorg. Chem.*, 1900, 25, 236.

[14] Bock, *Wied. Annalen*, 1887, 30, 631.

[15] On the constitution of the polysulphides see this series, Vol. VII.; Küster, *Zeitsch. anorg. Chem.*, 1905, 44, 431; 46, 113; Küster and Heberlein, *ibid.*, 1905, 43, 53.

[16] Thomas and Rule, *Trans. Chem. Soc.*, 1917, 111, 1063.

[17] Friedrich, *loc. cit.*

[18] Bloch and Höhn, *Ber.*, 1908, 41, 1961.

by heating sodium sulphide to fusion with appropriate proportions of sulphur, and extracting the melt with water.

Böttger[1] concentrated a solution similarly prepared, and isolated the disulphide as pentahydrate in the form of sulphur-yellow crystals. The anhydrous disulphide was prepared by Rule and Thomas[2] by the action of sodium on an alcoholic solution of sodium tetrasulphide, Na_2S_4. It is a pale-yellow, crystalline powder, becoming darker in colour with rise of temperature, and melting to a dark-red liquid. Friedrich[3] found for the melting-point 445° C. For the heat of formation in solution Sabatier[4] gives 104·6 Cal.

The trisulphide in the form of trihydrate was similarly prepared by Böttger as golden-yellow crystals. The anhydrous substance is produced by the interaction of sodium monosulphide and the calculated amount of sulphur in boiling toluene.[5] Its melting-point is given by Friedrich[6] as 320° C. Its heat of formation in solution is 106·4 Cal.[7]

Sabatier prepared the tetrasulphide by heating the monosulphide with excess of sulphur in a current of hydrogen or its sulphide, the product consisting of transparent red crystals. Rule and Thomas[8] found the tetrasulphide to be the only definite compound produced by the action of sulphur on an alcoholic solution of sodium hydrogen sulphide :

$$2NaSH+3S=Na_2S_4+H_2S.$$

It forms microscopic cubes of dark-yellow colour with an olive-green tinge, and is very hygroscopic. At 267° C. it melts to a dark-red liquid. Friedrich[9] gives the melting-point as 255° C. On heating, the aqueous solution deposits sulphur. A pale-yellow hexahydrate[10] and an octahydrate[11] have also been described. The heat of formation in solution is 98·4 Cal.[12] It is the most stable of the polysulphides.[13]

The pentasulphide was prepared by Hugot[14] by the action of excess of sulphur on a solution of sodium in liquid ammonia, but it is probable that his product was not free from excess of sulphur. Friedrich[15] gives the melting-point as 185° C. Schöne mentions a hexahydrate, and Böttger a dark orange-yellow octahydrate.

Bloxam[16] recommends the action of hydrogen sulphide on solid sodium sulphide as the best mode of preparing the polysulphides.

Sodium hydrogen sulphide, NaSH.—When benzene or ether is added to a concentrated solution of sodium ethoxide in alcohol saturated with hydrogen sulphide, a quantitative yield of anhydrous sodium hydrogen sulphide is obtained :

$$C_2H_5ONa+H_2S=C_2H_5OH+NaSH.$$

[1] Böttger, *Annalen*, 1884, 223, 338.
[2] Rule and Thomas, *Trans. Chem. Soc.*, 1914, 105, 177.
[3] Friedrich, *Metall und Erz*, 1914, 11, 79.
[4] Sabatier, *Compt. rend.*, 1880, 90, 1557.
[5] Locke and Anstell, *Amer. Chem. J.*, 1898, 20, 592.
[6] Friedrich, *Metall und Erz*, 1914, 11, 79.
[7] Sabatier, *loc. cit.*
[8] Rule and Thomas, *loc. cit.*
[9] Friedrich, *loc. cit.*
[10] Schöne, *Annalen*, 1878, 193, 241.
[11] Böttger, *ibid.*, 1884, 223, 335.
[12] Sabatier, *loc. cit.*
[13] Küster, *Zeitsch. anorg. Chem.*, 1905, 44, 431 ; 46, 113
[14] Hugot, *Compt rend* 1899, 129, 388.
[15] Friedrich, *loc. cit.*
[16] Bloxam, *Zeitsch. anorg. Chem.*, 1908, 60, 113.

It is a white, crystalline solid, very deliquescent, freely soluble in water, and moderately soluble in alcohol. When exposed to air it evolves hydrogen sulphide,[1] and is completely decomposed by heat into this gas and sodium monosulphide.[2] The anhydrous salt is also obtained by the interaction at 300° C. of sodium monosulphide and hydrogen sulphide free from carbon dioxide and oxygen.[3] Sabatier's[4] method is to saturate a solution of sodium sulphide with hydrogen sulphide, and concentrate in an atmosphere of the same gas. A solution can be obtained by saturating sodium-hydroxide solution with hydrogen sulphide. A dihydrate and a trihydrate have been described.[5]

The heat of formation of the solid from the elements is given by Sabatier as 55·7 Cal.; that in solution by Thomsen[6] as 58·48 Cal., and by Berthelot[7] as 60·7 Cal. For the heat of solution of the anhydrous salt at 17·5° C. Sabatier gives 4·4 Cal., and for that of the dihydrate —1·5 Cal.; it follows that the heat of hydration of the dihydrate is 5·9 Cal.

The preparation in solution of a compound of the formula NaOSH has been described by Gutmann.[8]

Sodium sulphite, Na_2SO_3.—The anhydrous sulphite can be prepared by heating equimolecular proportions of sodium hydrogen sulphite and sodium hydrogen carbonate:[9]

$$NaHSO_3+NaHCO_3=Na_2SO_3+H_2O+CO_2.$$

It is also precipitated by the action of ammonia on a solution containing sodium chloride and ammonium sulphite in equimolecular proportions.[10] Hartley and Barrett[11] have described a method of preparation from sulphur dioxide and sodium carbonate. It is a white, crystalline salt.

For the solubility of this substance in 100 grams of water at 20° C. Kremers[12] gives 28·7 grams; at 40° C., 49·5 grams; and at 100° C. Fourcroy[13] gives 33 grams. At 10° C. the heat of solution[14] of the anhydrous salt is 2·5 Cal.

Hartley and Barrett[11] state that the only stable forms are the anhydrous salt and the heptahydrate, $Na_2SO_3,7H_2O$. Neither they nor Schultz-Sellack[15] could isolate the decahydrate described by Muspratt.[16] The anhydrous salt belongs to the hexagonal system, and at 15° C. has the density 2·6334. The heptahydrate is monoclinic, its density at 15° C. being 1·5939. At 10° C. the heat of solution of the heptahydrate according to de Forcrand[14] is —11·1 Cal., and the heat of hydration 13·6 Cal.

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[1] Rule, *Trans. Chem. Soc.*, 1911, 99, 558.
[2] Thomas and Rule, *ibid.*, 1913, 103, 871.
[3] Verein Chemischer Fabriken in Mannheim, *German Patent*, 1908, No. 194882.
[4] Sabatier, *Ann. Chim. Phys.*, 1881, [5], 22, 15.
[5] Bloxam, *Trans. Chem. Soc.*, 1900, 77, 753.
[6] Thomsen, *Thermochemistry* (Longmans, 1908), 322.
[7] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 106.
[8] Gutmann, *Ber.*, 1908, 41, 3351.
[9] Payelle and Sivler, *German Patent*, No. 80390.
[10] Dresel and Lennhof, *ibid.*, No. 80185; compare Duvieusart, *ibid.*, 1909, No. 210804.
[11] Hartley and Barrett, *Trans. Chem. Soc.*, 1909, 95, 1178.
[12] Kremers, *Pogg. Annalen*, 1856, 99, 50.
[13] Fourcroy, *Comey's Dictionary of Solubilities*, London, 1896, 464.
[14] de Forcrand, *Ann. Chim. Phys.*, 1884, [6], 3, 243.
[15] Schultz-Sellack, *J. prakt. Chem.*, 1870, [2], 2, 459.
[16] Muspratt, *Phil. Mag.*, 1847, [3], 30, 414.

Dilute solutions readily undergo atmospheric oxidation, but Lumière and Seyewetz[1] found that a 20 per cent. solution is stable, and Ehrenfeld[2] states that the presence of excess of alkali prevents oxidation, while cuprous oxide exerts a catalytic accelerating effect on the transformation. A similar catalysis is occasioned by cupric sulphate,[3] but substances such as potassium cyanide and mannitol exercise a retarding influence,[4] affording an example of "negative catalysis." Solutions of sodium sulphite are sensitive to light, paper immersed in such a solution being capable of development by silver nitrate and other reagents.[5]

References are appended to investigations of the solubility,[6] formation of hydrates,[7] molecular depression of the freezing-point,[8] and electric conductivity.[8]

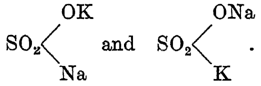
Sodium hydrogen sulphite, $NaHSO_3$.—The primary sulphite can be isolated by precipitating with alcohol a solution of sodium carbonate saturated with sulphur dioxide:

$$Na_2CO_3+2SO_2+H_2O=2NaHSO_3+CO_2.$$

Besides the anhydrous salt, there is a trihydrate,[9] and also a tetrahydrate.[10] Barth[11] has investigated the electric conductivity.

Sodium potassium sulphite, $NaKSO_3$.—When sodium hydrogen sulphite is neutralized by potassium hydroxide or carbonate, a double sulphite of sodium and potassium is formed. It is known as anhydrous salt, and also as monohydrate and dihydrate. For the heat of solution of the anhydrous form Hartog[12] gives —1·19 Cal.

Röhrig[13] and Schwicker[14] claim to have prepared two isomeric forms of this salt, and attribute to them the constitutional formulæ



$$SO_2\left\langle\begin{matrix}OK\\Na\end{matrix}\right. \quad \text{and} \quad SO_2\left\langle\begin{matrix}ONa\\K\end{matrix}\right. .$$

Schwicker's procedure for making the compounds was to neutralize potassium hydrogen sulphite with sodium carbonate, and sodium hydrogen sulphite with potassium carbonate. The first isomeride is represented as *potassium sodio-sulphonate*, and crystallizes with two molecules of water; the second is assumed to be *sodium potassio-sulphonate*, and crystallizes with one molecule of water.

Barth[15] failed to distinguish the supposed isomerides in aqueous

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[1] Lumière and Seyewetz, *Rev. gén. Chim.*, 1896, 7, 111.

[2] Ehrenfeld, *Zeitsch. anorg. Chem.*, 1908, 59, 161.

[3] Bigelow, *Zeitsch. physikal. Chem.*, 1898, 26, 493.

[4] Titoff, *Zeitsch. physical. Chem.*, 1903, 45, 641.

[5] Liesegang, *Photogr. Arch.*, 1893, 34, 353.

[6] Hartley and Barrett, *Trans. Chem. Soc.*, 1909, 95, 1178; Mitscherlich, *Pogg. Annalen*, 1827, 12, 140.

[7] Meyerhoffer, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 560; Traube, *Zeitsch. Kryst. Min.*, 1893, 22, 143.

[8] Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 185.

[9] Evans and Desch, *Chem. News*, 1895, 71, 248.

[10] Clarke, *Gmelin, Kraut, and Friedheim's Handbuch der anorg. Chem.*, 7th ed., Heidelberg, 1906, 2, i., 321.

[11] Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 185.

[12] Hartog, *Compt. rend.*, 1889, 109, 181.

[13] Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 250.

[14] Schwicker, *Ber.*, 1889, 22, 1728.

[15] Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 176.

solution, an illustration of his difficulty being the identity in their electric conductivities. Since both isomerides might yield the same ions, Barth's evidence is inconclusive; but his work on the mercury salts appears to confirm the assumption of the sulphonic formula.

Schwicker claimed to have prepared distinct derivatives by the action of ethyl iodide, but a repetition of his work by Fraps[1] led to negative results. Arbusoff[2] investigated the interaction of methyl iodide and the double sulphites obtained by Schwicker's method, the sodium atom in each instance being replaced by a methyl-group, with formation of the same compound,

$$CH_3{\cdot}SO_3K.$$

If two isomerides do exist, that with potassium attached directly to sulphur must be unstable, and change readily into the isomeric form.[3]

Sodium pyrosulphite, $Na_2S_2O_5$.—When excess of sulphur dioxide is passed into sodium-carbonate solution at low temperature, anhydrous sodium pyrosulphite separates[4]; at ordinary temperature the hydrate $Na_2S_2O_5,\frac{1}{2}H_2O$ is formed.[5] This substance may be regarded as an anhydride of sodium hydrogen sulphite: $2NaHSO_3-H_2O=Na_2S_2O_5$. The heat of formation of the anhydrous salt from its elements is given by de Forcrand[6] as 348·4 Cal., and the heat of solution at 10° C. as 5·2 Cal. The electric conductivity has been investigated by Walden.[7] The salt is employed to retard oxidation of photographic developers.

Sodium sulphate, Na_2SO_4.—The sulphate is often called "Glauber's salt," on account of its application in the seventeenth century as a medicine by the physician Glauber, the specific being known as "sal mirabile Glauberi." Its purgative action seems to be a phenomenon dependent on osmosis.

The anhydrous sulphate is a constituent of oceanic salt deposits, and is called *thenardite.* An isomorphous mixture with potassium sulphate is known as *glaserite*; a double salt with magnesium sulphate as *astrakanite*, and with calcium sulphate as *glauberite.*

Sodium sulphate is an intermediate product in the manufacture of sodium carbonate by the Le Blanc process (p. 143). It is also a by-product in the manufacture of nitric acid by the interaction of sodium nitrate and sulphuric acid:[8]

$$2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3.$$

In the Stassfurt deposits sodium chloride and magnesium sulphate monohydrate or *kieserite* are present, and on cooling the solution to −3° C. sodium sulphate crystallizes out. A mixture of sodium chloride, magnesium sulphate, and sand also reacts at dull red heat to form

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[1] Fraps, *Amer. Chem. J.*, 1900, 23, 202.

[2] Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 447; compare Godby, *Proc. Chem. Soc.*, 1907, 23, 241.

[3] Garrett (*Trans. Chem. Soc.*, 1915, 107, 1324) measured the molecular extinctions of solutions of the isomerides, but found no selective absorption, so that his method gave inconclusive results.

[4] Schultz, *Pogg. Annalen*, 1868, 133, 137; compare Carey and Hurter, *British Patent*, 1882, No. 4512.

[5] Röhrig, *Gmelin, Kraut, and Friedheim's Handbuch der anorg. Chem.*, 7th ed., 1906, 2, i., 321.

[6] de Forcrand, *Ann. Chim. Phys.*, 1884, [6], 3, 243.

[7] Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

[8] See this series, Vol. VI.

sodium sulphate and magnesium silicate, with evolution of chlorine.[1] In Hargreaves's [2] process sodium chloride reacts with a mixture of sulphur dioxide, steam, and air, producing sodium sulphate and hydrochloric acid. Sodium sulphate is also produced by treating the calcium sulphide of the alkali-waste with sodium hydrogen sulphate formed in the manufacture of nitric acid : [3]

$$2NaHSO_4+CaS=Na_2SO_4+CaSO_4+H_2S.$$

Sodium sulphate is a white, tetramorphous substance, crystallizing below 200° C. in the rhombic or monoclinic system, from 200° to 500° C. in another rhombic form, and above 500° C. in the hexagonal system.[4] It forms a heptahydrate and decahydrate. For the melting-point of the anhydrous salt Ruff and Plato [5] give 880° C. ; Wolters,[6] 881° C. ; McCrae,[7] 881·5° and 885·2° C. ; Arndt [8] and Nacken,[9] 883° C. ; Heycock and Neville,[10] 883·2° C.; Ramsay and Eumorfopoulos,[11] van Klooster,[12] and Dana and Foote,[13] 884° C.; Bocke,[14] 888° C.; and Hüttner and Tammann,[15] 897° C. Nacken observed neither decomposition nor volatilization at the melting-point. The transition-point of the monoclinic into the second rhombic form is given by Nacken [9] as 234° C., by Hüttner and Tammann [15] as 235° C., and by Bocke [14] as 239° C. The density of the anhydrous solid is given by Retgers [16] as 2·673 at 15° C., by Krickmeyer [17] as 2·671 at 20° C. ; for that of the fused salt from the melting-point to 1000° C., Brunner [18] gives the interpolation-formula

$$d_t=2{\cdot}065-0{\cdot}00045(t-900°)\,;$$

and for the decahydrate Clarke [19] gives 1·465, Andreae [20] 1·4665, and Rosický [21] 1·49.

For the temperature range 28° to 57° C. Schüller [22] found for the specific heat 0·2293, and for 17° to 98° C. Regnault [23] found 0·2312. For the heat of formation from the elements Thomsen [24] gives 328·6 Cal., and Berthelot [25] 328·1 Cal. Thomsen's [26] value for the heat of neutraliza-

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[1] Townsend, *British Patent*, 1879, No. 1703.
[2] Hargreaves, *Bull. Soc. d'Enc.*, 1873, 358.
[3] Chemische Fabrik Griesheim-Elektron, *German Patent*, No. 88227.
[4] Wyrouboff, *Bull. Soc. franç. Min.*, 1890, 13, 227 ; *Bull. Soc. chim.*, 1901, [3], 25, 110.
[5] Ruff and Plato, *Ber.*, 1903, 36, 2357.
[6] Wolters, *Jahrb. Min. Beil.-Bd.*, 1914, 30, 55 ; *Zeitsch. Kryst. Min.*, 1914, 53, 514.
[7] McCrae, *Ann. Physik*, 1895, [3], 55, 95.
[8] Arndt, *Zeitsch. Elektrochem.*, 1906, 12, 337.
[9] Nacken, *Nachr. K. Ges. Wiss. Göttingen*, 1907, 602.
[10] Heycock and Neville, *Trans. Chem. Soc.*, 1895, 67, 160.
[11] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.
[12] van Klooster, *Zeitsch. anorg. Chem.*, 1914, 85, 49.
[13] Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186.
[14] Bocke, *Zeitsch. anorg. Chem.*, 1906, 50, 355.
[15] Hüttner and Tammann, *ibid.*, 1905, 43, 215.
[16] Retgers, *Zeitsch. physikal. Chem.*, 1890, 6, 193.
[17] Krickmeyer, *ibid.*, 1896, 21, 53.
[18] Brunner, *Zeitsch. anorg. Chem.*, 1904, 38, 350.
[19] Schiff, *Clarke's Constants of Nature*, 2nd ed., Washington, 1888, 1, 77.
[20] Andreae, *Zeitsch. physikal. Chem.*, 1913, 82, 109.
[21] Rosický, *Zeitsch. Kryst. Min.*, 1908, 45, 473.
[22] Schüller, *Pogg. Annalen*, 1869, 136, 70, 235.
[23] Regnault, *ibid.*, 1841, 53, 60, 243.
[24] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 232.
[25] Berthelot, *Thermochimie*, Paris, 1897, 1, 207.
[26] Thomsen, *Thermochemistry* (Longmans, 1908), 115.

tion is 31·38 Cal., and for the heat of solution of the anhydrous sulphate he found 0·46 Cal.[1] For the heat of solution of the decahydrate Thomsen[2] gives −18·8 Cal., and Berthelot[3] −18·1 Cal. The heat of hydration of the anhydrous salt to the decahydrate is given by Thomsen[2] as 19·22 Cal., and by Berthelot[3] as 18·64 Cal.

The solubility of the anhydrous salt diminishes with rise of temperature from 33° to 120° C., as indicated in the table of solubility.

Solubility of Sodium Sulphate.

Solid Phase, $Na_2SO_4,10H_2O$.

Temperature, °C.	0	10	20	30	32·75
Grams Na_2SO_4 in 100 grams water	5·0	9·0	19·4	40·8	50·65

Solid Phase, $Na_2SO_4,7H_2O$.

Temperature, °C.	0	5	10	15	20	25
Grams Na_2SO_4 in 100 grams water	19·5	24	30	37	44	53

Solid Phase, Na_2SO_4.

Temperature, °C.	33	35	40	50	60	80	100
Grams Na_2SO_4 in 100 grams water	50·6	50·2	48·8	46·7	45·3	43·7	42·5
Temperature, °C.	120	140	160	230			
Grams Na_2SO_4 in 100 grams water	41·95	42	44·25	46·4			

Löwel[4] gives the transition-point of the heptahydrate into the anhydrous salt (*E*) as 24·4° C., and that of the decahydrate into the anhydrous salt (*F*) is given by Richards and Wells[5] as 32·383° C., and by Dickinson and Mueller[6] as 32·384° C. The solubility relations are graphically represented in fig. 9 (p. 120).

A saturated solution of sodium sulphate containing 42·2 grams of sulphate per 100 grams of water boils at 101·9° C. at 751 mm. pressure,[7] or 108·668° C. at 760 mm. pressure.[8]

Sodium sulphate readily forms a supersaturated solution in water.[9] When a solution is cooled to about 5° C., the heptahydrate crystallizes out. The crystals of the decahydrate weather in air, owing to loss of water of crystallization.

Reduction of sodium sulphate with charcoal at red heat produces sodium sulphide and carbon monoxide, along with sodium polysulphides and carbon dioxide. Addition of alcohol to a solution of sodium sulphate in aqueous hydrogen peroxide precipitates a complex derivative of the formula $Na_2SO_4,9H_2O,H_2O_2$.[10]

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[1] Thomsen, *J. prakt. Chem.*, 1878, [2], 17, 175; compare Pickering, *Trans. Chem. Soc.*, 1884, 45, 686; Berthelot and Ilosvay, *Ann. Chim. Phys.*, 1883, [5], 29, 336.

[2] Thomsen, *loc. cit.*

[3] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 106.

[4] Löwel, *ibid.*, 1857, [3], 49, 50.

[5] Richards and Wells, *Zeitsch. physikal. Chem.*, 1903, 43, 471.

[6] Dickinson and Mueller, *J. Amer. Chem. Soc.*, 1907, 29, 1318.

[7] Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 209.

[8] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.

[9] Compare Ostwald, *Principles of Inorganic Chemistry* (Macmillan, 1904), 492.

[10] Tanatar, *Zeitsch. anorg. Chem.*, 1901, 28, 255.

Sodium sulphate forms double salts with potassium sulphate[1] and magnesium sulphate.[2]

References are appended to investigations of the surface tension[3] and the electric conductivity[4] of the fused salt, the dissociation pressure,[5] and the heat of fusion[6]; properties of aqueous solutions, such as the transition-points of the hydrates,[7] vapour-pressure,[8] boiling-point,[9] molecular depression of the freezing-point,[10] density,[11] expansion,[12] specific heat,[13] viscosity,[14] diffusion,[15] optical properties,[16] electric conductivity,[17] and electrolysis.[18]

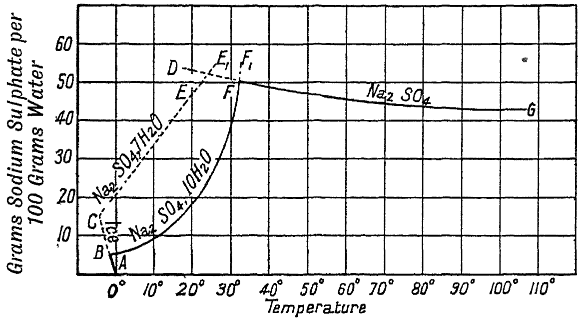

FIG. 9.—Solubility-curve of sodium sulphate.

Sodium hydrogen sulphate, $NaHSO_4$.—The primary sulphate is formed by the interaction of equimolecular proportions of sodium chloride and sulphuric acid, or by crystallizing the normal salt from

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[1] Retgers, *Zeitsch. physikal. Chem.*, 1890, 6, 205; van 't Hoff and Barschall, *Sitzungsber. K. Akad. Wiss. Berlin*, 1903, 359; *Zeitsch. physikal. Chem.*, 1906, 56, 212; Bandrowsky, *Zeitsch. physikal. Chem.*, 1895, 17, 240; Gossner, *Zeitsch. Kryst. Min.*, 1904, 39, 155.

[2] Nacken, *Nachr. K. Ges. Wiss. Göttingen*, 1907, 602.

[3] Quincke, *Pogg. Annalen*, 1869, 138, 141.

[4] Arndt, *Zeitsch. Elektrochem.*, 1906, 12, 337; Braun, *Ber.*, 1874, 7, 958.

[5] Lescœur, *Ann. Chim. Phys.*, 1890, [6], 21, 529.

[6] Cohen, *Zeitsch. physikal. Chem.*, 1894, 14, 53.

[7] Löwenherz, *ibid.*, 1895, 18, 70; Dawson and Jackson, *Trans. Chem. Soc.*, 1908, 93, 344; van 't Hoff and Saunders, *Sitzungsber. K. Akad. Wiss. Berlin*, 1898, 387; Kurnakoff and Schemtschushny, *Trans. Russ. Min. Soc.*, 1902, [2], 37, ii., 49; de Coppet, *Zeitsch. physikal. Chem.*, 1897, 22, 239; Cohen and Bredig, *ibid.*, 1904, 14, 535.

[8] Cohen, *ibid.*, 1894, 14, 53; Tammann, *Wied. Annalen*, 1885, 24, 530.

[9] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.

[10] Raoult, *Zeitsch. physikal. Chem.*, 1888, 2, 489; Loomis, *Wied. Annalen*, 1896, 57, 503.

[11] Pasca, *Trans. Roy. Soc. Canada*, 1900, 6, 27; James Barnes, *Trans. Nova Scotia Inst. Sci.*, 1900, 10, 49; Ostwald, *J. prakt. Chem.*, 1877, [2], 16, 385; 1878, [2], 18, 328; Kohlrausch, *Wied. Annalen*, 1885, 26, 161; Ruppin, *Zeitsch. physikal. Chem.*, 1894, 14, 467; Archibald, *Trans. Nova Scotia Inst. Sci.*, 1877, 9, 335.

[12] Nicol, *Ber.*, 1882, 15, 1931; Marignac, *Annalen Suppl.*, 1872, 8, 335; Zepernick and Tammann, *Zeitsch. physikal. Chem.*, 1895, 16, 659; Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 347.

[13] Pagliani, *Atti R. Accad. Sci. Torino*, 1880–81, 16, 595; 1881–82, 17, 97; Teudt, *Dissertation*, Erlangen, 1900; Thomsen, *Pogg. Annalen*, 1871, 142, 337.

[14] Arrhenius, *Zeitsch. physikal. Chem.*, 1887, 1, 285; Wagner, *ibid.*, 1890, 5, 31.

[15] Schuhmeister, *Sitzungsber. K. Akad. Wiss. Wien*, 1879, 79, ii., 603.

[16] Le Blanc and Rohland, *Zeitsch. physikal. Chem.*, 1896, 19, 261; Perkin, *Trans. Chem. Soc.*, 1893, 63, 57.

[17] Kohlrausch and Grüneisen, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1215; Kohlrausch, *ibid.*, 1901, 1026; 1902, 572; Jahn, *Zeitsch. physikal. Chem.*, 1907, 58, 641.

[18] Turrentine, *J. Physical Chem.*, 1908, 12, 448.

solution in sulphuric acid. At ordinary temperature monoclinic crystals of the monohydrate are deposited, at 50° C. triclinic crystals of the anhydrous substance.[1]

Sodium hydrogen sulphate is a white salt, of density[2] 2·435 at 13° C. Its heat of formation from the elements is given by Thomsen[3] as 267·4 Cal., and by Berthelot[4] as 269·1 Cal.; from sulphuric acid and sodium hydroxide it is 14·75 Cal. The heat of solution is given by Thomsen[5] as 1·19 Cal., but by Berthelot as —0·8 Cal.

Other investigations concern the molecular volume[6]; and such properties of the solution as viscosity,[7] density,[8] and electric conductivity.[9]

Various sulphates of sodium and hydrogen have been prepared. With absolute sulphuric acid sodium sulphate reacts, forming a complex crystalline derivative[10] melting at 40° C., and having the formula $Na_2SO_4,8H_2SO_4$. d'Ans[11] has prepared another example with the composition $Na_2SO_4,NaHSO_4$. Kendall and Landon[12] have described $2Na_2SO_4,9H_2SO_4$, an unstable substance at its melting-point, 60° C. (by extrapolation); $Na_2SO_4,2H_2SO_4$, unstable at its melting-point; and Na_2SO_4,H_2SO_4, melting at 186° C. Other compounds of similar type have been prepared.[13]

Sodium monopersulphate, Na_2SO_5.—This salt is produced by the interaction of barium perhydroxide and sodium hydrogen sulphate:[14]

$$Ba(OH)_4+2NaHSO_4=Na_2SO_5+BaSO_4+3H_2O.$$

Sodium pyrosulphate, $Na_2S_2O_7$.—The pyrosulphate is produced by the action of sulphur dioxide on sodium sulphate, or by heating the primary sulphate:

$$2NaHSO_4=Na_2S_2O_7+H_2O.$$

On ignition, it yields the normal sulphate and sulphur trioxide.

Sodium persulphate, $Na_2S_2O_8$.—The persulphate is formed in solution by the electrolysis of a concentrated aqueous solution of sodium sulphate at low temperature and high current-density. The solid persulphate can be obtained by double decomposition of ammonium persulphate and sodium carbonate either in the solid state or in concentrated solution, the crystalline salt being isolated from the solution either by addition of alcohol or by concentration at reduced pressure.[15] When dry and protected from sunlight, it keeps almost unchanged for years.[16]

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[1] Marignac, *Compt. rend.*, 1857, 45, 650.

[2] Spring, *Bull. Acad. roy. Belg.*, 1904, 290.

[3] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 233.

[4] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 106.

[5] Thomsen, *Thermochemistry* (Longmans, 1908), 49, 328.

[6] Spring, *Bull. Acad. roy. Belg.*, 1904, 290.

[7] Moore, *Physical Rev.*, 1896, 3, 321.

[8] Marignac, *Annalen Suppl.*, 1872, 8, 335.

[9] Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 185.

[10] Bergius, *Zeitsch. physikal. Chem.*, 1910, 72, 338.

[11] d'Ans, *Ber.*, 1906, 39, 1534.

[12] Kendall and Landon, *J. Amer. Chem. Soc.*, 1920, 42, 2131.

[13] Compare d'Ans, *Zeitsch. anorg. Chem.*, 1913, 80, 295; Foote, *J. Ind. Eng. Chem.*, 1919, 11, 629.

[14] Merck, *German Patent*, 1909, No. 213457; compare Willstätter and Hauenstein, *Ber.*, 1909, 42, 1839.

[15] Löwenherz, *German Patents*, Nos. 77340 and 81404.

[16] Elbs and Neher, *Chem. Zeit.*, 1921, 45, 1113.

Sodium thiosulphate, $Na_2S_2O_3$.—The thiosulphate is manufactured from the alkali-waste of the Le Blanc process by atmospheric oxidation in presence of sodium sulphate, which reacts with the calcium thiosulphate first formed to yield sodium thiosulphate :[1]

$$Ca(SH)_2+4O=CaS_2O_3+H_2O\,;$$
$$CaS_2O_3+Na_2SO_4=Na_2S_2O_3+CaSO_4.$$

The salt crystallizes from the solution as the monoclinic pentahydrate, the ordinary commercial form. It is obtained in the anhydrous state by oxidizing dry sodium hydrogen sulphide with air at 100° to 150° C. :[2]

$$2NaSH+4O=Na_2S_2O_3+H_2O.$$

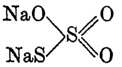
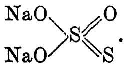
The thiosulphate is also produced by addition of iodine to an aqueous solution containing sodium sulphite and sodium sulphide :[3]

$$Na_2SO_3+Na_2S+2I=Na_2S_2O_3+2NaI.$$

A convenient method for preparing sodium thiosulphate in the laboratory consists in dividing a hot saturated solution of sodium carbonate into two equal portions, passing sulphur dioxide through one until absorption ceases, and then adding the other half. The solution of sodium sulphite thus produced is boiled with sulphur until no more dissolves, filtered, and allowed to crystallize. The reactions involved correspond with the equations

$$(1)\ Na_2CO_3+2SO_2+H_2O=2NaHSO_3+CO_2\,;$$
$$(2)\ 2NaHSO_3+Na_2CO_3=2Na_2SO_3+CO_2+H_2O\,;$$
$$(3)\ Na_2SO_3+S=Na_2S_2O_3.$$

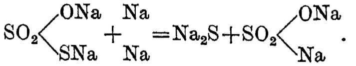
The constitution of sodium thiosulphate can be represented by two formulæ :

I.  ; II. 

$$\text{I. }\begin{matrix}\mathrm{NaO}\\ \mathrm{NaS}\end{matrix}\!>\!\mathrm{S}\!\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right.\ ;\quad \text{II. }\begin{matrix}\mathrm{NaO}\\ \mathrm{NaO}\end{matrix}\!>\!\mathrm{S}\!\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{S}\end{matrix}\right..$$

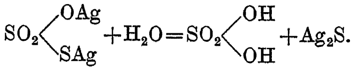
The preference is given to the first formula, as Schorlemmer[4] has pointed out that the second is not in good accord with some of the reactions of the salt :

(1) Sodium thiosulphate in solution is converted by sodium-amalgam into sodium sulphite and sodium sulphide :



$$\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{ONa}\\ \mathrm{SNa}\end{matrix}\right.+\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}=\mathrm{Na_2S}+\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{ONa}\\ \mathrm{Na}\end{matrix}\right..$$

(2) On warming with water, silver thiosulphate decomposes, precipitating silver sulphide and forming sulphuric acid :



$$\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{OAg}\\ \mathrm{SAg}\end{matrix}\right.+\mathrm{H_2O}=\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.+\mathrm{Ag_2S}.$$

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[1] Compare Schütz, *Zeitsch. angew. Chem.*, 1911, 24, 721.

[2] Verein Chem. Fabriken in Mannheim, *German Patent*, 1908, No. 194881.

[3] Spring, *Ber.*, 1874, 7, 1157.

[4] Schorlemmer, *J. Chem. Soc.*, 1869, 22, 256; compare Roscoe and Schorlemmer, *A Treatise on Chemistry*, vol. i.

For the density of the anhydrous salt Gerlach[1] gives 1·667 at mean temperature compared with water at 4° C.; for the pentahydrate Kopp[2] gives 1·736, Dewar[3] 1·729 at 17° C. and 1·7635 at the temperature of liquid air. For the specific heat of the anhydrous salt between 25° and 100° C. Pape[4] gives 0·221; for the pentahydrate between 11° and 44° C. Trentinagali[5] 0·4447, and for the liquid between 13° and 98° C., 0·569. The molecular heat[6] of the anhydrous salt is 34·91, and of the pentahydrate 86·22. Berthelot gives the heat of formation of the anhydrous salt from its elements as 256·3 Cal.[7] or 262·6 Cal.,[8] and Thomsen[9] that of the pentahydrate as 265·07 Cal. Berthelot found for the heat of solution of the anhydrous salt 1·7 Cal. at 15° C.; his value for that of the pentahydrate at 11° C. is −10·8 Cal., and Thomsen's[10] −11·37 Cal., so that the heat of hydration of the anhydrous salt to pentahydrate is about 13 Cal.

Nine hydrates, including thirteen crystalline forms, have been described.[11] The pentahydrate melts at 48·45° C., and the dihydrate[12] at 50·3° C. Each exists in two isomeric forms. According to Müller,[13] the unstable form of the pentahydrate crystallizes at −20° C. and melts at 33° C.; the stable modification crystallizes at −40° C. and melts at 48° C. The transition-point of the pentahydrate to the dihydrate is 48·17° C., and of the dihydrate to the anhydrous salt 68·5° C. The solubility of the pentahydrate, the dihydrate, and the anhydrous salt, expressed in grams of $Na_2S_2O_3$ per 100 grams of solution, are given in the table.[14]

Temperature, °C.	0	5	10	15	20	25	30	35	40	45
Pentahydrate	33·4	35·3	37·4	39·1	41·2	43·2	45·2	47·7	50·8	55·3
Dihydrate	52·7	53·4	53·9	54·6	55·2	56·0	57·1	58·2	59·4	60·7
Temperature, °C.	40	45	50	55	60	65	70	75	80	
Dihydrate	59·4	60·7	62·3	63·9	65·7	68·0				
Anhydrous salt	67·4	67·6	67·8	68·2	68·5	68·8	69·1	69·4	69·9	

In contact with the solid the saturated solution boils at 126° C., and contains 348 grams of the anhydrous salt in 100 grams of water.[15]

Concentrated solutions of sodium thiosulphate are moderately stable, but in dilute solution atmospheric carbon dioxide tends to liberate the unstable thiosulphuric acid, a substance readily changed

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[1] Gerlach, *Chem. Industr.*, 1886, 9, 241.
[2] Kopp, *Annalen*, 1855, 93, 129.
[3] Dewar, *Chem. News*, 1902, 85, 277.
[4] Pape, *Pogg. Annalen*, 1865, 125, 513.
[5] Trentinaglia, *Sitzungsber. K. Akad. Wiss. Wien*, 1876, [2], 72, 669.
[6] Schottky, *Physikal. Zeitsch.*, 1909, 10, 634.
[7] Berthelot, *Thermochimie*, Paris, 1897, 1, 207.
[8] Berthelot, *Ann. Chim. Phys.*, 1879, [5], 17, 468.
[9] Thomsen, *Thermochemistry* (Longmans, 1908), 328.
[10] Thomsen, *ibid.*, 49.
[11] Young, Mitchell, and Burke, *J. Amer. Chem. Soc.*, 1904, 26, 1389, 1413; 1906, 28, 315.
[12] Gernez, *Compt. rend.*, 1909, 149, 77.
[13] Müller, *Zeitsch. physikal. Chem.*, 1914, 86, 177.
[14] Young, Mitchell, and Burke, *loc. cit.*; Taylor, *Proc. Roy. Soc. Edin.*, 1897–98, 22, 249.
[15] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.

into sulphurous acid and sulphur. Siebenschuh[1] states that, after being kept for fourteen days, protection from light ensures the stability of the solution. Hampshire and Pratt[2] kept a solution for eight months without alteration in strength.

When a mineral acid is added to a dilute solution of sodium thiosulphate, the liquid remains clear for a time, and then becomes turbid owing to deposition of sulphur which at first was in solution:[3]

$$H_2S_2O_3=H_2O+SO_2+S.$$

The logarithms of the times elapsing before appearance of turbidity are proportional to the concentration of the hydrogen ions in the mineral acids added, so that for isohydric solutions the time of reaction is independent of the acid employed.[4] When hydrochloric acid is added slowly to a boiling solution of sodium thiosulphate, the sulphur is oxidized to sulphur dioxide:[5]

$$SO_2+S+2H_2O=H_2SO_4+H_2S.$$

The salt reacts with ozone in accordance with the equation[6]

$$3Na_2S_2O_3+2O_3=2Na_2SO_4+Na_2SO_3+2O_2+3S.$$

With hydrogen peroxide the first product is sodium tetrathionate, and the solution becomes alkaline:

$$2Na_2S_2O_3+H_2O_2=Na_2S_4O_6+2NaOH.$$

The subsequent stages of the reaction are more complex.[7]

With silver halides sodium thiosulphate forms a soluble sodium silver thiosulphate, and is employed as a "fixing" material for photographic plates and paper to remove the portion of silver salt unaffected by light:

$$AgBr+Na_2S_2O_3=NaAgS_2O_3+NaBr.$$

In the bleaching industry it finds application as an "anti-chlor," the excess of chlorine in the bleached material being removed by its aid in accordance with the equation

$$Na_2S_2O_3+4Cl_2+5H_2O=2NaCl+2H_2SO_4+6HCl.$$

Sodium thiosulphate is employed in iodometry, being converted by the action of iodine into sodium tetrathionate:

$$2Na_2S_2O_3+2I=Na_2S_4O_6+2NaI.$$

According to Kolthoff,[8] the reaction represented by the equation takes place in neutral or slightly acidic solution, and also in presence of strong acid. When the solution is strongly alkaline, all the thiosulphate is

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[1] Siebenschuh, *Stahl und Eisen*, 1909, 29, 1692.

[2] Hampshire and Pratt, *Pharm. J.*, 1913, [4], 37, 142; compare Bohrisch, *Pharm. Zeit.*, 1914, 59, 360.

[3] Landolt, *Ber.*, 1883, 16, 2958.

[4] von Oettingen, *Zeitsch. physikal. Chem.*, 1900, 33, 1; Colefax, *Trans. Chem. Soc.*, 1892, 61, 176, 199.

[5] Colson, *Compt. rend.*, 1909, 149, 77.

[6] Yamauchi, *Amer. Chem. J.*, 1913, 49, 55.

[7] Nabl, *Ber.*, 1900, 33, 3093, 3554; Tarugi and Vitali, *Gazzetta*, 1909, 39, i., 418; compare Willstätter, *Ber.*, 1903, 36, 1831.

[8] Kolthoff, *Pharm. Weekblad*, 1919, 56, 572.

oxidized directly to sulphate without the intermediate formation of tetrathionate, weak alkali having a similar, though only partial, effect.

The action of hypochlorite solutions on sodium thiosulphate is in accordance with the equations[1]

$$3Na_2S_2O_3+5Cl_2+5H_2O=Na_2SO_4+Na_2S_4O_6+8HCl+H_2SO_4+2NaCl\,;$$

or

$$3Na_2S_2O_3+5NaOCl+5H_2O=2Na_2SO_4+Na_2S_4O_6+5NaCl+5H_2O.$$

In presence of acids or sodium hydrogen carbonate, the reaction accords with the equation

$$Na_2S_2O_3+4Cl_2+5H_2O=2NaHSO_4+8HCl.$$

Kurtenacker[2] found that cyanogen bromide and iodide react with sodium thiosulphate in neutral solution in accordance with the equation

$$3CNBr+5S_2O_3''+H_2O=3Br'+2HCN+CNS'+SO_4''+2S_4O_6''.$$

In acidic solution the thiosulphate is converted into tetrathionate:

$$CNBr+2S_2O_3''+H^{\cdot}=Br'+HCN+S_4O_6''.$$

The reaction in neutral solution probably involves two stages, the solution becoming temporarily alkaline through the formation of sodium cyanide, which reacts with the generated tetrathionate in accordance with the equation

$$Na_2S_4O_6+3NaCN+H_2O=NaCNS+Na_2SO_4+Na_2S_2O_3+2HCN.$$

The thiosulphate produced then reacts with the halogen cyanide.

A mixture of crystallized sodium thiosulphate and ammonium nitrate finds application as a freezing-mixture.[3]

References are appended to investigation of the refractivity[4] of the solid; to properties of solutions such as the transition-points of the hydrates,[5] supersaturation,[6] electric conductivity,[7] density,[8] vapour-pressure,[9] boiling-point,[10] molecular depression of the freezing-point,[11] refractivity,[12] solubility in alcohol,[13] and electrolysis[14]; and to the formation of mixed thiosulphates of sodium and potassium and their isomerism.[15]

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[1] Diénert and Wandenbulcke, *Compt. rend.*, 1919, 169, 29.

[2] Kurtenacker, *Zeitsch. anorg. Chem.*, 1921, 116, 243; compare, however, Meineke, *ibid.*, 1893, 2, 157; Dixon and Taylor, *Trans. Chem. Soc.*, 1913, 103, 974.

[3] Schubardt, *German Patent*, 1911, No. 233596.

[4] Dufet, *Bull. Soc. franç. Min.*, 1888, 11, 123, 191.

[5] Trentinaglia, *Sitzungsber. K. Akad. Wiss. Wien*, 1876, [2], 72, 669; Richards and Churchill, *Zeitsch. physikal. Chem.*, 1899, 28, 314; Dawson and Jackson, *Trans. Chem. Soc.*, 1908, 93, 344; Guthrie, *Phil. Mag.*, 1878, [5], 6, 41.

[6] Blümcke, *Zeitsch. physikal. Chem.*, 1896, 20, 586.

[7] Küster and Thiel, *Zeitsch. anorg. Chem.*, 1899, 21, 401.

[8] Damien, *Ann. École Norm.*, 1881, [2], 10, 233.

[9] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; compare Lescœur, *Ann. Chim. Phys.*, 1896, [7], 9, 537.

[10] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.

[11] Richards and Faber, *Amer. Chem. J.*, 1899, 21, 172; compare Faktor, *Pharm. Post*, 1902, 34, 769.

[12] Bary, *Compt. rend.*, 1892, 114, 827; compare Miers and Isaac, *Trans. Chem. Soc.*, 1906, 89, 413.

[13] Parmentier, *Compt. rend.*, 1896, 122, 135; compare Bruner, *ibid.*, 1895, 121, 59.

[14] Thatcher, *Zeitsch. physikal. Chem.*, 1904, 47, 641.

[15] Schwicker, *Ber.*, 1889, 22, 1730.

Sodium dithionate, $Na_2S_2O_6$.[1]—The dithionate is obtained by the action of sodium carbonate on barium dithionate.[2] It is the principal product formed by boiling sodium silver sulphite with water : [3]

$$2AgSO_3Na = Na_2S_2O_6 + 2Ag.$$

It is known in the forms of dihydrate [4] and hexahydrate.[5]

For the density of the dihydrate Topsöe [6] gives 2·189. Thomsen [7] found for the heat of formation of the anhydrous compound 398·8 Cal.; for its heat of solution −5·37 Cal., and for that of the dihydrate −11·65 Cal., the heat of hydration being 6·28 Cal. The vapour-pressure [8] and electric conductivity [9] of solutions have also been studied.

Sodium trithionate, $Na_2S_3O_6$.—The trithionate can be prepared from sodium thiosulphate by oxidation with hydrogen peroxide,[10] or by electrolysis in acid or alkaline solution.[11] It is also formed by heating a solution of sodium mercuric thiosulphate : [12]

$$Na_2Hg(S_2O_3)_2 = Na_2S_3O_6 + HgS.$$

The trihydrate can be prepared by the interaction of sulphur dioxide and sodium thiosulphate.[13]

Sodium trithionate forms transparent plates, very soluble in water. The heat of formation in aqueous solution from the elements is given by Berthelot [14] as 393·6 Cal. The heat of solution of the trihydrate is −10·1 Cal.

Sodium tetrathionate, $Na_2S_4O_6$.—The tetrathionate is prepared from the thiosulphate either by the action of iodine (p. 124) or by oxidation with cupric chloride.[15] It can be precipitated from solution by addition of alcohol. With sodium carbonate it yields sodium thiosulphate : [16]

$$4Na_2S_4O_6 + 5Na_2CO_3 = 7Na_2S_2O_3 + 2Na_2SO_4 + 5CO_2.$$

The heat of formation in aqueous solution is given by Berthelot [17] as 387·2 Cal. A dihydrate exists, its heat of solution being −9·5 Cal.

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[1] On the constitution and properties of the polythionates of the alkali-metals, see Colefax, *Trans. Chem. Soc.*, 1892, 61, 176, 199, 1083; 1908, 93, 811; Marshall, *J. Soc. Chem. Ind.*, 1897, 16, 396; Gutmann, *Ber.*, 1905, 38, 1728, 3277; 1906, 39, 509; 1907, 40, 3614; 1908, 41, 300, 1650; Julius Meyer and H. Eggeling, *Ber.*, 1907, 40, 1531; Price and Twiss, *Trans. Chem. Soc.*, 1907, 91, 2021; Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726.

[2] See this series, Vol. III.

[3] Baubigny, *Compt. rend.*, 1909, 149, 735, 858; 1910, 150, 466.

[4] Holst, *Arch. Pharm.*, 1891, 229, 174.

[5] Kraut, *Annalen*, 1861, 118, 95.

[6] Topsöe, *Arch. Sci. phys. nat.*, 1872, [2], 45, 223.

[7] Thomsen, *Thermochemistry* (Longmans, 1908), 210, 326.

[8] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; *Wied. Annalen*, 1885, 24, 530.

[9] Ostwald, *Zeitsch. physikal. Chem.*, 1887, 1, 106.

[10] Willstätter, *Ber.*, 1903, 36, 1831.

[11] Thatcher, *Zeitsch. physikal. Chem.*, 1904, 47, 641.

[12] Spring, *Ber.*, 1874, 7, 1159.

[13] Villiers, *Compt. rend.*, 1888, 106, 1356.

[14] Berthelot, *Ann. Chim. Phys.*, 1889, [6], 17, 455.

[15] Kessler, *Jahresbericht*, 1847–48, 375.

[16] Gutmann, *Ber.*, 1908, 41, 300.

[17] Berthelot, *loc. cit.*

The tetrathionate is converted by the action of sodium sulphite into trithionate and thiosulphate :[1]

$$Na_2S_4O_6+Na_2SO_3=Na_2S_3O_6+Na_2S_2O_3.$$

With alkali-metal cyanides the tetrathionate reacts in accordance with the equation[2]

$$Na_2S_4O_6+3NaCN+H_2O=NaCNS+Na_2SO_4+Na_2S_2O_3+2HCN.$$

At the boiling-point, in presence of excess of cyanide, the thiosulphate formed reacts further to produce thiocyanate and sulphite.

Sodium pentathionate, $Na_2S_5O_6$.—This salt has not been obtained in the pure state, but is said to be one of the products of the decomposition of acid solutions of sodium thiosulphate, the sulphur dioxide liberated reacting with the thiosulphate :[3]

$$5Na_2S_2O_3+3SO_2=2Na_2S_5O_6+3Na_2SO_3.$$

It is also said to react with sodium sulphite, yielding the trithionate and thiosulphate :[3]

$$Na_2S_5O_6+2Na_2SO_3=Na_2S_3O_6+2Na_2S_2O_3.$$

Sodium hyposulphite, $Na_2S_2O_4$.—The hyposulphite was first prepared in solution by Schützenberger[4] by reducing a solution of sodium hydrogen sulphite with zinc, but the yield is unsatisfactory. Bernthsen and Bazlen[5] obtained the pure substance by reducing the primary sulphite with zinc-dust in presence of sulphurous acid,

$$2NaHSO_3+SO_2+Zn=Na_2S_2O_4+ZnSO_3+H_2O,$$

precipitating the zinc and removing the excess of acid by addition of milk of lime, the hyposulphite being salted out in the form of dihydrate by addition of sodium chloride. They recommend increasing the stability of the dihydrate by washing with acetone, at first dilute and finally pure, and drying in a vacuum. Jellinek[6] advises heating the dihydrate at 60° C. in vacuum, the process transforming it into the stable anhydrous salt. The hyposulphite can also be produced under special experimental conditions[7] by the electrolytic reduction of sodium hydrogen sulphite, Jellinek[8] having obtained a 7 to 8 per cent. solution by this means. Prepared by this process, it finds application in the reduction of indigo to indigo-white.[9]

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[1] Raschig, *Zeitsch. angew. Chem.*, 1920, 33, 260.

[2] Kurtenacker and Fritsch, *Zeitsch. anorg. Chem.*, 1921, 117, 202; compare Gutmann, *Ber.*, 1906, 39, 509; Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726.

[3] Raschig, *Zeitsch. angew. Chem.*, 1920, 33, 260.

[4] Schützenberger, *Compt. rend.*, 1869, 69, 196; 1872, 75, 879.

[5] Bernthsen and Bazlen, *Ber.*, 1900, 33, 126; Bazlen, *Ber.*, 1905, 38, 1057.

[6] Karl Jellinek, *Zeitsch. anorg. Chem.*, 1911, 70, 93.

[7] Frank, *Zeitsch. Elektrochem.*, 1904, 10, 450; Chaumat, *German Patent*, 1910, No. 221614; Elbs and Becker, *Zeitsch. Elektrochem.*, 1904, 10, 361; Julius Meyer, *Zeitsch. anorg. Chem.*, 1903, 34, 43.

[8] Karl Jellinek and E. Jellinek, *Zeitsch. physikal. Chem.*, 1919, 93, 325.

[9] Höchster Farbwerke, *German Patent*, 1902, No. 139567.

The anhydrous hyposulphite is also formed by the interaction of sulphur dioxide and sodium hydride :[1]

$$2NaH+2SO_2=Na_2S_2O_4+H_2.$$

The anhydrous salt is converted into the dihydrate by crystallization from water.

A laboratory method[2] for the preparation of sodium hyposulphite depends on the interaction of sodium formaldehydesulphoxylate,[3] $NaCH_3O_3S,2H_2O$, and sodium hydrogen sulphite, the product having a purity of 80 to 85 per cent., and the yield being 55 to 60 per cent. of that theoretically possible. The sodium formaldehydesulphoxylate can be obtained[2] by the reduction of commercial "hydrosulphite" by zinc-dust and zinc oxide in presence of formaldehyde solution, the crude product being recrystallized from water at 70° C.

Sodium hyposulphite dihydrate forms colourless vitreous prisms, readily soluble in water. On heating it loses its water of crystallization, melts at red heat, and burns with a blue flame, evolving sulphur dioxide. On addition of acid in small proportion the solution develops a red colour, due to separation of sulphur. Molecular-weight determinations by the cryoscopic method indicate it to be the salt of a dibasic acid, and to be represented by the formula $Na_2S_2O_4$.[4]

At temperatures between 0° and 30° C. the salt decomposes in aqueous solution in accordance with the scheme[5]

$$2Na_2S_2O_4=Na_2S_2O_5+Na_2S_2O_3;$$
$$Na_2S_2O_5+H_2O=2NaHSO_3.$$

Hydrogen sulphide has no action on dry sodium hyposulphite, but in presence of water it reacts as indicated by the equation

$$Na_2S_2O_4+H_2S=Na_2S_2O_3+H_2O+S.$$

The sulphur is obtained in a weighable form, and Sinnatt[6] advocates the estimation of sodium hyposulphite by this method.

The method devised by Seyewetz and Bloch[7] for the valuation of this substance depends on the oxidizing action of an ammoniacal solution of silver chloride :

$$Na_2S_2O_4+2AgCl+4NH_4OH=2(NH_4)_2SO_3+2NaCl+2H_2O+2Ag.$$

Hollingsworth Smith[8] has improved the speed of the operation, and has also eliminated the defect due to solid impurities in the hyposulphite being weighed with the silver.

Sodium hyposulphite is oxidized by iodine to sodium hydrogen

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[1] Moissan, *Compt. rend.*, 1902, 135, 647.

[2] Heyl and Greer, *Amer. J. Pharm.*, 1922, 94, 80.

[3] Orloff, *J. Russ. Phys. Chem. Soc.*, 1907, 39, 1588; compare Bazlen, *Ber.*, 1905, 38, 1057. The technical name of this product is "Rongalite." It is a reducer for vat dyestuffs.

[4] Julius Meyer, *Zeitsch. anorg. Chem.*, 1903, 34, 43; compare Orloff, *J. Russ. Phys. Chem. Soc.*, 1908, 39, 1588.

[5] Karl Jellinek and E. Jellinek, *Zeitsch. physikal. Chem.*, 1919, 93, 325.

[6] Sinnatt, *J. Soc. Dyers*, 1914, 30, 189.

[7] Seyewetz and Bloch, *Bull. Soc. chim.*, 1906, [3], 35, 293; compare Fradiss, *Bull. Assoc. Chimistes*, 1899, 16, 453; Knecht and Hibbert, *Ber.*, 1907, 40, 3819; Helwig, *Amer. Dyestuff Reporter*, 1920, 7, ii., 12.

[8] Hollingsworth Smith, *J. Amer. Chem. Soc.*, 1921, 43, 1307.

sulphate, a reaction applied by Bazlen and Bernthsen to the quantitative estimation of the salt:[1]

$$Na_2S_2O_4+6I+4H_2O=2NaHSO_4+6HI.$$

The action of selenium and tellurium on sodium hyposulphite has been investigated by Tschugaev and Chlopin.[2]

The hyposulphite was employed by Julius Meyer[3] in the preparation of metallic colloidal solutions. It finds technical application as a reducer in the dye-industry. When administered intravenously, it exerts a toxic effect.[4]

Sodium selenides.—The *monoselenide*, Na_2Se, is formed by the action of selenium on a solution of excess of sodium in liquid ammonia, and separates out.[5] It can also be produced by the interaction of selenium and sodium hyposulphite, $Na_2S_2O_4$.[6] It melts above 875° C., and on exposure to air its solution in water acquires a reddish colour, and deposits selenium. In solution it is extensively hydrolyzed, and under these conditions may be regarded as a mixture of sodium hydrogen selenide, NaSeH, and sodium hydroxide. Four hydrates are known, with 4½, 9, 10, and 16 molecules of water respectively.[7] For the heat of formation of the anhydrous compound Fabre[8] gives 59·7 Cal., and for the heat of solution at 14° C., 18·6 Cal. He has also investigated the heat of solution of the hydrates.

When excess of selenium reacts with a solution of sodium in liquid ammonia, *sodium tetraselenide*, Na_2Se_4, separates.[9] By fusion of sodium with selenium, Mathewson[10] has isolated between 500° and 250° C. the *diselenide* Na_2Se_2, *triselenide* Na_2Se_3, *tetraselenide* Na_2Se_4, and *hexaselenide* Na_2Se_6. They are dark-grey substances, unstable in air, and readily soluble in water to red solutions.

Sodium selenite, Na_2SeO_3.—The selenite is formed by heating a mixture of selenious acid and sodium chloride.[11] At ordinary temperature the aqueous solution deposits the pentahydrate, above 60° C. the anhydrous salt.[12] For the heat of formation from its elements in aqueous solution Thomsen gives 238·4 Cal.

Berzelius mentions a salt which was either *sodium hydrogen selenite*, $NaHSeO_3$, or *pyroselenite*, $Na_2Se_2O_5$.

Sodium selenate, Na_2SeO_4.—The selenate is prepared from sodium selenite by electrolytic oxidation with platinum electrodes at ordinary temperature.[13] A by-product analogous to the dithionate obtained in the electrolytic oxidation of sodium sulphite is not formed.[14]

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[1] Bazlen and Bernthsen, *Ber.*, 1910, 43, 501.

[2] Tschugaev and Chlopin, *Ber.*, 1914, 47, 1269.

[3] Julius Meyer, *Zeitsch. anorg. Chem.*, 1903, 34, 43.

[4] Heyl and Greer, *Amer. J. Pharm.*, 1922, 94, 80.

[5] Hugot, *Compt. rend.*, 1899, 129, 299.

[6] Tschugaev and Chlopin, *loc. cit.*

[7] Fabre, *Ann. Chim. Phys.*, 1887, [6], 10, 505; Clever and Muthmann, *Zeitsch. anorg. Chem.*, 1895, 10, 17.

[8] Fabre, *Ann. Chim. Phys.*, 1887, [6], 10, 505.

[9] Hugot, *Compt. rend.*, 1899, 129, 299.

[10] Mathewson, *J. Amer. Chem. Soc.*, 1907, 29, 867.

[11] Cameron and McCallan, *Chem. News*, 1889, 59, 258.

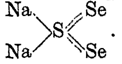
[12] Nilson, *Bull. Soc. chim.*, 1874, [2], 21, 253.

[13] Müller, *Ber.*, 1903, 36, 4262.

[14] Compare Förster and Friessner, *Ber.*, 1902, 35, 2515.

Sodium selenate is known in the anhydrous form and as decahydrate. From observations made by Funk,[1] Meyerhoffer[2] gives the solubility of the hydrate in 100 grams of water at 0° C. as 13·25 grams, and at 30° C. as 78·5 grams; and that of the anhydrous selenate at 40° C. as 82·5 grams, and at 100° C. as 72·75 grams. The decrease of solubility of the anhydrous salt with rise of temperature is reminiscent of the behaviour of the corresponding form of sodium sulphate. For the approximate transition-point of the hydrate into the anhydrous compound, Funk gives 32° C. The density of the hydrate[3] is 1·616. For the heat of formation from its elements of the selenate in aqueous solution Thomsen[4] gives 262·3 Cal., and for sodium hydrogen selenate, $NaHSeO_4$, 203·2 Cal.

Sodium sulphodiselenide, Na_2SSe_2, was obtained as pentahydrate by Messinger[5] by boiling selenium with a solution of sodium hydrogen sulphide in a current of hydrogen. Acids decompose it, liberating hydrogen sulphide and precipitating selenium. Messinger assigns it the constitution



$$\begin{matrix}Na \\ Na\end{matrix}\!>\!S\!\begin{matrix}=Se \\ =Se\end{matrix}$$

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Sodium tellurides.—Davy[6] prepared *sodium monotelluride*, Na_2Te, by the direct union of sodium and tellurium, and also by reduction with carbon of mixtures of an alkali-metal carbonate and tellurium oxide. In the neighbourhood of 250° C., sodium and tellurium unite with explosive violence to form the monotelluride. When the combination takes place in an inert atmosphere, the product has a bronze colour and a crystalline fracture. When dissolved in water in absence of air, it yields hydrated, acicular crystals, soluble at 40° C. in their own water of crystallization. When excess of tellurium has been employed in the preparation of the monotelluride, the mother-liquor of the crystals contains sodium and tellurium in the proportion Na_4Te_3. Isolation of this substance in crystalline form is prevented by its decomposition during evaporation, the crystalline monotelluride and free tellurium being obtained.[7] By the action of tellurium on a solution of sodium in liquid ammonia, Hugot[8] prepared *sodium monotelluride*, Na_2Te, and *sodium tritelluride*, Na_2Te_3. The monotelluride can also be produced by the action of tellurium on sodium hyposulphite, $Na_2S_2O_4$.[9] In a current of hydrogen at 250° C., sodium and tellurium unite with explosive energy, forming the monotelluride, a colourless crystalline substance, soluble in water.[10] It reduces auric chloride and platinum chloride to the corresponding metal, forming tellurium tetrachloride, $TeCl_4$. Its solution dissolves tellurium, yielding a polytelluride of the formula Na_4Te_3. From the results of thermal analysis, Pellini and Quercigh[11] infer the existence of two other polytellurides, with the formulæ Na_3Te_2 and Na_3Te_7.

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[1] Funk, *Ber.*, 1900, 33, 3696.

[2] Meyerhoffer, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 561.

[3] Rosický, *Zeitsch. Kryst. Min.*, 1908, 45, 473.

[4] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 1, 295.

[5] Messinger, *Ber.*, 1897, 30, 805.

[6] Davy, *Phil. Trans.*, 1810, 27, 16.

[7] Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 902.

[8] Hugot, *Compt. rend.*, 1899, 129, 299.

[9] Tschugaev and Chlopin, *Ber.*, 1914, 14, 1269.

[10] Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 902.

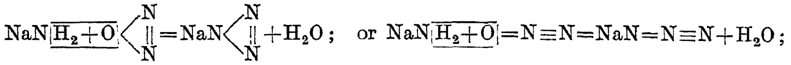
[11] Pellini and Quercigh, *Atti R. Accad. Lincei*, 1910, [5], 19, ii., 350.

Sodium tellurate,[1] $Na_2TeO_4,2H_2O$.—The tellurate is prepared in a similar manner to the selenate.[2] It is not readily soluble, and undergoes reduction easily to tellurium.[3] It is only known in the form of dihydrate.

Sodium chromates.—An account is given in this series, Vol. VII., of the modes of preparation and of the properties of sodium chromate and dichromate.

Sodium nitride, Na_3N.—The nitride is formed by submitting sodium to the action of the silent electric discharge in an atmosphere of nitrogen.[4] It is decomposed by water, with energetic evolution of ammonia. Fischer and Schröter[5] also claim to have prepared it, but they give no analyses or formula.

Sodium hydrazoate, NaN_3.—The hydrazoate is formed by neutralizing hydrazoic acid with sodium hydroxide;[6] by the interaction of sodamide and nitrous oxide:[7]



$$\mathrm{NaN}\boxed{H_2+O}\!\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. = \mathrm{NaN}\!\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + H_2O\text{; or } \mathrm{NaN}\boxed{H_2+O}=N\equiv N=\mathrm{NaN}=N\equiv N+H_2O\text{;}$$

and by decomposing hydrazoyl chloride with sodium hydroxide:[8]

$$N_3Cl+2NaOH=NaN_3+NaOCl+H_2O.$$

Sodium hydrazoate forms colourless crystals, which melt without decomposition, but explode at a temperature higher than the melting-point. At 10° C. 100 grams of water dissolve 40·16 grams, at 17° C. 41·7 grams.

Sodamide, $NaNH_2$.—Sodamide is formed by the action of liquid ammonia on the metal,[9] or by passing dry ammonia over fused sodium[10] or one of its alloys.[11] An apparatus for its preparation has been described by Wöhler and Stang-Lund.[12]

Sodamide is a white substance. According to Wöhler and Stang-Lund,[12] it melts at 210° C., and not between 149° and 155° C., as stated by Titherley[13]; but McGee[14] found that it melts sharply at 208° C. He was unable to prepare the blue solutions of sodium in the amide described by Titherley,[15] and found no solvent action on glass below 240° C. Contact of the amide with glass for several days at 270°

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[1] On sodium tellurite, compare Lenher and Wolesensky, *J. Amer. Chem. Soc.*, 1913, 35, 718.

[2] Funk, *Ber.*, 1900, 33, 3696.

[3] Müller, *Ber.*, 1903, 36, 4262.

[4] Zehnder, *Wied. Annalen*, 1894, 52, 56.

[5] Fischer and Schröter, *Ber.*, 1910, 43, 1465.

[6] Dennis and Benedict, *Zeitsch. anorg. Chem.*, 1898, 17, 19.

[7] Wislicenus, *Ber.*, 1892, 25, 2084; Curtius, *Ber.*, 1890, 23, 3023; 1891, 24, 3341; Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 278.

[8] Raschig, *Ber.*, 1908, 41, 4194.

[9] Compare Joannis, *Compt. rend.*, 1887, 109, 900; 1891, 112, 392; 1892, 115, 820; *Ann. Chim. Phys.*, 1906, [8], 7, 5; Ruff and Geisel, *Ber.*, 1906, 39, 828.

[10] Gay-Lussac and Thénard, *Recherches Physico-Chimiques*, Paris, 1811, 1, 354; Titherley, *Trans. Chem. Soc.*, 1894, 65, 504; de Forcrand, *Compt. rend.*, 1895, 121, 66.

[11] Gold- und Silber-Scheideanstalt vormals Rössler, *German Patent*, 1901, No. 117623.

[12] Wöhler and Stang-Lund, *Zeitsch. Elektrochem.*, 1918, 24, 261.

[13] Titherley, *Trans. Chem. Soc.*, 1894, 65, 504.

[14] McGee, *J. Amer. Chem. Soc.*, 1921, 43, 586.

[15] Titherley, *loc. cit.*

to 300° C. is attended by slight action, probably due to the presence of sodium hydroxide. Sodamide begins to sublime at 400° C. At 500° C. it decomposes with evolution of nitrogen and hydrogen, leaving a residue of sodium and sodium nitride. Between 200° and 300° C. in an atmosphere of hydrogen, it becomes partially converted into sodium hydride and ammonia :[1]

$$NaNH_2+H_2=NaH+NH_3.$$

It is employed in organic syntheses, an example being the conversion of phenylglycine into indoxyl in the manufacture of synthetic indigo.

When exposed to the action of air in presence of a small proportion of water, finely divided sodamide undergoes autoxidation, becoming transformed into a yellowish-red *peroxide*, probably having the formula $NaNH_2,O_2$. At the ordinary temperature there is no autoxidation in dry air, but between 100° and 110° C. the peroxide is slowly generated. In dry air this substance is stable.[2]

Sodium hydrazide, $NH_2{\cdot}NHNa$.—The hydrazide is produced by the interaction of hydrazine hydrate and sodamide :[3]

$$NH_2\,NH_2,H_2O+NH_2Na=NH_2{\cdot}NH_2+NH_3+NaOH\,;$$
$$NH_2{\cdot}NH_2+NH_2Na=NH_2{\cdot}NHNa+NH_3.$$

It can also be formed by the interaction of sodium and pure hydrazine, ammonia and a small proportion of hydrogen being evolved.[4] The colourless, glistening leaflets are both spontaneously inflammable and violently explosive.

Sodium hyponitrite, $Na_2N_2O_2$.—The hyponitrite can be prepared by reducing sodium nitrite with sodium-amalgam[5] and precipitating the solid by addition of alcohol to the solution. The reduction can also be effected by means of sulphur dioxide.[6]

Sodium hyponitrite is readily soluble in water, the concentrated solution being stable in presence of a large proportion of sodium hydroxide. On crystallization the salt is deposited as pentahydrate, this substance losing its water of crystallization in a desiccator or on exposure to air. The anhydrous salt is the more stable form ; it melts with decomposition at 300° C. The cryoscopic method gives the double molecular formula, $Na_2N_2O_2$.

Sodium nitrite, $NaNO_2$.—The nitrite is obtained by reducing sodium nitrate with metals such as lead or iron,[7] with sulphur[8] or carbon,[9] or with material containing these substances. In Dittrich's process[9] the nitrate is heated with slaked lime and sawdust, the yield being almost quantitative, whereas the action of coal and graphite is too energetic :

$$2NaNO_3+Ca(OH)_2+C=2NaNO_2+CaCO_3+H_2O.$$

Other processes for the preparation of the nitrite are the electrolytic

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[1] Miles, *Proc. Roy. Soc. Edin.*, 1915, 35, 134; compare Titherley, *Trans. Chem. Soc.*, 1894, 65, 504.

[2] Schrader, *Zeitsch. anorg. Chem.*, 1919, 108, 44.

[3] Stollé, *J. prakt. Chem.*, 1911, [2], 83, 200.

[4] Schlenk and Weichselfelder, *Ber.*, 1915, 48, 669.

[5] Jackson, *Proc. Chem. Soc.*, 1893, 9, 210; Divers, *Trans. Chem. Soc.*, 1899, 75, 85, 87, 95 ; Hantzsch and Kaufmann, *Annalen*, 1896, 292, 317.

[6] Divers and Haga, *Trans. Chem. Soc.*, 1899, 75, 77.

[7] Pelet and Corni, *Bull. Soc. Vaudoise Sci. nat.*, 1907, [5], 43, 177.

[8] Compare G. T. Morgan, *J. Soc. Chem. Ind.*, 1908, 27, 483.

[9] Dittrich, *German Patent*, 1909, No. 212203.

reduction of the nitrate[1]; the action of nitrous fumes containing excess of nitric oxide on a solution of sodium hydroxide or carbonate[2]; and the action of oxygen on ammonia in presence of platinized asbestos as catalyst, the ammonium nitrite produced being transformed by treatment with sodium hydroxide, and the evolved ammonia being available for further oxidation.[3]

Sodium nitrite is a white, crystalline salt. Its melting-point is given by Divers[2] as 213° C., but by Matignon and Marchal[4] as 276·9° C. (corr.), and by Bruni and Meneghini[5] as 284° C. At 15° C. 100 grams of water dissolve 83·3 grams. The heat of solution is —3·52 Cal., and the heat of formation in solution from the elements is 88·52 Cal.[4]

In aqueous solution at 100° C. and between 50 and 55 atmospheres of pressure, sodium nitrite is not oxidized by prolonged contact with oxygen, even in presence of a catalyst.[4] When heated in an atmosphere of oxygen for nine hours at 175 atmospheres of pressure, the temperature being gradually raised from 395° to 530° C., the solid is almost completely oxidized to sodium nitrate, but the reaction is too slow for practical application:[6]

$$2[NaNO_2]+(O_2)=2[NaNO_3]+45 \text{ Cal.}$$

When heated, sodium nitrite decomposes in accordance with the equation:[7]

$$3NaNO_2=Na_2O+NaNO_3+2NO.$$

Heating in an atmosphere of nitrogen peroxide yields nitric oxide and sodium nitrate:[7]

$$NaNO_2+NO_2=NO+NaNO_3.$$

At 60° C. in an atmosphere of carbon dioxide free from air, a 5 per cent. solution of sodium nitrite is decomposed by metallic copper, with evolution of nitrous fumes, but there is not sufficient evidence to enable the course of the reaction to be indicated by means of an equation.[8]

When an anolyte of sodium nitrite dissolved in twice its weight of water is electrolyzed with a silver anode, a complex salt of the formula $NaAg(NO_2)_2$ is formed at the anode. On evaporation of the solution over sulphuric acid *in vacuo*, it separates in bright yellow crystals.[9]

The nitrite finds extensive application in the manufacture of certain synthetic dyestuffs.

References are appended to the solubility in alcohol,[10] and such properties of the aqueous solution as density,[11] vapour-pressure,[12] and electric conductivity.[13]

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[1] Förster, *Elektrochemie wässriger Lösungen*, Leipsic, 1905, 325.

[2] Divers, *Trans. Chem. Soc.*, 1899, 75, 85, 87, 95.

[3] Warren, *Chem. News*, 1891, 63, 290.

[4] Matignon and Marchal, *Compt. rend.*, 1920, 170, 232.

[5] Bruni and Meneghini, *Zeitsch. anorg. Chem.*, 1909, 64, 193.

[6] Matignon and Monnet, *Compt. rend.*, 1920, 170, 180.

[7] Oswald, *Ann. Chim. Phys.*, 1914, [9], 1, 32.

[8] Peters, *Zeitsch. anorg. Chem.*, 1919, 107, 313.

[9] Jeffery, *Trans. Faraday Soc.*, 1920, 15, 16.

[10] Lobry de Bruyn, *Rec. trav. chim.*, 1892, 11, 156.

[11] Boguski, *Bull. Acad. Sci. Cracow*, 1898, 123.

[12] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9.

[13] Schümann, *Ber.*, 1900, 33, 532; Roczkowsky and Niementowsky, *Zeitsch. physikal. Chem.*, 1897, 22, 147; compare Holborn, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 749.

Disodium nitrite, Na_2NO_2.—Maxted[1] describes this nitrite as a bright yellow precipitate, obtained by the interaction of a solution of sodium in liquid ammonia free from moisture and dry sodium nitrite. It is also formed by the electrolysis of a solution of sodium nitrite in dry liquid ammonia. When brought into contact with water, the compound reacts with explosive violence, evolving hydrogen.

Sodium nitrate, $NaNO_3$.—Immense deposits of sodium nitrate are situated in Chile, hence the name "Chile saltpetre." The local name is "Caliche." The origin of the deposits is a matter of dispute.[2] The crude product is contaminated with clay and sand, and is purified by crystallization from water. An important impurity is sodium iodate, a valuable source of iodine.[3] Analyses have been given by Machattie[4] (I.) and Schulze[5] (II.), the numbers expressing percentages :

	$NaNO_3$.	$NaIO_3$.	NaCl.	Na_2SO_4.	$NaClO_3$.	KNO_3.	$MgSO_4$.	$CaSO_4$.	H_2O.	In-soluble.	Un-identi-fied.
(I.)	70·92	1·9	22·39	1·8	..	..	0·51	0·87	0·99	0·92	..
(II.)	36·93	..	30·31	0·66	0·61	7·69	17·79	..	1·43	1·11	3·47

The chlorides can be decomposed by heating with nitric acid, hydrogen chloride being expelled.

Sodium nitrate is a white substance, and crystallizes in cube-like, doubly refracting[6] rhombohedra isomorphous with calcspar. For its melting-point Haigh[7] gives 306·8° C., Lorenz[8] 310° C., Person[9] 310·5° C., Bruni and Meneghini[10] 312° C., Braun[11] 314° C., Carnelley[12] 316° and 319° C., and Carveth[13] 318° C. For the freezing-point Schaffgotsch[14] gives 313° C. The density is given by Krickmeyer[15] as 2·267 at 20° C., by Haigh[16] as 2·266 at 20° C., by Retgers[17] as 2·265 at 15° C., by Brill and Evans[18] as 2·175 at 13° C., and by Andreae[19] as 2·261. Between 320° and 515° C. it is given, according to Lorenz, by the expression $D=2{\cdot}12-0{\cdot}0007t$. For the specific heat between 27° and 59° C.

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[1] Maxted, *Trans. Chem. Soc.*, 1917, 111, 1016.

[2] Compare Ostwald, *Principles of Inorganic Chemistry* (Macmillan, 1904), 489.

[3] This series, Vol. VIII.

[4] Machattie, *Chem. News*, 1875, 31, 263.

[5] Schulze, *Zeitsch. Landw. Vers.-Wesen, Austria*, 1909, 12, 586. The absence of iodate is probably due to the fact that the sample was taken from a consignment of fertilizer already worked up for iodine.

[6] Compare Schrauf and others, p. 136, reference 3.

[7] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[8] Lorenz, Frei, and Jabs, *Zeitsch. physikal. Chem.*, 1908, 61, 468.

[9] Person, *Ann. Chim. Phys.*, 1849, [3], 27, 250.

[10] Bruni and Meneghini, *Zeitsch. anorg. Chem.*, 1909, 64, 193.

[11] Braun, *Pogg. Annalen*, 1875, 154, 190.

[12] Carnelley, *Trans. Chem. Soc.*, 1876, 29, 489 ; 1878, 33, 273.

[13] Carveth, *J. Physical Chem.*, 1898, 2, 209.

[14] Schaffgotsch, *Pogg. Annalen*, 1857, 102, 293.

[15] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 53.

[16] Haigh, *loc. cit.*

[17] Retgers, *Zeitsch. physical. Chem.*, 1889, 3, 289.

[18] Brill and Evans, *Trans. Chem. Soc.*, 1908, 93, 1442.

[19] Andreae, *Zeitsch. physikal. Chem.*, 1913, 82, 109.

Schüller[1] found 0·2650, Regnault[2] for the previously fused salt 0·2782, and Person[3] for the liquid between 320° and 430° C. 0·41. The latent heat of fusion for 1 gram-molecule at 310·5° C. is given by Person[3] as 5·5 Cal. The heat of formation from the elements is stated by Thomsen[4] to be 111·25 Cal., and by Berthelot[5] to be 110·7 Cal.; that from nitric acid and sodium hydroxide is given by Thomsen[6] as 13·68 Cal., and by Berthelot as 13·5 Cal. For the heat of solution Thomsen[7] gives —5·0 Cal., and Berthelot[8] between 10° and 15° C. —4·7 Cal. The heptahydrate[9] melts at —15·7° C.

The table summarizes the results obtained by the Earl of Berkeley[10] in his work on the solubility of sodium nitrate:

Temperature, °C.	Grams of $NaNO_3$ in 100 grams of Water.	Temperature, °C.	Grams of $NaNO_3$ in 100 grams of Water.
0	73	60	124·6
10	80·5	70	136
20	88	80	148
30	96·2	90	161
40	104·9	100	175·5
50	114	119	208·8

Gerlach[11] gives the boiling-point of the saturated solution in contact with the solid as 120° C., and its strength as 222 grams per 100 grams of water; the Earl of Berkeley and Applebey's[12] value for the boiling-point is 120·20° C. at 760 mm.

In the fused state sodium nitrate is dissociated to the extent of 61·7 per cent., and its mean molecular refraction between 320° and 440° C. is 11·54.[13]

The molecular electric conductivity of sodium nitrate between 321·5° and 487·3° C. is given by the formula[14]

$$\mu_t = 41{\cdot}56 + 0{\cdot}205(t - 300).$$

Sodium nitrate is a very deliquescent substance,[15] and is therefore unsuited for the manufacture of explosives. It is employed in agriculture as a fertilizer, and by double decomposition with potassium chloride yields potassium nitrate. Large quantities are reduced to

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[1] Schüller, *Pogg. Annalen*, 1869, 136, 70, 235.
[2] Regnault, *ibid.*, 1841, 53, 60, 243.
[3] Person, *Ann. Chim. Phys.*, 1847, [3], 21, 295.
[4] Thomsen, *Thermochemistry* (Longmans, 1908), 324, 325.
[5] Berthelot, *Ann. Chim. Phys.*, 1873, [4], 30, 440.
[6] Thomsen, *Thermochemistry* (Longmans, 1908), 115.
[7] Thomsen, *J. prakt. Chem.*, 1878, [2], 17, 175.
[8] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 521.
[9] Ditte, *Compt. rend.*, 1875, 80, 1164.
[10] Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 209.
[11] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.
[12] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.
[13] G. Meyer and Heck, *Zeitsch. Elektrochem.*, 1922, 28, 21.
[14] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.
[15] Compare Kortwright, *J. Physical Chem.*, 1899, 3, 328.

sodium nitrite, an important reagent in the manufacture of coal-tar dyestuffs.

References are appended to investigations of the molecular weight[1] and surface tension[2] of the fused salt; of the optical properties[3] and electric conductivity[4]; of such properties of aqueous solutions[5] as boiling-point,[6] density,[7] viscosity,[8] diffusion,[9] specific heat,[10] vapour-pressure,[11] molecular weight of the dissolved salt,[12] molecular depression of the freezing-point[13] and elevation of the boiling-point,[14] electric conductivity,[15] and refractivity[16]; of the solubility in organic solvents[17]; and of the formation of double salts with potassium nitrate and sodium carbonate.[18]

Sodium phosphides.—By heating in vacuum at 400° to 450° C. the black product formed by the interaction of sodium and phosphorus, a lemon-yellow substance of the formula Na_2P_5, is obtained.[19] It has a density somewhat above 2, is unstable in air, and is decomposed by water with formation of solid phosphorus hydride.

Tomkinson and Barker[20] describe the product formed by heating sodium and red phosphorus as a grey mass, which reacts violently with water, yielding spontaneously inflammable hydrogen phosphide. They also state that under suitable experimental conditions sodium reacts with yellow phosphorus to form a white, crystalline product.

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[1] Lorenz and Kaufler, *Ber.*, 1908, 41, 3727.

[2] Quincke, *Pogg. Annalen*, 1869, 138, 141.

[3] Schrauf, *Sitzungsber. K. Akad. Wiss. Wien*, 1860, 41, 769; Cornu, *Ann. Chim. Phys.*, 1867, [4], 11, 385; Kohlrausch, *Wied. Annalen*, 1878, 4, 28.

[4] Foussereau, *Ann. Chim. Phys.*, 1885, [6], 5, 317; Braun, *Pogg. Annalen*, 1875, 154, 161; Bouty and Poincaré, *Ann. Chim. Phys.*, 1889, [6], 17, 52; Lorenz and Kalmus, *Zeitsch. physikal. Chem.*, 1907, 59, 17, 244.

[5] de Coppet, *Zeitsch. physikal. Chem.*, 1897, 22, 239; Étard, *Ann. Chim. Phys.*, 1874, [7], 2, 527.

[6] Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1905, December.

[7] Barnes and Scott, *J. Physical Chem.*, 1898, 2, 536; Page and Knightley, *Trans. Chem. Soc.*, 1872, 10, 566.

[8] Arrhenius, *Zeitsch. physikal. Chem.*, 1887, 1, 285; Mützel, *Wied. Annalen*, 1891, 43, 15; Meyerhoffer and Saunders, *Zeitsch. physikal. Chem.*, 1899, 28, 461.

[9] Scheffer, *Zeitsch. physikal. Chem.*, 1888, 2, 390.

[10] Thomsen, *Pogg. Annalen*, 1871, 142, 337; Marignac, *Ann. Chim. Phys.*, 1876, [5]. 8, 410; Person, *ibid.*, 1851, [3], 33, 437; Teudt, *Dissertation*, Erlangen, 1900.

[11] Dieterici, *Wied. Annalen*, 1891, 42, 513; Smits, *Zeitsch. physikal. Chem.*, 1902, 39, 385; Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; Nicol, *Phil. Mag.*, 1886, [5], 22, 507.

[12] Lincoln and Klein, *J. Physical Chem.*, 1907, 11, 318.

[13] Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, 6, 387; Loomis, *Wied. Annalen*, 1896, 57, 505; Jones, Barnes, and Hyde, *Amer. Chem. J.*, 1902, 27, 28; Jones and Getman, *ibid.*, 439.

[14] Smits, *Zeitsch. physikal. Chem.*, 1902, 39, 385.

[15] Kohlrausch and Maltby, *Sitzungsber. K. Akad. Wiss. Berlin*, 1899, 665; Ostwald, *Lehrbuch der allgemein. Chem.*, 2nd ed., Leipsic, 1893, 746; Kohlrausch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1026; 1902, 572; Déguisne, *Dissertation*, Strasbourg, 1895; Bein, *Wied. Annalen*, 1862, 46, 29; *Zeitsch. physikal. Chem.*, 1898, 27, 1; 28, 439; Hittorf, *Pogg. Annalen*, 1853, 89, 177; 1856, 98, 1; 1858, 103, 1; 1859, 106, 338, 513; *Zeitsch. physikal. Chem.*, 1901, 39, 612; 1903, 43, 49.

[16] Borgesius, *Wied. Annalen*, 1895, 54, 233; Miers and Isaac, *Trans. Chem. Soc.*, 1906, 89, 413.

[17] Schiff, *Annalen*, 1861, 118, 365; Bodländer, *Zeitsch. physikal. Chem.*, 1891, 7, 316; Lobry de Bruyn, *Rec. trav. chim.*, 1892, 11, 147; *Zeitsch. physikal. Chem.*, 1892, 10, 787; Taylor, *J. Physical Chem.*, 1897, 1, 722; Bathrick, *ibid.*, 1896, 1, 162.

[18] Kreman and Žitek, *Monatsh.*, 1909, 30, 311.

[19] Hackspill and Bossuet, *Compt. rend.*, 1912, 154, 209.

[20] Tomkinson and Barker, *Chem. News*, 1920, 121, 104, 177.

At low temperatures ammonia reacts with sodium and red phosphorus to form a reddish-brown, amorphous mass, considered by Hugot[1] to be sodium phosphide. With excess of sodium, yellow crystals of the formula $Na_3P_2H_3$ are formed. They react with water and acids, evolving phosphine:

$$Na_3P_2H_3+3H_2O=3NaOH+2PH_3.$$

Sodium dihydrophosphide, $NaPH_2$, is a white substance formed by treating a solution of sodium in liquid ammonia with phosphine, and evaporating the ammonia.[2] *Trisodium phosphide*, Na_3P, is produced simultaneously. The mixture reacts with water, evolving phosphine.

Sodium hypophosphite, NaH_2PO_2.—The hypophosphite is formed by the interaction of sodium hydroxide and phosphorus:

$$P_4+3NaOH+3H_2O=3NaH_2PO_2+PH_3.$$

It can also be obtained by decomposing the calcium or barium salt by the action of sodium carbonate in alcoholic solution.

Sodium hypophosphite is a powerful reducer. On heating it evolves phosphine, the reaction being often so violent as to cause explosion:[3]

$$5NaH_2PO_2=Na_4P_2O_7+NaPO_3+2PH_3+2H_2.$$

At 21·5° C. the heat of formation from sodium hydroxide and the acid is 15·16 Cal.,[4] and that from the elements in solution is 198·4 Cal.[5] The electric conductivity has been studied by Arrhenius.[6]

Sodium phosphites.—*Disodium hydrogen phosphite*, $Na_2HPO_3,5H_2O$, is obtained by concentration of a solution of phosphorous acid neutralized with sodium carbonate, and over sulphuric acid changes to the anhydrous salt. The pentahydrate is very deliquescent. The anhydrous salt melts at 53° C., and above this temperature is oxidized to sodium phosphate, with evolution of phosphine.[7] The heat of formation from the elements is 285·1 Cal.,[8] and from the acid and sodium hydroxide in solution 28·45 Cal.[9] The heat of hydration of the anhydride to the pentahydrate is 13·7 Cal.

Sodium dihydrogen phosphite, $NaH_2PO_3,2\frac{1}{2}H_2O$, crystallizes when a solution of equimolecular proportions of phosphorous acid and sodium hydroxide is cooled to $-23°$ C. The heat of formation of the anhydrous salt from the elements is 333·8 Cal.,[8] and from the acid and sodium hydroxide in solution 14·83 Cal.[10] The heat of hydration of the hydrate is 6·05 Cal.

When anhydrous sodium dihydrogen phosphite is heated at 160° C. it is converted into *disodium dihydrogen pyrophosphite*, $Na_2H_2P_2O_5$. It forms microscopic crystals, reconverted by heating in solution into the parent substance. The heat of formation from the elements is 599 Cal.[11]

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[1] Hugot, *Compt. rend.*, 1895, 121, 206; 1898, 126, 1719.

[2] Joannis, *ibid.*, 1894, 119, 557.

[3] Rammelsberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1872, 412.

[4] Compare Arrhenius, *Zeitsch. physikal. Chem.*, 1892, 9, 339.

[5] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 1, 421.

[6] Arrhenius, *loc. cit.*

[7] Amat, *Compt. rend.*, 1890, 110, 191.

[8] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 1, 98.

[9] Thomsen, *Thermochemistry* (Longmans, 1908), 96.

[10] Thomsen, *ibid.*, 98.

[11] Amat, *loc. cit.*

Sodium hypophosphates.—When a solution of hypophosphoric acid is neutralized with sodium carbonate, methyl-orange being employed as indicator, the hexahydrate of *disodium dihydrogen hypophosphate*, $Na_2H_2P_2O_6$, is formed.[1] The crystals dissolve in water, yielding a solution of slight acidity, the solubility in cold water being 2·2 per cent., and in hot water about 20 per cent. The refractivity of the solid[2] and the electric conductivity of the solution[3] have been investigated.

Excess of sodium carbonate converts this salt into the normal *sodium hypophosphate*, $Na_4P_2O_6$, which crystallizes as decahydrate, isomorphous with the corresponding pyrophosphate.[4] It yields a slightly alkaline solution, its solubility being given by Salzer as about 2 per cent. With an equimolecular proportion of disodium dihydrogen hypophosphate it yields a *trisodium hydrogen hypophosphate*, $Na_3HP_2O_6$. This substance crystallizes as nonahydrate, its solubility at ordinary temperatures being given by Salzer as about 4·5 per cent. The solution has an alkaline reaction.

Sodium orthophosphates.—*Normal sodium orthophosphate*, Na_3PO_4, is obtained by the interaction of equimolecular proportions of disodium hydrogen phosphate and sodium hydroxide. It is known in the anhydrous form, and as heptahydrate,[5] decahydrate,[6] and dodecahydrate. For the density of the anhydrous salt at 17·5° C. Clarke[7] gives 2·536, and for that of the dodecahydrate at ordinary temperature he gives 1·620, and Dufet[8] 1·6445. The solution in water is strongly alkaline; at 15° C. 100 grams of water dissolve 10·5 grams of the dodecahydrate.[9] The heat of formation from the elements is 452·4 Cal.[10]; that from phosphoric acid and sodium hydroxide is given by Thomsen[11] as 34·029 Cal., and by Berthelot[12] as 33·6 Cal. At 18° to 20° C. the heat of solution of the dodecahydrate is —14·5 Cal.[13]

References are appended to work on the transition-point,[14] and refractivity[15]; and to properties of solutions, such as hydrolytic dissociation,[16] density,[17] vapour-pressure,[18] and electric conductivity.[19]

Disodium hydrogen orthophosphate, Na_2HPO_4, is obtained in the form of dodecahydrate by neutralizing phosphoric acid with sodium carbonate. It is the ordinary sodium phosphate of commerce, and is a white,

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[1] Salzer, *Annalen*, 1877, 187, 331; 1878, 194, 28; Joly, *Compt. rend.*, 1885, 101, 1058.

[2] Dufet, *Bull. Soc. franç. Min.*, 1887, 10, 77.

[3] Rosenheim, Stadler, and Jacobsohn, *Ber.*, 1906, 39, 2837.

[4] Rosenheim and Pritze, *Ber.*, 1908, 41, 2708.

[5] Hall, *Trans. Chem. Soc.*, 1887, 51, 94.

[6] Rammelsberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1864, 680.

[7] Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 114.

[8] Dufet, *Bull. Soc. franç. Min.*, 1887, 10, 77.

[9] Schiff, *Annalen*, 1860, 113, 350.

[10] Berthelot and Louguinine, *Ann. Chim. Phys.*, 1876, [5], 9, 28; compare Mixter, *Amer. J. Sci.*, 1909, [4], 28, 103.

[11] Thomsen, *Thermochemistry* (Longmans, 1908), 99.

[12] Berthelot and Louguinine, *loc. cit.*

[13] Joly, *Compt. rend.*, 1887, 104, 1704.

[14] Richards and Churchill, *Zeitsch. physikal. Chem.*, 1899, 28, 314; d'Ans and Schreiner, *ibid.*, 1910, 75, 95.

[15] Baker, *Trans. Chem. Soc.*, 1885, 47, 353; Dufet, *loc. cit.*

[16] Salm, *Zeitsch. physikal. Chem.*, 1906, 57, 471; Shields, *ibid.*, 1893, 12, 167.

[17] Schiff, *loc. cit.*

[18] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; *Wied. Annalen*, 1885, 24, 530.

[19] Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

crystalline salt, its solubility[1] at 10° C. per 100 grams of water being 3·9 grams, and at 30° C. 24·1 grams.

Solubility of Disodium Hydrogen Orthophosphate (Shiomi).[2]

Temperature, °C. . .	10·26	25·15	40·29	60·23	99·77
Grams Na_2HPO_4 in 100 g. H_2O	3·55	12·02	54·88	83·00	102·15

There are three breaks in the curve: at 36·45° C., corresponding with the transition from dodecahydrate to heptahydrate; at 48° C. (probably heptahydrate to dihydrate); and at 95·2° C. (probably dihydrate to anhydrous salt). Later work[3] has indicated the dodecahydrate to exist in two forms, α and β, their transition-temperature being 29·6° C. The transition-temperature of the α-hydrate to the heptahydrate was found to be 35·0° C. The solubilities of the two dodecahydrates were also determined.

For the density of the dodecahydrate Clarke[4] gives 1·535, and at the temperature of liquid air Dewar[5] gives the value 1·545. For the specific heat of the crystalline salt between −20° and 2° C. Person[6] found 0·454, and for the fused salt between 44° and 97° C. 0·758; for the solid dodecahydrate Nernst and Lindemann[7] give 0·3723, and for the heptahydrate 0·3230. Thomsen[8] gives 50·04 Cal. as the heat of formation of the dihydrate from sodium hydroxide and phosphoric acid.[9] The latent heat of fusion of the dodecahydrate at 36·1° C. is given by Person[10] as 23·9 Cal.

For the transition-points of the dodecahydrate to the heptahydrate and of the heptahydrate to the dihydrate d'Ans and Schreiner[11] give

$$Na_2HPO_4{,}12H_2O(35{\cdot}4^\circ\ C.)\longrightarrow Na_2HPO_4{,}7H_2O(48{\cdot}35^\circ\ C.)\longrightarrow$$
$$\longrightarrow Na_2HPO_4{,}2H_2O.$$

At a pressure of 0·1 atm. Biltz[12] gives the transition-points on the absolute scale as

$$Na_2HPO_4{,}12H_2O(317^\circ)\longrightarrow Na_2HPO_4{,}7H_2O(319^\circ)\longrightarrow$$
$$\longrightarrow Na_2HPO_4{,}2H_2O(346^\circ)\longrightarrow Na_2HPO_4.$$

The transition-point of the dodecahydrate into the heptahydrate is given by Person[13] as 36·4° C., Baur[14] 36·6° C., and Tilden[15] 35° C.; and the transition-point into the anhydrous salt by Muller[16] as 43·5° C.

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[1] Mulder, *Bydragen*, etc., Rotterdam, 1864, 100; d'Ans and Schreiner, *Zeitsch. physikal. Chem.*, 1910, 75, 95.
[2] Shiomi, *Mem. Coll. Sci. Eng. Kyōtō*, 1909, 1, 406.
[3] Hammick, Goadby, and Booth, *Trans. Chem. Soc.*, 1920, 117, 1589.
[4] Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 114.
[5] Dewar, *Chem. News*, 1902, 85, 277.
[6] Person, *Pogg. Annalen*, 1847, 70, 300.
[7] Nernst and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247.
[8] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 233.
[9] Compare Berthelot and Louguinine, *Ann. Chim. Phys.*, 1876, [5], 9, 28.
[10] Person, *ibid.*, 1849, [3], 27, 252, 259.
[11] d'Ans and Schreiner, *Zeitsch. physikal. Chem.*, 1910, 75, 95.
[12] Biltz, *ibid.*, 1909, 67, 561.
[13] Person, *loc. cit.*
[14] Baur, *Zeitsch. physikal. Chem.*, 1895, 18, 180.
[15] Tilden, *Trans. Chem. Soc.*, 1884, 45, 268.
[16] Muller, *J. Chim. phys.*, 1909, 7, 534.

When heated, disodium hydrogen phosphate gives up its water of crystallization, and then decomposes, forming sodium pyrophosphate.

Other investigations include the refraction constants,[1] and the dissociation-pressure of the water of crystallization of the dodecahydrate at the transition-point[2]; and such properties of solutions as density,[3] specific heat,[4] boiling-point,[5] vapour-pressure,[6] molecular depression of the freezing-point,[7] electric conductivity,[8] and hydrolytic dissociation.[9]

Treatment of disodium hydrogen orthophosphate with phosphoric acid converts it into *sodium dihydrogen orthophosphate*, NaH_2PO_4, which crystallizes as monohydrate and dihydrate. For the density of the monohydrate Schiff[10] gives 2·040, and for that of the dihydrate Dufet[11] gives 1·9096. On heating, the salt loses its water of crystallization at 100° C., and at 200° C. is converted by further dehydration into disodium dihydrogen pyrophosphate, $Na_2H_2P_2O_7$, and at a higher temperature this substance is transformed into sodium metaphosphate, $NaPO_3$.[12] At 180° C. transformation into the pyrophosphate is very slow, about 178 hours being required for complete conversion.[13]

At 0° C. 100 grams of water dissolve 59·9 grams, and at 18° C. 84·6 grams of the salt,[14] yielding an acid solution. For the heat of formation from the elements Berthelot[15] gives 355·0 Cal.; from the interaction of phosphoric acid and sodium hydroxide he gives 14·7 Cal., and Thomsen[16] 14·829 Cal.

Attention has also been directed to the refractivity[17] of the salt; and to such properties of its solution as vapour-pressure,[18] molecular depression of the freezing-point,[19] electric conductivity,[20] and hydrolytic dissociation.[21]

Sodium pyrophosphate, $Na_4P_2O_7$.—The pyrophosphate is obtained in its anhydrous form by heating disodium hydrogen orthophosphate :

$$2Na_2HPO_4=Na_4P_2O_7+H_2O.$$

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[1] Dufet, *Bull. Soc. franç. Min.*, 1887, 10, 77.

[2] Frowein, *Zeitsch. physikal. Chem.*, 1887, 1, 362; compare Müller-Erzbach, *Ber.*, 1887, 20, 137; Lescœur, *Ann. Chim. Phys.*, 1890, [6], 21, 551; Pfaundler, *Ber.*, 1871, 4, 75.

[3] Schiff, *Annalen*, 1859, 110, 70.

[4] Marignac, *Ann. Chim. Phys.*, 1876, [5], 8, 410.

[5] Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 413.

[6] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; *Wied. Annalen*, 1885, 24, 530.

[7] Loomis, *Wied. Annalen*, 1897, 60, 532.

[8] Foster, *Physical Rev.*, 1899, 8, 257; Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

[9] Friedenthal, *Zeitsch. Elektrochem.*, 1904, 10, 114; Salm, *ibid.*, 342; Shields, *Zeitsch. physikal. Chem.*, 1893, 12, 167; Boidin, *Bull. Assoc. chim. Sucr. Dist.*, 1904, 22, 112.

[10] Schiff, *Annalen*, 1858, 108, 21.

[11] Dufet, *loc. cit.*

[12] Graham, *Pogg. Annalen*, 1834, 32, 56.

[13] Balareff, *Zeitsch. anorg. Chem.*, 1921, 118, 123.

[14] Joly and Dufet, *Compt. rend.*, 1886, 102, 1391.

[15] Berthelot, *Thermochimie*, Paris, 1897, 1, 310.

[16] Thomsen, *Thermochemistry* (Longmans, 1908), 99.

[17] Dufet, *loc. cit.*

[18] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; *Wied. Annalen*, 1885, 24, 530.

[19] Petersen, *Zeitsch. physikal. Chem.*, 1893, 11, 184.

[20] Walden, *ibid.*, 1887, 1, 529; Arrhenius, *ibid.*, 1892, 9, 339; Déguisne, *Dissertation*, Strasbourg, 1895.

[21] Salm, *Zeitsch. Elektrochem.*, 1904, 10, 342; Friedenthal, *ibid.*, 114.

The product is a white substance, its melting-point being given by Carnelley[1] as 888° C. and by Le Chatelier[2] as 957° C. and also[3] as 970° C. For the density Schröder[4] gives 2·534, and Mohr[5] 2·385. Between 17° and 98° C. Regnault[6] found the specific heat to be 0·2283. The heat of solution is given by Thomsen[7] as 11·85 Cal.

Sodium pyrophosphate crystallizes from water as the monoclinic decahydrate. Its density is given by Playfair and Joule[8] as 1·836, Mohr[9] 1·773, and Dufet[10] 1·824; and its heat of solution by Thomsen[11] as —11·67 Cal. At 20° C. 100 grams of water dissolve 6·2 grams, and at 80° C. 30 grams,[12] yielding a solution of faint alkaline reaction.

Other investigations concern the refractivity[13]; and properties of the solution such as density,[14] vapour-pressure,[15] and electric conductivity.[16]

Disodium dihydrogen pyrophosphate, $Na_2H_2P_2O_7$.—This substance is formed by heating sodium dihydrogen phosphate at about 200° C.:

$$2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O.$$

Above 300° C. it is converted into sodium metaphosphate.

In addition to the anhydrous salt, a tetrahydrate,[17] and also a hexahydrate[18] of density[19] 1·848, are known. The aqueous solution has an acidic reaction, and reacts with sodium hydroxide to form the normal pyrophosphate.

Sodium metaphosphate, $NaPO_3$.—The metaphosphate is prepared by the interaction of sodium nitrate and phosphoric acid at 330° C.[20] It is a white, vitreous mass, almost insoluble in water, and melting[21] at 617±2° C. It is sometimes called "Maddrell's salt," after its discoverer.[22] The *semihydrate*, $NaPO_3,\frac{1}{2}H_2O$, is formed by heating sodium ammonium hydrogen phosphate at 160° to 170° C., and subsequently raising the temperature to 320° C.[23] Tammann[24] has proved the existence

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[1] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[2] Le Chatelier, *Bull. Soc. chim.*, 1887, [2], 47, 300.

[3] Le Chatelier, *Compt. rend.*, 1894, 118, 350.

[4] Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

[5] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 118.

[6] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[7] Thomsen, *J. prakt. Chem.*, 1878, [2], 17, 175; *Thermochemistry* (Longmans, 1908), 49.

[8] Playfair and Joule, *Mem. Chem. Soc.*, 1843–1845, 2, 401.

[9] Compare Clarke, *loc. cit.*

[10] Dufet, *Bull. Soc. franç. Min.*, 1887, 10, 77.

[11] Thomsen, *loc. cit.*

[12] Poggiale, *J. Pharm. Chim.*, 1863, [3], 44, 273.

[13] Dufet, *loc. cit.*

[14] Fouqué, *Ann. Observat. Paris*, 1868, 9, 172.

[15] Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; *Wied. Annalen*, 1885, 24, 530.

[16] Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

[17] Rammelsberg, *Gesamt. Abhandl.*, 1888, 127.

[18] Bayer, *J. prakt. Chem.*, 1869, 106, 501.

[19] Dufet, *loc. cit.*

[20] von Knorre, *Zeitsch. anorg. Chem.*, 1900, 24, 378.

[21] Carnelley, *loc. cit.*

[22] Maddrell, *Phil. Mag.*, 1847, [3], 30, 322.

[23] Langheld, Oppmann, and E. Meyer, *Ber.*, 1912, 45, 3753.

[24] Tammann, *J. prakt. Chem.*, 1892, [2], 45, 421; *Zeitsch. physikal. Chem.*, 1890, 6, 124; compare Warschauer, *Zeitsch. anorg. Chem.*, 1903, 36, 188; Fleitmann, *Pogg. Annalen*, 1849, 78, 361; Fleitmann and Henneberg, *Annalen*, 1848, 65, 307; Jawein and Thillot, *Ber.*, 1889, 22, 655; Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 118; Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; Wiesler, *Zeitsch. anorg. Chem.*, 1901, 28, 182; Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 529.

of a number of polymeric forms, the di-, tri-, tetra-, and hexa-metaphosphates having been described. The metaphosphate can also exist in metameric forms. In the crystalline state it is unimolecular, and in the glacial condition at least termolecular.[1]

Sodium polyphosphate.—Ignition of the residue left on evaporation of a solution of sodium hydroxide or carbonate with sufficient phosphoric acid gives a vitreous polyphosphate in an impure condition. It dissolves slowly in cold water, but more rapidly on warming. The solution is almost neutral to methyl-orange and to phenolphthalein. It has been found impossible to purify the substance or determine its composition, on account of its energetic action on vessels of glass, porcelain, silica, nickel, and platinum, but it probably has the formula $Na_4P_6O_{17}$.[2]

Sodium arsenide, Na_3As, has been studied by Hugot.[3]

Sodium arsenites.—No crystalline arsenite has been obtained, but solutions of the *meta-arsenite,* $NaAsO_2$, the *diarsenite* $NaHAs_2O_4$, and *trisodium orthoarsenite,* Na_3AsO_3, have been prepared.[4]

Sodium arsenates.—Excess of sodium hydroxide converts arsenic acid into *trisodium orthoarsenate,* Na_3AsO_4, mean density [5] 2·835. From solution it crystallizes as dodecahydrate, density [6] 1·832, m.p. 86·3° C. At ordinary temperature 100 grams of water dissolve 28·6 grams of the salt, yielding a strongly alkaline solution. The heat of formation in aqueous solution from the elements is given by Thomsen [7] as 381·5 Cal., and that of the solid by Mixter [8] as 360·8 Cal.

Other salts described are *disodium hydrogen orthoarsenate,*[9] Na_2HAsO_4, converted by heat into *sodium pyroarsenate,*[10] $Na_4As_2O_7$; and *sodium dihydrogen orthoarsenate,*[11] NaH_2AsO_4.

Sodium antimonate.—This substance is precipitated by the interaction of potassium antimonate and a concentrated solution of a sodium salt, its formation affording a means of testing for sodium. The white, amorphous salt may be regarded as the hydrated *meta-antimonate,* $NaSbO_3,3\frac{1}{2}H_2O$; or, since one molecule of water is expelled above 200° C., it may be considered a *pyroantimonate,* $Na_2H_2Sb_2O_7,6H_2O$.[12] Its heat of formation from the elements is 346·4 Cal.[13]

Sodium carbide, Na_2C_2.—When acetylene reacts with sodium, either in the metallic state,[14] or as hydride,[15] or in solution in liquid ammonia, a substance of the formula C_2Na_2,C_2H_2 is produced. When heated in

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[1] Holt and Myers, *Trans. Chem. Soc.*, 1913, 103, 532.

[2] J. H. Smith, *J. Soc. Chem. Ind.*, 1917, 36, 419.

[3] Hugot, *Compt. rend.*, 1898, 127, 553.

[4] Compare Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49; von Zawidski, *Ber.*, 1903, 36, 1427; Auerbach, *Zeitsch. anorg. Chem.*, 1903, 37, 360; Thomsen, *Ber.*, 1874, 7, 935.

[5] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 121.

[6] Dufet, *Bull. Soc. franç. Min.*, 1887, 10, 77.

[7] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 1, 299.

[8] Mixter, *Amer. J. Sci.*, 1909, [4], 28, 103.

[9] Compare Clarke, *loc. cit.*; Tilden, *Trans. Chem. Soc.*, 1884, 45, 269; Dufet, *loc. cit.*; Thomsen, *loc. cit.*; Schiff, *Annalen*, 1858, 107, 293; 108, 326; 1860, 113, 183, 350; Tammann, *Mém. Acad. St. Pétersbourg*, 1887, [7], 35, No. 9; Walden, *Zeitsch. physikal. Chem.*, 1888, 2, 49.

[10] Compare Walden, *loc. cit.*; Pickering, *Trans. Chem. Soc.*, 1907, 91, 307.

[11] Joly and Dufet, *Compt. rend.*, 1886, 102, 1391; Reyher, *Zeitsch. physikal. Chem.*, 1888, 2, 744; Thomsen, *loc. cit.*; Tammann, *loc. cit.*; Walden, *loc. cit.*

[12] Heffter, *Pogg. Annalen*, 1852, 86, 417.

[13] Mixter, *Amer. J. Sci.*, 1909, [4], 28, 103.

[14] Matignon, *Compt. rend.*, 1897, 124, 775, 1026.

[15] Moissan, *ibid.*, 1898, 127, 913; 1903, 137, 463.

vacuum, or in a current of hydrogen at 220° C., it evolves acetylene, leaving sodium carbide. The carbide is very reactive, readily undergoing decomposition with deposition of carbon, and decomposing water with evolution of acetylene.[1]

Sodium carbonate, Na_2CO_3.—The carbonate is present in the ashes of sea-plants, its principal source prior to the French Revolution, when Le Blanc devised a method for its production. It is also found in the form of solid deposits,[2] and in solution in many natural waters. Pozzi-Escot[3] believes the Peru deposits to have originated in the reduction to sodium sulphide, by means of plants and algæ, of sodium sulphate dissolved from the soil, the sulphide formed being converted into sodium carbonate or sodium hydrogen carbonate by the action of carbon dioxide from the air, or from the decomposition of vegetable matter.

Sodium carbonate is manufactured from sodium chloride by three processes: Le Blanc's process, Solvay's ammonia-soda process, and the electrolytic process.[4]

Le Blanc's Process.—This process involves three stages: the conversion of sodium chloride into sodium sulphate, or "salt-cake process"; the reduction of the sulphate to sulphide by means of carbon, and the conversion of the sulphide into sodium carbonate by the action of calcium carbonate, or "black-ash process"; and the extraction of the sodium carbonate with water, or "lixiviation process":

$$NaCl+H_2SO_4=NaHSO_4+HCl;$$
$$NaCl+NaHSO_4=Na_2SO_4+HCl;$$
$$Na_2SO_4+2C=Na_2S+2CO_2;$$
$$Na_2S+CaCO_3=Na_2CO_3+CaS.$$

The salt-cake process takes place in two stages, the reaction represented by the second equation being carried on at a higher temperature in a reverberatory furnace. The hydrochloric acid constitutes a valuable by-product.

The sulphate prepared by the salt-cake process is pulverized, and mixed with an equal weight of chalk and half its weight of coal or coke. The mixture is then fused in a rotatory furnace. At first only carbon dioxide is evolved, but at the end of the operation carbon monoxide is generated, and burns as it escapes into the atmosphere:

$$2CaCO_3+2C=2CaO+4CO.$$

The sodium carbonate is lixiviated with water to separate it from the calcium sulphide or "alkali-waste," and from other impurities such as sodium chloride, sulphate, silicate, and aluminate; calcium oxide, sulphite, and thiosulphate; iron oxide; and alumina.

Ammonia-soda Process.—This process is said[5] to have been devised by the apothecary Gerolamo Forni in 1836. It was perfected by Solvay, and on the continent of Europe it has largely displaced the older Le Blanc process. A solution of sodium chloride is treated alternately with ammonia and carbon dioxide under pressure, sodium

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[1] Compare de Forcrand, *ibid.*, 1895, 120, 1215; 1897, 124, 1153; Matignon, *ibid.*, 1897, 125, 1033.

[2] Compare Reichert, *Zeitsch. Kryst. Min.*, 1909, 47, 205.

[3] Pozzi-Escot, *Bull. Soc. chim.*, 1919, [4], 25, 614.

[4] For full details of alkali manufacturing processes, see Lunge's *Manufacture of Sulphuric Acid and Alkali*, 3rd ed. (Gurney and Jackson, 1911), vols. ii. and iii.

[5] Vanzetti, *Chem. Zeit.*, 1910, 34, 229.

hydrogen carbonate separating out from the concentrated solution of ammonium chloride. On heating, the sodium hydrogen carbonate is converted into sodium carbonate, the evolved carbon dioxide being utilized again in the formation of sodium hydrogen carbonate. The ammonia is recovered from the ammonium-chloride solution by distilling it with lime obtained as a by-product in the generation of the carbon dioxide from limestone. The reactions[1] involved are represented by the equations

$$2NaCl+2NH_3+2CO_2+2H_2O=2NH_4Cl+2NaHCO_3;$$
$$2NaHCO_3=Na_2CO_3+CO_2+H_2O;$$
$$CaCO_3=CaO+CO_2;$$
$$2NH_4Cl+CaO=2NH_3+CaCl_2+H_2O.$$

The process yields a purer initial product than the Le Blanc method, but has the disadvantage of leaving the chlorine of the sodium chloride in the form of calcium chloride, for which the demand is limited.

The equilibrium of the four salts sodium chloride, sodium hydrogen carbonate, ammonium chloride, and ammonium hydrogen carbonate has been studied by Toporescu,[2] and he has constructed a diagram to facilitate calculation of the proportion of each salt which will crystallize on progressive evaporation of a solution of known initial composition. His diagrammatic method has been applied by Le Chatelier[3] to ascertaining the proportion of water or salt which must be added to get the maximum yield of pure sodium hydrogen carbonate under manufacturing conditions.

The use of sodium nitrate as a substitute for sodium chloride in the ammonia-soda process has been studied by Fedotiew and Koltunow.[4]

Electrolytic Process.—The production of sodium carbonate by the electrolysis of sodium-chloride solution is gradually supplanting the older methods. In the operation a diaphragm is employed, and the details are described on pp. 97 and 98. The solution of sodium hydroxide formed is converted into carbonate by the action of carbon dioxide, the sodium hydrogen carbonate formed being decomposed by heat.

Sodium carbonate is also manufactured to some extent from other materials, such as cryolite, a double fluoride of sodium and aluminium found in Greenland, and sodium nitrate.

Properties.—Anhydrous sodium carbonate is a white solid, density[5] 2·476, m.p.[6] 851° to 853° C. Its specific heat is 0·246 between 18° and 48° C. (Kopp[7]), and 0·2728 between 16° and 98° C. (Regnault[8]). Its heat of formation from the elements is given as 272·64,[9] 270·8,[10] or 271·97 Cal.[11]

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[1] Compare also Mason, *Chem. Zeit.*, 1914, 38, 513.

[2] Toporescu, *Compt. rend.*, 1922, 174, 870.

[3] Le Chatelier, *ibid.*, 870.

[4] Fedotiew and Koltunow, *Zeitsch. anorg. Chem.*, 1914, 85, 247.

[5] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 126; Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

[6] Compare Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 1, 241; Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360; Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215; Arndt, *Zeitsch. Elektrochem.*, 1906, 12, 337.

[7] Kopp, *Annalen Suppl.*, 1864–65, 3, i., 289.

[8] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[9] Thomsen, *Thermochemistry* (Longmans, 1908), 232, 326.

[10] Berthelot, *Thermochimie*, Paris, 1897, 1, 214.

[11] de Forcrand, *Compt. rend.*, 1909, 149, 719.

Sodium carbonate forms three hydrates. The *decahydrate* is monoclinic, and has the density 1·455,[1] other values being 1·446 at 17° C. and 1·493 at the temperature of liquid air.[2] At 20° C. 100 grams of water dissolve 21·4 grams, reckoned as Na_2CO_3. The *heptahydrate* appears to exist in both a rhombic and a metastable rhombohedral[3] form, but only between narrow limits of temperature. Its solubility diminishes with rise of temperature. The solubility of the *monohydrate*[4] at 50° C. is 47·5 grams Na_2CO_3 in 100 grams of water. The transition-points of the hydrates are given by Wells and McAdam[5]: 10 to 7 (D), 32·0° C.; 7 to 1 (F), 35·37° C.; 10 to 1 (intersection CD and GF), 32·96° C. Some of their solubility-data are given in the table, and the solubility-curve in fig. 10 (p. 146):

$Na_2CO_3,10H_2O$.		$Na_2CO_3,7H_2O$.		Na_2CO_3,H_2O.	
Temperature, °C.	Grams Na_2CO_3 in 100 grams Water.	Temperature, °C.	Grams Na_2CO_3 in 100 grams Water.	Temperature, °C.	Grams Na_2CO_3 in 100 grams Water.
27·84	34·20	30·35	43·50	29·86	50·53
29·33	37·40	31·82	45·16	31·80	50·31
30·35	40·12	32·86	46·28	35·37	49·67
31·45	43·25	34·37	48·22	37·91	49·11
31·72	44·21	35·15	49·23	40·93	48·52
32·06	45·64	35·62	50·08	43·94	47·98

The transition-temperature of the decahydrate to the heptahydrate is given by Richards and Fiske[6] as 32·017° C.

According to Berzelius, and also Schindler,[7] the decahydrate in air at 12·5° C. becomes transformed into a *pentahydrate*. The existence of other hydrates described is even more doubtful. The boiling solution of sodium carbonate absorbs carbon dioxide from the atmosphere. Dubovitz[8] found that exposure of the solid carbonate to atmospheric carbon dioxide and moisture for thirteen days produced between 15 and 20 per cent. of the primary salt, $NaHCO_3$, and that with a large excess of carbon dioxide and moisture complete conversion could be attained.[9]

Sodium hydrogen carbonate, $NaHCO_3$.—The primary salt is an intermediate product in the ammonia-soda process, and can be prepared

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[1] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, I, 126; Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

[2] Dewar, *Chem. News*, 1902, 85, 277.

[3] Loewel, *Ann. Chim. Phys.*, 1851, [3], 33, 382.

[4] Epple, *Dissertation*, Heidelberg, 1899.

[5] Wells and McAdam, *J. Amer. Chem. Soc.*, 1907, 29, 721.

[6] Richards and Fiske, *ibid.*, 1914, 36, 485.

[7] Schindler, *Mag. Pharm.*, 33, 14, 319.

[8] Dubovitz, *Chem. Zeit.*, 1921, 45, 890.

[9] For a double carbonate of sodium and potassium, see the section on potassium carbonate (p. 183).

by the action of carbon dioxide on a solution of the normal carbonate, preferably in 80 per cent. alcohol.

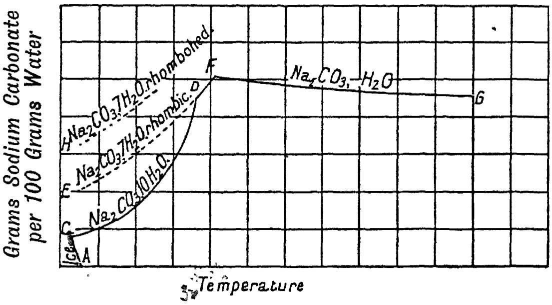


FIG. 10.—Solubility-curve of sodium carbonate.

The salt forms white, monoclinic crystals, of mean density[1] 2·206. On heating it is decomposed :

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

On heating in aqueous solution a similar decomposition takes place:[2]

$$NaHCO_3 + H_2O = NaOH + H_2O + CO_2 ;$$
$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O.$$

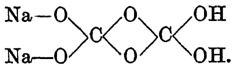
The heat of formation of the salt from the elements is given as 229·3,[3] 228·38,[4] and 227·0 Cal.[5] The solubility-data given by Dibbits[6] are summarized in the table :

Temperature, °C. . . .	0	10	20	30	40	50	60
Grams $NaHCO_3$ in 100 g. water	6·9	8·2	9·6	11·1	12·7	14·5	16·4

Its solution in water has a faint alkaline reaction. In presence of steam, sodium hydrogen carbonate is converted by sodium sulphide into the normal carbonate :[7]

$$2NaHCO_3 + Na_2S = 2Na_2CO_3 + H_2S.$$

The constitution of the primary carbonate is represented by Bicher[8] by the bimolecular formula Na_2CO_3,H_2CO_3 or



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[1] Compare, Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, I, 129 ; Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

[2] MacCoy, *Amer. Chem. J.*, 1903, 29, 437.

[3] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, I, 298.

[4] de Forcrand, *Compt. rend.*, 1909, 149, 719.

[5] Berthelot, *Ann. Chim. Phys.*, 1873, [4], 29, 470.

[6] Dibbits, *J. prakt. Chem.*, 1874, [2], 10, 439.

[7] Verein Chemischer Fabriken in Mannheim, *German Patent*, 1908, No. 194994.

[8] Bicher, *Chem. Zeit.*, 1910, 34, 765.

A double salt with the normal carbonate, $Na_2CO_3,NaHCO_3,2H_2O$,[1] occurs in Venezuela as *Urao*, and in Egypt as *Trona*. It is formed on concentrating a solution of the two salts in molecular proportions,[2] and has been observed[3] to be a product of the efflorescence of the normal decahydrate during a period of twenty years.

Sodium percarbonate, $Na_2C_2O_6$.—The percarbonate is said[4] to be formed by the electrolytic oxidation of the normal carbonate, but it has not been isolated by this method. A substance of the formula $2Na_2CO_3,3H_2O_2$ is obtained by the interaction of 3 molecules of hydrogen peroxide in aqueous solution and 2 molecules of sodium carbonate, the product being subsequently dried *in vacuo*.[5] Other percarbonates have been described,[6] but their existence is still a subject of debate.

Sodium cyanide, NaCN.—The cyanide is formed by the action of hydrocyanic acid on sodium hydroxide; by heating sodium ferrocyanide in absence of air, or with sodium carbonate and charcoal; from atmospheric nitrogen by heating anhydrous sodium carbonate with iron-filings in air[7]; by heating sodium in ammonia at 350° C., and converting the resulting sodamide into cyanide by heating with charcoal[8]; and by the action of ammonia on a mixture of fused sodium cyanide, sodium, and charcoal, the sodium cyanamide, Na_2CN_2, formed being converted by the charcoal into sodium cyanide.[9]

Sodium cyanide forms colourless crystals, very soluble in water, the weak acidic character of the hydrocyanic acid inducing hydrolytic dissociation, thus imparting to the solution a strong alkaline reaction, and an odour of hydrocyanic acid.[10] The anhydrous salt is converted by boiling with 75 per cent. alcohol into the dihydrate, a substance converted by slow evaporation over lime into the yellow, crystalline monohydrate.[11]

For the heat of formation of sodium cyanide from its elements, Berthelot[12] gives 22·6 Cal., and Joannis[13] 23·1 Cal. The heat of neutralization of hydrocyanic acid by sodium hydroxide is between 2·77 and 2·9 Cal., its low value being due to the heat absorbed by the ionization of the weak acid. At 9° C. the heat of solution of the anhydrous salt is 0·5 Cal., and of the dihydrate 4·4 Cal.[13] It is very poisonous.

Sodium thiocyanate, NaCNS.—The thiocyanate can be prepared by the action of sodium carbonate on thiocyanic acid or ammonium thiocyanate, or by fusion of potassium ferrocyanide with anhydrous sodium thiosulphate.

The anhydrous salt forms very deliquescent, rhombic plates, its heat

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[1] Chatard, *Amer. J. Sci.*, 1889, [3], 38, 59.

[2] Compare Habermann and Kurtenacker, *Zeitsch. anorg. Chem.*, 1909, 63, 65.

[3] Cumming, *Chem. News*, 1910, 102, 311.

[4] Constam and Arthur von Hansen, *Zeitsch. Elektrochem.*, 1896, 3, 137.

[5] Henkel & Co., *British Patent*, 1916, No. 100997.

[6] Compare Tanatar, *Ber.*, 1899, 32, 1544; Wolffenstein and Peltner, *Ber.*, 1908, 41, 280; Riesenfeld and Reinhold, *Ber.*, 1909, 42, 4377; Wolffenstein, *Ber.*, 1910, 43, 639; Merck, *German Patent*, 1909, No. 213457.

[7] Täuber, *Ber.*, 1899, 32, 3150.

[8] Behringer, *German Patent*, No. 90999.

[9] Rössler, *German Patents*, Nos. 124977 and 126241.

[10] Compare James Walker, *Zeitsch. physikal. Chem.*, 1900, 32, 137.

[11] Joannis, *Ann. Chim. Phys.*, 1882, [5], 26, 484.

[12] Berthelot, *Compt. rend.*, 1880, 91, 79.

[13] Joannis, *loc. cit.*

of solution being 39·2 Cal.[1] With sulphurous acid it yields complex derivatives.[2]

Sodium ferrocyanide.—The modes of preparation and the properties of sodium ferrocyanide, of sodium ferricyanide, and of similar salts are described in Vol. IX., Part II.

Sodium silicates.—The *metasilicate*, Na_2SiO_3, is formed by the interaction of calculated quantities of sodium hydroxide and freshly precipitated silicic acid, and on addition of alcohol separates in monoclinic crystals, m.p. 1007° C.,[3] or 1056° C.,[4] or 1088° C.[5] Its aqueous solution is strongly alkaline. A rhombic nonahydrate melting at 47° C., a monoclinic hexahydrate melting at 63·5° C., and a hexagonal tetrahydrate melting at 83° to 85° C. have been described.[6] An *octahydrate* possibly exists at low temperature.[7] With excess of sodium hydroxide another silicate, probably the ortho-form, Na_4SiO_4, is produced.[8] According to Niggli,[9] fusion of sodium carbonate and silica develops the equilibrium indicated by the scheme

$$Na_2CO_3+Na_2SiO_3 \rightleftharpoons Na_4SiO_4+CO_2,$$

the proportion of orthosilicate increasing with rise of temperature.

Fusion of silica with sodium carbonate yields a mixture of silicates, excess of silica producing the so-called " water-glass," a thick, syrup-like liquid employed as a cement and in the preservation of eggs. The commercial product contains 3 or 4 molecules of silica to each molecule of sodium oxide.[10]

The interaction of silica and sodium chloride, characteristic of such processes as salt-glazing, coking salty coals, and chloridizing roasts, has been investigated up to 1000° C. by Clews and Thompson.[11] There are three distinct reactions corresponding with the equations

$$(1)\ 4x\mathrm{NaCl}+y\mathrm{SiO_2}+x\mathrm{O_2}=2x\mathrm{Na_2O},y\mathrm{SiO_2}+2x\mathrm{Cl_2}\ ;$$
$$(2)\ 2x\mathrm{NaCl}+y\mathrm{SiO_2}+x\mathrm{H_2O}=x\mathrm{Na_2O},y\mathrm{SiO_2}+2x\mathrm{HCl}\ ;$$
$$(3)\ 4\mathrm{HCl}+\mathrm{O_2}=2\mathrm{H_2O}+2\mathrm{Cl_2}.$$

In moist air all three reactions occur, the second predominating, although up to 1000° C. the magnitude of reaction is very small. The first reaction also takes place in dry air, and the second in moist nitrogen.

Sodium boride.—Metallic sodium and boric anhydride react to form a sodium boride.[12]

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[1] Joannis, *Ann. Chim. Phys.*, 1882, [5], 26, 484.

[2] Fox, *Zeitsch. physikal. Chem.*, 1902, 41, 458.

[3] Kultascheff, *Zeitsch. anorg. Chem.*, 1903, 35, 187; compare Guertler, *ibid.*, 1904, 40, 268.

[4] van Klooster, *Zeitsch. anorg. Chem.*, 1910, 69, 135.

[5] Jaeger, *J. Washington Acad. Sci.*, 1914, 1, 49; Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186.

[6] Erdenbrecher, *Mikrokosmos*, 1921, 15, 55.

[7] Ammon, *Silikate der Alkalien und Erden*, 1862, 12; compare Vesterberg, *Rep. 8th Internat. Congress Appl. Chem.*, 1912, 2, 235.

[8] Jordis, *Zeitsch. anorg. Chem.*, 1908, 58, 98.

[9] Niggli, *J. Amer. Chem. Soc.*, 1913, 35, 1693.

[10] Compare Graham-Otto, *Lehrbuch der anorg. Chem.*, 5th ed., Brunswick, 1878–1889, 3, 434; Morey and Fenner, *J. Amer. Chem. Soc.*, 1914, 36, 215.

[11] Clews and Thompson, *Trans. Chem. Soc.*, 1922, 121, 1442. References to the literature and to patent specifications are given.

[12] Moissan, *Compt. rend.*, 1892, 114, 319.

Sodium hypoborate, NaH_3BO.—On cooling the mixture produced by the interaction of a very concentrated solution of potassium hydroxide and boron hydride, B_4H_{10}, the very deliquescent sodium hypoborate is obtained.[1]

Sodium borates.—The anhydrous *metaborate*, $NaBO_2$, is formed by fusing borax with sodium carbonate, being obtained in hexagonal prisms, m.p.[2] 966° C., density[3] 0·2571 between 17° and 97° C. When the syrup-like solution obtained by concentrating equivalent proportions of sodium hydroxide and boric acid or borax is allowed to crystallize over concentrated sulphuric acid, the *tetrahydrate* separates in triclinic crystals. The *dihydrate*[4] and other hydrates[5] have also been described. The aqueous solution of the metaborate has an alkaline reaction, due to hydrolytic dissociation.[6] The *orthoborate* is formed by fusing boric anhydride with sodium peroxide.[7]

The most important borate of sodium is *disodium tetraborate* or *borax*, $Na_2B_4O_7,10H_2O$, found in Thibet as the mineral *tincal*, and also in California. The native variety is purified by crystallization, but most of the borax of commerce is obtained by fusing native boric acid with sodium carbonate.

The anhydrous salt is obtained by heating the decahydrate, and is a white substance of density[8] 2·367. Its melting-point is given as 561° C.,[9] 730° C.,[10] 741° C.,[11] and 878° C.,[12] the fused substance solidifying to a colourless, transparent, vitreous mass known as the "borax bead." In the melted state it dissolves metallic oxides, producing characteristic colorations, and finds application in analysis. It is also employed in soldering metals to remove the superficial layer of oxide, and to prevent oxidation during the process by excluding the air. Its specific heat is 0·229 between 17° and 47° C. (Kopp[13]), and 0·2382 between 16° and 98° C. (Regnault[14]). Its heat of formation is 748·1 Cal.[15]

The *decahydrate* or ordinary borax forms monoclinic crystals of density 1·723 (Hassenfratz[16]); or 1·694 at 17° C., and 1·728 at the temperature of liquid air (Dewar[17]). Its specific heat[18] is 0·385 between 19° and 50° C. A *pentahydrate* belonging to the rhombohedral division of the hexagonal system crystallizes above 60° C. Its density[19] is 1·815. The pentahydrate is stable from 60° C., the transition-point from the decahydrate, to 125° C. At 130° C. the stable form is the *trihydrate ;*

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[1] Stock and Kuss, *Ber.*, 1914, 47, 810; see potassium hypoborate, p. 185.
[2] van Klooster, *Zeitsch. anorg. Chem.*, 1916, 69, 122.
[3] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.
[4] Dukelski, *Zeitsch. anorg. Chem.*, 1906, 50, 38.
[5] Atterberg, *ibid.*, 1906, 48, 367.
[6] Compare James Walker, *Zeitsch. physikal. Chem.*, 1900, 32, 137.
[7] Mixter, *Amer. J. Sci.*, 1908, [4], 26, 125.
[8] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415.
[9] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.
[10] Ponomarev, *Zeitsch. anorg. Chem.*, 1914, 89, 383.
[11] Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186.
[12] Victor Meyer and Riddle, *Ber.*, 1893, 26, 2448.
[13] Kopp, *Annalen Suppl.*, 1864–65, 3, i., 289.
[14] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.
[15] Berthelot, *Ann. Chim. Phys.*, 1873, [4], 29, 470.
[16] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 107.
[17] Dewar, *Chem. News*, 1902, 85, 277.
[18] Kopp, *loc. cit.*
[19] Payen, *Jahresber.*, 1828, 171.

at 150° C. it is the dihydrate; and at 180° C. it is the *monohydrate.* The last molecule of water is retained up to 318° C.[1]

By fusing borax with boron trioxide, two definite *acid borates* are produced. One of them has the formula $Na_2O,3B_2O_3$, and melts at 694° C.; the other melts at 783° C., and has the formula $Na_2O,4B_2O_3$.[2] The crystallization of solutions with the composition ratio

$$Na_2O : B_2O_3 = 1 : 5$$

yields a *disodium pentaborate*, $Na_2O,5B_2O_3,10H_2O$.[3]

Sodium perborate, $NaBO_3,4H_2O$.—A perborate of the formula indicated is formed by the action of excess of hydrogen peroxide on a solution of borax and sodium hydroxide,[4] and the action of a mineral acid or hydrogen peroxide on a mixture of sodium peroxide and boric acid:[5]

$$2B(OH)_3+2Na_2O_2+H_2SO_4+4H_2O=2(NaBO_3,4H_2O)+Na_2SO_4;$$
$$2B(OH)_3+Na_2O_2+H_2O_2+4H_2O=2(NaBO_3,4H_2O).$$

It is also produced in the electrolysis of an aqueous solution of sodium metaborate,[6] or of sodium carbonate and borax.[7] Alsgaard[8] recommends electrolyzing a solution containing borax, sodium carbonate, sodium hydrogen carbonate, potassium dichromate, and sodium silicate with a copper pipe as cathode and a platinum anode, the current being 6 ampères at 7 to 8 volts, and the temperature 10° C. Foerster[9] considers the formula $NaBO_2,H_2O_2,3H_2O$ to be more in accord with the properties of the compound than $NaBO_3,4H_2O$.

Sodium perborate tetrahydrate is stable in air, but in aqueous solution it loses oxygen.[10] The solution is alkaline in reaction. The velocity of decomposition and catalysis of sodium perborate have been studied by Seorgi and Nocentini.[11] Addition of alcohol precipitates a salt, probably $NaBO_4$, readily decomposed with evolution of oxygen either in the dry state or on solution in water. The tetrahydrate loses its water of crystallization, forming a stable monohydrate.[12] At 15° C. the solubility[13] is 2·55 grams $NaBO_3$ in 100 grams of water. The salt finds application as a therapeutic agent, and is employed in bleaching. Its behaviour in solution is similar to that of hydrogen peroxide.

From a solution in water of sodium peroxide and boric acid another *perborate*, or "perborax," $Na_2B_4O_8,10H_2O$, separates.[14] On solution in

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[1] Hoffmann, *J. Soc. Chem. Ind.*, 1916, 39, 411.

[2] Ponomarev, *Zeitsch. anorg. Chem.*, 1914, 89, 383.

[3] Rosenheim and Leyser, *Zeitsch. anorg. Chem.*, 1921, 119, 1.

[4] Tanatar, *Zeitsch. physikal. Chem.*, 1898, 26, 132; 1899, 29, 162; *Zeitsch. anorg. Chem.*, 1901, 26, 345.

[5] Jaubert, *German Patent*, 1909, No. 207580.

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

[7] Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, *British Patents*, 1916, Nos. 100153 and 102359.

[8] Alsgaard, *J. Physical Chem.*, 1922, 26, 137; compare *Tidskr. kem. Pharm. Terap. Kristiania*, 1916, Nos. 17 and 18.

[9] Foerster, *Zeitsch. angew. Chem.*, 1921, 34, 354.

[10] Melikoff and Pissarjewski, *Ber.*, 1898, 31, 678.

[11] Seorgi and Nocentini, *Gazzetta*, 1921, 51, i., 289.

[12] Bruhat and Dubois, *loc. cit.*

[13] Lion, *Rev. gén. Chim.*, 1905, [7], 8, 163.

[14] Jaubert, *Compt. rend.*, 1904, 139, 796; compare also Chem. Werke vorm. Byk, *German Patent*, 1913, No. 256920.

water it yields hydrogen peroxide. At 22° C. its solubility is 7·1 grams of $Na_2B_4O_8$ in 100 grams of water, the solution being strongly alkaline.

DETECTION AND ESTIMATION OF SODIUM.

All sodium salts impart a characteristic yellow coloration to the Bunsen flame, the test being so delicate as to detect 3×10^{-10} grams. The extreme delicacy of the test and the wide distribution of traces of sodium chloride throughout the atmosphere render the persistence or otherwise of the coloration an important factor in determining the presence or absence of sodium in the substance under examination. In the spectroscope, sodium gives a yellow line, coincident with the D-line of the solar spectrum.

Most salts of sodium are soluble in water, but the pyroantimonate, $Na_2H_2Sb_2O_7$, dissolves only to the extent of 1 part in 350 parts of boiling water. It is produced by addition of potassium pyroantimonate to a neutral or alkaline solution of a sodium salt. The double chloride with tin, and the double sulphite with platinum, $Na_6Pt(SO_3)_4,7H_2O$, are less soluble than the corresponding potassium salts.

In quantitative analysis sodium is estimated as sulphate, formed by evaporation with concentrated sulphuric acid. If potassium be present, its amount is determined by precipitation as double chloride with platinum from the solution of the mixed sulphates.[1]

The salts of sodium react with a solution of potassium nitrite and the nitrates of bismuth and cæsium, yielding a yellow, crystalline precipitate of the formula $5Bi(NO_2)_3,9CsNO_2,6NaNO_2$. This reaction is applicable to the detection and estimation of sodium.[2]

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[1] On the separation from potassium and rubidium, compare Wernadski, *Bull. Soc. franç. Min.*, 1913, 36, 258.

[2] Ball, *Trans. Chem. Soc.*, 1909, 95, 2126; 1910, 97, 1408.

CHAPTER V.

POTASSIUM.

Symbol, K. Atomic weight, 39·10 (O=16).

Occurrence.—Potassium is present in many rocks in the form of silicates, such as *orthoclase*, $K_2O,Al_2O_3,6SiO_2$; *mica*, $K_2O,3Al_2O_3,4SiO_2$; and *leucite*, $K_2O,Al_2O_3,4SiO_2$. It is a constituent of the waters of mineral springs and of the ocean. The deposits at Stassfurt in North Germany, formed by evaporation of large volumes of land-locked sea-water, contain enormous quantities of *carnallite*, a double chloride of potassium and magnesium of the formula $KCl,MgCl_2,6H_2O$; *kainite*, a mixture of potassium and magnesium sulphates with potassium and sodium chlorides; and *sylvine* or potassium chloride. From these and other similar deposits in the same locality most of the potassium salts of commerce were obtained prior to August 1914. The outbreak of the great European War stopped the supply, and the ensuing dearth of potassium salts gave a valuable stimulus to research on their production from orthoclase, which contains about 2·4 per cent. of K_2O (compare p. 161). Potassium salts are a constituent of the soil, and are present in large quantities in plants. In these vegetable products the metal is usually combined with organic acids such as oxalic, tartaric, and malic.

History.—The history of potassium is discussed in the chapter on sodium (pp. 81 and 82).

Preparation.—The metal was first isolated by Davy[1] by electrolysis of the hydroxide, and shortly afterwards Gay-Lussac and Thénard[2] obtained it by the action of iron on the carbonate. Charcoal can be substituted for iron, one process consisting in the decomposition at low red heat of potassium hydrogen tartrate,[3] with formation of a mixture of charcoal and potassium carbonate, the reduction to metal being subsequently effected at a higher temperature:

$$K_2CO_3+2C=2K+3CO.$$

If the temperature is too low, there is danger of the liberated potassium combining with carbon monoxide to form a highly explosive compound, potassium carbonyl, $C_6(OK)_6$. Another modification[4] of the method consists in heating a mixture of tar and potassium carbonate or hydroxide

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[1] Sir Humphry Davy, *Phil. Trans.*, 1808, 1; 1809, 39; 1810, 16.

[2] Gay-Lussac and Thénard, *Recherches chimiques*, Paris, 1811, I, 74.

[3] Compare Wöhler, *Pogg. Annalen*, 1825, 4, 23, 474.

[4] Thompson and White, *British Patent*, 1887, No. 8426.

at dull redness, and subsequently raising the temperature of small portions of the carbonaceous mass to bright redness, the molten metal being tapped off. The fused hydroxide can also be allowed to flow over heated charcoal, and the metal distilled off.[1]

When equivalent weights of sodium and potassium hydroxide are mixed, and fused in absence of air, sodium monoxide is formed, hydrogen evolved, and potassium distils at a temperature of about 670° C. The metal can be condensed, and the process is claimed to be applicable to its manufacture.[2]

Latterly the production of potassium by the electrolytic process has become of industrial importance, partly on account of the purity of the product, and partly because the attendant risk is much less than with the chemical methods. The ordinary Castner[3] process for the isolation of sodium is inapplicable to potassium, Lorenz[4] having shown that part of the potassium is dissolved in the molten state by the fused hydroxide, and part is vaporized and after condensation in minute drops is diffused throughout the liquid mass. The effect is that the liberated metal tends to combine with the anion at the anode. The difficulty is avoided by surrounding the iron-wire cathode with a cylinder of magnesite to prevent diffusion of the metal to the anode, by employing as low a temperature as possible, and by excluding air. An anode of sheet iron is immersed in the fused hydroxide outside the magnesite chamber. As substitutes for the hydroxide, potassium nitrate,[5] and also potassium chloride with an admixture of fluoride to lower the melting-point,[6] are employed. With the nitrate the cathode is an aluminium vessel.

Physical Properties.—Potassium is a soft, silver-white[7] metal of high lustre. Its melting-point is given as 60° C.,[8] 62·4° C.,[9] 62·5° C.,[10] and 63·5° C.[11] A wide discrepancy exists between the values given for the boiling-point, among them being 667° C.[12]; 667° C. at 760 mm. pressure,[13] 719° to 731° C.,[14] 757·5° C.,[15] 365° C. at 0 mm.,[16] and about 90° C. in the vacuum of the cathode light.[17] For the density are recorded the values 0·8629[18] and 0·859[19] at 0° C., 0·8621[20] at 20° C., and 0·851

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[1] Netto, *British Patents*, 1887, Nos. 14602 and 17412.

[2] Wickel and Loebel, *German Patent*, 1919, No. 307175.

[3] Castner, *British Patent*, 1890, No. 13356.

[4] Lorenz and Clarke, *Zeitsch. Elektrochem.*, 1903, 9, 269; compare Le Blanc and Brode, *ibid.*, 1902, 8, 817.

[5] Darling and Forrest, *German Patent*, No. 83097.

[6] Stoerck, *ibid.*, No. 68335.

[7] Bornemann (*Zeitsch. angew. Chem.*, 1922, 35, 227) has described a method of preparing and preserving the metal untarnished.

[8] Masing and Tammann, *Zeitsch. anorg. Chem.*, 1910, 67, 183.

[9] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

[10] Bunsen, *Annalen*, 1863, 125, 368; Holt and Sims, *Trans. Chem. Soc.*, 1894, 65, 432; Kurnakoff and Pushin, *Zeitsch. anorg. Chem.*, 1902, 30, 109; van Bleiswyk, *ibid.*, 1912, 74, 152.

[11] Rengade, *Compt. rend.*, 1913, 156, 1897; *Bull. Soc. chim.*, 1914, [4], 15, 130.

[12] Perman, *Trans. Chem. Soc.*, 1889, 55, 326.

[13] Hansen, *Ber.*, 1909, 42, 210.

[14] Carnelley and Williams, *Trans. Chem. Soc.*, 1879, 35, 563; 1880, 37, 125.

[15] Ruff and Johannsen, *Ber.*, 1905, 38, 3601.

[16] Hansen, *loc. cit.*

[17] Krafft and Bergfeld, *Ber.*, 1905, 38, 254.

[18] Vicentini and Omodei, *Wied. Annalen Beibl.*, 1888, 12, 176.

[19] Hackspill, *Compt. rend.*, 1911, 152, 259.

[20] Richards and Brink, *J. Amer. Chem. Soc.*, 1907, 29, 117.

(solid) and 0·8298 (liquid)[1] at 62·1° C. The atomic volume calculated from the value at 20° C. is 45·35. The metal has a lower density and a higher atomic volume than sodium.

At ordinary temperature potassium has a wax-like consistence, its hardness[2] being 0·5, the corresponding values for the other alkali-metals being lithium 0·6, sodium 0·4, rubidium 0·3, and cæsium 0·2. At low temperatures the metal becomes hard and brittle. Like sodium, it crystallizes in cubes and also in quadratic octahedra.[3] In reflected light it has a greenish-blue colour, that of light transmitted through very thin layers being violet-blue. At the boiling-point its vapour is green, at bright redness violet.

Between −78·5° and 23° C. the specific heat is given[4] as 0·1662, corresponding with the atomic heat 6·5. The specific heat increases rapidly with rise in temperature, the value recorded[5] between 22·3° and 56·5° C. being 0·1922. For the specific heat of the solid at the melting-point, Rengade[6] gives 0·1914. The latent heat of fusion has been found by Joannis[7] to be 15·7 Cal. per kilogram, and by Rengade[8] to be 14·63 Cal. The metal is a good conductor of heat and electricity,[9] and displays slight magnetic properties.[10] The "velocity of sound" method indicates the monatomicity of potassium vapour.[11]

Potassium and many of its salts are said to exhibit radioactivity, the amount of radium present in a gram of the chloride, sulphate, carbonate, or nitrate being given[12] as 3×10^{-14}. Some authorities deny the existence of radioactive properties.

Chemical Properties.—Potassium is a very reactive substance, decomposing water with formation of the hydroxide so energetically as to ignite the evolved hydrogen. This phenomenon has been attributed[13] to the free motion of the hydrogen being impeded by the high density and large molecular volume of the potassium vapour, and the consequent localization of the heat generated by the action. With sodium the hydrogen is not in ordinary circumstances ignited, since the metallic vapour has a low density and small molecular volume ; although ignition of the hydrogen may be effected by keeping the sodium stationary by supporting it on filter-paper floating on water. The action of the metal on ice begins at −105° C.[14] When exposed to air the bright

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[1] Vicentini and Omodei, *Wied. Annalen Beibl.*, 1888, 12, 176.

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

[3] Long, *J. Chem. Soc.*, 1860, 13, 122.

[4] Schüz, *Wied. Annalen*, 1892, 46, 177.

[5] Bernini, *Physikal. Zeitsch.*, 1906, 7, 168.

[6] Rengade, *Bull. Soc. chim.*, 1914, [4], 15, 130.

[7] Joannis, *Ann. Chim. Phys.*, 1887, [6], 12, 381.

[8] Rengade, *loc. cit.*

[9] Compare Bernini, *Physikal. Zeitsch.*, 1904, 5, 241 ; Guntz and Broniewski, *Compt. rend.*, 1908, 147, 1474 ; Hackspill, *ibid.*, 1910, 151, 305 ; Müller, *Metallurgie*, 1910, 730, 755.

[10] Bernini, *Physikal. Zeitsch.*, 1905, 6, 109.

[11] Wenz, *Ann. Physik*, 1910, [4], 33, 951.

[12] Satterly, *Proc. Camb. Phil. Soc.*, 1911, 16, 67 ; compare Henriot, *Compt. rend.*, 1909, 148, 910 ; Henriot and Vavon, *ibid.*, 149, 30 ; Campbell, *Proc. Camb. Phil. Soc.*, 1908, 14, 557 ; 1909, 15, 11 ; Strong, *Amer. Chem. J.*, 1909, 42, 147 ; Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576 ; Elster and Geitel, *ibid.*, 1910, 11, 275 ; Henriot, *Le Radium*, 1910, 7, 40 ; *Compt. rend.*, 1911, 152, 851 ; Büchner, *Le Radium*, 1912, 9, 259 ; Hahn and Rothenbach, *Physikal. Zeitsch.*, 1919, 20, 194.

[13] Banerjee, *Chem. News*, 1910, 102, 319.

[14] Hackspill and Bossuet, *Compt. rend.*, 1911, 152, 874.

surface of the metal soon tarnishes, owing to the effect of moisture. The metal also combines energetically with oxygen and the halogens, an example being the liberation of silicon and boron from their oxides and chlorides. Its solution in liquid ammonia reacts with ozone.[1]

Potassium Ion.—With the exception of rubidium and cæsium, potassium has the greatest electroaffinity or tendency to ionization, a fact regarded by Abegg and Bodländer as according with the ready solubility of most of its salts, and the comparatively slight tendency of its ions to form complex salts or hydrates. The potassium salts are strong electrolytes, being highly dissociated in dilute aqueous solution. Only those with coloured anions yield coloured solutions, an indication that the potassium ion is colourless. The conductivity of the potassium ion is 64·5 at 18° C., and 74·8 at 25° C. The transport-number[2] is 0·514.

Atomic Weight.—In connexion with the atomic weight of sodium, reference has been made to the general methods employed by Berzelius, by Stas, and by Marignac in determining the atomic weights of sodium, potassium, silver, chlorine, bromine, and iodine. At this point it will suffice to summarize the results obtained by these methods, and those derived from the work of modern investigators.

There are numerous early determinations of the composition of potassium chlorate, giving the ratio $KClO_3 : KCl$. The results are summarized in the table:

Experimenter.	Year.	$KClO_3 : KCl = 100 : x$, where $x =$
Berzelius[3] . . .	1818	60·851 ±0·0006
Penny[4] . . .	1839	60·8225±0·0014
Pelouze[5] . . .	1842	60·843 ±0·0053
Marignac[6] . . .	1842	60·839 ±0·0013
Gerhardt[7] . . .	1845	60·8757±0·0020
,, . . .	,,	60·9487±0·0011
Maumené[8] . .	1846	60·791 ±0·0009
Stas[9] . . .	1860	60·8428±0·0012
,, . . .	,,	60·8490±0·0017

In Stas's first series of experiments the chlorate was decomposed by heat; in the second, it was decomposed by hydrochloric acid. From the foregoing results Clarke[10] has computed the weighted mean (p. 88)

$$KClO_3 : KCl = 100 : 60·846 \pm 0·00038 \qquad . \quad . \quad (A)$$

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[1] Compare sodium, p. 86.

[2] Tolman, *J. Amer. Chem. Soc.*, 1911, 33, 121.

[3] Berzelius, *Trommsdorf's N. J. Pharm.*, 1818, ii., 2, 44; *Pogg. Annalen*, 1826, 8, 1; *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 3, 1189.

[4] Penny, *Phil. Trans.*, 1839, 129, 20.

[5] Pelouze, *Compt. rend.*, 1842, 15, 959.

[6] Marignac, *Œuvres Complètes*, Geneva, 1902, 1; 57.

[7] Gerhardt, *Compt. rend.*, 1845, 21, 1280.

[8] Maumené, *Ann. Chim. Phys.*, 1846, [3], 18, 71.

[9] Stas, *Œuvres Complètes*, Brussels, 1894, 1, 404.

[10] Clarke, *A Recalculation of the Atomic Weights*, Washington, Smithsonian Miscellaneous Collections, 2nd ed., 1897; 3rd ed., 1910.

Early analyses of potassium bromate by Marignac[1] and of potassium iodate by Millon[2] gave

$KBrO_3$: KBr=100 : 71·3245±0·0207 . . . (B)
KIO_3 : KI=100 : 77·527±0·005 . . . (C)

Analyses of potassium chloride form two groups, one based on the ratio Ag : KCl, and the other on the ratio AgCl : KCl. The results of the first group are given in the table :

Experimenter.	Years.	Ag : KCl=100 : x, where x=
Marignac[3] . . .	1843	69·062 ±0·0017
Stas[4] . . .	1860–1882	(i.) 69·1036±0·0003
		(ii.) 69·1033±0·0003
		(iii.) 69·1190±0·0003
		(iv.) 69·1230±0·0002

In Stas's third series of experiments a correction was applied for the solubility in water of silver chloride. The fourth series was published after his death. The data derived from his later work were vitiated by the use of solutions of too high concentration. As the weighted mean of the preceding results Clarke gives

Ag : KCl=100 : 69·114±0·00013 . . . (D)

The values for the ratio AgCl : KCl are given in the table :

Experimenter.	Years.	AgCl : KCl=100 : x, where x=
Berzelius[5] . . .	1813	51·997
Marignac[6] . . .	1842–1843	52·011±0·0018
Maumené[7] . .	1846	51·878±0·0049

Assigning equal weight to the values of Berzelius and of Maumené, the weighted mean computed by Clarke's method of the preceding results is

AgCl : KCl=100 : 52·006±0·0011 . . . (E)

Early analyses of potassium bromide only give the ratio Ag : KBr :

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[1] Marignac, *Œuvres Complètes*, Geneva, 1902, 1, 84.
[2] Millon, *Ann. Chim. Phys.*, 1843, [3], 9, 400.
[3] Marignac, *Œuvres Complètes*, Geneva, 1902, 1, 77.
[4] Stas, *Œuvres Complètes*, Brussels, 1894, 1, (i.) 361, 363; (ii.) 363; (iii.) 766, 775; (iv.) 468.
[5] Berzelius, *Pogg. Annalen*, 1813, 8, 47; *Afhandlingar i Fysik, Kemi, etc.*, Stockholm, 1806–1818, 5, 388. The result has been reduced to vacuum standard.
[6] Marignac, *Œuvres Complètes*, Geneva, 1902, 1, 60, 78. The result has been reduced to vacuum standard.
[7] Maumené, *Ann. Chim. Phys.*, 1846, [3], 18, 63.

Experimenter.	Year.	Ag : KBr = 100 : *x*, where *x* =
Marignac [1] . . .	1843	110·343 ± 0·005
Stas [2]	1865	110·346 ± 0·002

The weighted mean is

Ag : KBr = 100 : 110·3459 ± 0·0019 . . (F)

Five analyses of potassium iodide by Marignac [3] in 1843 gave

Ag : KI = 100 : 153·800 . . . (G)

From the foregoing seven mean results lettered from A to G the atomic weight of potassium can be induced. For this purpose the antecedent data calculated by Stas from his experiments have been chosen, (O = 16), Cl = 35·457, Br = 79·952, I = 126·850, Ag = 107·930. The values obtained for the atomic weight of potassium are :

(A) 39·136 (C) 38·739 (E) 39·113 (G) 39·038
(B) 39·438 (D) 39·138 (F) 39·144

The values (B) and (C), derived from analyses of potassium bromate and iodate, are obviously worthless. The results (A), (D), and (F) depend mainly on the careful work of Stas, and their arithmetic mean is 39·139. The results (E) and (G) are based on Marignac's work on potassium chloride and iodide, and approximate reasonably to those of Stas. Excluding (B) and (C), the arithmetic mean of the results is

K = 39·113.

From his own experiments Stas induced the value K = 39·142, and recalculation in terms of O = 16 of the value accepted as the atomic weight of potassium for many years gives 39·14 or 39·15.

The work of modern investigators, particularly that of Richards and his coadjutors at Harvard, has proved Stas's value for the atomic weight of silver to be too high, and his relative values for silver and chlorine to be erroneous. These inaccuracies vitiate the preceding calculations; but there would be no advantage in deriving them from more accurate antecedent data, as modern research has disclosed appreciable errors in even the most painstaking of the earlier work, and furnished more reliable ratios for inducing the atomic weight of potassium. In the subjoined account the calculations have been made with the atomic weights O = 16·000, Ag = 107·880, Cl = 35·457, Br = 79·916, N = 14·008.

In connexion with their work on cæsium, Richards and Archibald [4] in 1903 made two analyses of potassium chloride, the results being

AgCl : KCl = 100 : 52·0215,

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[1] Marignac, *Œuvres Complètes*, Geneva, 1902, 1, 82.
[2] Stas, *Œuvres Complètes*, Brussels, 1894, 1, 747.
[3] Marignac, *Œuvres Complètes*, Geneva, 1902, 1, 86.
[4] Richards and Archibald, *Proc. Amer. Acad.*, 1903, 38, 457

whence K=39·109; and

$$Ag : KCl = 100 : 69{\cdot}1145,$$

whence K=39·104.

In the following year Archibald[1] published the results of four additional experiments:

$$AgCl : KCl = 100 : 52{\cdot}024,$$

whence K=39·113; and

$$Ag : KCl = 100 : 69{\cdot}114,$$

whence K=39·103.

Richards and Archibald also made three other experiments, potassium nitrate being heated with silica, and the loss in weight determined:

$$N_2O_5 : K_2O = 100 : 87{\cdot}232,$$

whence K=39·112.

An account of the elaborate research of Richards and Stähler[2] on potassium chloride appeared in 1907. The salt employed was prepared by the action of hydrogen chloride on potassium nitrate purified by repeated recrystallization with special precautions. After several crystallizations, the chloride was fused in a current of nitrogen. The silver was obtained by reducing the nitrate with ammonium formate. After electrolytic purification, it was fused in a lime-boat in a current of hydrogen, and finally *in vacuo*. In the analyses the silver required to precipitate the chlorine from a known weight of potassium chloride was determined, and also the weight of silver chloride produced:

$$5 \text{ experiments.} \quad AgCl : KCl = 100 : 52{\cdot}0118 \pm 0{\cdot}0004,$$

whence **K=39·095**;

$$7 \text{ experiments.} \quad Ag : KCl = 100 : 69{\cdot}1073 \pm 0{\cdot}0004,$$

whence **K=39·096.**

A parallel research on potassium bromide by Richards and Mueller[3] gave results in good agreement with those of Richards and Stähler:

$$4 \text{ experiments.} \quad AgBr : KBr = 100 : 63{\cdot}3727 \pm 0{\cdot}0003,$$

whence **K=39·096**;

$$11 \text{ experiments.} \quad Ag : KBr = 100 : 110{\cdot}3190 \pm 0{\cdot}0004,$$

whence **K=39·096.**

A very careful redetermination of the ratio $KClO_3 : KCl$ by Stähler and Meyer[4] in 1911 gave

$$KClO_3 : KCl = 164{\cdot}382 : 100,^5$$

or

$$KCl : 3O = 100 : 64{\cdot}382,$$

whence **K=39·098.**

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[1] Archibald, *Trans. Roy. Soc. Canada*, 1904, 3, 47.

[2] Richards and Stähler, *Carnegie Institution of Washington*, 1907, Publication No. 69, p. 1; *J. Amer. Chem. Soc.*, 1907, 29, 623; *Chem. News*, 1907, 96, 133.

[3] Richards and Mueller, *Carnegie Institution of Washington*, 1907, Publication No. 69, p. 27; *J. Amer. Chem. Soc.*, 1907, 29, 639; *Chem. News*, 1907, 96, 156.

[4] Stähler and Meyer, *Zeitsch. anorg. Chem.*, 1911, 71, 378.

[5] By combining this ratio with the potassium-chloride ratios of Richards and Stähler and the Ag : Cl ratio of Richards and Wells, the atomic weights of silver, chlorine, and potassium can be calculated. Taking O=16, the computation gives K=39·097. See also p. 87.

Neglecting the work of Richards and Archibald, which lacks the experimental accuracy of the later investigations, five modern values for the atomic weight of potassium fall within the limits of 39·095 and 39·098, and indicate the great probability of the value

$$\mathbf{K=39{\cdot}096.}$$

The current table of the International Committee on Atomic Weights gives [1]

$$\mathbf{K=39{\cdot}10.}$$

Alloys of Potassium and Sodium.[2]—Potassium and sodium unite to an alloy of the formula Na_2K.[3] In absence of air at 200° to 250° C., potassium reacts with sodium hydroxide to form a liquid alloy NaK_2: [4]

$$3K+NaOH=KOH+NaK_2.$$

At 350° C. sodium and potassium hydroxide interact in accordance with the equation

$$3Na+2KOH=2NaOH+NaK_2.$$

At 225° to 275° C. the reaction is different, and is expressed by the equation

$$2Na+KOH=NaOH+NaK.$$

On exposure to air these alloys ignite instantly.

COMPOUNDS OF POTASSIUM.

Potassium hydride, KH.—Moissan[5] prepared the hydride by a method analogous to that employed by him for the corresponding sodium derivative, the excess of potassium being dissolved by liquid ammonia. Ephraim and Michel[6] passed hydrogen into potassium at 350° C., and found the reaction to be promoted by the presence of calcium. The hydride forms white crystals of density 0·80. The vapour-tension for each temperature-interval of 10° between 350° and 410° C. corresponds with the values 56, 83, 120, 168, 228, 308, and 430 mm. respectively.[7] In chemical properties potassium hydride resembles the sodium compound, but is less stable. Its stability is greater than that of rubidium hydride or cæsium hydride. Carbon dioxide converts it into potassium formate.

Potassium fluoride, KF.—The fluoride is produced by the interaction of hydrofluoric acid and potassium carbonate or hydroxide; by heating potassium silicofluoride or borofluoride with lime; and by the action of potassium on fluorine, hydrofluoric acid, or silicon fluoride or boride.

The anhydrous salt forms crystals belonging to the cubic system,

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[1] Compare Hinrichs, *Compt. rend.*, 1909, 148, 484; Dubreuil, *Bull. Soc. chim.*, 1910, [4], 7, 119; W. A. Noyes and H. C. P. Weber, *J. Amer. Chem. Soc.*, 1908, 30, 13.

[2] For potassium-amalgam see this series, Vol. III.

[3] Van Bleiswyk, *Zeitsch. anorg. Chem.*, 1912, 74, 152.

[4] Jaubert, *Ber.*, 1908, 41, 4116.

[5] Moissan, *Compt. rend.*, 1902, 134, 18; compare Troost and Hautefeuille, *ibid.*, 1874, 78, 807; Elster and Geitel, *Physikal. Zeitsch.*, 1910, 11, 257.

[6] Ephraim and Michel, *Helv. Chim. Acta*, 1921, 4, 762.

[7] Compare Keyes, *J. Amer. Chem. Soc.*, 1912, 34, 779.

melting at 789° C.,[1] 846° C.,[2] 859·9° C.,[3] or 867° C.,[4] and boiling at 1505° C.[5] The vapour-pressure in atmospheres is given by the expression

$$\log p = -41900/4{\cdot}57T + 5{\cdot}138.$$

Its mean density[6] is 2·481. It yields a deliquescent, crystalline dihydrate, $KF,2H_2O$, m.p. 41° C.; and a stable, transparent, crystalline tetrahydrate, $KF,4H_2O$, m.p. 19·3° C.[7] The heat of formation is 110·6 Cal.[8] The latent heat of fusion is 0·108 Cal. per gram.[9] The molecular electric conductivity of potassium fluoride between 863·0° and 975° C. is given by the formula[10]

$$\mu_t = 101{\cdot}8 + 0{\cdot}3163(t - 900).$$

The heat of solution of the anhydrous salt at 20° C. is 3·6 Cal., and that of the dihydrate −1·0 Cal. The solubility of the dihydrate per 100 grams of water is 92·3 grams at 18° C.,[11] and 96·3 grams at 21° C.,[12] the solution being neutral. Electrolysis of the aqueous solution produces a considerable proportion of ozone.

Potassium hydrogen fluoride, KF, HF.—Potassium fluoride combines with hydrofluoric acid to form a *primary fluoride*, KF,HF or KHF_2, crystallizing in tetragonal plates, and decomposed at red heat with evolution of hydrofluoric acid. Its heat of formation[13] from the fluoride and hydrogen fluoride is 21·1 Cal., and its heat of solution is −6·0 Cal. Other unstable compounds of potassium fluoride with 2 and with 3 molecules of hydrogen fluoride have been prepared.[14]

Precipitation with alcohol of a solution of potassium fluoride and hydrogen peroxide yields an unstable compound of the formula KF,H_2O_2.[15]

Potassium chloride, KCl.—The chloride is found in nature as *sylvine*: in combination as *carnallite*, $KCl,MgCl_2,6H_2O$; *kainite*, $KCl,MgSO_4,3H_2O$; and as *douglasite*, $K_2FeCl_4,2H_2O$. It is also a constituent of the ashes of plants, and of the residues from the manufacture of alcohol from beet-molasses.

Potassium chloride can be synthesized from potassium and chlorine, the elements combining directly under the influence of heat, or at ordinary temperature in presence of moisture. At −80° C. the metal does not combine with chlorine. The salt can be prepared by the action of hydrochloric acid on the carbonate.

In addition to kainite and sylvine, the salt deposits at Stassfurt

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[1] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[2] von Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and von Wartenberg, *ibid.*, 162.

[3] Ruff and Plato, *Ber.*, 1903, 36, 2357; Plato, *Zeitsch. physikal. Chem.*, 1907, 58, 350.

[4] Karandéeff, *Zentr. Min.*, 1909, 728.

[5] von Wartenberg and Schulz, *loc. cit.*

[6] Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 16.

[7] de Forcrand, *Compt. rend.*, 1911, 152, 1073; compare Ditte, *ibid.*, 1896, 123, 1282; Mylius and Funk, *Ber.*, 1897, 30, 1718.

[8] Guntz, *Ann. Chim. Phys.*, 1884, [6], 3, 18.

[9] Plato, *Zeitsch. physikal. Chem.*, 1907, 58. 350.

[10] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.

[11] Mylius and Funk, *loc. cit.*

[12] Ditte, *loc. cit.*

[13] Guntz, *Ann. Chim. Phys.*, 1884, [6], 3, 18.

[14] Moissan, *Compt. rend.*, 1888, 106, 547.

[15] Tanatar, *Zeitsch. anorg. Chem.*, 1901, 28, 255.

("Abraumsalze") contain 55 to 65 per cent. of carnallite, associated with 20 to 25 per cent. of rock-salt, 10 to 20 per cent. of kieserite, $MgSO_4,H_2O$, and 2 to 4 per cent. of tachydrite, $CaCl_2,2MgCl_2,12H_2O$. The technical preparation of potassium chloride from these deposits depends on the ready solubility of carnallite, and the crystallization of potassium chloride from hot saturated solutions of this substance.[1] Kainite is employed as a source of potassium chloride, and the compound is also obtained by fractional crystallization of the salts present in sea-water and in the ash of seaweed.

A process for the production of potassium chloride from orthoclase was patented by Bassett,[2] but has not been worked technically. It was discovered independently and investigated by Ashcroft,[3] and consists in heating finely divided orthoclase with sodium chloride in equal proportion by weight at 900° to 1000° C., 85 per cent. of the potassium in the mineral being replaced by sodium in accordance with the scheme

$$K_2O,Al_2O_3,6SiO_2+2NaCl \rightleftharpoons Na_2O,Al_2O_3,6SiO_2+2KCl.$$

The potassium chloride can be separated from the insoluble sodium felspar by lixiviation, and from the excess of sodium chloride by fractional crystallization. This process might afford a new method for the manufacture of potassium chloride. It has also been found possible to extract the salt from the dust of the blast-furnace.[4]

Potassium chloride forms colourless cubes, and has also been obtained in octahedra, rhombododecahedra, and icositetrahedra. Its melting-point is given as 762° C.,[5] 772·3° C.,[6] 774° C.,[7] 775° C.,[8] 778° C.,[9] and 790° C.[10] It volatilizes without decomposition, the molecular weight derived from the vapour density,[11] and also that from the depression of the freezing-point of mercuric chloride,[12] corresponding with the simple formula KCl. For the density are given the mean value 1·977,[13] and also 1·989 at 16° C.,[14] 1·991 at 20° C.,[15] 1·994 at 20·4° C.,[16] 1·951 at 23·4° C.,[17] 1·612 at the melting-point.[18] The specific heat is given as 0·171 between 13° and 46° C.,[19] 0·1730 between 14° and 99° C.,[20] 0·1840 between 20° and 726° C., and for the fused salt 0·2671 between 807° and

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[1] Compare van 't Hoff and Meyerhoffer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1897, 487; *Zeitsch. physikal. Chem.*, 1899, 30, 64; Meyerhoffer, *German Patents*, 1896, Nos. 92812 and 98344.

[2] H. P. Bassett, *U.S.A. Patent*, 1913, No. 1072686.

[3] Ashcroft, *Chem. Trade J.*, 1917, 61, 529.

[4] Chance, *ibid.*, 1918, 62, 44; *J. Soc. Chem. Ind.*, 1918, 37, 87.

[5] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[6] Plato, *Zeitsch. physikal. Chem.*, 1906, 55, 721.

[7] Schaefer, *Jahrb. Min. Beil.-Bd.*, 1919, 43, 132.

[8] Arndt, *Zeitsch. Elektrochem.*, 1906, 12, 337; Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137; Korreng, *Jahrb. Min. Beil.-Bd.*, 1914, 37, 51.

[9] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[10] Schemtschushny and Rambach, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1785.

[11] Nernst, *Nachr. K. Ges. Wiss. Göttingen*, 1903, 75.

[12] Beckmann, *Zeitsch. anorg. Chem.*, 1907, 55, 180.

[13] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 20 and 21.

[14] Retgers, *Zeitsch. physikal. Chem.*, 1889, 3, 289.

[15] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[16] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 53.

[17] Buchanan, *Proc. Chem. Soc.*, 1905, 21, 122.

[18] Quincke, *Pogg. Annalen*, 1869, 138, 141.

[19] Kopp, *Annalen Suppl.*, 1864–5, 3, i., 289.

[20] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

935° C.[1] The latent heat of fusion per gram is recorded as 0·063 Cal.[2] and 0·086 Cal.[3] At 801° C. the vapour-pressure is 1·54 mm.; at 948° C. it is 8·33 mm.; and at 1044° C. it is 24·1 mm.[4] The molecular electric conductivity between 775·7° and 943·5° C. is given by the formula [5]

$$\mu_t = 115{\cdot}4 + 0{\cdot}2575(t - 800).$$

The heat of formation from the elements is given as 105·6 Cal.[6] and 105·7 Cal.[7]

SOLUBILITY[8] OF POTASSIUM CHLORIDE IN 100 GRAMS OF WATER.

Temperature, °C.	Solubility in Grams.	Temperature, °C.	Solubility in Grams.	Temperature, °C.	Solubility in Grams.
0	27·6*	30	37·0	90	54·0
5	29·3	40	40·0	100	56·7
10	31·0	50	42·6	130	66·0
15	32·4†	60	45·5	147	70·8
20	34·0	70	48·3	180	77·5
25	35·5	80	51·1		

* The density of the solution is 1·150. † Density 1·172.

The boiling-point of the saturated solution[9] in contact with excess of the salt is 108·6° C. at 760 mm.

At 25° C. 100 grams of ethyl alcohol dissolve 0·022 gram of potassium chloride.[10]

Double chlorides of potassium and other metals have also been prepared.[11] Potassium chloride does not form either compounds or mixed crystals with lithium chloride.[12]

Potassium bromide, KBr.—The bromide is prepared by the action of bromine on warm, concentrated potassium-hydroxide solution, the bromate simultaneously formed being converted into bromide by subsequent heating :

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

It forms white cubes,[13] m.p. 733° C.,[14] 740° C.,[15] 745·5° C.,[16] or 750° C.[17]

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[1] Plato, *Zeitsch. physikal. Chem.*, 1906, 55, 721.
[2] Schemtschushny and Rambach, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1785.
[3] Plato, *Zeitsch. physikal. Chem.*, 1907, 58, 350.
[4] Jackson and J. J. Morgan, *J. Ind. Eng. Chem.*, 1921, 13, 110.
[5] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.
[6] Thomsen, *J. prakt. Chem.*, 1875, [2], 11, 242.
[7] Berthelot, *Ann. Chim. Phys.*, 1884, [6], 1, 97.
[8] Compare Andreae, *J. prakt. Chem.*, 1884, [2], 29, 470.
[9] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.
[10] Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1904.
[11] Compare Liebisch and Korreng, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 192.
[12] Schaefer, *Jahrb. Min. Beil.-Bd.*, 1919, 43, 132.
[13] Compare Oettel, *Zeitsch. Elektrochem.*, 1906, 12, 604.
[14] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.
[15] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.
[16] McCrae, *Wied. Annalen*, 1895, 55, 95.
[17] Ruff and Plato, *Ber.*, 1903, 36, 2357.

The mean density is 2·690,[1] other values found being 2·756 at 20° C.,[2] 2·679 at 23·4° C.,[3] and 2·73 at 25° C.[4] The specific heat is 0·1132 between 16° and 98° C.,[5] or 0·102 between the temperature of liquid air and 15° C.[6] The molecular electric conductivity of potassium bromide between 745·2° and 868·6° C. is given by the formula[7]

$$\mu_t = 90{\cdot}09 + 0{\cdot}1906(t - 750).$$

The heat of formation of potassium bromide from the elements is given as 95·3 Cal.[8] and 95·6 Cal.[9] At 20° C. 100 grams of water dissolve 65 grams of the bromide[10]; and at 25° C. 100 grams of ethyl alcohol dissolve 0·142 gram.[11]

In aqueous solution potassium bromide reacts with bromine, *polybromides* with the formulæ KBr_3 and KBr_5 being formed in solution.[12] In the neighbourhood of its melting-point the salt evolves bromine freely.[13] Potassium bromide finds application in medicine as a soporific, and in photographic development as a "restrainer."

Potassium iodide, KI.—The iodide is obtained by neutralizing the carbonate with hydriodic acid, and also by the interaction of potassium hydroxide and iodine, the iodate simultaneously produced being converted into iodide by heat or by the action of a reducer such as carbon :

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

It is manufactured by the action of iron-filings on iodine in presence of water, the soluble iodide Fe_3I_8 formed being decomposed by potassium hydroxide, a process accompanied by precipitation of the oxide Fe_3O_4 and formation of a solution of potassium iodide. The salt crystallizes on concentration of the aqueous solution. It can also be prepared from the ashes of seaweed, and from the iodate present in Chile saltpetre.

Potassium iodide forms crystals belonging to the cubic system, melting at 677·3° C.,[14] 680° C.,[15] 684·1° C.,[16] 705° C.,[17] or 722·7° C.[18] Its density is given by various investigators as 3·079,[19] 3·043 at 24·3° C.,[20] and 3·115 at 25° C.[21] The specific heat is given as 0·0766,[22] and 0·0819

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[1] Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 31.

[2] Krickmeyer. *Zeitsch. physikal. Chem.*, 1896, 21, 53.

[3] Buchanan, *Proc. Chem. Soc.*, 1905, 21, 122.

[4] Richards and Mueller, *J. Amer. Chem. Soc.*, 1907, 29, 639; compare Brunner, *ibid.*, 1904, 38, 350; Lorenz, Frei, and Jabs, *Zeitsch. physikal. Chem.*, 1908, 61, 468.

[5] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[6] Nordmeyer, *Ber. Deut. physikal. Ges.*, 1908, 6, 2021.

[7] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.

[8] Thomsen, *J. prakt. Chem.*, 1875, [2], 11, 242.

[9] Berthelot, *Thermochimie*, Paris, 1897, 1, 181.

[10] de Coppet, *Ann. Chim. Phys.*, 1883, [5], 30, 416.

[11] Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1904.

[12] Böricke, *Zeitsch. Elektrochem.*, 1905, 11, 57.

[13] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.

[14] McCrae, *Wied. Annalen*, 1895, 55, 95.

[15] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

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

[17] Ruff and Plato, *Ber.*, 1903, 36, 2357.

[18] McCrae, *loc. cit.*

[19] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 34.

[20] Buchanan, *Proc. Chem. Soc.*, 1905, 21, 122.

[21] Baxter and Brink, *J. Amer. Chem. Soc.*, 1908, 30, 46.

[22] Nernst and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247.

between 20° and 99° C.[1] The heat of formation from the solid elements is 80·1 Cal.[2]

The molecular electric conductivity of potassium iodide between 691·5° and 814° C. is given by the formula [3]

$$\mu_t=85{\cdot}41+0{\cdot}1564(t-700).$$

The salt dissolves in water to form a neutral solution, readily decomposed by atmospheric oxygen and carbon dioxide with separation of iodine.

SOLUBILITY OF POTASSIUM IODIDE IN 100 GRAMS OF WATER.[4]

Temperature, °C.	Solubility in Grams.	Temperature, °C.	Solubility in Grams.	Temperature, °C.	Solubility in Grams.
−10	115·1	40	160	90	200
0	127·5	50	168	100	208
10	136·0	60	176	110	215
20	144	70	184	120	223
30	152	80	192		

The boiling-point of a solution in contact with excess of the salt is 118·4° C., and the liquid contains 222·6 grams of dissolved salt per 100 grams of water.[5]

At 25° C. 100 grams of ethyl alcohol dissolve 2·16 grams of potassium iodide.[6]

Potassium iodide finds application in medicine. The chief impurities present in the " pure " commercial product are iodate, carbonate, and chloride of potassium.

On heating potassium iodide with ammonium bromide in a long narrow tube of hard glass, iodine is liberated. By the aid of this test one-tenth of a milligram of the iodide can be detected.[7]

Various *polyiodides* of potassium have been mentioned as formed by addition of iodine to solutions of potassium iodide in water and in organic solvents. There seems to be much uncertainty as to whether they are true poly-derivatives or only mixtures of potassium iodide and iodine, but Foote and Chalker[8] state that the compounds KI_3 and KI_7 have a definite existence.

Potassium hypochlorite,[9] KOCl.—An aqueous solution of the hypo-

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[1] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[2] Thomsen, *J. prakt. Chem.*, 1875, [2], 11, 242.

[3] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.

[4] Mulder, *Seidell's Solubilities*, 2nd ed. (Crosby Lockwood and Son, 1920), 537; compare Mulder, *Scheikunde*, Rotterdam, 1864, 63.

[5] Mulder, *Scheikunde*, Rotterdam, 1864, 63.

[6] Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1904.

[7] Guareschi, *Atti R. Accad. Sci. Torino*, 1915, 50, 354.

[8] Foote and Chalker, *Amer. Chem. J.*, 1908, 39, 561; compare Dawson, *Trans. Chem. Soc.*, 1908, 93, 1308.

[9] For *potassium chlorite*, $KClO_2$, see chlorous acid, this series, Vol. VIII.

chlorite is formed analogously to that of sodium hypochlorite by the action of chlorine on a dilute aqueous solution of the hydroxide at low temperatures; by the interaction of potassium salts and bleaching-powder solution; and by the electrolysis of potassium-chloride solution without a diaphragm. It is also formed to some extent by passing an alternating current through a solution of potassium chloride.[1] The heat of formation of the substance in aqueous solution is given as 84·35 Cal.[2] and 88·0 Cal.[3] This solution was formerly employed as a bleaching agent, under the name " Eau de Javelle."

Potassium chlorate, $KClO_3$.—The chlorate is obtained by methods similar to those employed for the corresponding sodium salt. The electrolysis of the chloride[4] affords a means of manufacture, and it is also obtained by the interaction of potassium chloride and calcium chlorate. Large quantities are made by the electrolytic oxidation of sodium chloride to chlorate, and conversion of this salt into potassium chlorate by treatment with potassium chloride. Sodium chlorate is much more soluble than potassium chlorate, so that the electrolytic process is not impeded by crystallization of the salt.

The electrochemical formation of chlorate from hypochlorite is regarded by Knibbs and Palfreeman[5] as involving two reactions, represented by the equations

$$OCl' + 2HOCl = ClO_3' + 2H^{\cdot} + 2Cl' ;$$
$$2OCl' + 2H^{\cdot} + 2Cl' = 2HOCl + 2Cl'.$$

The net result is the disappearance of three hypochlorite ions, with formation of 1 chlorate ion and 2 chloride ions. Although apparently termolecular, the first reaction is unimolecular, since the concentration of the hypochlorous acid remains constant. The second reaction is practically instantaneous.[6] Chloride can be produced by the electrolysis of chlorate, possibly in accordance with the equation

$$4MClO_3 = 3MClO_4 + MCl,$$

M representing an atom of a univalent metal. The formation of chloride is promoted by rise of temperature, but is almost inhibited by the presence of a chromate.[7]

Potassium chlorate forms monoclinic crystals,[8] its melting-point being given as 357·10° C.,[9] 370° C.,[10] and 372° C.[11] When a solution obtained by treatment of crude Californian petroleum with concentrated sulphuric acid and dilution with water is added to a solution in water of the ordinary tabular potassium chlorate, and the mixture con-

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[1] Coppadoro, *Gazzetta*, 1905, 35, ii., 604.

[2] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 5, 337.

[3] Thomsen, *Thermochemistry* (Longmans, 1908), 328.

[4] Wallach, *Zeitsch. Elektrochem.*, 1906, 12, 677. See also this series, Vol. VIII.

[5] Knibbs and Palfreeman, *Trans. Faraday Soc.*, 1921, 16, 402.

[6] Compare Oechsli, *Zeitsch. Elektrochem.*, 1903, 9, 807; Bennett and Mack, *Trans. Amer. Elektrochem. Soc.*, 1916, 29, 323.

[7] Knibbs and Palfreeman, *loc. cit.*

[8] Ries, *Zeitsch. Kryst. Min.*, 1905, 41, 243.

[9] Carpenter, *Chem. and Met. Eng.*, 1921, 24, 569.

[10] Le Chatelier, *Bull. Soc. chim.*, 1887, [2], 47, 300.

[11] Carnelley, *Trans. Chem. Soc.*, 1876, 29, 489.

centrated on the water-bath, the salt separates in long fibrous crystals of silky appearance.[1]

The density of potassium chlorate is 2·344 at 17° C.,[2] 2·3384,[3] or in mean[4] 2·331. The specific heat is given as 0·194 between 16° and 49° C.,[5] and 0·2096 between 16° and 98° C.[6] The values recorded for the heat of formation from the elements are 93·8 Cal.[7] and 95·8 Cal.[8]

SOLUBILITY OF POTASSIUM CHLORATE IN 100 GRAMS OF WATER.[9]

Temperature, °C.	Solubility in Grams.	Temperature, °C.	Solubility in Grams.
0	3·3	80	39·6
10	5·0	90	47·5
20	7·1	100	56·0
30	10·1	120	73·3
40	14·5	136	99
50	19·7	160	148
60	26·0	190	183
70	32·5		

Potassium chlorate is employed for various purposes as an oxidizer, examples being the manufacture of dyes such as aniline-black, and the production of safety matches and fireworks.

With concentrated hydrochloric acid potassium chlorate evolves chlorine and chlorine peroxide, a reaction useful in certain analytical operations. The mixture is called "euchlorine."[10]

Action of Heat on Potassium Chlorate.—When heated to 357° C., potassium chlorate undergoes no perceptible decomposition, but the particles cake together, and under the microscope exhibit signs of incipient fusion.[11] At a slightly higher temperature the salt melts, and there is rapid evolution of oxygen between 370° and 380° C., several reactions being initiated.

1. Potassium perchlorate is formed by autoxidation, the exothermic reaction corresponding with the equation

$$KClO_3+3KClO_3=3KClO_4+KCl+61{\cdot}3 \text{ Cal.}$$

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[1] Wolcott, *J. Ind. Eng. Chem.*, 1921, 13, 215.

[2] Retgers, *Zeitsch. physikal. Chem.*, 1890, 5, 436.

[3] Andreae, *ibid.*, 1913, 82, 109.

[4] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 72.

[5] Kopp, *Annalen Suppl.*, 1864–65, 3, i., 289.

[6] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[7] Berthelot, *Ann. Chim. phys.*, 1877, [5], 10, 383.

[8] Thomsen, *J. prakt. Chem.*, 1875, [2], 11, 142.

[9] Interpolated by Meyerhoffer (*Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 543) from the data of Gay-Lussac, *Ann. Chim. Phys.*, 1819, 11, 314; and of Tilden and Shenstone, *Trans. Roy. Soc.*, 1884, 175, 34; compare Tschugajev and Chlopin, *Zeitsch. anorg. Chem.*, 1914, 86, 154.

[10] Compare Pebal, *Annalen*, 1875, 177, 1.

[11] McLeod, *Trans. Chem. Soc.*, 1889, 55, 184.

Scobai[1] has proved the reaction to take place in accordance with this equation by measuring the velocity of formation of potassium perchlorate at 395° C., and has also demonstrated its quadrimolecular nature.

2. Simultaneously, a unimolecular reaction occurs, potassium chlorate decomposing with formation of potassium chloride, and evolution of oxygen :

$$2KClO_3=2KCl+3O_2.$$

3. A sufficient rise in temperature initiates the decomposition of the potassium perchlorate, chiefly in accordance with the equation

$$KClO_4=KCl+2O_2;$$

and at 445° C. there is complete decomposition in the sense indicated,[2] except for a small proportion of potassium chlorate simultaneously regenerated.[3]

The decomposition is much facilitated by the presence of certain oxides, such as manganese dioxide. The part played by these agents has been the subject of considerable controversy. Repeated use of the oxide produces no measurable diminution in its activity.[4] The action has been suggested[5] to be entirely mechanical, and analogous to that of sand and other substances in promoting the ebullition of water. On this assumption, all bodies in a fine state of division might be expected to exert a similar influence, a view at variance with the results of experiment. The oxides of metals capable of yielding more than one oxide, such as iron, nickel, copper, and cobalt, facilitate the reaction; but the oxides of zinc and magnesium are without effect. Probably higher and lower oxides of manganese are formed alternately at the expense of the chlorate.[6] In presence of the oxide there is no apparent formation of potassium perchlorate,[7] the manganese dioxide inducing the decomposition of the chlorate into chloride and oxygen at a temperature lower than that necessary for the autoxidation of the chlorate to perchlorate with appreciable velocity.[8]

Potassium perchlorate, $KClO_4$.—Careful heating of potassium chlorate causes partial autoxidation to perchlorate :

$$4KClO_3=3KClO_4+KCl.$$

The slight solubility of the perchlorate in dilute alcohol affords a means of separating it from the chloride. According to Blau and Weingland,[9] the decomposition of the chlorate is best carried out in quartz flasks at 480° C. without a catalyst, but when between 96 and 97 per cent. of the chlorate has been transformed the perchlorate begins to decompose, so that the change is never complete. The decomposition of the perchlorate is much accelerated by the presence of traces of iron oxide,

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[1] Scobai, *Zeitsch. physikal. Chem.*, 1903, 44, 319.
[2] Frankland and Dingwall, *Trans. Chem. Soc.*, 1887, 51, 279.
[3] Teed, *Proc. Chem. Soc.*, 1885, 1, 105 ; 1886, 2, 141 ; Frankland and Dingwall, *loc. cit.*
[4] McLeod, *Trans. Chem. Soc.*, 1889, 55, 184.
[5] Veley, *Phil. Trans.*, 1888, [A], 179, 270.
[6] Sodeau, *Trans. Chem. Soc.*, 1902, 81, 1066.
[7] Eccles, *J. Chem. Soc.*, 1876, 29, 857 ; Teed, *Trans. Chem. Soc.*, 1887, 51, 283.
[8] Sodeau, *loc. cit.* ; compare this series, Vol. VII., Part I.
[9] Blau and Weingland, *Zeitsch. Elektrochem.*, 1921, 27, 1.

copper, nickel, boron trioxide, or potassium hydroxide, so that vessels made of iron are unsuitable for its preparation.

When sulphuric acid reacts with potassium chlorate without application of heat, a yield of 11 per cent. of the perchlorate is obtained. Boiling with phosphoric acid of 85 per cent. strength gives a 15 per cent. yield; and evaporation to dryness with nitric acid produces a 30 per cent. yield. Hydrochloric acid does not form any perchlorate.[1]

A good yield of the perchlorate is obtained by the electrolysis of potassium chlorate with a platinum anode and a nickel cathode, the current density being 0·15 ampère per square decimètre. Even when revolving rapidly, the electrodes become incrusted with perchlorate; but this difficulty may be avoided by electrolyzing sodium chlorate, and forming potassium perchlorate by double decomposition (p. 105).[2] Knibbs and Palfreeman[3] regard the electrolytic formation of perchlorate as being analogous to that of persulphate, and give the scheme

$$-O_2ClO- + -OClO_2 = [O_2ClO-]_2;$$
$$[O_2ClO-]_2 + H_2O = O_2ClO \cdot OH + O_2ClOH.$$

The salt forms colourless, rhombic crystals, melting at 610° C.[4] Its density is given as 2·524 at 10·8° C.,[5] and 2·520 at ordinary temperature.[6] The specific heat[7] is 0·190 between 14° and 45° C. The heat of formation from the elements is 112·5 Cal.[8] The solubility at 25° C. is 1·96 grams per 100 grams of water.[9] Above 400° C. the salt decomposes with evolution of oxygen and formation of KCl. Its insolubility in alcohol renders it of service in the estimation of potassium.

Potassium hypobromite, $KOBr$.—The hypobromite can be prepared from the hydroxide or carbonate by the action of bromine, or from the bromide by electrolysis, by methods analogous to those described for sodium hypobromite.

Potassium bromate, $KBrO_3$.—The bromate is formed by the interaction of bromine and concentrated potassium hydroxide, or by the electrolytic oxidation of the bromide. The hexagonal crystals[10] melt[11] at 434° C., their mean density[12] being 3·27. The heat of formation from the elements is given as 84·06 Cal.[13] and 84·3 Cal.[14] The solubility[15] at 20° C. is 6·9 grams per 100 grams of water. When heated above its melting-point, $KBrO_3$ is decomposed into the bromide and oxygen.

Potassium perbromate, $KBrO_4$.—The perbromate has been prepared

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[1] Lenher, Stone, and Skinner, *J. Amer. Chem. Soc.*, 1922, 44, 143.

[2] Blau and Weingland, *Zeitsch. Elektrochem.*, 1921, 27, 1.

[3] Knibbs and Palfreeman, *Trans. Faraday Soc.*, 1921, 16, 402.

[4] Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 125.

[5] Muthmann, *Zeitsch. Kryst. Min.*, 1894, 22, 497.

[6] Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 73.

[7] Kopp, *Annalen Suppl.*, 1864–65, 3, i., 289.

[8] Berthelot, *Ann. Chim. Phys.*, 1882, [5], 27, 226.

[9] Muir, *Chem. News*, 1876, 33, 15; compare Rothmund, *Zeitsch. physikal. Chem.*, 1909, 69, 528.

[10] Ries, *Zeitsch. Kryst. Min.*, 1905, 41, 243.

[11] Carnelley and O'Shea, *Trans. Chem. Soc.*, 1884, 45, 409.

[12] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 73.

[13] Thomsen, *Thermochemistry* (Longmans, 1908), 328.

[14] Berthelot, *Thermochimie*, Paris, 1897, 1, 187.

[15] Kremers, *Pogg. Annalen*, 1856, 97, 15; compare Rothmund, *Zeitsch. physikal. Chem.*, 1909, 69, 528.

by the action of potassium hydroxide on perbromic acid, and forms crystals isomorphous with those of potassium perchlorate.[1]

Potassium hypoiodite, KOI.—The hypoiodite has not been isolated, but is formed in aqueous solution by the interaction of iodine and a dilute solution of potassium hydroxide :

$$I_2+2KOH=KOI+KI+H_2O.$$

The solution is employed in analysis as an oxidizer, the hypoiodite being reduced to iodide. It is unstable, one part of the hypoiodite undergoing oxidation at the expense of the remainder :[2]

$$3KOI=KIO_3+2KI.$$

Potassium iodate, KIO_3.—The iodate is formed by the oxidation of potassium iodide, either electrolytically, or by means of potassium permanganate or chlorate. The colourless, monoclinic[3] crystals melt[4] at 560° C., and have a density[5] of 3·89. The heat of formation from the elements is given as 124·49 Cal.[6] and 126·1 Cal.[7] At 20° C. the solubility is 8·1 grams per 100 grams of water, the boiling-point of the saturated solution being 102° C.[8] A semi-hydrate has been described.[9] On heating, potassium iodate decomposes with evolution of oxygen, the decomposition being facilitated by the presence of MnO_2.

When the iodate is crystallized from acid solution, a *di-iodate*, KIO_3,HIO_3, is formed.[10] It finds application in the determination of the concentration of hydrogen ions,[11] and also in volumetric analysis, since it reacts with potassium iodide and hydrochloric acid according to the equation

$$KIO_3,HIO_3+10KI+11HCl=11KCl+12I+6H_2O.$$

A *tri-iodate*, $KIO_3,2HIO_3$, has also been prepared.[10]

Potassium periodate, KIO_4.—The periodate is produced by oxidizing a mixture of potassium iodate and hydroxide either electrolytically or with chlorine. It crystallizes in quadratic pyramids, melting at 582° C.,[12] and of density 3·618[13] at 15° C. At 13° C. its solubility is 0·66 gram per 100 grams water.[13] The heat of formation from the elements is 107·7 Cal.[14] In aqueous solution it is converted by potassium iodide into the iodate :

$$3KIO_4+KI=4KIO_3.$$

From an aqueous solution of the periodate and potassium hydroxide a *basic periodate*, $K_4I_2O_9,9H_2O$, crystallizes.

Potassium manganate and permanganate.—The methods of preparation and the properties of these are given in Vol. VIII.

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[1] Kämmerer, *J. prakt. Chem.*, 1863, 90, 190.
[2] Schwicker, *Zeitsch. physikal. Chem.*, 1895, 16, 303.
[3] Ries, *Zeitsch. Kryst. Min.*, 1905, 41, 243.
[4] Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 125.
[5] Clarke, *Amer. J. Sci.*, 1877, [3], 14, 281.
[6] Thomsen, *Thermochemistry* (Longmans, 1908), 328.
[7] Berthelot, *Ann. Chim. Phys.*, 1878, [5], 13, 27.
[8] Kremers, *Pogg. Annalen*, 1856, 97, 15.
[9] Ditte, *Ann. Chim. Phys.*, 1870, [4], 21, 47.
[10] Meerburg, *Chem. Weekblad*, 1904, 1, 474.
[11] Compare Sand, *Ber.*, 1906, 39, 2038.
[12] Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 125.
[13] Barker, *ibid.*, 1908, 93, 15.
[14] Berthelot, *Thermochimie*, Paris, 1897, 1, 187.

Potassium monoxide, K_2O.—The monoxide is formed by incomplete oxidation of potassium by dry oxygen at reduced pressure, and removal of the excess of metal by distillation in vacuum.[1] The product forms microscopic octahedra, which become pale-yellow at 200° C., and have a density of 2·32 at 0° C. Above 400° C. in vacuum it is decomposed into the metal and the peroxide. The heat of formation of the monoxide from its elements is 86·80 Cal.[2] It is reduced by hydrogen to the hydride and hydroxide. With water it reacts energetically to form the hydroxide, the heat of solution being 75·0 Cal.[3] It also combines with fluorine, chlorine, and iodine. The heat of formation from the elements is 86·8 Cal.[3]

Potassium peroxides.—Several peroxides have been described.[4] The *tetroxide*, K_2O_4, or K_2O_2,O_2,[5] is produced by burning the metal in air or oxygen. de Forcrand[6] heats the potassium first in a current of nitrogen, then in air, and finally in pure oxygen at a temperature between 180° and 200° C. The product is a sulphur-yellow, very hygroscopic powder, its heat of formation from the elements being 137·74 Cal. It is decomposed by water, with evolution of oxygen and formation of potassium hydroxide and hydrogen peroxide:[7]

$$K_2O_4+2H_2O=2KOH+H_2O_2+O_2.$$

With dilute sulphuric acid it yields hydrogen peroxide.

When the tetroxide is heated at 480° C. under a pressure of 1 mm. of mercury, it is converted into *potassium trioxide*, K_2O_3, a yellow, crystalline substance, from which dilute sulphuric acid generates hydrogen peroxide. Its heat of formation from the elements is 124·34 Cal.[8]

At —50° C. oxygen reacts with a solution of potassium in liquid ammonia to form the tetroxide and trioxide, and also *potassium dioxide*, K_2O_2.[9] The heat of formation of the dioxide from its elements is about 108·8 Cal.[10]

Potassium hydroxide, KOH.—The hydroxide can be prepared by methods similar to those employed for the corresponding sodium derivative. The chief processes are the electrolysis of the chloride, and the interaction of the carbonate or sulphate[11] in aqueous solution with slaked lime. In the sulphate process, evaporation of the mother-liquid yields the anhydrous hydroxide, the monohydrate, or the dihydrate, the formation of each product depending on the concentration.[12] For laboratory use, the substance can be prepared free from carbonate by a method described by Jorissen and Filippo.[13]

Potassium hydroxide is a white solid, melting[14] at 360·4° C., and with

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[1] Rengade, *Compt. rend.*, 1906, 143, 1152; 1907, 144, 753.
[2] de Forcrand, *ibid.*, 1914, 158, 991.
[3] Rengade, *ibid.*, 1907, 145, 236.
[4] Compare Calvert, *Zeitsch. physikal. Chem.*, 1901, 38, 513.
[5] Riesenfeld and Mau, *Ber.*, 1911, 44, 3595.
[6] de Forcrand, *Compt. rend.*, 1914, 158, 843.
[7] Riesenfeld and Mau, *Ber.*, 1911, 44, 3595.
[8] de Forcrand, *Compt. rend.*, 1914, 158, 991.
[9] Joannis, *ibid.*, 1893, 116, 1372.
[10] de Forcrand, *ibid.*, 1914, 158, 991.
[11] Compare Herold, *Zeitsch. Elektrochem.*, 1905, 11, 417.
[12] Salzbergwerk Neustassfurt, *German Patent*, 1906, No. 189835.
[13] Jorissen and Filippo, *Chem. Weekblad*, 1909, 6, 145.
[14] Hevesy, *Zeitsch. physikal. Chem.*, 1910, 73, 667.

density[1] 2·044. The heat of formation from the elements is given as 102·76 Cal.,[2] 103·2 Cal.,[3] and 104·6 Cal.[4]; that from the monoxide and water as 49·72 Cal.[5] The latent heat of fusion per mol. is 1·60 Cal.[6] At 795° C. the vapour-pressure is 8 mm.[7]

The solubility of potassium hydroxide has been studied by Pickering,[8] some of his results being given in the appended table:

Solubility of Potassium Hydroxide.

Temperature, °C.	−40	−30	−20	−10	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140
Grams of KOH per 100 grams of water	61·2	82·4	87·9	92·3	99·2	106·1	112·7	122·2	136·9	143·9	150	157·9	163·4	177·7	187·3	201·2	214·4	235·5	281·6

The density of the solution saturated at 15° C. is 1·536.

In chemical properties the potassium derivative resembles sodium hydroxide, the aqueous solution being a strong base,[9] a solution containing 6·7 gram-molecules of the hydroxide per litre having the maximum OH′-concentration.[10] The hydroxide readily absorbs ozone, the product being possibly the heptoxide, K_2O_7.[11]

Three hydrates have been isolated, the monohydrate, dihydrate, and tetrahydrate, melting respectively at 143° C., 35·5° C., and −32·7° C., the transition-point of the first and second being 32·5° C., and of the second and third −33° C.[12]

The action of aqueous solutions of potassium hydroxide on sulphur is similar to that of sodium hydroxide or of concentrated ammonium hydroxide (pp. 111 and 220).

Potassium monosulphide, K_2S.—The sulphide can be formed by direct union of the elements,[13] by reduction of potassium sulphate with hydrogen or charcoal, and by the interaction of aqueous solutions of potassium hydroxide and potassium hydrogen sulphide. It is also produced by the action of sulphur on a solution of excess of potassium in liquid ammonia.[14] On evaporation of its aqueous solution in vacuum at low temperature, the pentahydrate[15] crystallizes. A dihydrate and a dodecahydrate are also known.[16] The anhydrous salt can be obtained

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[1] Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415.

[2] de Forcrand, *ibid.*, 1908, [8], 15, 433.

[3] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 235.

[4] Berthelot, *Thermochimie*, Paris, 1897, 1, 178.

[5] de Forcrand, *loc. cit.*

[6] Hevesy, *Zeitsch. physikal. Chem.*, 1910, 73, 667.

[7] Jackson and J. J. Morgan, *J. Ind. Eng. Chem.*, 1921, 13, 110.

[8] Pickering, *Trans. Chem. Soc.*, 1893, 63, 908.

[9] On the heat of neutralization by hydrochloric acid, hydrobromic acid, hydriodic acid, and nitric acid compare Richards and Rowe, *J. Amer. Chem. Soc.*, 1922, 44, 684.

[10] Kohlrausch, *Wied. Annalen*, 1879, 6, 1, 145.

[11] Traube, *Ber.*, 1912, 45, 2201.

[12] Pickering, *Trans. Chem. Soc.*, 1893, 63, 908.

[13] Rengade and Costeanu, *Compt. rend.*, 1913, 156, 791.

[14] Hugot, *ibid.*, 1899, 129, 388.

[15] Schöne, *Pogg. Annalen*, 1867, 131, 380.

[16] Bloxam, *Trans. Chem. Soc.*, 1900, 77, 753; Sabatier, *Ann. Chim. Phys.*, 1881, [5], 22, 22.

by eliminating the water from the hydrates by means of a current of dry hydrogen.

In properties potassium monosulphide resembles the sodium salt. The anhydrous substance forms small cubic octahedra, isomorphous with the monosulphide of rubidium, but not with that of cæsium.[1] At the laboratory temperature its density is 1·805.[2] The heat of formation of the solid from its elements is 87·1 Cal.,[3] and the heat of solution is 22·7 Cal. In dilute solution it has a strongly alkaline reaction, owing to almost complete hydrolysis to the hydroxide and primary sulphide.

Potassium polysulphides.—Several polysulphides have been described. According to Thomas and Rule,[4] the complete series K_2S_x exists, x being any whole number up to a maximum of 6. The values obtained for the molecular weights in alcoholic solution by the ebullioscopic method favour the simple formula K_2S_x, and not K_4S_x.

The *trisulphide*, K_2S_3, is formed by the action of excess of sulphur on a solution of potassium in liquid ammonia.[5] The *tetrasulphide*, K_2S_4, the most stable member of the series, can be prepared by heating a mixture of potassium carbonate and sulphur at 800° C. in a current of carbon dioxide,[6] or by the action of hydrogen sulphide on the fused pentasulphide. It yields an octahydrate, a trihydrate, and a semihydrate. Its heat of formation from the elements is 116·6 Cal.[7]

The *pentasulphide*, K_2S_5, is formed at lower temperatures from the carbonate by the action of excess of sulphur, thiosulphate being also produced by heating the two substances in a closed vessel at 250° C., the mixture constituting one variety of the so-called "liver of sulphur." A better method for preparing the pentasulphide is to saturate a solution of potassium ethoxide with hydrogen sulphide and add the equivalent amount of sulphur.[8] By this process it has not been found possible to prepare the disulphide, trisulphide, tetrasulphide, or hexasulphide, even when the calculated proportions of the materials are employed, the product being invariably the pentasulphide. Thus prepared, the substance forms an orange-red, very hygroscopic, crystalline solid. At 220° C. it melts with decomposition. When in contact with air, or in aqueous solution, it undergoes gradual decomposition, with liberation of sulphur.

Polysulphides of the formulæ K_4S_5 and K_4S_8 have also been prepared by the interaction of the solid primary sulphide with hydrogen sulphide.[9] Aqueous solutions of the monosulphide are unsuited for preparing individual polysulphides.

Potassium hydrogen sulphide, KSH.—The anhydrous primary sulphide can be obtained by the action of hydrogen sulphide on potassium suspended in ether.[10] It can also be prepared by saturating an

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[1] Rengade and Costeanu, *Compt. rend.*, 1914, 158, 946.
[2] Compare Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 415.
[3] Compare Sabatier, *ibid.*, 1881, [5], 22, 22.
[4] Thomas and Rule, *Trans. Chem. Soc.*, 1917, 111, 1063.
[5] Hugot, *Compt. rend.*, 1899, 129, 388.
[6] Schöne, *Pogg. Annalen*, 1867, 131, 380.
[7] Sabatier, *loc. cit.*
[8] Rule and Thomas, *Trans. Chem. Soc.*, 1914, 105, 2819.
[9] Bloxam, *Zeitsch. anorg. Chem.*, 1908, 60, 113.
[10] Bloxam, *Trans. Chem. Soc.*, 1900, 77, 753; compare Bloxam, *ibid.*, 1895, 67, 277.

aqueous solution of potassium hydroxide with hydrogen sulphide,[1] evaporating to dryness in vacuum, and eliminating the water from the resulting $\frac{1}{4}$-hydrate[2] or $\frac{1}{2}$-hydrate[3] by a current of dry hydrogen. It can be precipitated quantitatively by adding benzene or ether to a solution of sodium ethoxide in absolute alcohol saturated with hydrogen sulphide:[4]

$$C_2H_5ONa+H_2S=NaSH+C_2H_5OH.$$

Potassium hydrogen sulphide forms white, miscroscopic cubes, more deliquescent than the corresponding sodium derivative. The heat of formation from the element is given as 64·0 Cal.,[5] and that in aqueous solution as 65·1 Cal.[6]

Potassium sulphite, K_2SO_3.—The sulphite can be prepared by passing sulphur dioxide into a solution of potassium carbonate till evolution of carbon dioxide ceases; or by dissolving a known weight of potassium hydroxide in water, saturating with sulphur dioxide, and adding an equal weight of the hydroxide. Evaporation of the solution yields the rhombic *dihydrate*, which is transformed into the anhydrous salt at 120° C., a white solid with heat of formation 272·6 Cal.[7] A *monohydrate* is also known.

Potassium hydrogen sulphite, $KHSO_3$.—The primary sulphite can be precipitated in monoclinic crystals by addition of alcohol to a solution of potassium carbonate into which excess of sulphur dioxide has been passed. It is unstable, readily losing sulphur dioxide. Its heat of formation in aqueous solution is 211·3 Cal.[8]

Potassium pyrosulphite, $K_2S_2O_5$.—On treatment of a hot saturated solution of potassium carbonate with sulphur dioxide, the pyrosulphite separates in monoclinic crystals, which are more stable than those of the primary sulphite. Its heat of formation from the elements is 369·4 Cal.[8] It is employed in the preparation of photographic developers under the name "potassium metabisulphite."

Potassium sulphate, K_2SO_4.—The sulphate occurs in nature in the form of double salts. Examples are *schönite*, $K_2SO_4,MgSO_4,6H_2O$; *polyhalite*, $K_2SO_4,MgSO_4,2CaSO_4,2H_2O$; and *glaserite*, $3K_2SO_4,Na_2SO_4$. It is a by-product in the manufacture of nitric acid from potassium nitrate and sulphuric acid, and can also be prepared by the action of sulphuric acid on potassium chloride. The main sources of potassium sulphate are kainite ($KCl,MgSO_4,3H_2O$) and sylvine (KCl), both present in the Stassfurt "Abraumsalze." Water decomposes kainite into a sparingly soluble double sulphate of potassium and magnesium, and the very soluble magnesium chloride; a similar product is obtained by the interaction of sylvine and kieserite ($MgSO_4,H_2O$). The magnesium chloride is removed by cold water, and the residual double sulphate treated with excess of an aqueous solution of potassium chloride:

$$K_2SO_4,MgSO_4+2KCl=2K_2SO_4+MgCl_2.$$

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[1] Compare Biltz and Wilke-Dörfurt, *Ber.*, 1905, 38, 125.
[2] Schöne, *Pogg. Annalen*, 1867, 131, 380.
[3] Bloxam, *Trans. Chem. Soc.*, 1900, 77, 753.
[4] Rule, *ibid.*, 1911, 99, 558.
[5] Sabatier, *Ann. Chim. Phys.*, 1881, [5], 22, 22.
[6] Thomsen, *Pogg. Annalen*, 1870, 139, 242.
[7] Berthelot, *Ann. Chim. Phys.*, 1884, [6], 1, 76.
[8] Berthelot, *ibid.*, 87.

Potassium sulphate forms white, rhombic crystals,[1] melting-point 1015° C.,[2] 1045° C.,[3] 1050° C.,[4] 1052° C.,[5] 1057° C.,[6] 1058·9° C.,[7] 1066·1° C.,[7] 1066·5° C.,[8] 1067° C.,[9] 1070° C.,[10] 1074° C.,[11] or 1078° C.[12] Its density is given as 2·6617,[13] 2·6627[14] at 16·4° C., 2·6633,[15] 2·666,[16] 2·670[17] at 20° C., and 2·6521[18] at 60° C. Its specific heat is 0·196 between 13° and 45° C.,[19] or 0·1901 between 15° and 98° C.[20] At 1130° C. the vapour-pressure is 0·4 mm.[21] The heat of formation from the elements is given as 344·3 Cal.[22] and 344·6 Cal.[23] The crystals are diamagnetic, and exhibit triboluminescence.[24] The salt does not form hydrates.[25] The solubility in water is given in the table.[26]

Solubility of Potassium Sulphate.

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100	120	143	170
Grams of K_2SO_4 in 100 g. of water.	7·35	9·22	11·11	12·97	14·76	16·50	18·17	19·75	21·4	22·8	24·1	26·5	28·8	32·9

A solution in contact with excess of salt boils at 101·392° C. under a pressure of 760 mm. of mercury.[27] The aqueous solution of the salt has a neutral reaction.

Potassium hydrogen sulphate, $KHSO_4$.—The primary sulphate is formed by the action of an equivalent proportion of sulphuric acid on the normal sulphate or on the nitrate or chloride. It is also produced by the interaction of potassium sulphate and ammonium hydrogen sulphate under the influence of steam superheated at 200° to 400° C.:[28]

$$K_2SO_4+NH_4HSO_4=2KHSO_4+NH_3.$$

When the proportion of steam is deficient, a pyrosulphate is produced.

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[1] For isomorphism, see p. 227.

[2] Le Chatelier, *Compt. rend.*, 1894, 118, 350.

[3] Le Chatelier, *Bull. Soc. chim.*, 1887, [2], 47, 300.

[4] Ruff and Plato, *Ber.*, 1903, 36, 2357.

[5] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[6] Müller, *N. Jahrb. Mineral Beil.-Bd.*, 1914, 30, 1; *Zeitsch. Kryst. Min.*, 1914, 53, 511.

[7] McCrae, *Wied. Annalen*, 1895, 55, 95.

[8] Heycock and Neville, *Trans. Chem. Soc.*, 1895, 67, 160.

[9] van Klooster, *Zeitsch. anorg. Chem.*, 1914, 85, 49.

[10] Amadori, *Atti R. Accad. Lincei*, 1913, [5], 22, i., 453.

[11] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215; Karandéeff, *Zentr. Min.*, 1909, 728.

[12] Victor Meyer, Riddle, and Lamb, *Ber.*, 1893, 26, 3129.

[13] Andreae, *Zeitsch. physikal. Chem.*, 1913, 82, 109.

[14] Andreae, *ibid.*, 1911, 76, 491.

[15] Tutton, *Trans. Chem. Soc.*, 1894, 65, 628.

[16] Retgers, *Zeitsch. physikal. Chem.*, 1889, 3, 289.

[17] Krickmeyer, *ibid.*, 1896, 21, 53.

[18] Tutton, *loc. cit.*

[19] Kopp, *Annalen Suppl.*, 1864–5, 3, i., 289.

[20] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[21] Jackson and J. J. Morgan, *J. Ind. Eng. Chem.*, 1921, 13, 110.

[22] Berthelot, *Thermochimie*, Paris, 1897, 1, 190.

[23] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 236.

[24] Trautz, *Zeitsch. physikal. Chem.*, 1905, 53, 1; compare Lindener, *Bull. Acad. St. Pétersbourg*, 1909, 961.

[25] Ogler, *Compt. rend.*, 1876, 82, 1055.

[26] Values interpolated by Meyerhoffer (*Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 546); compare Tilden and Shenstone, *Proc. Roy. Soc.*, 1883, 35, 345; Andreae, *J. prakt. Chem.*, 1884, [2], 29, 470; Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207.

[27] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.

[28] Dominik, *Przemysl Chem.*, 1921, 5, 10, 37, 63.

Potassium hydrogen sulphate is dimorphous, crystallizing in the rhombic and also in the monoclinic system. Its melting-point is given as 200° C.[1] and 210° C.,[2] and its mean density as 2·355.[3] The heat of formation from the elements is recorded as 276·1 Cal.[4] and 277·1 Cal.[5] The solubility in water is given in the table.

Solubility of Potassium Hydrogen Sulphate.

Temperature, °C.	0	20	40	100
Grams of $KHSO_4$ in 100 grams of water	36·3	51·4	67·3	121·6

The boiling-point of a solution in contact with excess of salt is 108° C.[6] The solution has a very acidic reaction. On heating above the melting-point it is converted into the pyrosulphate.

Several other potassium hydrogen sulphates have been described.[7] Examples of such compounds are $K_2SO_4,3H_2SO_4$ with melting-point 91·5° C., and K_2SO_4,H_2SO_4 with melting-point 218·6° C.[8]

Potassium pyrosulphate, $K_2S_2O_7$.—The pyrosulphate is produced by heating potassium hydrogen sulphate, or by the action of sulphur trioxide on the normal sulphate. It forms colourless crystals, melting[9] above 300° C., and of density 2·277. The heat of formation is 474·2 Cal.[10]

Potassium persulphate, $K_2S_2O_8$.—The persulphate is formed in the electrolysis of the primary sulphate or normal sulphate in concentrated solution,[11] with a current density of 5 ampères per sq. cm. The use of a diaphragm is unnecessary, and the yield is much higher when the electrolyte contains hydrofluoric acid. The compound is also manufactured by double decomposition from ammonium persulphate. Any excess of this salt can be eliminated[12] by crystallizing from hot water in presence of sufficient barium hydroxide to decompose the ammonium derivative. The heat of formation of potassium persulphate is 454·5 Cal.,[13] and the solubility at 0° C. is 1·76 grams per 100 grams of water.[14] With concentrated sulphuric acid it forms complex derivatives containing a large proportion of oxygen.[15] It unites with hydrogen peroxide to form an unstable compound, probably having the formula $K_2S_2O_8,H_2O_2$. This substance decomposes spontaneously into potassium hydrogen sulphate and oxygen.[16] Although it has no action on a

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[1] Mitscherlich, *Pogg. Annalen*, 1830, 18, 152, 173.

[2] Schultz-Sellack, *Jahresber.*, 1871, 217.

[3] Compare Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 89.

[4] Berthelot, *Ann. Chim. Phys.*, 1873, [4], 29, 435.

[5] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 236.

[6] Kremers, *Pogg. Annalen*, 1856, 97, 15.

[7] Stortenbeker, *Rec. trav. chim.*, 1902, 21, 401; *van Bemmelen-Festschrift*, 1910, 329; d'Ans, *Zeitsch. anorg. Chem.*, 1909, 63, 225; 1913, 80, 295; Bergius, *Zeitsch. physikal. Chem.*, 1910, 72, 338; Arzalier, *Compt. rend.*, 1908, 147, 129.

[8] Kendall and Landon, *J. Amer. Chem. Soc.*, 1920, 42, 2131.

[9] Schultz-Sellack, *Jahresber.*, 1871, 217.

[10] Berthelot, *Ann. Chim. Phys.*, 1873, [4], 30, 442.

[11] Marshall, *Trans. Chem. Soc.*, 1891, 59, 771.

[12] Mackenzie and Marshall, *ibid.*, 1908, 93, 1726.

[13] Berthelot, *Ann. Chim. Phys.*, 1892, [6], 26, 538, 550.

[14] Marshall, *Trans. Chem. Soc.*, 1891, 59, 772.

[15] Compare this series, Vol. VII.

[16] Friend, *Trans. Chem. Soc.*, 1906, 89, 1092.

cold solution of potassium permanganate, its presence prevents the accurate estimation of hydrogen peroxide by titration with permanganate in the usual manner. This phenomenon is due to a catalytic, mutual reduction of the persulphate and peroxide, the proportion of permanganate required being less than that indicated by theory. If protected from sunlight, dry potassium persulphate can be preserved almost unchanged for years.[1]

Potassium thiosulphate, $K_2S_2O_3$.—The thiosulphate is prepared by boiling potassium sulphite in aqueous solution with sulphur. Its heat of formation is 278·0 Cal.[2] A monohydrate has been isolated.[3]

Potassium dithionate, $K_2S_2O_6$.—The dithionate is prepared by the interaction of barium dithionate and potassium carbonate. It forms hexagonal crystals, of density [4] 2·278 at 20° C. The heat of formation from the elements is 415·72 Cal.[5] At 16° C. the solubility is 6·06 grams per 100 grams of water.[6]

Potassium trithionate, $K_2S_3O_6$.—The trithionate is prepared by the action of sulphurous acid on potassium thiosulphate, and separates in rhombic crystals, of density 2·304 at 20° C. Its heat of formation is given as 405·85 Cal.[7] and 416·0 Cal.[8] It dissolves readily in water, forming a neutral solution.

Potassium tetrathionate, $K_2S_4O_6$.—The tetrathionate is formed by the interaction of potassium thiosulphate in aqueous solution and iodine, the salt being precipitated from the reaction-mixture by addition of alcohol. It is crystalline, and has a density of 2·296. The heat of formation from the elements is 397·21 Cal.[7]

Potassium pentathionate, $K_2S_5O_6$.—The pentathionate and tetrathionate are produced simultaneously by concentrating a solution of sulphurous acid saturated with hydrogen sulphide, filtering off the precipitated sulphur, and adding the calculated quantity of potassium acetate. The salts are separated mechanically by means of a mixture of bromoform and xylene in such proportions as to cause the pentathionate to float and the tetrathionate to sink. The pentathionate has a density of 2·1123 at 20° C. Its heat of formation is 390·1 Cal.[9]

An unstable *hexathionate* is said to have been isolated from the mother-liquor obtained in the preparation of the pentathionate.[10]

In general character the potassium polythionates resemble the corresponding sodium salts.

Potassium hyposulphite, $K_2S_2O_4$.—The hyposulphite is obtained in the form of trihydrate by a method analogous to that employed for the sodium salt. A solution of potassium sulphite containing free sulphurous acid is treated with zinc-dust, and filtered after precipitation of the zinc by addition of slaked lime. On mixing the solution with alcohol, the trihydrate is deposited in very unstable yellow crystals. When boiled with acetone or methyl alcohol and dried in vacuum, they

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[1] Elbs and Neher, *Chem. Zeit.*, 1921, 45, 1113.
[2] Berthelot, *Ann. Chim. Phys.*, 1889, [6], 17, 468.
[3] Berthelot, *ibid.*, 1876, [5], 9, 157.
[4] Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 299.
[5] Thomsen, *Thermochemistry* (Longmans, 1908), 250.
[6] Heeren, *Pogg. Annalen*, 1826, 7, 72.
[7] Thomsen, *Thermochemistry* (Longmans, 1908), 328.
[8] Berthelot, *Ann. Chim. Phys.*, 1889, [6], 17, 449.
[9] Berthelot, *ibid.*, 468.
[10] Debus, *Annalen*, 1888, 244, 110.

yield the anhydrous salt in the form of very stable white crystals,[1] also produced by the interaction of sulphur dioxide and potassium hydride.[2]

Potassium selenides.—The *monoselenide*, K_2Se, is formed by the action of selenium on excess of potassium dissolved in liquid ammonia; with excess of selenium the *tetraselenide*, K_2Se_4, is produced.[3] Each compound resembles the corresponding sodium derivative. With solutions of potassium carbonate, hydrogen selenide reacts forming a number of hydrates of the monoselenide. The heat of formation of the anhydrous mono-derivative is given as 79·4 Cal.[4] The *triselenide* has been isolated,[5] and Fabre has also described the *primary selenide*, KSeH.

Potassium selenites.—Little is known of the selenites, but a *normal selenite*, a *primary selenite*, and a *pyroselenite* have been described.[6]

Potassium selenate, K_2SeO_4.—Electrolytic oxidation of the solution of selenite formed by the interaction of selenious acid and potassium carbonate yields potassium selenate,[7] rhombic crystals[8] of density[9] 3·066 at 20° C. At the same temperature its solubility is 111 grams per 100 grams of water.[10] Electrolytic oxidation of its solution acidified with selenic acid converts the selenate into *potassium perselenate*.[11]

Potassium tellurides.—The *monotelluride*, K_2Te, was originally produced by Davy[12] by direct combination of the elements. At 250° C. the reaction is even more energetic than that between sodium and tellurium. When prepared in an atmosphere of hydrogen, the product has a crystalline structure, and a dark iridescent-purple colour. With water it yields a purple solution, being reprecipitated by alcohol in the form of small, ill-defined crystals.[13]

The monotelluride and the *tritelluride*, K_2Te_3, have been prepared by the interaction of tellurium and a solution of potassium in liquid ammonia.[14]

Potassium tellurate,[15] K_2TeO_4.—At 20° C. the solubility of the tellurate is 27·53 grams per 100 grams of water.[16]

Potassium chromates.—The modes of preparation and an account of the properties of potassium chromate and dichromate are given in Volume VII.

Potassium nitride, K_3N.—The nitride is said[17] to be formed by heating potassamide, but the statement has not been confirmed by the

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[1] Bazlen, *Ber.*, 1905, 38, 1057; *German Patent*, No. 119676.

[2] Moissan, *Compt. rend.*, 1902, 135, 647.

[3] Hugot, *ibid.*, 1899, 129, 299.

[4] Fabre, *Ann. Chim. Phys.*, 1887, [6], 10, 506.

[5] Clever and Muthmann, *Zeitsch. anorg. Chem.*, 1895, 10, 117.

[6] Compare Muthmann and Schäfer, *Ber.*, 1893, 26, 1014.

[7] Müller, *Ber.*, 1903, 36, 4262.

[8] For isomorphism, see p. 227.

[9] Tutton, *Trans. Chem. Soc.*, 1897, 71, 846.

[10] Étard, *Ann. Chim. Phys.*, 1894, [7], 2, 550; compare Tutton, *loc. cit.*

[11] Dennis and Brown, *J. Amer. Chem. Soc.*, 1901, 23, 358.

[12] Davy, *Phil. Trans.*, 1810, 27, 16.

[13] Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 902.

[14] Hugot, *Compt. rend.*, 1899, 129, 388.

[15] On potassium tellurite, compare Lenher and Wolensky, *J. Amer. Chem. Soc.*, 1913, 35, 718.

[16] Rosenheim and Weinheber, *Zeitsch. anorg. Chem.*, 1911, 69, 261.

[17] Gay-Lussac and Thénard, *Recherches physico-chimiques*, 1811, 1, 337; Davy, *Phil. Trans.*, 1809, 40, 150.

results of more recent investigation.[1] Although Fischer and Schröter [2] claim to have prepared it, they give no analyses or formula.

Potassium hydrazoate, KN_3.—On concentrating a solution of hydrazoic acid neutralized with potassium hydroxide, the hydrazoate separates in doubly refracting crystals. It is not very explosive, but melts and decomposes above 350° C. The aqueous solution has a slight alkaline reaction, the solubility at 17° C. being 49·6 grams per 100 grams of water.[3]

Potassamide, KNH_2.—Gaseous ammonia reacts with fused potassium to form potassamide, and it is also produced by the interaction of potassium hydride and liquefied ammonia.[4] It is a white substance, melting at 338° C.[5] At 400° to 500° C. it volatilizes in a current of hydrogen. It reacts with water to form potassium hydroxide and ammonia.

Potassium hyponitrite, $K_2N_2O_2$.—The hyponitrite can be prepared from potassium nitrite by reduction with potassium-amalgam, or electrolytically.[6] Its heat of formation in aqueous solution is 116·2 Cal.[7]

Potassium nitrite, KNO_2.—The nitrite is made by the reduction of potassium nitrate by heating it alone, or with metals such as lead and iron, or with substances containing sulphur or carbon. It is also formed from potassium nitrate by electrolysis with a silver cathode and a copper anode, the yield being almost quantitative.[8] The pure salt can be obtained by precipitating the aqueous solution with methyl alcohol.[9] Another method for the production of the nitrite depends on the double decomposition of silver nitrite and lithium chloride.[10]

The pure, anhydrous nitrite is not hygroscopic, but as usually prepared the substance is a very deliquescent, crystalline solid, its aqueous solution having a slight alkaline reaction. At 15·5° C. the solubility is 300 grams per 100 grams of water.[11] The heat of formation in aqueous solution from the elements is 88·9 Cal.[12] The products of electrolytic reduction are hyponitrite, ammonia, and hydroxylamine.

At 350° C. potassium nitrite begins to decompose in accordance with the equations

$$3KNO_2=K_2O+KNO_3+2NO\ ;$$
$$5KNO_2=K_2O+3KNO_3+2N.$$

Heating with nitrogen peroxide oxidizes the nitrite to nitrate : [10]

$$KNO_2+NO_2=KNO_3+NO.$$

Potassium nitrite readily reacts with cold sulphuric acid of 17 per cent. strength, yielding a mixture of nitric oxide and higher oxides of

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[1] Titherley, *Trans. Chem. Soc.*, 1894, 65, 511.

[2] Fischer and Schröter, *Ber.*, 1910, 43, 1465.

[3] Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 261; Dennis and Benedict, *Zeitsch. anorg. Chem.*, 1898, 17, 19.

[4] Ruff and Geisel, *Ber.*, 1906, 39, 828.

[5] Wöhler and Stang-Lund, *Zeitsch. Elektrochem.*, 1918, 24, 261; compare Titherley, *Trans. Chem. Soc.*, 1894, 65, 504.

[6] Zorn, *Ber.*, 1879, 12, 1509.

[7] Berthelot, *Ann. Chim. Phys.*, 1889, [6], 18, 574.

[8] Compare Duparc, Couchet, and Schlosser, *Zeitsch. Elektrochem.*, 1906, 12, 665; Müller and Weber, *ibid.*, 1903, 9, 955, 978; Müller and Spitzer, *ibid.*, 1905, 11, 917.

[9] Donath, *Chem. Zeit.*, 1911, 35, 773.

[10] Oswald, *Ann. Chim. Phys.*, 1914, [9], 1, 32.

[11] Divers, *Trans. Chem. Soc.*, 1899, 75, 86.

[12] Berthelot, *Thermochimie*, Paris, 1897, 1, 193.

nitrogen. If the mixed gases are passed through a solution of an alkali-metal hydroxide, pure nitric oxide is isolated. For laboratory purposes this method affords a convenient means of preparing the gas, 10 grams of potassium nitrite producing about 2·5 litres of the oxide.

Potassium nitrate, KNO_3.—The nitrate is manufactured from natural saltpetre earths found in Bengal, and to a less extent in Egypt and elsewhere. The nitrate in these earths is produced by the oxidation of organic matter by the action of " nitrifying " bacteria in presence of atmospheric oxygen, a warm, moist climate being particularly favourable for the process. The nitrate is extracted by lixiviating the earth in vessels of earthenware or wood, and concentrating the aqueous solution in iron pots by solar or artificial heat.

Artificial saltpetre earths can be prepared by allowing stable refuse to nitrify in contact with a porous soil containing calcium carbonate, the nitrate being isolated by lixiviation and purified by crystallization. The salt is also manufactured from sodium nitrate by the action of potassium chloride, since it crystallizes out from a hot concentrated solution of these two substances as the temperature falls. When prepared from Chile saltpetre, it often contains sodium nitrate, and chloride, chlorate, and perchlorate of potassium.

The extraordinary demand for nitric acid and nitrates brought about by the abnormal conditions consequent on the great European War of 1914 and succeeding years gave a powerful impetus to the development of synthetic methods for the fixation of atmospheric nitrogen. For an account of these developments reference should be made to Volume VI. of this series.

At ordinary temperature, potassium nitrate crystallizes in the rhombic system, at higher temperatures the crystals formed are rhombohedral. The transition-point is 129·5° C.[1] The second form is said[2] to exist in two modifications, α and β. Among the values given for the melting-point are 333° C.,[3] 334·5° C.,[4] and 339° C.[5]; for that of the rhombohedral form 334° C.[6] For the density the mean value is given as 2·092,[7] other determinations giving 2·1047,[8] 2·109[9] at 16° C., 2·109[10] at 20° C., and $2{\cdot}044-0{\cdot}0006t$[11] at temperatures ranging from 350° C.[8] 500° C. The heat of formation from the elements is given as 119 Cal.[12] and 119·5 Cal.[13] The molecular electric conductivity of potassium nitrate between 346·1° and 500·4° C. is given by the formula[14]

$$\mu_t=36{\cdot}21+0{\cdot}1875(t-350).$$

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[1] van Eyck, *Zeitsch. physikal. Chem.*, 1905, 51, 721.

[2] Wallerant, *Compt. rend.*, 1905, 140, 264; 1906, 142, 100, 168.

[3] Lorenz, Frei, and Jabs, *Zeitsch. physikal. Chem.*, 1908, 61, 468.

[4] Stern, *ibid.*, 1909, 65, 667; Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[5] van Eyck, *loc. cit.*; Person, *Ann. Chim. Phys.*, 1847, [3], 21, 295; Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[6] Roozeboom, *Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 374.

[7] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 109 and 110.

[8] Andreae, *Zeitsch. physikal. Chem.*, 1913, 82, 109.

[9] Retgers, *ibid.*, 1889, 3, 289.

[10] Haigh, *loc. cit.*

[11] Lorenz, Frei, and Jabs, *loc. cit.*

[12] Berthelot, *Thermochimie*, Paris, 1897, 1, 193.

[13] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 236.

[14] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.

Potassium nitrate does not form hydrates. Its solubility[1] in water increases rapidly with rise of temperature, as indicated by the table:

Solubility of Potassium Nitrate.

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100	110	120	125
Grams KNO_3 in 100 g. of water.	13·3	20·9	31·6	45·8	63·9	85·5	110·0	138	169	202	246	300	394	493

The boiling-point of a solution in contact with excess of salt is 115·55° C. at 760 mm. pressure.[2] The salt exhibits triboluminescence, and is diamagnetic.

On heating, potassium nitrate is converted into the nitrite, with evolution of oxygen. It finds application as an oxidizer, notably in the detonation of gunpowder, the cheaper sodium nitrate being inadmissible on account of its hygroscopic nature. The usual composition of this explosive is 75 per cent. of potassium nitrate, 15 per cent. of carbon, and 10 per cent. of sulphur. In contact with the fused nitrate, carbon and sulphur become ignited, and burn with evolution of the corresponding dioxide and nitrogen, and formation of other products. In dilute solution the nitrate is partially transformed by the action of ultraviolet rays into potassium nitrite and oxygen.[3]

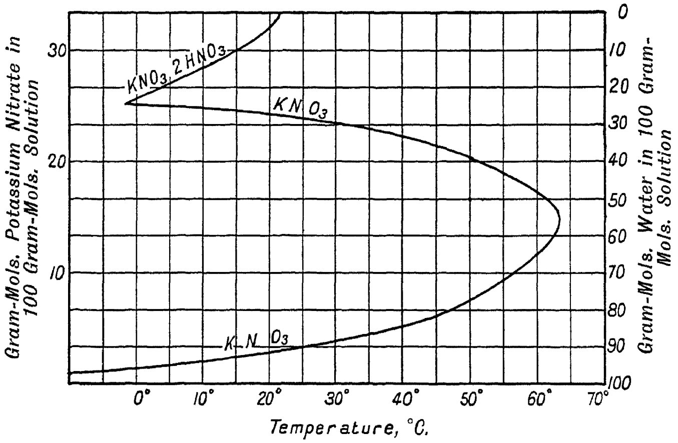

FIG. 11.—Behaviour of $KNO_3,2HNO_3$ with water.

Two *acid potassium nitrates* have been isolated[4]: a dinitrate, $.O_3,HNO_3$, stable at 22° to 28° C., and a trinitrate, $KNO_3,2HNO_3$, melting at 22° C. The behaviour of the trinitrate with water is graphically represented in fig. 11 (compare fig. 12, p. 235).

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[1] Compare Schreinemakers and de Baat, *Zeitsch. physikal. Chem.*, 1909, 65, 553; Andreae, *J. prakt. Chem.*, 1884, [2], 29, 470; Tilden and Shenstone, *Trans. Roy. Soc.*, 1884, 175, 34; Tschugajev and Chlopin, *Zeitsch. anorg. Chem.*, 1914, 86, 154; Findlay, Idwal Morgan, and Morris, *Trans. Chem. Soc.*, 1914, 105, 779.

[2] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489; compare Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207; Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1905, December.

[3] Thiele, *Zeitsch. angew. Chem.*, 1909, 22, 2472.

[4] Groschuff, *Ber.*, 1904, 37, 1489.

Potassium phosphides.—Phosphine reacts with a solution of potassium in liquefied ammonia to form *potassium dihydrophosphide*, KH_2P, white crystals decomposed by moist air with evolution of phosphine.[1] On heating, it is converted into *tripotassium phosphide*, K_3P. A solution of potassium in liquefied ammonia reacts with red phosphorus to form *potassium pentaphosphide*, KP_5.[2] The black product formed from potassium and phosphorus loses its excess of metal in vacuum at 400° to 450° C., yielding *dipotassium pentaphosphide*, K_2P_5. It is a lemon-yellow substance with a density of about 2, is unstable in air, and is decomposed by water with formation of solid phosphorus hydride.[3]

Potassium hypophosphite, KH_2PO_2.—The hypophosphite is formed by the action of phosphorus on alcoholic potash. It resembles the corresponding sodium derivative.

Potassium phosphites and hypophosphates.—*Monopotassium* and *dipotassium hydrogen phosphite*, *potassium pyrophosphite*, and *potassium hypophosphate* are obtained by methods analogous to those employed for the corresponding sodium salts.

Potassium orthophosphates.—The normal salt, *potassium orthophosphate*, K_3PO_4, is obtained by heating basic slag or native calcium phosphate with charcoal and potassium sulphate. The potassium sulphide simultaneously formed is converted into phosphate by addition of phosphoric acid, or the potassium phosphate is precipitated by addition of alcohol. The aqueous solution of the salt is very alkaline in reaction, owing to hydrolytic dissociation. The heat of formation from the elements in solution is 483·6 Cal.[4]

The interaction of the calculated quantities of phosphoric acid and potassium carbonate in aqueous solution yields *dipotassium hydrogen phosphate*, K_2HPO_4. It is only known in solution, and in this form has a slightly alkaline reaction to litmus, but is neutral to phenolphthalein. Its heat of formation in aqueous solution is 429·2 Cal.[4]

Calcium phosphate reacts with potassium hydrogen sulphate and sulphuric acid to form *potassium dihydrogen phosphate*, KH_2PO_4, the most important of the potassium phosphates. It forms doubly refracting crystals melting at 96° C.,[5] of density 2·3325[6] at 9·2° C., and 2·338[7] at 20° C., and of specific heat 0·208 between 17° and 48° C.[8] The heat of formation in aqueous solution is 374·4 Cal.[9] When heated at 244° C., it loses water, yielding the acid pyrophosphate, $K_2H_2P_2O_7$.[10]

Potassium pyrophosphate, $K_4P_2O_7$.—The pyrophosphate is produced by heating dipotassium hydrogen phosphate, or by neutralizing anhydrous phosphoric acid with potassium hydroxide dissolved in absolute alcohol. Its specific heat is 0·1910 between 17° and 98° C.[11] It is soluble in water, forming a slightly alkaline solution, and yields a trihydrate.

Potassium metaphosphates.—In mode of formation and character the

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[1] Joannis, *Compt. rend.*, 1894, 119, 557.
[2] Hugot, *ibid.*, 1895, 121, 206.
[3] Hackspill and Bossuet, *ibid.*, 1912, 154, 209.
[4] Berthelot, *Thermochimie*, Paris, 1897, 1, 193.
[5] Tilden, *Trans. Chem. Soc.*, 1884, 45, 266.
[6] Muthmann, *Zeitsch. Kryst. Min.*, 1894, 22, 497.
[7] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 53.
[8] Kopp, *Annalen Suppl.*, 1864–5, 3, i., 289.
[9] Berthelot, *loc. cit.*
[10] Balareff, *Zeitsch. anorg. Chem.*, 1921, 118, 123.
[11] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

metaphosphates are analogous to the corresponding sodium derivatives. *Potassium metaphosphate*, KPO_3, has a mean density of 2·258 [1] at 14·5° C., and melts at 810° C.[2] It dissolves with difficulty in water.

Potassium arsenite, K_3AsO_3.—The arsenite is very unstable, but from its solution containing excess of arsenious acid *potassium hydrogen diarsenite*, $KHAs_2O_4$ or $K_2H_2As_4O_8$, can be isolated by covering it with a layer of alcohol.[3]

At 25° C. the ternary system *potassium oxide—arsenious oxide—water* indicates the existence of two arsenites of potassium soluble in water without decomposition.[4] They have the formulæ $K_2As_4O_7$ and $K_6As_4O_9,12H_2O$.

Potassium arsenates.—*Potassium arsenate*, K_3AsO_4; *dipotassium hydrogen arsenate*, K_2HAsO_4; and *potassium dihydrogen arsenate*, KH_2AsO_4, have been prepared. Their heats of formation are respectively 396·2 Cal., 339·8 Cal., and 234·0 Cal.[5] The last mentioned has a density of 2·851 at ordinary temperatures,[6] and of 2·8675 at 9·2° C.[7] *Potassium meta-arsenate*, $KAsO_3$, has a specific heat of 0·1563 between 17° and 99° C.[8]

Potassium carbide, K_2C_2.—The carbide is prepared by methods similar to those employed for the sodium compound, and also resembles this substance in properties.

Potassium carbonate, K_2CO_3.—The carbonate is a constituent of the ashes of wood and other vegetable products, and is obtained by extracting with water, the purified product being known as "pearl-ash." The origin of the world "potash" has occasioned some controversy. It has been attributed by some to the name of the chemist Pott (1692–1777), but it appears to have been in use before his birth. Three other explanations have been advanced: the use of pots, and later boilers, in the concentration of the aqueous extract of the crude ashes [9]; the employment of pots in the incineration of the wood [10]; and the fact that ashes collected under the cooking-pots on the hearth fires of the Middle Ages.[11] The first of these three explanations seems to be the most plausible.

Modern manufacturing methods depend on the conversion of potassium chloride into carbonate by electrolysis; by the Le Blanc process; or by the action of magnesium carbonate, carbon dioxide, and water:

$$3MgCO_3+2KCl+CO_2+H_2O=2MgKH(CO_3)_2+MgCl_2.$$

The precipitated double carbonate is decomposed by hot water: [12]

$$2MgKH(CO_3)_2=2MgCO_3+K_2CO_3+CO_2+H_2O.$$

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[1] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 118.

[2] van Klooster, *Zeitsch. anorg. Chem.*, 1910, 69, 122.

[3] Compare Pasteur, *Annalen*, 1848, 68, 309; *J. Pharm. Chim.*, 1848, 13, 397; Stavenhagen, *J. prakt. Chem.*, 1895, 51, 1; Auerbach, *Zeitsch. anorg. Chem.*, 1903, 37, 364.

[4] Schreinemakers and de Baat, *Rec. trav. chim.*, 1920, 39, 423.

[5] Berthelot, *Thermochimie*, Paris, 1897, 1, 193.

[6] Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 121.

[7] Muthmann, *Zeitsch. Kryst. Min.*, 1894, 22, 497.

[8] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[9] von Lippman, *Chem. Zeit.*, 1908, 32, 977; König, *ibid.*, 1140.

[10] Reisenegger, *ibid.*, 1071.

[11] Witt, *ibid.*, 1029.

[12] Auerbach, *Zeitsch. Elektrochem.*, 1904, 10, 161.

Potassium carbonate is also manufactured from the spent wash of the spirit-distiller, and from the residual liquor of the wool-scourer.

Potassium carbonate is a white solid. Its melting-point is given by various experimenters as 878·6° C.,[1] 880° C.,[2] 885° C.,[3] 873·1° C., 887·5° C., 891° C.,[4] 894° C.,[5] 897·3° C., 897·7° C.,[6] 900° C.[7] For the density the mean value is given[8] as 2·29; a more recent determination[9] gives 2·3312 at 17° C. Its specific heat is 0·206 between 17° and 47° C.,[10] and 0·2162 between 23° and 99° C.[11] At 970° C. the vapour-pressure is 1·68 mm.; and at 1130° C. it is 5·0 mm.[12] The heat of formation from the elements is recorded as 275·37 Cal.,[13] 278·8 Cal.,[14] and 281·1 Cal.[15] Potassium carbonate exhibits diamagnetism.

Several hydrates have been described, but their constitutions are not definitely settled.[16] At 25° C. the solubility is 113·5 grams per 100 grams of water,[16] and at 130° C. it is 196 grams.[17] The aqueous solution has a strong alkaline reaction, due to hydrolytic dissociation. It forms various primary carbonates by interaction with atmospheric carbon dioxide,[18] and unites with hydrogen peroxide yielding compounds of the formulæ $K_2CO_3,3H_2O_2$ and $K_2CO_3,2H_2O_2,\frac{1}{2}H_2O$.[19]

Potassium sodium carbonate, $K_2CO_3,Na_2CO_3,12H_2O$.—A double salt of this formula is a constituent of vegetable ashes. At 35° C. it decomposes in accordance with the equation

$$3(K_2CO_3,Na_2CO_3,12H_2O)=2K_2CO_3+K_2CO_3,3Na_2CO_3,10H_2O+26H_2O.$$

The double carbonate thus generated decomposes at a temperature of about 130° C.[20]

Potassium hydrogen carbonate, $KHCO_3$.—Carbon dioxide precipitates the primary carbonate from a concentrated solution of potassium carbonate in the form of monoclinic crystals of density[21] 2·17. The heat of formation from the elements is given as 231·63 Cal.[22] and 233·3 Cal.[23] In dilute aqueous solution it has an alkaline reaction, owing to hydrolytic dissociation in accordance with the equation

$$KHCO_3+H_2O=KOH+H_2O+CO_2.$$

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[1] Victor Meyer, Riddle, and Lamb, *Ber.*, 1893, 26, 3129.

[2] Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

[3] Le Chatelier, *Bull. Soc. chim.*, 1887, [2], 47, 300.

[4] Niggli, *J. Amer. Chem. Soc.*, 1913, 35, 1693.

[5] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[6] McCrae, *Wied. Annalen*, 1895, 55, 95.

[7] Arndt, *Zeitsch. Elektrochem.*, 1906, 12, 337.

[8] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 126; Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

[9] Earl of Berkeley, *Proc. Chem. Soc.*, 1906, 22, 321.

[10] Kopp, *Annalen Suppl.*, 1864–5, 3, i., 289.

[11] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[12] Jackson and J. J. Morgan, *J. Ind. Eng. Chem.*, 1921, 13, 110.

[13] de Forcrand, *Compt. rend.*, 1909, 149, 719.

[14] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 111.

[15] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 236.

[16] Meyerhoffer, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 542.

[17] Mulder, *Scheikunde*, Rotterdam, 1864, 97.

[18] de Forcrand, *Compt. rend.*, 1909, 149, 719, 825.

[19] Kazanesky, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 388.

[20] Bain and Oliver, *Trans. Roy. Soc. Canada*, 1916, [3], 10, 65.

[21] Compare Clarke, *Constants of Nature*, 2nd. ed., Washington, 1888, 1, 129; Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873.

[22] de Forcrand, *loc. cit.*

[23] Berthelot, *loc. cit.*

The solubility in water at 20° C. is stated to be 26·31 grams per 100 grams of water,[1] and also 33·2 grams.[2] On heating, the salt is converted into the normal carbonate:

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O.$$

The dissociation-pressure has been investigated by Caven and Sand.[3]

Potassium percarbonate, $K_2C_2O_6$.—Electrolysis of a solution of the normal carbonate between —30° and 40° C. yields a 90 per cent. percarbonate,[4] a very unstable substance, readily converted into the primary carbonate and oxygen. It is a white, crystalline powder, and is decomposed energetically by water with evolution of oxygen.[5]

Potassium thiocarbonate, K_2CS_3.—The interaction of potassium sulphide and carbon disulphide produces the thiocarbonate, a yellow substance very soluble in water.[6]

Potassium cyanide, KCN.—The cyanide is manufactured by methods similar to those employed for the corresponding sodium derivative. Potassium ferrocyanide is heated either in absence of air, or with potassium carbonate and charcoal, or with sodium, the potassium cyanide being extracted by lixiviation with water or dilute alcohol. It is also obtained by the action of a mixture of steam and nitrogen on potassium carbonate or carbide,[7] the manufacture of cyanides by the aid of atmospheric nitrogen being now an important industrial process.

The salt forms colourless cubes melting at 601·2° C.,[8] and of density[9] 1·52. The heat of formation from the elements is given as 30·1 Cal.[10] and 32·5 Cal.[11] A solution in contact with excess of salt boils at 103·3° C. and contains 122·2 grams per 100 grams of water at that temperature.[12] Owing to hydrolytic dissociation the aqueous solution has an odour of hydrocyanic acid and a strongly alkaline reaction.[13] No hydrate has been isolated. Oxidation with sodium hypobromite converts the salt into cyanate, formate, and carbonate.[14] Its strong reducing power at elevated temperatures renders it a valuable reagent in blowpipe analysis.

With gold, potassium cyanide forms complex derivatives, and it is employed in the extraction of the metal (p. 324). As a double cyanide with other metallic cyanides, such as those of silver, gold, and nickel, it is an important reagent in electroplating. It is also employed in photography. Like hydrocyanic acid, it is extremely poisonous.

Potassium thiocyanate, KCNS.—The thiocyanate is formed by fusing potassium cyanide with sulphur, or a mixture of potassium

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[1] de Forcrand, *Compt. rend.*, 1909, 149, 719, 825.

[2] Dibbits, *J. prakt. Chem.*, 1874, [2], 10, 439.

[3] Caven and Sand, *Trans. Chem. Soc.*, 1914, 105, 2753.

[4] Riesenfeld and Reinhold, *Ber.*, 1909, 42, 4377; compare Constam and Hansen, *Zeitsch. Elektrochem.*, 1896, 3, 137; Brown, *J. Amer. Chem. Soc.*, 1905, 27, 1222.

[5] Compare Biltz and Gahl, *Zeitsch. Elektrochem.*, 1905, 11, 409.

[6] Compare Delachanal, *Ann. Chim. Phys.*, 1877, [5], 12, 141.

[7] Caro and Frank, *German Patents*, 1895, Nos. 88363 and 92587; 1896, No. 95660.

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

[9] Bödeker, *Jahresber.*, 1860, 17.

[10] Berthelot, *Thermochimie*, Paris, 1897, 1, 195.

[11] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 467.

[12] Griffiths, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 542.

[13] Compare Shields, *Zeitsch. physikal. Chem.*, 1893, 12, 167; James Walker, *ibid.*, 1900, 32, 137.

[14] Dehn, *J. Amer. Chem. Soc.*, 1909, 31, 1220.

ferrocyanide and potassium carbonate with the same reagent. The colourless, deliquescent crystals melt[1] at 161·2° or 172·3° C., their density being 1·886.[2] At 430° C. the salt develops a blue colour, but becomes white again on cooling. The heat of formation from the elements is 50·5 Cal.,[3] and at 20° C. the solubility[4] is 217 grams per 100 grams of water. Sulphur dioxide reacts with it in aqueous solution to form a complex derivative.[5] Sodium hypobromite reacts energetically with potassium thiocyanate, evolving heat and forming potassium cyanate and sulphate.[6]

Potassium ferrocyanide and ferricyanide.— The modes of preparation and the properties of potassium ferrocyanide, of potassium ferricyanide, and of similar salts are described in Vol. IX., Part II.

Potassium silicates.—Potash water-glass is prepared similarly to the corresponding sodium product. When the calculated proportion of potassium hydroxide and silicic acid is employed, addition of alcohol to the solution precipitates *potassium metasilicate*, K_2SiO_3. When kept for a prolonged period over sulphuric acid, the syrup-like potash water-glass deposits hygroscopic plates, probably $K_4SiO_4,2KOH,8H_2O$.[7]

Niggli[8] has demonstrated that on fusion of potassium carbonate and silica an equilibrium between the disilicate (see below) formed and the carbonate is attained :

$$K_2CO_3+K_2Si_2O_5 \rightleftharpoons 2K_2SiO_3+CO_2.$$

With rise of temperature the proportion of metasilicate increases.

By heating mixtures of water and finely powdered glasses at high temperatures, Morey and Fenner[9] have prepared *potassium hydrogen disilicate*, $KHSi_2O_5$, in the form of orthorhombic crystals which do not lose water even at 350° C.; and *potassium disilicate*, $K_2Si_2O_5$, a hygroscopic salt readily acted upon by water, and melting at 1015°±10° C.[8]

Potassium fluosilicate, K_2SiF_6.—The fluosilicate is precipitated in the form of microscopic crystals of slight solubility by the action of fluosilicic acid on solutions of potassium salts :

$$H_2SiF_6+2KCl=K_2SiF_6+2HCl.$$

It is decomposed by alkali-metal hydroxides with formation of a fluoride and silicic acid, and can be estimated by this method with phenolphthalein as indicator :

$$4KOH+K_2SiF_6=6KF+H_4SiO_4.$$

Potassium hypoborate, KH_3OB.—The hypoborate is a very deli-

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[1] Pohl, *Sitzungsber. K. Akad. Wiss. Wien*, 1851, 6, 587; Paternò and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [5], 16, i., 465.

[2] Bödeker, *Jahresber.*, 1860, 17.

[3] Joannis, *Ann. Chim. Phys.*, 1882, [5], 26, 482.

[4] Rüdorff, *Pogg. Annalen*, 1872, 145, 611; compare H. W. Foote, *Amer. Chem. J.*, 1903, 30, 330.

[5] Walden, *Ber.*, 1899, 32, 2862; Fox, *Zeitsch. physikal. Chem.*, 1902, 41, 458; Walden and Centnerszwer, *ibid.*, 1903, 42, 456; Smits, *ibid.*, 1905, 51, 193.

[6] Dehn, *J. Amer. Chem. Soc.*, 1909, 31, 1220.

[7] Jordis, *Zeitsch. anorg. Chem.*, 1908, 58, 98.

[8] Niggli, *J. Amer. Chem. Soc.*, 1913, 35, 1693.

[9] Morey and Fenner, *ibid.*, 1914, 36, 215.

quescent substance, formed by the interaction of boron hydride, B_4H_{10}, and a very concentrated solution of potassium hydroxide :[1]

$$B_4H_{10}+4KOH=4KH_3OB+H_2.$$

The hydride of the formula B_2H_6 acts similarly :

$$B_2H_6+2KOH=2KH_3OB+H_2.$$

Potassium borates.—Fusion of boron trioxide with the equivalent proportion of potassium carbonate yields the *metaborate*, KBO_2, white, monoclinic crystals[2] melting at 947° C., and of specific heat[3] 0·2248 between 16° and 98° C. It dissolves in water, forming a strongly alkaline solution, from which a 1·5-hydrate[4] and a 1·25-hydrate[5] are said to crystallize. At 0° C. Rosenheim and Leyser[6] observed the formation of crystals with $4H_2O$, and at 30° C. that of crystals with $1{\cdot}25H_2O$. The salt is gradually transformed by atmospheric carbon dioxide into the tetraborate and carbonate.

Dipotassium tetraborate, $K_2B_4O_7$, of specific heat[7] 0·2198 between 18° and 99° C., has been isolated[8] in the form of hydrates, and a *pentaborate*, $KB_5O_8,4H_2O$, has also been prepared. This pentaborate separates from solutions in which the ratio

$$B_2O_3 : KOH=3 : 1$$

or higher. Its solubility is only slightly greater than that of potassium perchlorate.[9]

Potassium perborates.—Potassium forms perborates by reactions similar to those employed for the preparation of the corresponding salts of sodium.[10] A perborate of the formula $KBO_3,\frac{1}{2}H_2O$ is precipitated as a crystalline powder by the interaction of a solution of potassium metaborate and 3 per cent. hydrogen peroxide. At 15° C. 100 grams of water dissolve 2·5 grams of the salt. In warm water it undergoes partial decomposition into boric acid, potassium hydroxide, and hydrogen peroxide. At ordinary temperature the dry salt is stable, but it decomposes suddenly between 150° and 160° C., leaving a residue of metaborate, and evolving oxygen.

A perborate with similar properties and the formula $KBO_3,\frac{1}{2}H_2O_2$ is produced by the action of 30 per cent. hydrogen peroxide on potassium metaborate. At 15° C. its solubility is 0·70 gram per 100 grams of water.

DETECTION AND ESTIMATION OF POTASSIUM.

Potassium salts impart a violet coloration to the Bunsen flame, the tint appearing reddish-violet through an indigo-prism or blue glass.

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

[2] van Klooster, *Zeitsch. anorg. Chem.*, 1910, 69, 122.

[3] Regnault, *Pogg. Annalen*, 1841, 53, 60, 243.

[4] Atterberg, *Öfers. Vetensk. Akad. Förhandl.*, 1874, No. 6, 16 ; *Zeitsch. anorg. Chem.*, 1906, 48, 367.

[5] Dukelski, *Zeitsch. anorg. Chem.*, 1906, 50, 38.

[6] Rosenheim and Leyser, *ibid.*, 1921, 119, 1.

[7] Regnault, *loc. cit.*

[8] Atterberg, *Zeitsch. anorg. Chem.*, 1906, 48, 367 ; Dukelski, *loc. cit.*

[9] Rosenheim and Leyser, *loc. cit.*

[10] Compare Girsewald and Wolokitin, *Ber.*, 1909, 42, 865.

The test serves to identify potassium in presence of sodium. The metal is detected and estimated quantitatively by precipitation with chloroplatinic acid as potassium chloroplatinate, K_2PtCl_6, or by conversion into perchlorate. The insolubility of these salts in alcohol facilitates the separation of potassium from sodium.[1] Acetone has the advantage of dissolving both chloroplatinic acid and sodium chloroplatinate, but not the potassium salt.[2] The metal is also estimated as sulphate, chloride, primary tartrate,[3] and cobaltinitrite.[4]

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[1] Morozewicz, *Bull. Acad. Sci. Cracow*, 1906, 796.

[2] Meillère, *J. Pharm. Chim.*, 1913, [7], 7, 281.

[3] Compare Marshall, *Chem. Zeit.*, 1914, 38, 585, 615.

[4] Compare Mitscherlich and Fischer, *Landw. Versuchs-Stat.*, 1912, 78, 75; van den Bos, *Chem. Weekblad*, 1913, 10, 182; McDougall, *J. Amer. Chem. Soc.*, 1912, 34, 1684; Burgess and Kamm, *ibid.*, 652; Zaleski, *Landw. Versuchs-Stat.*, 1913, 83, 221. On the separation of potassium from rubidium and cæsium, compare Wernadski, *Bull. Soc. franç. Min.*, 1913, 36, 258.

CHAPTER VI.

RUBIDIUM.

Symbol, Rb. Atomic weight, 85·45 (O=16).

Occurrence.—Rubidium is widely distributed in nature, being found in small quantities in association with the other alkali-metals. It constitutes about 1 per cent. of lepidolite, and is present in the Stassfurt salt deposits, in the soil, in many natural waters, and in the ashes of numerous plants.

History.—Rubidium was discovered[1] by the aid of the spectroscope in 1861 in the mineral water of Dürkheim, and also in lepidolite. Its name is derived from the two dark red lines in its spectrum (*rubidus*, dark-red).

Preparation.—The main source of rubidium compounds is the residual mother-liquor obtained in the extraction of potassium chloride from carnallite. The solution contains *rubidium-carnallite*, $RbCl,MgCl_2$, a substance transformed by addition of aluminium sulphate into *rubidium-alum*, $RbAl(SO_4)_2,12H_2O$. Separation from the potassium and cæsium salts also present is effected by fractional crystallization of the alum,[2] of the chloroplatinate[3] Rb_2PtCl_6, of rubidium-iron-alum,[4] and of the double chloride with stannous chloride[5] or with antimony trichloride.[6]

The metal can be isolated by ignition of the tartrate, the carbon liberated by the decomposition of the tartaric acid radical reducing the carbonate simultaneously formed; from the chloride by electrolysis in the fused state,[7] or by the action of calcium[8]; and from the hydroxide by electrolysis,[9] or by reduction with magnesium.[10]

Physical Properties.—Rubidium is a silver-like metal of lustrous appearance, but rapidly tarnishes through atmospheric oxidation. It is the softest metal, except cæsium, its hardness on Rydberg's scale being

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[1] Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 342; 1863, 119, 1; *Annalen*, 1862, 122, 347; 1863, 125, 367.

[2] Redtenbacher, *J. prakt. Chem.*, 1865, 95, 148.

[3] Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 373.

[4] Erdmann, *Arch. Pharm.*, 1894, 232, 3.

[5] Sharples, *Amer. J. Sci.*, 1869, [2], 47, 178; Stolba, *Dingler's Polytech. J.*, 1870, 197, 336; 198, 225.

[6] Muthmann, *Ber.*, 1893, 26, 1019; compare Godeffroy, *Ber.*, 1874, 7, 241; Wells, *Zeitsch. anorg. Chem.*, 1893, 4, 344.

[7] Bunsen and Kirchhoff, *loc. cit.*

[8] Hackspill, *Compt. rend.*, 1905, 141, 106; *Bull. Soc. chim.*, 1911, [4], 9, 446.

[9] Hevesy, *Zeitsch. anorg. Chem.*, 1910, 67, 242.

[10] Graefe and Eckardt, *ibid.*, 1899, 22, 158; Erdmann and Köthner, *Annalen*, 1897, 294, 56.

0·3. Its melting-point is given as 37·0° C.,[1] 37·8° C.,[2] 38° C.,[3] 38·5 C.,[4] and 39° C.,[5] and its boiling-point as 696° C. at 760 mm. pressure,[6] the vapour being greenish-blue in colour. At 180° C. the vapour has a purple-red colour, which changes to orange above 350° C.[7] Its density is given as 1·52 (Bunsen and Kirchhoff[8]), 1·5248 at 0° C. (Hackspill[9]), 1·522 at 15° C. (Erdmann and Köthner[10]), and 1·532 at 20° C. (Richards and Brink[11]). The table on p. 2 indicates that in melting-point and density rubidium and cæsium are more closely related to one another than to the other alkali-metals, and a similar resemblance has been observed regarding the crystallography of the salts of the two metals.[12] According to Rengade,[13] the specific heat of the solid at its melting-point is 0·019, and the heat of fusion per gram is 0·00615 Cal.

Several rubidium salts exhibit radioactivity,[14] among them the sulphate,[15] chloride, and chlorate.[16] The action of the sulphate on the photographic plate is more powerful than that of potassium sulphate.[17]

Chemical Properties.—In its chemical character rubidium occupies a position intermediate between potassium and cæsium. It combines with atmospheric oxygen and decomposes water more energetically than potassium, and the bright metal ignites spontaneously in dry oxygen. It begins to react with ice at —108° C.[18] When dissolved in liquid ammonia, the metal combines with ozone.[19] Some of its salts are poisonous.

Rubidium Ion.—The univalent metal yields univalent ions, analogous to those of potassium, but has a greater electroaffinity, its salts being more readily ionized. This property manifests itself in the large heat of ionization,[20] 62·6 Cal., in the ready solubility of most of its salts, and in the comparatively slight tendency to form complex molecules.[21] Only salts with strong anions, such as ClO_3', ClO_4', NO_3', $Al(SO_4)_2'$, and $PtCl_6''$, exhibit slight solubility.

Atomic Weight.—Like the other alkali-metals, rubidium is univalent, forming compounds of the type RbX, so that its hydrogen equivalent

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[1] Guntz and Broniewski, *J. Chim. phys.*, 1909, 7, 464.

[2] Eckardt, *Ann. Physik*, 1900, 1, 790.

[3] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

[4] Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 373; Erdmann and Köthner, *Annalen*, 1897, 294, 56.

[5] Rengade, *Compt. rend.*, 1913, 156, 1897; *Bull. Soc. chim.*, 1914, [4], 15, 130.

[6] Ruff and Johannsen, *Ber.*, 1905, 38, 3601.

[7] Dunoyer, *Le Radium*, 1912, 9, 218.

[8] Bunsen and Kirchhoff, *loc. cit.*

[9] Hackspill, *Compt. rend.*, 1911, 152, 259.

[10] Erdmann and Köthner, *loc. cit.*

[11] Richards and Brink, *J. Amer. Chem. Soc.*, 1907, 29, 117.

[12] Tutton, *Trans. Chem. Soc.*, 1897, 71, 846; *Zeitsch. Kryst. Min.*, 1898, 29, 124; Sachs, *ibid.*, 1903, 38, 496; Marshall, *J. Amer. Chem. Soc.*, 1900, 22, 48.

[13] Rengade, *Bull. Soc. chim.*, 1914, [4], 15, 130.

[14] Hahn and Rothenbach, *Physikal. Zeitsch.*, 1919, 20, 194.

[15] Campbell, *Proc. Camb. Phil. Soc.*, 1909, 15, 11.

[16] Strong, *Amer. Chem. J.*, 1909, 42, 147.

[17] Büchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 18, 91; compare Elster and Geitel, *Physikal. Zeitsch.*, 1910, 11, 275; Henriot, *Le Radium*, 1910, 7, 40; *Compt. rend.*, 1911, 152, 851.

[18] Hackspill and Bossuet, *Compt. rend.*, 1911, 152, 874.

[19] Compare sodium, p. 86.

[20] Ostwald, *Grundriss der allgem. Chem.*, 3rd ed., Leipsic, 1899, 281.

[21] Compare Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, 20, 462; Erdmann, *Arch. Pharm.*, 1894, 232, 25.

is the same as its atomic weight. Its properties and those of its compounds indicate it to be a member of the first group of the periodic system, with an atomic weight of the order Rb=85. This view finds confirmation in the isomorphism of its salts with those of potassium and cæsium (Vol. I., p. 74); in the close approximation in the molecular heats of the carbonate and chloride to those of the corresponding salts of sodium and potassium; and in the depression of the freezing-points of such solvents as bismuth chloride and mercuric chloride produced by rubidium chloride.

The various attempts to determine the atomic weight of rubidium are given in the appended table. The values computed for the atomic weight as given in the last column are not in the original memoirs, but have been calculated from the ratios in the adjoining column, employing for the purpose the modern atomic weights of silver, chlorine, and bromine, Ag=107·880, Cl=35·457, and Br=79·916. This method facilitates direct comparison of the results of the early investigators with the values at present accepted.

Investigator.	Number of Experiments.	Mean Values of Ratios determined.	Atomic Weight of Rubidium.
Bunsen[1] .	4	AgCl : RbCl =100 : 84·253	85·31
Piccard[2] .	4	AgCl : RbCl =100 : 84·290	85·36
Godeffroy[3] .	4	AgCl : RbCl =100 : 84·3345	85·43
Heycock[4] .	..	Ag : RbCl =100 : 111·925	85·28
,, .	2	Ag : RbBr=100 : 153·238	85·40
Archibald[5] .	14	AgCl : RbCl =100 : 84·3485	**85·448**
,, .	14	Ag : RbCl =100 : 112·0545	85·430
,, .	7	AgBr : RbBr=100 : 88·0533	**85·447**
,, .	7	Ag : RbBr=100 : 153·283	**85·448**

The most reliable results are those of Archibald shown in heavy-face type, the mean value for the atomic weight of rubidium being 85·448.[6]

The current table of the International Committee on Atomic Weights gives the value

Rb=85·45.

COMPOUNDS OF RUBIDIUM.[7]

Rubidium hydride, RbH.—The hydride has been prepared[8] by a method analogous to that employed for sodium hydride. It can also be produced by heating rubidium carbonate with metallic magnesium in an

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[1] Bunsen, *Pogg. Annalen*, 1861, 113, 339.

[2] Piccard, *J. prakt. Chem.*, 1862, 86, 449.

[3] Godeffroy, *Annalen*, 1876, 181, 180.

[4] Heycock, *Brit. Assoc. Reports*, 1882, 449.

[5] Archibald, *Trans. Chem. Soc.*, 1904, 85, 776.

[6] Compare Brauner, *Abegg and Auerbach's Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, 421.

[7] For *rubidium-amalgam*, see this series, Vol. III.

[8] Moissan, *Compt. rend.*, 1903, 136, 587, 1177.

atmosphere of hydrogen at 650° C. for five days.[1] It is a white, crystalline substance,[2] with density about 2. The vapour-tension for each temperature-interval of 10° between 350° and 450° C. corresponds with the values 100, 114, 130, 160, 200, 253, 322, 424, and 567 mm. respectively. A possible source of error may be the presence of carbon dioxide as the result of decomposition of the magnesium carbonate formed; but soda-lime was employed to absorb any carbon dioxide liberated, and the measurements were made rapidly.[1] The tension increases rapidly to 85 mm. at 230° C., and then slowly to 100 mm. at 370° C.

This hydride is more stable than that of cæsium, but less stable than that of sodium or of potassium.[2] It is very reactive. When heated in vacuum at 300° C. it decomposes into its constituent elements. At ordinary temperatures it is attacked by the halogens. Carbon dioxide converts it into rubidium formate:

$$RbH+CO_2=H{\cdot}COORb.$$

Under reduced pressure sulphur dioxide converts it into rubidium hyposulphite, $Rb_2S_2O_4$.

Rubidium fluoride, RbF.—The fluoride is obtained in anhydrous crystals by concentrating a solution of sodium carbonate neutralized with hydrofluoric acid.[3] Its melting-point is given as 753° C.[4] and 775° C.[5] The boiling-point is 1410° C., and the vapour-pressure in atmospheres is given by the expression [6]

$$\log p=-40000/4{\cdot}57T+5{\cdot}243.$$

It is very soluble in water, its heat of solution[7] being 5·80 Cal. Two hydrates are known,[8] $2RbF,3H_2O$, which melts at 36° C., and $RbF,3H_2O$. They are very hygroscopic. With hydrogen fluoride the fluoride yields the *primary salt* RbF,HF. Other acid fluorides, RbF,2HF, and RbF,3HF, have also been prepared.

Rubidium chloride, RbCl.—The chloride is produced by the interaction of hydrochloric acid and rubidium carbonate, and also by heating rubidium chloroplatinate. It forms lustrous cubes, stated to melt at 710° C.,[9] 712° to 713° C.,[10] 713° C.,[11] 714° C.,[12] 717° C.,[13] and 726° C.,[14] and to boil at 1383° C.[15] The vapour-pressure in atmospheres is given by the expression [15]

$$\log p=-37800/4{\cdot}57T+4{\cdot}998.$$

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[1] Ephraim and Michel, *Helv. Chim. Acta*, 1921, 4, 762.

[2] Elster and Geitel, *Physikal. Zeitsch.*, 1910, 11, 257.

[3] Eggeling and Julius Meyer, *Zeitsch. anorg. Chem.*, 1905, 46, 174.

[4] Carnelley, *Trans. Chem. Soc.*, 1898, 33, 273.

[5] Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and Wartenberg, *ibid.*, 162.

[6] Wartenberg and Schulz, *loc. cit.*

[7] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[8] de Forcrand, *ibid.*, 1208.

[9] Carnelley, *loc. cit.*

[10] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[11] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[12] Richards and Meldrum, *ibid.*, 1917, 39, 1816.

[13] Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and Wartenberg, *ibid.*, 162.

[14] Schemtschushny and Rambach, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1785.

[15] Wartenberg and Schulz, *loc. cit.*

Its density is recorded as 2·209,[1] 2·706 at 22·9° C. (Buchanan [2]), and 2·762 at 20° C. (Haigh [3]). Its specific heat is 0·112 between 16° and 45° C.,[4] and the latent heat of fusion per gram is 0·038 Cal.[5] The heat of formation in aqueous solution from the elements is 105·94 Cal.[6] The salt does not form hydrates, but is very soluble in water.[7]

Solubility of Rubidium Chloride.

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100
Grams of RbCl per 100 grams of water.	77·0	84·4	91·1	97·6	103·5	109·3	115·5	121·4	127·2	133·1	138·9

The boiling-point of the saturated solution in contact with excess of the salt is 113·71° C. at 760 mm. pressure,[8] and the heat of solution is —4·5 Cal.[9] At 25° C. 100 grams of ethyl alcohol dissolve 0·078 gram.[10] The salt unites with free halogens, yielding various *polyhalides*,[11] and also forms double chlorides with other metallic chlorides.[12] It exhibits radioactivity.[13]

Rubidium bromide, RbBr.—The methods for the formation of the bromide are similar to those employed for the production of rubidium chloride. The salt is colourless, crystallizes in cubes, and is stated to melt at 681° C.[14] and 683° C.,[15] and to boil at 1350° C.[16] The vapour-pressure in atmospheres is given by the expression [16]

$$\log p = -36980/4{\cdot}57T + 4{\cdot}964.$$

Its density is given as 2·780,[17] and also 3·210 at 23° C.[18] Bromine is evolved at the melting-point, and is also displaced by the action of iodine.[19] It dissolves in water much more freely than potassium bromide, the solubility at 16° C. being 105 grams in 100 grams of water.[20] The heat of solution is —5·96 Cal.[21] It forms polyhalides, such as $RbBr_3$ and $RbBr_2I$.[22]

Rubidium iodide, RbI.—The iodide is formed by the action of hydriodic acid on rubidium carbonate, and crystallizes in colourless

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[1] Compare Schröder, *Annalen*, 1878, 192, 295.
[2] Buchanan, *Proc. Chem. Soc.*, 1905, 21, 122.
[3] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.
[4] Kopp, *Annalen Suppl.*, 1864–5, 3, i., 289.
[5] Schemtschushny and Rambach, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1785.
[6] de Forcrand, *Compt. rend.*, 1906, 143, 98.
[7] Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207.
[8] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.
[9] de Forcrand, *Compt. rend.*, 1911, 152, 27.
[10] Turner and Bissett, *Trans. Chem. Soc.*, 1913, 103, 1904.
[11] Wells and Wheeler, *Zeitsch. anorg. Chem.*, 1892, 1, 442 ; 2, 257.
[12] Liebisch and Korreng, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 192.
[13] Büchner, *Le Radium*, 1912, 9, 259.
[14] Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568 ; compare Albrecht and Wartenberg, *ibid.*, 162.
[15] Carnelley, *Trans. Chem. Soc.*, 1898, 33, 273.
[16] Wartenberg and Schulz, *loc. cit.*
[17] Compare Schröder, *loc. cit.*
[18] Buchanan, *loc. cit.*
[19] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.
[20] Reissig, *Annalen*, 1863, 127, 34.
[21] de Forcrand, *Compt. rend.*, 1911, 152, 27.
[22] Wells and Wheeler, *loc. cit.*

cubes, its melting-point being given as 641·5° C.[1] and 642° C.[2] The boiling-point is 1305° C.,[3] and the vapour-pressure in atmospheres is given by the expression [3]

$$\log p = -37000/4{\cdot}57T + 5{\cdot}148.$$

Its density is stated to be 3·023,[4] 3·447,[5] 3·428 [6] at 24·3° C., and 3·438 [7] at 25° C. At 17·4° C. its solubility is 152 grams in 100 grams of water,[8] the heat of solution being −6·5 Cal.[9] *Polyiodides* such as RbI_3,[10] RbI_7, and RbI_9[11] have been isolated.

Rubidium chlorate, $RbClO_3$.—The chlorate is obtained by the interaction of rubidium sulphate and barium chlorate. On heating, it decomposes like potassium chlorate. It is less soluble in water than the corresponding potassium salt, the solubility at 19° C. being 5·1 grams in 100 grams of water.[12]

Rubidium perchlorate, $RbClO_4$.—When rubidium chlorate is heated to a moderate temperature, it is converted into a mixture of perchlorate and chloride. The perchlorate is isomorphous with the corresponding potassium salt, but is less soluble in water, the solubility at 21·3° C. being 1·09 grams in 100 grams of water.[13]

Rubidium iodate, $RbIO_3$.—Iodic anhydride reacts with rubidium carbonate to form the iodate, and the salt is also produced by passing chlorine into a hot concentrated solution of rubidium iodide and hydroxide.[14] It forms monoclinic crystals isomorphous with those of potassium iodate, and of density 4·559 at 14° C. At 23° C. the solubility is 2·1 grams in 100 grams of water.[15] It yields *acid iodates*,[15] such as $RbIO_3,HIO_3$ and $RbIO_3,2HIO_3$, and also compounds of the type $RbIO_3,F_2$[16] and $RbIO_3,HIO_3,4HF$.[17]

Rubidium periodate, $RbIO_4$.—When a mixture of rubidium iodate and hydroxide in hot concentrated solution is oxidized with chlorine, the periodate is formed in colourless quadratic crystals isomorphous with those of potassium periodate, and with the density 3·918 at 16° C. At 13° C. its solubility is 0·65 gram in 100 grams of water.[18]

Rubidium monoxide, Rb_2O.—When rubidium is partially oxidized by diluted oxygen, and the excess of metal removed by distillation, the

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[1] Victor Meyer, Riddle, and Lamb, *Ber.*, 1893, 26, 3129.

[2] Carnelley, *Trans. Chem. Soc.*, 1898, 33, 273.

[3] Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568; compare Albrecht and Wartenberg, *ibid.*, 162.

[4] Compare Schröder, *Annalen*, 1878, 192, 295.

[5] Erdmann, *Arch. Pharm.*, 1894, 232, 25.

[6] Buchanan, *Proc. Chem. Soc.*, 1905, 21, 122.

[7] Baxter and Brink, *J. Amer. Chem. Soc.*, 1908, 30, 46.

[8] Reissig, *Annalen*, 1863, 127, 34.

[9] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[10] Wells and Wheeler, *Zeitsch. anorg. Chem.*, 1892, 1, 442; 2, 257; compare Foote and Chalker, *Amer. Chem. J.*, 1908, 39, 561.

[11] Abegg and Hamburger, *Zeitsch. anorg. Chem.*, 1906, 50, 403.

[12] Reissig, *loc. cit.*

[13] Louguinine, *Annalen*, 1862, 121, 123.

[14] Barker, *Trans. Chem. Soc.*, 1908, 93, 15.

[15] Wheeler, *Amer. J. Sci.*, 1902, [3], 44, 123.

[16] Weinland and Lauenstein, *Zeitsch. anorg. Chem.*, 1899, 20, 30; Weinland and Alfa, *ibid.*, 1899, 21, 53.

[17] Weinland and Köppen, *ibid.*, 1900, 22, 260; Weinland and Barttlingck, *Ber.*, 1903, 36, 1401.

[18] Barker, *loc. cit.*

monoxide is obtained in transparent, pale-yellow crystals which become deeper yellow at 250° C.[1] Its density is 3·72. At 400° C. it is decomposed into the metal and dioxide; and at 250° C. it reacts with hydrogen, forming equimolecular proportions of the hydroxide and hydride. It also reacts with fluorine, chlorine, and iodine. Its heat of formation[2] is 83·5 Cal.

Rubidium peroxides.—Three peroxides have been prepared by the action of excess of oxygen on the metal.[3] The *dioxide*, Rb_2O_2, forms yellow needles melting about 600° C., and of density 3·65[4] at 0° C. Its heat of formation from the elements is about 107·6 Cal.[5] The *trioxide*, Rb_2O_3, is produced by heating the metal with the theoretical proportion of oxygen, and is a black solid, melting below 500° C., and of density 3·53 at 0° C. It dissolves readily in water, forming hydrogen peroxide, and evolving oxygen. Its heat of formation from the elements is about 125·6 Cal.[5] The *tetroxide*, Rb_2O_4, is formed as a yellowish-brown substance by the action of oxygen at reduced pressure on the metal,[6] or as a brownish-black mass by the further oxidation of the dioxide. At ordinary pressure in an atmosphere of oxygen it melts between 600° and 650° C. to a dark brown liquid, but in vacuum decomposes at a lower temperature. Its heat of formation from the elements is 137·6 Cal.[7]

Rubidium hydroxide, RbOH.—The hydroxide is formed by dissolving the metal in water, or by the action of barium hydroxide on rubidium sulphate. It is a very deliquescent substance, and is volatilized by heat. Its melting-point[8] is 301° C., and its density[9] 3·203 at 11° C. The latent heat of fusion per mol. is 1·614 Cal.[10]; the heat of formation from the elements is 101·99 Cal.[11] A monohydrate and a dihydrate have been described.[12]

Rubidium peroxide hydrate, $RbO{\cdot}OH,H_2O_2$.—Hydrogen peroxide reacts with rubidium hydroxide in alcoholic solution to form the peroxide hydrate, a white, deliquescent solid, stable below 0° C., but decomposing at higher temperatures with evolution of oxygen, and formation of a substance which is probably a hydrated tetroxide.[13]

Rubidium sulphides.[14]—The tetrahydrate of the *monosulphide*, $Rb_2S,4H_2O$, is formed by the interaction of equivalent proportions of rubidium hydrogen sulphide and hydroxide, and is precipitated in colourless crystals by addition of alcohol and ether. The anhydrous salt is produced by the action of excess of rubidium on sulphur, the uncombined metal being removed by distillation in vacuum. It forms

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[1] Rengade, *Compt. rend.*, 1906, 142, 1153; 143, 1152; 1907, 144, 753; 145, 236.

[2] Rengade, *ibid.*, 1908, 146, 129; *Bull. Soc. chim.*, 1908, [4], 3, 190, 194; de Forcrand, *Compt. rend.*, 1914, 158, 991.

[3] Rengade, *Compt. rend.*, 1907, 144, 920.

[4] Rengade, *Ann. Chim. Phys.*, 1907, [8], 11, 348.

[5] de Forcrand, *loc. cit.*

[6] Compare Erdmann and Köthner, *Annalen*, 1897, 294, 56.

[7] de Forcrand, *Compt. rend.*, 1914, 158, 843.

[8] Hevesy, *Zeitsch. physikal. Chem.*, 1910, 73, 667.

[9] Hevesy, *Zeitsch. anorg. Chem.*, 1910, 67, 242.

[10] Hevesy, *Zeitsch. physikal. Chem.*, 1910, 73, 667.

[11] de Forcrand, *Ann. Chim. Phys.*, 1908, [8], 15, 433.

[12] de Forcrand, *Compt. rend.*, 1909, 149, 1341.

[13] Peltner, *Ber.*, 1909, 42, 1777.

[14] Biltz and Wilke-Dörfurt, *Ber.*, 1905, 38, 123; *Zeitsch. anorg. Chem.*, 1906, 48, 297; 50, 67.

microscopic white needles belonging to the cubic system, and isomorphous with those of the corresponding salt of potassium, but not with those of cæsium monosulphide. Its density is 2·912, and it melts at the temperature of softening of glass. It dissolves in water with a hissing sound, the heat of solution being 24·6 Cal. The heat of formation of the solid from its elements is 87·1 Cal., and that from rubidium hydroxide and hydrogen sulphide is 8·0 Cal. Rubidium monosulphide is readily oxidized, is combustible, and weathers in air.[1]

The monosulphide is converted by sulphur in an atmosphere of hydrogen into the *pentasulphide*, Rb_2S_5, deliquescent, red crystals melting at 223° to 224° C., and of density 2·618 at 15° C. When heated in nitrogen it yields the *trisulphide*, Rb_2S_3, consisting of hygroscopic, dark-yellow crystals melting at 213° C.; but in hydrogen the hygroscopic *disulphide*, Rb_2S_2, is formed, a substance melting about 420° C. and boiling above 950° C. Both the disulphide and the trisulphide yield a monohydrate. The *tetrasulphide*, Rb_2S_4, is formed by heating the monosulphide with the calculated amount of sulphur. It yields a yellow, crystalline dihydrate. *Rubidium hydrogen sulphide*, RbSH, is produced by saturating a solution of rubidium hydroxide with hydrogen sulphide.

Rubidium sulphate, Rb_2SO_4.—The sulphate forms rhombic crystals isomorphous[2] with those of potassium sulphate, melting[3] at 1074° C., the density at 20° C. being 3·6113, and at 60° C. 3·5943.[4] It exists in two modifications,[5] the transition-point being 657° C. The heat of formation from the elements is 344·68 Cal., and the heat of solution —6·66 Cal. at 15° C.[6] The solubility[7] is given in the appended table:

Solubility of Rubidium Sulphate.

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100
Grams of Rb_2SO_4 per 100 g. of water	36·4	42·6	48·2	53·5	58·5	63·1	67·4	71·4	75·0	78·7	81·8

The boiling-point of the saturated solution in contact with excess of sulphate is 103·5° C. at 760 mm. pressure.[8] With aluminium and ferric sulphates it forms well-crystallized alums. It exhibits radioactivity.[9]

Rubidium hydrogen sulphate, $RbHSO_4$.—The primary sulphate has a density at 16° C. of 2·892.[10] Its heat of formation from the elements is 277·37 Cal., and its heat of solution —3·73 Cal.[11] On ignition it is converted into *rubidium pyrosulphate*, $Rb_2S_2O_7$.

Rubidium persulphate, $Rb_2S_2O_8$.—The persulphate is formed by the

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[1] Rengade and Costeanu, *Compt. rend.*, 1913, 156, 791; 1914, 158, 946.

[2] See p. 227.

[3] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[4] Tutton, *Trans. Chem. Soc.*, 1894, 65, 628; 1896, 69, 344.

[5] Hüttner and Tammann, *loc. cit.*

[6] de Forcrand, *Compt. rend.*, 1906, 143, 98.

[7] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 566; compare Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207; Étard, *Ann. Chim. Phys.*, 1894, [7], 2, 550.

[8] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.

[9] Büchner, *Le Radium*, 1912, 9, 259.

[10] Spring, *Bull. Acad. roy. Belg.*, 1904, 290.

[11] de Forcrand, *loc. cit.*

electrolysis at a low temperature of a saturated solution of rubidium sulphate containing sulphuric acid.[1] Its *solubility* at 22·5° C. is 3·4 grams in 100 grams of water.

Rubidium thiosulphate, $Rb_2S_2O_3$.—Interaction of rubidium carbonate and barium thiosulphate produces the dihydrate of rubidium thiosulphate.[2] It is hygroscopic, and readily soluble in water.

Rubidium dithionate, $Rb_2S_2O_6$.—The dithionate is formed by the action of rubidium sulphate on barium dithionate.[3]

Rubidium trithionate, $Rb_2S_3O_6$.—When rubidium persulphate reacts with somewhat more than twice the molecular proportion of strontium thiosulphate in solution, rubidium tetrathionate is formed :

$$Rb_2S_2O_8+2SrS_2O_3=Rb_2S_4O_6+2SrSO_4.$$

The strontium sulphite produced by decomposition of the excess of strontium thiosulphate then reacts with the rubidium tetrathionate, forming trithionate :

$$Rb_2S_4O_6+SrSO_3=Rb_2S_3O_6+SrS_2O_3.$$

In presence of sulphurous acid a similar reaction takes place. The trithionate forms rhombic crystals isomorphous with those of the corresponding potassium salt, the density being 2·845.[4]

Rubidium tetrathionate, $Rb_2S_4O_6$.—The tetrathionate is prepared by the method just indicated,[4] and is also formed by the action of iodine on the thiosulphate.[5]

Rubidium selenate, Rb_2SeO_4.—Neutralization of selenic acid with rubidium carbonate yields the selenate in colourless crystals,[6] of density 3·8995 at 20° C. At 12° C. its solubility is 158·9 grams in 100 grams of water. Addition of an equivalent proportion of selenic acid converts it into *rubidium hydrogen selenate,* $RbHSeO_4$, its solubility at 17·5° C. being 140 grams in 100 grams of water.[7]

Rubidium tellurates.—The *normal tellurate,* $Rb_2TeO_4,3H_2O$, and the *primary tellurate,* $2RbHTeO_4,H_2O$, are prepared like the corresponding selenates, but do not appear to be isomorphous with them.[8]

Rubidium nitride, Rb_3N, and **rubidamide,** $RbNH_2$.—The nitride is formed along with the amide by heating the hydride in nitrogen.[9] The amide is also produced by the action of ammonia on the metal at 200° to 300° C.,[10] as well as at lower temperatures.[11] The amide is a white, deliquescent, crystalline substance, melting at 285° to 287° C., and boiling about 400° C.

Rubidium hydrazoate, RbN_3.—The hydrazoate is produced by the

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[1] Foster and Smith, *J. Amer. Chem. Soc.*, 1899, 21, 934; compare Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726.

[2] Julius Meyer and Eggeling, *Ber.*, 1907, 40, 1351.

[3] Weinland and Alfa, *Zeitsch. anorg. Chem.*, 1899, 21, 53.

[4] Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726.

[5] Julius Meyer and Eggeling, *loc. cit.*

[6] For isomorphism, see p. 227.

[7] Pellini, *Atti R. Accad. Lincei*, 1906, [5], 15, i., 711.

[8] Norris and Kingman, *Amer. Chem. J.*, 1901, 26, 318.

[9] Moissan, *Compt. rend.*, 1903, 136, 587, 1177; compare Fischer and Schröter, *Ber.*, 1910, 43, 1465.

[10] Titherley, *Trans. Chem. Soc.*, 1897, 71, 469.

[11] Ruff and Geisel, *Ber.*, 1906, 39, 828.

interaction of rubidium sulphate and barium hydrazoate.[1] It forms tetragonal plates melting at 330° to 340° C., which display marked double refraction. It is not very explosive, but melts between 330° and 340° C. with evolution of gas. The solubility at 16° C. is 107·1 grams in 100 grams of water, the solution having a slightly alkaline reaction.

Rubidium nitrite, $RbNO_2$.—Barium nitrite and rubidium sulphate interact to form rubidium nitrite, a yellowish, crystalline substance, very soluble in water.[2]

Rubidium nitrate, $RbNO_3$.—The nitrate is trimorphous,[3] crystallizing in hexagonal,[4] cubic, and bi-refractive forms, the transition-points in the order named being 161·4° C. and 218·9° to 219·3° C. The crystals are very hard, melt at 313° C.,[5] and have a density of 3·131[6] at 15° C. and 3·112 at 20° C.[7] The molecular electric conductivity of rubidium nitrate between 318·8° and 493° C. is given by the formula[8]

$$\mu_t = 33{\cdot}51 + 0{\cdot}145(t - 300).$$

The solubility in water[9] is given in the table:

Solubility of Rubidium Nitrate.

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100
Grams of $RbNO_3$ per 100 g. of water	19·5	33·0	53·3	81·3	116·7	155·6	200	251	309	375	452

A saturated solution containing 617 grams in 100 grams of water boils at 118·3° C. under a pressure of 734 mm. of mercury. In chemical properties the salt resembles potassium nitrate. It exhibits radioactivity.[10] With nitric acid it yields *acid* nitrates,[11] $RbNO_3,HNO_3$, melting at 62° C., and $RbNO_3,2HNO_3$, melting at 39° to 46° C.

Rubidium phosphide, Rb_2P_5.—The phosphide is formed by the interaction of phosphorus and rubidium hydride, and also by Hackspill and Bossuet's method (p. 136). In properties it resembles closely the corresponding potassium derivative, and has a density of 2·5.[12]

Rubidium phosphates.—The three phosphates are prepared by the interaction of phosphoric acid and rubidium hydroxide or carbonate in appropriate proportions.[13] The *primary phosphate*, RbH_2PO_4, is acidic in aqueous solution; the other two are alkaline. When heated at 244° C. the primary phosphate loses water, yielding the acid pyrophosphate, $Rb_2H_2P_2O_7$.[14] The *secondary phosphate* forms a monohydrate,

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[1] Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 280; compare Dennis and Benedikt, *Zeitsch. anorg. Chem.*, 1898, 17, 20.

[2] Ball and Abram, *Trans. Chem. Soc.*, 1914, 103, 2130.

[3] Schwarz, *Landolt, Börnstein, and Meyerhoffer's Tabellen*, 3rd ed., Berlin, 1905, 283.

[4] Compare Jaeger, *Zeitsch. Kryst. Min.*, 1907, 43, 588; Duffour, *Bull. Soc. franç. Min.*, 1913, 36, 136.

[5] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[6] Retgers, *Zeitsch. physikal. Chem.*, 1889, 4, 597.

[7] Haigh, *loc. cit.*

[8] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.

[9] Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207; compare Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 566.

[10] Büchner, *Le Radium*, 1912, 9, 259.

[11] Wells and Metzger, *Amer. Chem. J.*, 1901, 26, 271.

[12] Compare Bossuet and Hackspill, *Compt. rend.*, 1913, 157, 720.

[13] Von Berg, *Ber.*, 1901, 34, 4181.

[14] Balareff, *Zeitsch. anorg. Chem.*, 1921, 118, 123.

and the *normal phosphate* a tetrahydrate. On heating the primary salt, the *metaphosphate* is formed; the secondary salt is converted into the *pyrophosphate* by heat. In properties the phosphates resemble the corresponding potassium derivatives.

Rubidium arsenite and arsenate.—Several derivatives of arsenious acid and arsenic acid have been prepared.[1] Their properties are analogous to those of the corresponding potassium salts.

Rubidium carbide, Rb_2C_2.—The carbide is formed by heating rubidium acetylide, Rb_2C_2,C_2H_2, in vacuum at 300° C., acetylene being evolved.[2] It crystallizes in brownish-red leaflets.[3]

Rubidium carbonate, Rb_2CO_3.—The carbonate is prepared in the anhydrous state by ignition of the residue from the evaporation of a solution of rubidium hydroxide and ammonium carbonate.[4] It melts about 837° C.,[5] and its specific heat[6] is 0·123 between 18° and 47° C. It is very deliquescent, the heat of solution in water being 9·077 Cal.[7] The solution is alkaline. Several hydrates have been described.[7] The heat of formation of the anhydrous salt from its elements is 274·9 Cal.[8]

Rubidium hydrogen carbonate, $RbHCO_3$.—The primary carbonate is produced by saturating a concentrated aqueous solution of rubidium carbonate with carbon dioxide.[9] It dissolves readily in water, the slightly alkaline solution being decomposed by heat, with evolution of carbon dioxide. The heat of solution at 15° C. is —4·731 Cal., and that of formation from its elements 231·92 Cal. The dissociation-pressure has been investigated by Caven and Sand.[10]

Rubidium percarbonate, $Rb_2C_2O_6$.—The percarbonate is produced by electrolytic oxidation of a concentrated aqueous solution of rubidium carbonate.[11] It resembles the corresponding potassium salt.

Peltner[12] has described rubidium percarbonates of the formulæ $Rb_2CO_4,2H_2O_2,H_2O$; $Rb_2CO_4,H_2O_2,2H_2O$; and $2Rb_2CO_4,5H_2O$. They are unstable hygroscopic substances, and on contact with water evolve oxygen.

Rubidium metasilicate, Rb_2SiO_3.—The properties of the metasilicate in dilute aqueous solution have been investigated.[13]

Rubidium pentaborate, $RbB_5O_8,5H_2O$.—The pentaborate separates from solutions in which the ratio

$$B_2O_3 : RbOH = 3 : 1$$

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[1] Bouchonnet, *Compt. rend.*, 1907, 144, 641.

[2] See this series, Vol. V., 88.

[3] Moissan, *Compt. rend.*, 1903, 136, 1221, 1522.

[4] Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 342; 1863, 119, 1; *Annalen*, 1862, 122, 347; 1863, 125, 367.

[5] Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 125.

[6] Kopp, *Annalen Suppl.*, 1864–5, 3, i., 289.

[7] de Forcrand, *Compt. rend.*, 1909, 149, 97.

[8] de Forcrand, *ibid.*, 719.

[9] de Forcrand, *ibid.*, 719, 825.

[10] Caven and Sand, *Trans. Chem. Soc.*, 1914, 105, 2755.

[11] Constam and Hansen, *Zeitsch. Elektrochem.*, 1896, 3, 144; compare Peltner, *Ber.*, 1909, 42, 1777; Riesenfeld and Reinhold, *ibid.*, 4377; Riesenfeld and Mau, *ibid.*, 1911, 44, 3589.

[12] Peltner, *loc. cit.*

[13] Kahlenberg and Lincoln, *J. Physical Chem.*, 1898, 2, 82; compare Ordway, *Amer. J. Sci.*, 1907, [4], 24, 473.

or higher. Its properties are similar to those of the corresponding potassium salt.[1]

DETECTION AND ESTIMATION OF RUBIDIUM.

Rubidium salts impart a reddish-violet coloration to the Bunsen flame, similar to that characteristic of potassium derivatives. Like potassium, rubidium forms several salts not readily soluble, among them the chloroplatinate, perchlorate, silicofluoride, bismuth thiosulphate, and primary tartrate. It can also be detected by the formation of $Bi(NO_2)_3,2RbNO_2,NaNO_2$, a yellow crystalline precipitate produced by adding a solution of bismuth nitrate and sodium nitrite to one of a rubidium salt.[2]

Rubidium chloride yields a complex rubidium-silver-gold chloride, separating in blood-red prisms. The formation of this precipitate is an aid in the microchemical identification of rubidium, and serves to detect one-tenth of a microgram of the element.[3]

The metal can be estimated as chloride or sulphate, or by heating the sulphate with sulphuric acid and the sulphate of an alkaline-earth metal such as calcium, a double sulphate of the type $Rb_2SO_4,CaSO_4$ being formed and weighed.[4]

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[1] Rosenheim and Leyser, *Zeitsch. anorg. Chem.*, 1921, 119, 1.

[2] Ball, *Trans. Chem. Soc.*, 1909, 95, 2126.

[3] Bayer, *Monatsh.*, 1920, 41, 223; compare Emich, *ibid.*, 243.

[4] Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726. On the separation from sodium and potassium, compare Vernadski, *Bull. Soc. franç. Min.*, 1913, 36, 258.

CHAPTER VII.

CÆSIUM.

Symbol, Cs. Atomic weight, 132·81 (O=16).

Occurrence.—The principal mineral containing cæsium is *pollucite*, a double silicate with aluminium having the approximate composition $Cs_4Al_4H_2Si_9O_{27}$, found in Maine and in Elba.[1] It accompanies the other alkali-metals, being found in traces in the Stassfurt salt deposits and in many mineral springs.

History.—The metal was discovered [2] by the spectroscopic method in 1860 in the waters of the Dürkheim spring. Its name is derived from the two characteristic blue lines of its spectrum (*cæsius*, sky-blue). Bunsen did not isolate the metal, but prepared its amalgam.

Preparation.—The isolation of cæsium compounds is facilitated by the relatively low solubility of certain double salts, such as the alums, chloroplatinates, and double chlorides with antimony, tin, and lead.[3] Its separation from rubidium depends on the solubility of its carbonate in alcohol, that of rubidium being only slightly soluble.

The metal was originally isolated by electrolysis of the cyanide in presence of barium cyanide.[4] It is best prepared by reduction of the hydroxide [5] or carbonate [6] by magnesium in a current of hydrogen, the vapour being condensed under petroleum; or by reduction of the chloride by calcium in vacuum.[7]

Physical Properties.—Cæsium is a pale-yellow [8] metal, m.p. 28·45° C.,[9] 28·25° C.,[10] 28·2° C.,[11] 26·5° C.,[12] 26·37° C.,[13] or 26° C.,[14] b.p. 670° C.,[15] its density being 1·9029 [16] at 0° C., 1·88 [17] at 15° C., 1·87 [18] at 20° C., 1·886

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[1] Pisani, *Compt. rend.*, 1864, 58, 714; *Annalen*, 1864, 132, 31.

[2] Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 342; 1863, 119, 1; *Annalen*, 1862, 122, 347; 1863, 125, 367.

[3] Sharples, *Amer. J. Sci.*, 1869, [2], 47, 178; Wells, *Zeitsch. anorg. Chem.*, 1893, 4, 344.

[4] Setterberg, *Annalen*, 1882, 211, 112.

[5] Erdmann and Menke, *J. Amer. Chem. Soc.*, 1899, 21, 259.

[6] Gräfe and Eckardt, *Zeitsch. anorg. Chem.*, 1899, 22, 158.

[7] Hackspill, *Compt. rend.*, 1905, 141, 106; *Bull. Soc. chim.*, 1911, [4], 9, 446; Rengade, *Compt. rend.*, 1906, 142, 1533; 1907, 145, 236; *Ann. Chim. Phys.*, 1907, [8], 11, 348.

[8] Rengade, *Bull. Soc. chim.*, 1909, [4], 5, 994.

[9] Rengade, *Compt. rend.*, 1913, 156, 1897; *Bull. Soc. chim.*, 1914, [4], 15, 130.

[10] Rengade, *Bull. Soc. chim.*, 1909, [4], 5, 994.

[11] Guntz and Broniewski, *J. Chim. phys.*, 1909, 7, 464.

[12] Setterberg, *Annalen*, 1882, 211, 112.

[13] Eckardt and Gräfe, *Zeitsch. anorg. Chem.*, 1900, 23, 378.

[14] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

[15] Ruff and Johannsen, *Ber.*, 1905, 38, 3601.

[16] Hackspill, *Compt. rend.*, 1911, 152, 259.

[17] Setterberg, *loc. cit.*

[18] Richards and Brink, *J. Amer. Chem. Soc.*, 1907, 29, 117.

at 26° C., 1·836 at 27° C., and 1·827[1] at 40° C. The atomic volume is 71, and is higher than that of any other element.[2] At absolute zero the density is 2·222, and the corresponding atomic volume is 59·77.[3] The specific heat is 0·04817 between 0° and 26° C.,[4] and is given by Rengade[5] as 0·0600 at 0° C. The heat of fusion of 1 gram is given as 3·73 cal., and also[5] as 3·76 cal. It is the softest metal, the hardness on Rydberg's[4] scale being 0·2. Neither the metal nor any of its salts displays radioactivity.[7]

Chemical Properties.—In chemical properties cæsium is closely related to potassium and rubidium. When brought into contact with air, it undergoes rapid oxidation; and the pure metal ignites in dry oxygen at the ordinary temperature.[8] It decomposes water energetically, the action on ice beginning at −116° C.[9] Its solution in liquid ammonia reacts with ozone.[10]

Cæsium Ion.—Cæsium forms colourless univalent ions. It is the most electropositive of the elements, its great electroaffinity corresponding with the ready solubility of its salts. The salts with strong anions are less soluble than the corresponding derivatives of the other alkali-metals.[11]

Atomic Weight.—The chemical properties of cæsium indicate its close relationship to the other alkali-metals. It is univalent, forming compounds of the type CsX, its atomic weight and hydrogen equivalent being the same. Its atomic weight is of the order Cs=133: a value confirmed by the specific-heat method (Vol. I., p. 88); by the isomorphism of the cæsium compounds with those of potassium, ammonium, and rubidium (Vol. I., p. 74); by the correspondence of the properties of the metal and its compounds with the periodic system; by the formation of a univalent cation; and by the depression of the freezing-point of bismuth chloride and mercuric chloride produced by cæsium chloride.

Early Determinations.

The earliest determination of the atomic weight of cæsium with any approach to accuracy was that of Johnson and Allen.[12] The mean of four experiments gave the value

$$AgCl : CsCl = 100 : 117{\cdot}499,$$

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[1] Eckardt and Gräfe, *Zeitsch. anorg. Chem.*, 1900, 23, 378.

[2] Compare Rudorf, *Das Periodische System*, Hamburg, 1904, 129.

[3] Herz, *Zeitsch. anorg. Chem.*, 1921, 120, 159; compare Herz, *ibid.*, 1919, 105, 171; Lorenz and Herz, *ibid.*, 1921, 117, 267.

[4] Eckardt and Gräfe, *loc. cit.*

[5] Rengade, *Bull. Soc. chim.*, 1914, [4], 15, 130.

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

[7] Compare Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576; Elster and Geitel, *ibid.*, 1910, 11, 275; Henriot, *Le Radium*, 1910, 7, 40; *Compt. rend.*, 1911, 152, 851; Büchner, *Le Radium*, 1912, 9, 259; compare Hahn and Rothenbach, *Physikal. Zeitsch.*, 1919, 20, 194.

[8] Rengade, *Compt. rend.*, 1906, 142, 1533; 1907, 145, 236; *Ann. Chim. Phys.*, 1907, [8], 11, 348.

[9] Hackspill and Bossuet, *Compt. rend.*, 1911, 152, 874.

[10] Compare the section on sodium, p. 86.

[11] Compare Abegg and Bodländer, *Zeitsch. anorg. Chem.*, 1899, 20, 462.

[12] Johnson and Allen, *Amer. J. Sci.*, 1863, [2], 35, 94.

whence the atomic weight of cæsium is

$$Cs = 132{\cdot}963.$$[1]

In 1863 Bunsen[2] obtained the ratio

$$AgCl : CsCl = 100 : 117{\cdot}467$$

as the mean of three experiments, the corresponding value for the atomic weight being

$$Cs = 132{\cdot}917.$$

Godeffroy[3] employed material of doubtful purity, his ratio being

$$AgCl : CsCl = 100 : 117{\cdot}164,$$

whence

$$Cs = 132{\cdot}484.$$

Modern Determinations.

With a view to calculating the atomic weight of cæsium, Richards and Archibald[4] in 1903 determined with great accuracy the values of five different and independent ratios. Their results are summarized in the table:

Number of Experiments.	Mean Values of Ratios determined.	Atomic Weight of Cæsium.
3	$AgCl : CsCl = 100 : 117{\cdot}398$	132·818
12	$Ag : CsCl = 100 : 155{\cdot}9635$	132·796
4	$NO : Cs_2O = 100 : 260{\cdot}693$	132·800
4	$AgBr : CsBr = 100 : 113{\cdot}2798$	132·819
3	$Ag : CsBr = 100 : 197{\cdot}1976$	132·821

The current table of the International Committee on Atomic Weights gives

$$\mathbf{Cs = 132{\cdot}81.}$$

Several investigators[5] have experimented with a view to proving the existence of a metal analogous to cæsium, but with a higher atomic weight. Careful examination of cæsium salts has given no indication of the presence of this "*eka*cæsium."

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[1] See remarks on the calculation of the atomic weight, p. 190. The atomic weights employed here and in succeeding calculations are $Ag = 107{\cdot}880$, $Cl = 35{\cdot}457$, $N = 14{\cdot}010$, and $Br = 79{\cdot}916$.

[2] Bunsen, *Pogg. Annalen*, 1863, 119, 1.

[3] Godeffroy, *Annalen*, 1876, 181, 176.

[4] Richards and Archibald, *Proc. Amer. Acad.*, 1903, 38, 443; *Zeitsch. anorg. Chem*, 1903, 34, 351.

[5] Richards and Archibald, *Zeitsch. anorg. Chem.*, 1903, 34, 353; *Proc. Amer. Acad.*, 1903, 38, 443; Baxter, *J. Amer. Chem. Soc.*, 1915, 37, 286; Dennis and Wyckoff, *ibid.*, 1920, 42, 985.

COMPOUNDS OF CÆSIUM.[1]

Cæsium hydride, CsH.—It is difficult to prepare the hydride in a state of purity. It can be obtained in the form of white crystals by the interaction of pure cæsium and pure hydrogen, its general characteristics being similar to those of the corresponding rubidium derivative.[2] Ephraim and Michel[3] produced it by heating a mixture of cæsium carbonate and metallic magnesium in hydrogen at 580° to 620° C. for three days. It is the least stable of the alkali-metal hydrides. Its density[4] is 2·7. Ephraim and Michel[3] found the vapour-tension for each interval of 10° between 340° and 440° C. to be 78, 100, 126, 160, 202, 256, 317, 402, 503, 630, and 787 mm.; but the measurements may have been vitiated by the presence of carbon dioxide arising from decomposition of the magnesium carbonate formed, by the sublimation of the metal, and by its solubility in the hydride.

Cæsium fluorides.—Evaporation of a solution of cæsium carbonate in hydrofluoric acid yields the *primary fluoride,* CsF,HF.[5] When heated, this substance is converted into the *normal fluoride,* CsF, which crystallizes in cubes, melts at 684° C.,[6] and boils at 1251° C.[6] Its vapour-pressure in atmospheres corresponds with the expression [6]

$$\log p = -34700/4{\cdot}57T + 4{\cdot}982.$$

The anhydrous fluoride yields two very deliquescent hydrates, $CsF,1{\cdot}5H_2O$, and $3CsF,2H_2O$.[7] The heat of solution of the anhydrous salt is 8·37 Cal.[8]

Cæsium chloride, CsCl.—The chloride is prepared similarly to that of rubidium. It forms cubes, melting at 626° C.,[9] 631° C.,[10] 645° C.,[11] 646° C.[12] or 647° C.,[13] and boiling at 1303° C.[14] The vapour-pressure in atmospheres is given by the expression [14]

$$\log p = -37400/4{\cdot}57T + 5{\cdot}190.$$

The substance has a density of 3·972 [15] or 3·987 [16] at 20° C., and 3·982 [17] at 23·1° C. Its latent heat of fusion per gram is 0·024 Cal.[18] The

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[1] Attention is called to the close analogy in modes of preparation and properties of the cæsium and rubidium compounds. For *cæsium-amalgam,* see this series, Vol. III.

[2] Moissan, *Compt. rend.,* 1903, 136, 587, 1177; Elster and Geitel, *Physikal. Zeitsch.,* 1910, 11, 257.

[3] Ephraim and Michel, *Helv. Chim. Acta,* 1921, 4, 762.

[4] Moissan, *loc. cit.*

[5] Chabrié, *Compt. rend.,* 1901, 132, 680.

[6] Wartenberg and Schulz, *Zeitsch. Elektrochem.,* 1921, 27, 568; compare Albrecht and Wartenberg, *ibid.,* 162.

[7] de Forcrand, *Compt. rend.,* 1911, 152, 1208.

[8] de Forcrand, *ibid.,* 27.

[9] Wartenberg and Schulz, *Zeitsch. Elektrochem.,* 1921, 27, 568; compare Albrecht and Wartenberg, *ibid.,* 162.

[10] Carnelley and Williams, *Trans. Chem. Soc.,* 1880, 37, 125.

[11] Richards and Meldrum, *J. Amer. Chem. Soc.,* 1917, 39, 1816.

[12] Schemtschushny and Rambach, *J. Russ. Phys. Chem. Soc.,* 1909, 41, 1785.

[13] Haigh, *J. Amer. Chem. Soc.,* 1912, 34, 1137.

[14] Wartenberg and Schulz, *loc. cit.*

[15] Richards and Archibald, *Zeitsch. anorg. Chem.,* 1903, 34, 353.

[16] Haigh, *loc. cit.*

[17] Buchanan, *Proc. Chem. Soc.,* 1905, 21, 122.

[18] Schemtschushny and Rambach, *loc. cit.*

hygroscopic salt is very readily soluble in water, yielding a neutral solution. The solubility[1] is given in the appended table :

Solubility of Cæsium Chloride.

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100
Grams of CsCl per 100 g. of water	161·4	174·7	186·5	197·3	208·0	218·5	229·0	239·5	250·0	260·1	270·5

The heat of solution is —4·68 Cal.,[2] and the heat of formation 109·86 Cal.[3] A saturated solution boils at 119·9° C. under 760 mm. pressure.[4] Cæsium chloride resembles the rubidium salt in forming a number of complex *polyhalides*.[5] It is a useful agent in photomicrography, since it forms well-defined double salts with many metals among them—silver, gold, platinum, mercury, lead, copper, and many others.[6] It has a decided toxic effect.

Cæsium bromide, $CsBr$.—The bromide is produced by the interaction of cæsium sulphate and barium bromide.[7] It forms anhydrous[8] cubic crystals, melting at 627° C., and boiling at 1300° C.[9] The vapour-pressure in atmospheres is given by the expression[10]

$$\log p = -36750/4{\cdot}57T + 5{\cdot}113.$$

The density of the crystals is 4·380[11] at 20° C., and 4·455[12] at 21·4° C. Its heat of solution is —6·73 Cal.[13] It is characterized by the formation of complex *polyhalides*.[14]

Cæsium iodide, CsI.—The iodide is prepared by the action of cæsium sulphate on barium iodide. It forms crystals, melting at 621·0° C.,[15] and boiling at 1280° C.,[16] the vapour-pressure in atmospheres corresponding with the expression[17]

$$\log p = -36600/4{\cdot}57T + 5{\cdot}165.$$

The density is given as 4·523,[18] 4·508[19] at 22·8° C., and 4·510[20] at 25° C. At 35·6° C. its solubility is 106 grams in 100 grams of water. Its heat of

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[1] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 533 ; Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207.

[2] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[3] de Forcrand, *ibid.*, 1906, 143, 98.

[4] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.

[5] Compare Wells and Wheeler, *Zeitsch. anorg. Chem.*, 1892, 1, 442 ; 2, 257 ; Wyckoff, *J. Amer. Chem. Soc.*, 1920, 42, 1100.

[6] Ducloux, *Anal. Assoc. Quím. Argentina*, 1921, 9, 215.

[7] Chabrié, *Compt. rend.*, 1901, 132, 680.

[8] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.

[9] Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568 ; compare Albrecht and Wartenberg, *ibid.*, 162.

[10] Wartenberg and Schulz, *loc. cit.*

[11] Richards and Archibald, *Zeitsch. anorg. Chem.*, 1903, 34, 353.

[12] Buchanan, *Proc. Chem. Soc.*, 1905, 21, 122.

[13] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[14] Wells and Wheeler, *Zeitsch. anorg. Chem.*, 1892, 1, 442 ; 2, 257.

[15] Victor Meyer, Riddle, and Lamb, *Ber.*, 1893, 26, 3129.

[16] Wartenberg and Schulz, *Zeitsch. Elektrochem.*, 1921, 27, 568 ; compare Albrecht and Wartenberg, *ibid.*, 162.

[17] Wartenberg and Schulz, *loc. cit.*

[18] Beketoff, *Bull. Acad. Sci. St. Pétersbourg*, 1892, 34, 197.

[19] Buchanan, *loc. cit.*

[20] Baxter and Brink, *J. Amer. Chem. Soc.*, 1908, 30, 46.

solution is —8·25 Cal.[1] A *tri-iodide* and a *pentaiodide* have been isolated,[2] and the existence of a *heptaiodide* and of an *enneaiodide*, CsI_9, is probable.[3]

Cæsium chlorate, $CsClO_3$.—The chlorate has been little investigated.[4]

Cæsium bromate, $CsBrO_3$.—The preparation of cæsium bromate has been effected by McCrosky and Buell,[5] and is stated to be carried out best in acid solution. It crystallizes without water of crystallization, and melts at a higher temperature than potassium bromate. At 30° C. 100 grams of water dissolve 4·53 grams of the salt.

Cæsium iodate, $CsIO_3$.—The iodate is precipitated by the action of chlorine on a hot concentrated solution of cæsium iodide and hydroxide.[6] It yields monoclinic crystals, isomorphous with the corresponding salts of rubidium and potassium, and of density 4·831 at 16° C. At 24° C. its solubility is 2·6 grams in 100 grams of water.[7]

Cæsium periodate, $CsIO_4$.—The periodate is prepared by the action of cæsium carbonate on periodic acid.[8] It forms orthorhombic plates, not isomorphous with the corresponding salts of rubidium and potassium.[9] It has a density of 4·259 at 15° C., and its solubility at 15° C. is 2·15 grams in 100 grams of water.

Cæsium monoxide, Cs_2O.—The monoxide is prepared by incomplete oxidation of the metal at ordinary temperature, the excess being removed by vacuum-distillation at 180° to 200° C.[10] It forms scarlet-red crystals,[11] which become purple-red at a temperature above the ordinary, and black at 150° C. At —180° C. their colour is bright yellow. The substance melts at 450° to 500° C., decomposing into the metal and the peroxide, Cs_2O_2. At 0° C. it has a density of 4·36[12] (water at 0° C.$=$1). Its heat of formation is 82·7 Cal.,[13] and its heat of solution is 83·2 Cal.[14] From the air it absorbs moisture and carbon dioxide, becoming white and deliquescent. It dissolves to a clear solution in water, the process being attended by a hissing sound and the production of flame. In moist carbon dioxide it ignites at the ordinary temperature. Hydrogen reduces it to the hydride and hydroxide.

Cæsium suboxides.—Two suboxides have been isolated,[15] Cs_7O, a bronze-coloured solid, melting at 3° C.; and Cs_7O_2, long prisms of permanganate colour. Both are formed by fusion of the monoxide with cæsium, the fusion-curve indicating the existence of two other suboxides, Cs_4O and Cs_3O.

Cæsium peroxides.—Three peroxides have been prepared by heating

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[1] de Forcrand, *Compt. rend.*, 1911, 152, 27.

[2] Wells and Wheeler, *Zeitsch. anorg. Chem.*, 1892, 1, 442; 2, 257.

[3] Abegg and Hamburger, *ibid.*, 1906, 50, 403; compare Foote, *Amer. Chem. J.*, 1903, 29, 203; Dawson and Goodson, *Trans. Chem. Soc.*, 1904, 85, 796.

[4] Compare Baur, *Zeitsch. physikal. Chem.*, 1895, 18, 184.

[5] McCrosky and Buell, *J. Amer. Chem. Soc.*, 1920, 42, 1786.

[6] Barker, *Trans. Chem. Soc.*, 1908, 93, 15.

[7] Wheeler, *Amer. J. Sci.*, 1902, [3], 44, 123.

[8] Wells, *Amer. Chem. J.*, 1901, 26, 278.

[9] Barker, *loc. cit.*

[10] Rengade, *Compt. rend.*, 1906, 143, 592; 1907, 144, 753.

[11] Rengade, *ibid.*, 1909, 148, 1199; *Bull. Soc. chim.*, 1909, [4], 5, 994.

[12] Rengade, *Bull. Soc. chim.*, 1907, [4], 1, 666.

[13] Rengade, *Compt. rend.*, 1908, 146, 129; de Forcrand, *ibid.*, 1914, 158, 991.

[14] Rengade, *ibid.*, 1908, 146, 129.

[15] Rengade, *ibid.*, 1909, 148, 1199; *Bull. Soc. chim.*, 1909, [4], 5, 994.

the metal in aluminium vessels with the calculated proportions of oxygen, or by the action of oxygen on a solution of the metal in liquid ammonia at −50° to −70° C. *Cæsium dioxide*,[1] Cs_2O_2, forms yellowish, acicular crystals, which become brown with rise of temperature, and at 400° to 450° C. melt to a black liquid. At 650° C. it begins to decompose with evolution of oxygen. It has a density of 4·47 at 15° C. It dissolves slowly in slightly acidulated water, forming hydrogen peroxide. The heat of formation from its elements is 107·0 Cal.[2] *Cæsium trioxide*,[1] Cs_2O_3, is a black substance, melting at 400° C., the density at 0° C. being 4·25. With water it evolves oxygen, forming hydrogen peroxide. The heat of formation of the trioxide from its elements is 127·46 Cal.[2] *Cæsium tetroxide*,[3] Cs_2O_4, is formed by oxidizing the metal between 300° and 350° C.[1] It is a golden-yellow, crystalline powder, melting in an oxygen atmosphere at 518° C., the density at 0° C. being 3·68, and at 19° C. 3·77.[3] It darkens with rise of temperature, and decomposes readily. With moisture it deliquesces and reacts in accordance with the equation

$$Cs_2O_4+2H_2O=2CsOH+H_2O_2+O_2.$$

Heating with carbon dioxide forms the carbonate and ozone:

$$Cs_2O_4+CO_2=Cs_2CO_3+O_3.$$

It is reduced by hydrogen. The heat of formation from the elements is 141·46 Cal.[4]

Cæsium hydroxide, CsOH.—The hydroxide is produced by the action of the metal on water, or of the sulphate on barium hydroxide. It is a solid, melting at 272·3° C., its latent heat of fusion per mol. being 1·609 Cal.[5] It is extremely deliquescent, and dissolves in water with evolution of much heat, the heat of solution being 16·423 Cal.[6] At 30° C. the saturated solution contains 75·08 per cent. of the base.[7] A *monohydrate*, melting at 180° C., has been isolated.[8] The heat of formation of the anhydrous compound from its elements is 101·03 Cal.[9]

Cæsium sulphides.[10]—In methods of preparation and properties the sulphides of cæsium resemble closely the corresponding salts of rubidium. The *monosulphide*,[11] Cs_2S, is prepared by heating sulphur with excess of cæsium, and removing the uncombined metal by distillation in vacuum. It forms white needles, melting at the temperature of softening of glass, readily oxidized and combustible. It weathers in air, and dissolves in water with a hissing sound. It is more soluble than the monosulphide of potassium or rubidium, and the three sulphides are not isomorphous.[12] Both the *disulphide*, Cs_2S_2, m.p. about 460° C., b.p. above 800° C., and the trisulphide, Cs_2S_3, m.p. 217° C., b.p. above 800° C.,

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[1] Rengade, *Compt. rend.*, 1906, 142, 1149; *Ann. Chim. Phys.*, 1907, [8], 11, 348.

[2] de Forcrand, *Compt. rend.*, 1914, 158, 991.

[3] Rengade, *loc. cit.*

[4] de Forcrand, *Compt. rend.*, 1910, 150, 1399.

[5] Hevesy, *Zeitsch. physikal. Chem.*, 1910, 73, 667.

[6] de Forcrand, *Compt. rend.*, 1906, 142, 1252; 1914, 158, 991.

[7] Schreinemakers and Meyeringh, *Chem. Weekblad*, 1908, 5, 811.

[8] de Forcrand, *Compt. rend.*, 1909, 149, 1341.

[9] Rieke and Endell, *Sprechsaal*, 1910, 43, 683.

[10] Biltz and Wilke-Dörfurt, *Ber.*, 1905, 38, 123; *Zeitsch. anorg. Chem.*, 1906, 48, 297; 50, 67.

[11] Rengade and Costeanu, *Compt. rend.*, 1913, 156, 791.

[12] Rengade and Costeanu, *ibid.*, 1914, 158, 946.

yield a monohydrate. The *tetrasulphide*, Cs_2S_4, is anhydrous. The *pentasulphide*, Cs_2S_5, melts at 204° to 205° C., and its density at 16° C. is 2·806.

Cæsium sulphites.[1]—The *normal sulphite*, Cs_2SO_3, is prepared by addition of an equivalent proportion of cæsium carbonate to an alcoholic solution of the salt saturated with sulphur dioxide. It forms white, readily soluble crystals.

The *primary sulphite*, $CsHSO_3$, is prepared by the action of sulphur dioxide on an alcoholic solution of the carbonate. It is a white, crystalline salt, very soluble in water.

Cæsium sulphate, Cs_2SO_4.—The sulphate is produced by the interaction of cæsium chloride and sulphuric acid.[2] It forms rhombic crystals,[3] melting at 995° C.[4] or 1019° C.[5] Its density at 16° C. is 4·260[6]; at 20° C., 4·2433; and at 60° C., 4·2218.[7]

The solubility[8] is given in the table:

Solubility of Cæsium Sulphate.

Temperature, °C.	0	10	20	30	40	50	60	70	80	90	100
Grams of Cs_2SO_4 per 100 grams of water	167·1	173·1	178·7	184·1	189·4	194·9	199·9	205·0	210·3	214·9	220·3

A saturated solution boils at 110° C. at 760 mm. pressure.[9] The salt is almost insoluble in alcohol. The heat of formation from the elements has been calculated[10] to be 349·8 Cal. It forms well-crystallized double salts with the sulphates of lithium, ferric iron, aluminium, and bivalent metals.

Cæsium hydrogen sulphate, $CsHSO_4$.—The primary sulphate crystallizes in rhombic prisms,[11] of density 3·352[12] at 16° C. Its heat of formation from the elements is 282·9 Cal., and its heat of solution —3·73 Cal.[13]

Another *acid sulphate*, $Cs_2O,8SO_3$, and the *pyrosulphate*, $Cs_2S_2O_7$, have been prepared.[14]

Cæsium persulphate, $Cs_2S_2O_8$.—The persulphate is produced by electrolysis of a concentrated solution of the sulphate.[15]

Cæsium thiosulphate, $Cs_2S_2O_3$.—The thiosulphate is formed on addition of sulphur to a boiling solution of the sulphite,[16] and also by the action of the carbonate on barium thiosulphate.[17] It crystallizes in small, very soluble needles.

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[1] Chabrié, *Compt. rend.*, 1901, 132, 680.

[2] Foote, *J. Amer. Chem. Soc.*, 1911, 33, 463.

[3] For isomorphism, see p. 227.

[4] Müller, *N. Jahrb. Mineral Beil.-Bd.*, 1914, 30, 1; *Zeitsch. Kryst. Min.*, 1914, 53, 511.

[5] Hüttner and Tammann, *Zeitsch. anorg. Chem.*, 1905, 43, 215.

[6] Spring, *Bull. Acad. roy. Belg.*, 1904, 290.

[7] Tutton, *Zeitsch. Kryst. Min.*, 1895, 24, 1.

[8] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 534; Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207.

[9] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.

[10] de Forcrand, *Compt. rend.*, 1906, 143, 98.

[11] Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 342; 1863, 119, 1; *Annalen*, 1862, 122, 347; 1863, 125, 367.

[12] Spring, *loc. cit.*

[13] de Forcrand, *loc. cit.*

[14] Weber, *Ber.*, 1884, 17, 2500.

[15] Foster and Smith, *J. Amer. Chem. Soc.*, 1899, 21, 934.

[16] Chabrié, *Compt. rend.*, 1901, 133, 295.

[17] Julius Meyer and Eggeling, *Ber.*, 1907, 40, 1351.

Cæsium dithionate, $Cs_2S_2O_6$.—The dithionate is produced by the action of the sulphate on barium dithionate.[1] It crystallizes in colourless, hexagonal plates, very soluble in water.

Cæsium trithionate, $Cs_2S_3O_6$.—The trithionate has been prepared by a method analogous to that employed for the rubidium salt.[2] It crystallizes in the triclinic system as an efflorescent monohydrate. The anhydrous salt has a density of 3·3 (approx.).

Cæsium tetrathionate, $Cs_2S_4O_6$.—The tetrathionate is an intermediate product in the production of the trithionate by Mackenzie and Marshall's method,[2] and is also formed by the action of iodine on the thiosulphate.[3]

Cæsium selenate, Cs_2SeO_4.—The normal selenate has been obtained in rhombic crystals,[4] of density 4·4528[5] at 20° C. At 12° C. its solubility is 245 grams in 100 grams of water. It is converted by selenic acid into *cæsium hydrogen selenate,* $CsHSeO_4$.[6]

Cæsamide, $CsNH_2$.—The amide is produced by the action of gaseous[7] or liquid[8] ammonia on the metal, or by that of gaseous ammonia on the hydride.[9] It crystallizes in white needles, melting at 260° C., and reacts energetically with water.

Cæsium hydrazoate, CsN_3.—The hydrazoate forms deliquescent crystals, melting at 310° to 318° C. It is not very explosive. Its solubility at 16° C. is 307·4 grams in 100 grams of water.[10]

Cæsium nitrite, $CsNO_2$.—The nitrite is prepared by the interaction of cæsium sulphate and barium nitrite, and forms a yellowish, hygroscopic, crystalline mass.[11] A number of double and triple salts of the nitrite with other metallic nitrites have been prepared.[12]

Cæsium nitrate, $CsNO_3$.—The nitrate crystallizes in hexagonal prisms, isomorphous with the corresponding salts of rubidium and potassium; they melt at 407° C.[13] or 414° C.[14] At 20° C. its density[13] is 3·643, and at 28° C. 3·687.[14]

The solubility in water[15] is given in the appended table:

Solubility of Cæsium Nitrate.

Temperature, °C. . .	0	10	20	30	40	50	60	70	80	90	100
Grams of $CsNO_3$ per 100 g. of water . .	9·33	14·9	23·0	33·9	47·2	64·4	83·8	107	134	163	197

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[1] Chabrié, *Compt. rend.*, 1901, 133, 295.

[2] Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726.

[3] Julius Meyer and Eggeling, *Ber.*, 1907, 40, 1351.

[4] For isomorphism, see p. 227.

[5] Tutton, *Zeitsch. Kryst. Min.*, 1895, 24, 1.

[6] Norris and Kingman, *Amer. Chem. J.*, 1901, 26, 318.

[7] Rengade, *Compt. rend.*, 1906, 142, 1533; 1907, 145, 236; *Ann. Chim. Phys.*, 1907, [8], 11, 348.

[8] Ruff and Geisel, *Ber.*, 1906, 39, 828.

[9] Moissan, *Compt. rend.*, 1903, 136, 587, 1177.

[10] Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 280; compare Dennis and Benedikt, *Zeitsch. anorg. Chem.*, 1898, 17, 20.

[11] Ball and Abram, *Trans. Chem. Soc.*, 1914, 103, 2130.

[12] Jamieson, *Amer. Chem. J.*, 1907, 38, 614.

[13] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[14] Richards and Archibald, *Zeitsch. anorg. Chem.*, 1903, 34, 353.

[15] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 534; Earl of Berkeley, *Phil. Trans.*, 1904, [A], 203, 207.

The molecular electric conductivity of cæsium nitrate between 446·6° and 556·3° C. is given by the formula [1]

$$\mu_t = 42{\cdot}13 + 0{\cdot}120(t - 450).$$

A saturated solution in contact with excess of the salt boils at 107·2° C. under 760 mm. pressure.[2] Its solubility in absolute alcohol is very slight. With nitric acid it yields *acid nitrates* [3] of the type $CsNO_3,HNO_3$, m.p. 100° C., and $CsNO_3,2HNO_3$, m.p. 32° to 36° C.

Cæsium phosphide, Cs_2P_5.—The phosphide resembles the corresponding potassium derivative (p. 181). It can be prepared by Hackspill and Bossuet's method (p. 181, reference 3).

Cæsium phosphates.—In constitution and properties the phosphates resemble the corresponding salts of rubidium. They are prepared by analogous methods.[4]

Cæsium carbide, Cs_2C_2.—The carbide is prepared from cæsium acetylide, Cs_2C_2,C_2H_2, by a method similar to that employed for the corresponding rubidium compound.[5]

Cæsium carbonate, Cs_2CO_3.—The normal carbonate is produced by the interaction of the hydroxide and ammonium carbonate.[6] It forms deliquescent, hydrated crystals, the anhydrous salt being very hygroscopic, and melting at red heat. When heated in vacuum it loses carbon dioxide. It is soluble in water to a very alkaline solution, the heat of solution being 11·84 Cal.[7] At 20° C. the saturated solution contains 72·34 per cent. of the anhydrous salt. Several hydrates are known. The heat of formation of the anhydrous salt is 274·54 Cal.[8]

Cæsium hydrogen carbonate, $CsHCO_3$.—The primary carbonate is formed by the action of carbon dioxide on the normal carbonate,[9] and crystallizes in long, anhydrous prisms, stable up to 125° C., but decomposing at 175° C. with evolution of carbon dioxide and formation of the normal carbonate. At 20° C. its solubility is higher than that of the corresponding potassium salt, being 67·77 grams in 100 grams of water : that of potassium hydrogen carbonate is 33·2 grams. At 15° C. the heat of solution is −4·317 Cal. The heat of formation from the elements is 232·92 Cal. The dissociation-pressure has been studied by Caven and Sand.[10] Other primary carbonates are formed by the action of atmospheric carbon dioxide on a solution of cæsium carbonate.

Cæsium percarbonate, $Cs_2C_2O_6$.—A solution of the percarbonate has been obtained by the electrolysis of a solution of cæsium carbonate.[11]

Cæsium metasilicate, Cs_2SiO_3.—An investigation has been made of the properties of the metasilicate in dilute aqueous solution.[12]

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[1] Jaeger and Kapma, *Zeitsch. anorg. Chem.*, 1920, 113, 27.

[2] Earl of Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, [A], 85, 489.

[3] Wells and Metzger, *Amer. Chem. J.*, 1901, 26, 271.

[4] Von Berg, *Ber.*, 1901, 34, 4181.

[5] Moissan, *Compt. rend.*, 1903, 136, 1221, 1522.

[6] Bunsen and Kirchhoff, *Pogg. Annalen*, 1861, 113, 342; 1863, 119, 1; *Annalen*, 1862, 122, 347; 1863, 125, 367.

[7] de Forcrand, *Compt. rend.*, 1909, 149, 97.

[8] de Forcrand, *ibid.*, 719.

[9] de Forcrand, *ibid.*, 719, 825; compare Bunsen and Kirchhoff, *loc. cit.*

[10] Caven and Sand, *Trans. Chem. Soc.*, 1914, 105, 2755.

[11] Riesenfeld and Reinhold, *Ber.*, 1909, 42, 4377.

[12] Kahlenberg and Lincoln, *J. Physical Chem.*, 1898, 2, 82.

DETECTION AND ESTIMATION OF CÆSIUM.

Cæsium compounds impart a reddish-violet coloration to the Bunsen flame, similar to that given by rubidium. The chloride forms an insoluble double chloride with stannic chloride of the formula Cs_2SnCl_6,[1] and also a double salt with antimony chloride.[2] Mackenzie and Marshall's method[3] described for rubidium (p. 199) is also applicable to the detection of cæsium.[4]

Cæsium chloride reacts with gold and silver solutions to form a complex cæsium-silver-gold chloride, crystallizing in opaque cubes. The microchemical identification of one-tenth of a microgram of cæsium is possible by means of this test.[5]

The separation of the metal from rubidium depends on the ready solubility of its carbonate in alcohol, that of rubidium being very slightly soluble. In its estimation the double salts with tin, lead, and antimony are employed.[6]

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[1] Stolba, *Dingler's Polytech. J.*, 1870, 197, 336; 198, 225.

[2] Muthmann, *Ber.*, 1893, 26, 1019; compare Godeffroy, *Ber.*, 1874, 7, 241.

[3] Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726.

[4] Compare Ball, *ibid.*, 1909, 95, 2126; 1910, 97, 1408.

[5] Bayer, *Monatsh.*, 1920, 41, 223; compare Emich, *ibid.*, 243.

[6] Sharples, *Amer. J. Sci.*, 1869, [2], 47, 178; Wells, *Zeitsch. anorg. Chem.*, 1893, 4, 344.

CHAPTER VIII.

AMMONIUM COMPOUNDS.

Occurrence.—Small quantities of ammonium salts are widely distributed over the surface of the earth and throughout the ocean. They are present in the Stassfurt deposits. The sulphate and chloride have been found in the neighbourhood of active volcanoes, and the borate is present in the boric-acid soffioni. A mineral called *struvite*, $MgNH_4PO_4$, is a product of the decomposition of animal excrement in the soil.

History.—The name *ammonium* is assigned to the radical NH_4, supposed to be present in the so-called *ammonium-amalgam*.[1] This substance was first prepared by Sebeck by electrolyzing ammonium salts in contact with mercury, and later by Berzelius and Pontin. Ampère regarded ammonia as the oxide of a metallic-like substance related to the alkalies.[2]

The name ammonia is probably derived from ἄμμος, sand.[3] The " hammoniacus sal " mentioned by Pliny [4] was probably rock-salt, and not the modern sal-ammoniac, similar terms being employed by Serapion and Avicenna in the eleventh century. Geber applied the name *sal ammoniacum* or *sal armoniacum* to ammonium chloride, and from the thirteenth to the seventeenth century these names were employed, as well as the name *sal armeniacus*. The term *sal ammoniacus* seems to have been definitely applied to ammonium chloride from the eighteenth century onwards. The confusion in nomenclature probably arose through the introduction of ammonium chloride into Europe from Asia about the eighth century under the name *Armenian salt*, this title being later confused with the name *sal ammoniacum* applied to rock-salt.

Geber's method for preparing ammonium chloride consisted in evaporating urine with sodium chloride, and subliming the residue. The Egyptians prepared it by subliming the soot formed by the combustion of camels' dung. It was first produced from hydrogen chloride and ammonia by Angelus Sala in 1620, and its qualitative composition was established by Glauber in 1648.

In 1595 Libavius obtained crystals of ammonium sulphate by evaporating impure sulphuric acid, and also by evaporating urine with sulphuric acid. It was investigated by Glauber, and received the name *sal ammoniacum secretum Glauberi*. At the close of the seventeenth century it was much in favour as a medicine. Glauber also prepared

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[1] See this series, Vol. III.

[2] Compare Kopp, *Geschichte der Chemie*, Brunswick, 1845, 3, 250.

[3] Compare Treumann, *Chem. Zeit.*, 1909, 33, 49 ; Schöne, *ibid.*, 77 ; von Lippmann, *ibid.*, 117, 186 ; Kout, *ibid.*, 297 ; Schramm, *ibid.*, 529.

[4] Pliny, *Naturalis Historiae*, Lugdini Batavorum, Rotterdam (Hackios), 1668, Vol. 3, Book 31, Chap. 7, p. 365.

ammonium nitrate, or *nitrum flammans*, by the action of ammonia on nitric acid. In the fifteenth century Valentinus obtained a red oil containing compounds of ammonia and sulphur by the distillation of a mixture of ammonium chloride, lime, and sulphur. At a later date this oil was named after Beguin *spiritus sulphuris volabilis Beguini.* In 1732 Boerhave discovered the solubility of sulphur in ammonia solution, and named the product "volatile liver of sulphur."

Preparation.—Being very sensitive to rise of temperature, the isolation of the ammonium radical by the electrolysis of solutions of ammonium salts in liquid ammonia is probably precluded by the thermal effect of the current. Its formation by the interaction of well-cooled ammonium chloride and a solution of potassium in liquid ammonia at −70° C. is indicated by a deficit of as much as 65 per cent. in the volume of the hydrogen evolved.[1]

The ammonium salts are formed by the interaction of gaseous ammonia and acids. Some of them are decomposed so readily as to make their isolation from solution impracticable, owing to hydrolytic dissociation and the volatility of the ammonia. The heat of neutralization by strong acids is 12·3 Cal., being 1·4 Cal. less than that of strong bases.[2]

Properties.—Although the radical ammonium has not been isolated, the analogy between its salts and those of the alkali-metals is so striking as to make it advantageous to consider both classes of compounds together. This similarity is displayed in such properties as crystalline form, optical character, solubility, electrolytic dissociation, and the strongly electropositive nature of the cations. Many ammonium salts are isomorphous with the corresponding salts of potassium, examples being the sulphate and chlorate. Numerous isomorphous double salts are also known, the alums furnishing a notable example. In its comparatively slight solubility ammonium hydrogen tartrate resembles the corresponding potassium salt, but the other simple salts of ammonium are very soluble. Crystallographic and optical measurements of the sulphates have shown that the radical ammonium occupies an intermediate position between rubidium and cæsium, but is more closely related to rubidium than to cæsium.[3] Its salts do not exhibit radioactivity.[4]

The ready vaporization of the ammonium salts constitutes a distinction between them and the salts of the alkali-metals. The conversion into vapour is attended by almost complete dissociation into ammonia and acid.

The anomalous character of ammonium hydroxide is the cause of another marked difference between the salts of ammonium and those of the alkali-metals, manifested in a much greater degree of hydrolysis in aqueous solution. When slightly warmed, a previously neutral solution of an ammonium salt reddens litmus. When the ammonia is in combination with a non-volatile acid, boiling expels it, and ultimately an acidic reaction develops in the solution.[5] The velocity of the action

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[1] Schlubach and Ballauf, *Ber.*, 1921, 54, [B], 2825.

[2] Thomsen, *Thermochemistry* (Longmans, 1908), 115.

[3] Tutton, *Trans. Chem. Soc.*, 1903, 83, 1049.

[4] Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576.

[5] Compare Dibbits, *Ber.*, 1872, 5, 820; Fittig, *Annalen*, 1863, 128, 189; Leeds, *Amer. J. Sci.*, 1874, [3], 7, 197; *Chem. News*, 1874, 29, 256; *Arch. Sci. phys. nat.*, 1874, 50, 214.

of bromine on ammonium salts furnishes a means of comparing the extent of their hydrolytic dissociation. Under certain conditions the action on free ammonia is represented by the equation

$$2NH_3+3Br_2=N_2+6HBr,$$

and for the ammonium salts its velocity increases with the hydrolytic dissociation.[1] Other methods of determining the degree of hydrolysis have also been devised.[2]

Ammonium ion and Valency.—Although no direct measurement of the electroaffinity of the ammonium ion has been possible, the slight tendency to hydration of its salts indicates that it is stronger than the potassium ion. It is colourless, and the *migration-velocity* at 18° C.[3] is given as 64·2, and at 25° C.[4] as 73. Like the alkali-metals, the radical ammonium is univalent, and forms salts with one equivalent of an acid.

AMMONIUM SALTS.

Ammonium fluoride, NH_4F.—The fluoride is formed by the interaction of gaseous hydrogen fluoride and anhydrous ammonia. It can be prepared by sublimation from a mixture of ammonium chloride and sodium fluoride.[5] It forms very brittle, colourless, hexagonal laminæ[6] of strongly saline taste. In dry air it is stable at ordinary temperature. When heated, it fuses, and then sublimes. The dry salt can absorb ammonia at ordinary temperature, the gas being expelled by heat. It is deliquescent, and dissolves in its own weight of water at 0° C.[7] In aqueous solution it undergoes extensive hydrolytic dissociation. In consequence of the presence of free hydrogen fluoride, the solution attacks glass, and should be stored in vessels made of platinum, silver, or gutta-percha.[8] Explosive, oily drops of nitrogen fluoride are said to be formed by its electrolysis,[9] but the statement lacks confirmation.[7] It is employed as a disinfectant in the brewing industry,[10] and is a powerful preservative, almost inhibiting the fermentation of invert-sugar.[11]

The heat of formation of the solid from gaseous ammonia and hydrogen fluoride is 37·3 Cal., and the heat of neutralization of the acid by ammonia in aqueous solution is 15·2 Cal.[12]

Ammonium hydrogen fluoride, NH_4F,HF.—Evaporation of a solution of the normal salt at a temperature between 36° and 40° C. expels ammonia, the primary salt crystallizing out. It can also be prepared by the action of ammonia on a solution of hydrogen fluoride, a small proportion of ammonium sulphide or carbonate being added.[13] It forms colourless rhombic prisms, readily soluble in water,[6] with a density of 1·211[14] at 12° C.

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[1] Ostwald and Raich, *Zeitsch. physikal. Chem.*, 1888, 2, 125.

[2] Compare Veley, *Trans. Chem. Soc.*, 1905, 87, 26; Hill, *ibid.*, 1906, 89, 1273; Naumann and Rücker, *J. prakt. Chem.*, 1905, [2], 74, 249; Naumann and Müller, *ibid.*, 215; Grossmann, *Zeitsch. anorg. Chem.*, 1902, 33, 149.

[3] Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, Leipsic, 1898.

[4] Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 228.

[5] Berzelius, *Lehrbuch der Chemie*, 6th ed., Leipsic, 1856, 3, 282.

[6] Marignac, *Ann. Mines*, 1859, [5], 15, 221.

[7] Ruff and Geisel, *Ber.*, 1903, 36, 2677.

[8] Rose, *Pogg. Annalen*, 1859, 108, 19.

[9] Warren, *Chem. News*, 1887, 55, 289.

[10] Will and Braun, *Zeitsch. ges. Brauw.*, 1904, 27, 521, 537, 553.

[11] Lührig and Sartori, *Pharm. Zentralhalle*, 1908, 49, 934.

[12] Guntz, *Compt. rend.*, 1883, 97, 1483; *Ann. Chim. Phys.*, 1884, [6], 3, 5, 17.

[13] Rose, *loc. cit.*

[14] Bödeker, *Beziehungen zwischen Dichte und Zusammensetzung*, Leipsic, 1860.

Ammonium chloride, NH_4Cl.—In nature the chloride is found in the neighbourhood of volcanoes, and it is a constituent of many varieties of coal, iron-ore, and mineral waters. It is formed by the action of gaseous hydrogen chloride on ammonia in presence of a trace of moisture[1]; by the interaction of ammonium hydrogen carbonate and soluble chlorides[2]; and by sublimation from a mixture of ammonium sulphate and sodium chloride.[3] It was formerly manufactured in Egypt by sublimation from the soot formed by burning camels' dung. Another process of manufacture consisted in subliming the soot produced by the combustion of a mixture of manure, sodium chloride, coal, and clay. The main source of ammonium chloride is the gas-manufacture, the ammoniacal liquor containing sulphide, cyanide, and carbonate of ammonium. After liberating the ammonia by the action of lime, and absorbing it by hydrochloric acid, solid ammonium chloride is obtained by concentrating the solution in leaden pans. It is purified by sublimation. Stas[4] has described a method of purifying the "pure" commercial product.

Ammonium chloride forms colourless crystals belonging to the cubic system, characterized by their saline taste. According to Wegscheider,[5] the crystals are dimorphous, and have the transition-point 184·5° C.; whereas Hachmeister[6] gives 174° C. Haigh[7] states that ammonium chloride sublimes without melting, but Rassow[8] gives the melting-point as 519·7° C., and the vapour-pressure at 520° C. as 37·5 atmospheres. Its density is given as 1·527[9] at 11·3° C.; 1·526[10] at 20° C.; 1·496 to 1·503[11] at 20° C.; 1·532[12] at 22° C.; and 1·578[13] at —188° C. Its specific heat is given as 0·3594 between 0° and 19° C.,[14] 0·373 between 15° and 45° C.,[15] and 0·391 between 23° and 100° C.[16] The heat of formation from its elements is 75·79 Cal.[17]

The solubility in water[18] is given in the table:

Solubility of Ammonium Chloride.

Temperature, °C.	—15	—10·9	—5·7	0	10	20	30	40
Grams of NH_4Cl in 100 g. of water	24·5	25·5	27·7	29·4	33·3	37·2	41·4	45·8
Temperature, °C.	50	60	70	80	90	100	110	
Grams of NH_4Cl in 100 g. of water	50·4	55·2	60·2	65·6	71·3	77·3	83·8	

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[1] Compare Baker, *Trans. Chem. Soc.*, 1894, 65, 611.

[2] Genteles, *British Patent*, 1878, No. 2224.

[3] French, *J. Soc. Chem. Ind.*, 1888, 7, 735.

[4] Stas, *Gesetze der chemischen Proportionen der Atomgewichten*, Leipsic, 1867, 49.

[5] Wegscheider, *Zeitsch. anorg. Chem.*, 1918, 103, 207.

[6] Hachmeister, *ibid.*, 1919, 109, 145.

[7] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

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

[9] Chauvenet and Urbain, *Compt. rend.*, 1913, 156, 1320.

[10] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[11] Le Blanc and Rohland, *Zeitsch. physikal. Chem.*, 1896, 19, 261.

[12] Krickmeyer, *ibid.*, 1896, 21, 53.

[13] Dewar, *Chem. News*, 1902, 85, 277.

[14] Brönsted, *Zeitsch. Elektrochem.*, 1912, 18, 714.

[15] Kopp, *Annalen Suppl.*, 1864–5, 3, 289.

[16] Neumann, *Pogg. Annalen*, 1865, 126, 120.

[17] Thomsen, *Thermochemistry* (Longmans, 1908), 251.

[18] Mulder, *Bijdragen tot de geschiedenis van het scheikundig gebonden water*, Rotterdam, 1864, 57. Below 0° C. the results are those of Meerburg, *Zeitsch. anorg. Chem.*, 1903, 37, 203.

A solution in contact with excess of the salt boils at 115·6° C., and at that temperature contains 87·3 grams per 100 grams of water. At 75° C. a similar solution contains 38·23 grams of the salt per 100 grams of the solution.[1] In dilute aqueous solution its degree of ionization is of the same order as that of potassium or sodium chloride.[2]

The volatilization of ammonium chloride by heat is attended by much dissociation[3] in presence of moisture, corresponding with 67 to 63 per cent., and a slight decrease in the extent of the dissociation between 280° and 330° C.[4] Absence of water-vapour almost entirely prevents the dissociation of ammonium chloride, and the combination of hydrogen chloride and ammonia.[5]

The heat of neutralization of ammonia and hydrogen chloride in aqueous solution is given as 12·27 Cal.[6] and 12·45 Cal.[7] At ordinary temperature this solution is not absolutely stable.[8] When heated, it evolves ammonia, and develops an acidic reaction.[9]

When ammonium chloride is heated in contact with air and platinum, there is partial oxidation with formation of nitric acid and liberation of chlorine. Heating the salt with gaseous hydrogen iodide also causes decomposition[10]; and heating with potassium forms potassium chloride, with evolution of ammonia and hydrogen. It is also decomposed by other metals. At a red heat it converts many salts and oxides into chlorides,[11] but the oxides of cobalt and nickel are reduced to the corresponding metal.[12] At 400° C. it reacts with carbonyl chloride, $COCl_2$, to form carbamyl chloride, $Cl{\cdot}CO{\cdot}NH_2$.[13] When heated with potassium dichromate, it is decomposed with evolution of nitrogen, nitric oxide, nitrogen peroxide, and chlorine.[14] It combines with ammonia to form complex derivatives,[15] an additive compound prepared by Kendall and Davidson[16] having the formula $NH_4Cl,3NH_3$, and the melting-point 10·7° C.

Ammonium chloride exerts a catalytic, accelerating effect on certain reactions, examples being the interaction of iodic acid and sulphurous acid,[17] and the inversion of sucrose by hydrochloric acid.[18] It is employed in the manufacture of ammonia and ammonium compounds, in pharmacy and the dye-industry, and in soldering.

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[1] Tschugaev and Chlopin, *Zeitsch. anorg. Chem.*, 1914, 86, 154.

[2] Noyes, *Zeitsch. physikal. Chem.*, 1882, 9, 608.

[3] Than, *Annalen*, 1861, 131, 131; Bineau, *Ann. Chim. Phys.*, 1863, [3], 68, 416; Ramsay and Young, *Zeitsch. physikal. Chem.*, 1887, 1, 244.

[4] Smith and Lombard, *J. Amer. Chem. Soc.*, 1915, 37, 38.

[5] Baker, *Trans. Chem. Soc.*, 1894, 65, 611; 1898, 73, 422; compare Gutmann, *Annalen*, 1897, 299, 267.

[6] Thomsen, *Thermochemistry* (Longmans, 1908), 115.

[7] Berthelot, *Compt. rend.*, 1873, 76, 1041, 1106.

[8] Leeds, *Chem. News*, 1879, 39, 17; *Amer. Chem. J.*, 1880, 2, 246; compare Cornwall, *ibid.*, 45.

[9] Watson Smith, *J. Soc. Chem. Ind.*, 1911, 30, 253; Leeds, *Amer. J. Sci.*, 1874, [3], 7, 197; *Chem. News*, 1874, 29, 256; *Arch. Sci. phys. nat.*, 1874, 50, 214.

[10] Hautefeuille, *Bull. Soc. chim.*, 1867, [2], 7, 198.

[11] Compare Gmelin-Kraut, *Handbuch der anorg. Chem.*, Heidelberg, 1872–1897, 2, i., 422.

[12] Santi, *Boll. chim. farm.*, 1904, 43, 673.

[13] Gattermann and Schmidt, *Ber.*, 1887, 20, 858.

[14] Frankforter, Roehrich, and Manuel, *J. Amer. Chem. Soc.*, 1910, 32, 176; compare de Luna, *Ann. Chim. Phys.*, 1863, [3], 68, 183.

[15] Troost, *Compt. rend.*, 1879, 88, 578.

[16] Kendall and Davidson, *J. Amer. Chem. Soc.*, 1920, 42, 1141.

[17] Landolt, *Sitzungsber. K. Akad. Wiss. Berlin*, 1887, 21, 745.

[18] Arrhenius, *Zeitsch. physikal. Chem.*, 1889, 4, 240.

Ammonium bromide, NH_4Br.—The bromide is produced by the interaction of ammonia and hydrogen bromide, either in the gaseous form or in solution, the second process being accompanied by the formation of hypobromite,[1] and possibly bromate.[2] Under certain conditions it is also formed by the action of bromine on ammonia :

$$4NH_3+3Br=3NH_4Br+N.$$

A method of preparing the pure substance has also been described.[3]

Ammonium bromide is a colourless, crystalline substance of strongly saline taste. On exposure to the air it gradually develops a yellow colour, the change being caused by the liberation of bromine. Rassow [4] gives the melting-point of the salt as 541·9° C. Its density is stated to be 2·327 [5] at 15° C. and 2·3956 [6] at 24° C. On heating it sublimes, and undergoes almost complete dissociation into ammonia and hydrogen bromide,[7] the degree of dissociation being 39 per cent. at 320° C. and 10 per cent. at 388° C.[8] On cooling, it condenses unchanged.[9] The heat of formation from the elements is 66·4 Cal.,[10] and from gaseous ammonia and hydrogen bromide 45·0 Cal.[11] Its solubility in water is given in the table : [12]

Solubility of Ammonium Bromide.

Temperature, °C. . .	10	20	40	60	80	100
Grams of NH_4Br in 100 grams of water . .	66·2	74·0	87·5	101·0	115·0	128·2

More recent work indicates the solubility per 100 grams of water to be 60·6 grams at 0° C., 99·2 grams at 50° C., and 145·6 grams at 100° C.[13]

The solution of a gram-molecule in 200 gram-molecules of water absorbs 4·4 Cal.[14] The heat of neutralization of ammonia and hydrogen bromide in dilute aqueous solution is 12·4 Cal.[15]

In concentrated aqueous solution ammonium bromide is converted by electrolysis or the action of bromine into *ammonium tribromide*, NH_4Br,Br_2,.[16] This substance is unstable, and forms large columnar crystals with a colour similar to that of potassium dichromate. Ammonium bromide combines with ammonia to form complex de-

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[1] Schönbein, *J. prakt. Chem.*, 1861, 84, 385.

[2] Bosetti, *Arch. Pharm.*, 1889, [3], 27, 120; compare Thümmel, *ibid.*, 1888, [3], 26, 1124.

[3] Richards and Müller, *Zeitsch. anorg. Chem.*, 1907, 53, 423.

[4] Rassow, *ibid.*, 1920, 114, 117.

[5] Eder, *Sitzungsber. K. Akad. Wiss. Wien*, 1882, 86, 284.

[6] Schiff and Monsacchi, *Zeitsch. physikal. Chem.*, 1896, 21, 277.

[7] Deville and Troost, *Compt. rend.*, 1859, 49, 239; 1863, 56, 891; *Annalen*, 1860, 113, 42; 1863, 127, 274.

[8] Smith and Lombard, *J. Amer. Chem. Soc.*, 1915, 37, 38.

[9] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.

[10] Thomsen, *J. prakt. Chem.*, 1880, [2], 21, 449; Berthelot, *Thermochimie*, Paris, 1897, 1, 222.

[11] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 2, 406; *J. prakt. Chem.*, 1877, [2], 16, 330.

[12] Eder, *Abhandl. K. Akad. Wiss. Berlin*, 1880, 82, ii., 1284; Guthrie, *Phil. Mag.*, 1875, [4], 49, 213; Eder, *Sitzungsber. K. Akad. Wiss. Wien*, 1882, 86, 1284; Gerlach, *Salzlösungen*, Freiberg, 1859.

[13] Smith and Eastlack, *J. Amer. Chem. Soc.*, 1916, 38, 1261.

[14] Thomsen, *J. prakt. Chem.*, 1877, [2], 16, 330.

[15] Arrhenius, *Zeitsch. physikal. Chem.*, 1887, 1, 635.

[16] Roozeboom, *Ber.*, 1881, 14, 2398.

rivatives,[1] an example being the substance[2] melting at 13·7° C., and having the formula $NH_4Br,3NH_3$.

Ammonium iodide, NH_4I.—The iodide is formed by methods analogous to those applicable to the bromide.[3] It is also a product of the decomposition of nitrogen iodide in presence of water or ammonium hydroxide.[4] It is best prepared by addition of alcohol to an aqueous solution of potassium iodide and ammonium sulphate in equimolecular proportions, potassium sulphate crystallizing and ammonium iodide remaining dissolved.[5] It can also be prepared by the interaction of ferrous iodide and ammonium carbonate, and by that of ammonium hydroxide and iodine in presence of hydrogen peroxide: [6]

$$2NH_3+2I+H_2O_2=2NH_4I+O_2.$$

Ammonium iodide crystallizes in colourless deliquescent cubes, of density 2·515[7] at 20° C. For the melting-point Rassow[8] gives 551° ± 3° C., an accurate determination being prevented by dissociation. Heating causes sublimation, accompanied by almost complete dissociation,[9] and in presence of air a certain degree of decomposition. The initial effect of heat is to cause the vapour to associate, the degree of association diminishing with rise of temperature.[10] The heat of formation from the elements is 49·31 Cal., and from gaseous ammonia and hydrogen iodide 43·46 Cal.[11] At 15° C. its solubility is 167 grams in 100 grams of water.[12] In concentrated aqueous solution it is converted by iodine into the tri-iodide,[13] NH_4I,I_2, tabular, rhombic crystals, isomorphous with the tri-iodides of the alkali-metals.[14] With ammonia, ammonium iodide yields additive compounds.[15] One example is the substance melting at $-8·0°$ C., with the formula $NH_4I,3NH_3$; and another that melting at $-5·1°$ C., with the formula $NH_4I,4NH_3$.

In aqueous solution ammonium iodide is gradually oxidized, the reaction being accelerated by light.[16] The salt finds application in the photographic industry.

Ammonium dichloroiodide, NH_4Cl_2I.—The liquid obtained by the action of chlorine on an aqueous solution of ammonium chloride containing iodine in suspension, until the free iodine has just disappeared, deposits scarlet prisms of ammonium dichloroiodide. This perhalide is also formed by the interaction of an aqueous solution of ammonium iodide and chlorine. It is the most stable of the trihalides, and can be

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[1] Troost, *Compt. rend.*, 1881, 92, 715; Roozeboom, *Zeitsch. physikal. Chem.*, 1888, 2, 460; *Rec. trav. chim.*, 1885, 4, 361.

[2] Kendall and Davidson, *J. Amer. Chem. Soc.*, 1920, 42, 1141.

[3] Compare Schönbein, *J. prakt. Chem.*, 1861, 84, 385.

[4] Guyard, *Compt. rend.*, 1883, 97, 526; *Mon. Scient.*, 1883, [3], 13, 1011.

[5] Jacobsen, *Neues Jahrb. Pharm.*, 1864, 20, 91.

[6] Broeksmit, *Pharm. Weekblad*, 1917, 54, 1373; compare Rupp, *Apoth. Zeit.*, 1918, 33, 406, 473.

[7] Le Blanc and Rohland, *Zeitsch. physikal. Chem.*, 1896, 19, 261.

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

[9] Deville and Troost, *Compt. rend.*, 1859, 49, 239; 1863, 56, 891; *Annalen*, 1860, 113, 42; 1863, 127, 274.

[10] Smith and Lombard, *J. Amer. Chem. Soc.*, 1915, 37, 38.

[11] Thomsen, *Thermochemistry* (Longmans, 1908), 251.

[12] Eder, *Dingler's Polytech. J.*, 1876, 221, 189.

[13] Johnson, *Chem. News*, 1878, 37, 270; *Trans. Chem. Soc.*, 1878, 33, 397.

[14] Wheeler, Barnes, and Pratt, *Amer. Chem. J.*, 1897, 19, 672.

[15] Kendall and Davidson, *J. Amer. Chem. Soc.*, 1920, 42, 1141.

[16] Leeds, *Pharm. J.*, 1879, [3], 9, 1017

preserved indefinitely in a sealed tube. At ordinary temperature in contact with air it is slowly transformed into iodine monochloride and ammonium chloride, and at 100° C. it decomposes rapidly into these two substances. It dissolves readily in water, yielding a deep-red solution.[1]

Ammonium tetrachloroiodide, NH_4Cl_4I.—This compound is the first of the ammonium perhalides mentioned in the literature. It was prepared originally by Filhol in 1839,[2] and was isolated by Chattaway [1] in the form of golden-yellow prisms by the action of chlorine on a saturated aqueous solution of ammonium dichloroiodide. When kept in a sealed tube it is stable; but in the air first loses chlorine, forming the dichloroiodide, this substance gradually changing into ammonium chloride and iodine monochloride.

Ammonium chlorobromoiodide, NH_4ClBrI.—Equivalent amounts of bromine and iodine react with a concentrated aqueous solution of ammonium chloride to form a brownish-red liquid, from which ammonium chlorobromoiodide can be obtained in garnet-red prisms. In a sealed tube it is stable, even at 200° C., but heating in air decomposes it into ammonium chloride and iodine bromide. It dissolves very readily in water, forming a deep-red solution.[1]

Ammonium hypochlorite, NH_4ClO.—An unstable solution of the hypochlorite is obtained by neutralizing aqueous hypochlorous acid with ammonia, by the action of chlorine on ammonium hydroxide,[3] and by addition of an ammonium salt to a dilute solution of bleaching powder.[4] It has not been isolated in the solid state.

Ammonium chlorate, NH_4ClO_3.—The chlorate is produced by neutralizing chloric acid with ammonia, and by double decomposition from the chlorates of calcium, strontium, and barium by means of ammonium carbonate, or from potassium chlorate by the action of ammonium hydrogen tartrate or silicofluoride.[5] It forms tetragonal,[6] highly explosive crystals,[7] melting slightly above 60° C. At 90° C. an explosive decomposition takes place in accordance with the equation [8]

$$NH_4ClO_3=NOCl+2H_2O.$$

It is employed in bronzing copper.

Ammonium perchlorate, NH_4ClO_4.—The perchlorate is formed by mixing solutions of barium perchlorate and ammonium sulphate, by the action of ammonium nitrate on sodium perchlorate,[9] and by that of ammonium chloride on calcium or magnesium perchlorate.[10] It forms rhombic,[11] doubly refracting crystals,[12] of density 1·88 at 25° C. Its solubility at 18° C. is 21·07 grams in 100 grams of water.[13] It is de-

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[1] Chattaway, *Trans. Chem. Soc.*, 1915, 107, 105; for corresponding organic derivatives see McCombie and Reade, *ibid.*, 1923, 123, 141.

[2] Filhol, *J. Pharm.*, 1839, 25, 431.

[3] Compare Dutoit and Miss Emily Aston, *Compt. rend.*, 1897, 125, 240.

[4] Cross and Bevan, *Proc. Chem. Soc.*, 1890, 6, 22.

[5] Wonfor, *Phil. Mag.*, 1824, 63, 75.

[6] Retgers, *Zeitsch. physikal. Chem.*, 1890, 5, 436.

[7] Groschuff, *Deutsch. Mech. Zeit.*, 1912, 145, 153.

[8] Salvadori, *Ann. Chim. Applicata*, 1916, 6, 116.

[9] Alvisi, *Patentblatt*, 1898, 20, 567.

[10] Miolatti, *German Patent*, No. 112682.

[11] Hofmann, Höbold, and Quoos, *Annalen*, 1912, 386, 304.

[12] Clark, *Ber.*, 1879, 12, 1398.

[13] Hofmann, Höbold, and Quoos, *loc. cit.*

composed by heat, slowly between 145° and 150° C., rapidly at 180° C.,[1] and is employed in the manufacture of explosives.[2]

Ammonium hypobromite.—Bromine is said to react with a well-cooled ammonium-hydroxide solution, with formation of an unstable solution of the hypobromite.[3]

Ammonium bromate, NH_4BrO_3.—Evaporation of an aqueous solution of ammonia and bromic acid, or of barium bromate and ammonium carbonate, yields the bromate in colourless needles. They are very unstable, and decompose with some energy at ordinary temperatures.[4]

Ammonium hypoiodite.—A very unstable solution of the hypoiodite is probably formed by addition of excess of ammonium hydroxide to an aqueous solution of iodine. The solution exerts a powerful bleaching action, but rapidly decomposes into iodine and iodate.[5]

Ammonium iodate, NH_4IO_3.—The iodate is produced by the action of ammonia or ammonium carbonate on iodic acid or iodine trichloride, and is also one of the products of the interaction of iodine and ammonia.[6] It forms colourless rhombic [7] crystals, of density 3·3085 [8] at 21° C., its solubility at 30° C. being 4·2 grams in 100 grams of water.[9] At 150° C. it decomposes energetically into oxygen, nitrogen, iodine, and water.[10] Acid salts derived from one molecule of the iodate and one molecule [11] or two molecules [12] of iodic acid have been described.

Ammonium periodate, NH_4IO_4.—Neutralization of periodic acid with ammonia yields the periodate in tetragonal crystals isomorphous with the corresponding potassium, sodium, and rubidium salts,[13] and also with the periodates of silver and lithium.[14] Its density at 18° C. is 3·056; and its solubility at 16° C. is 2·7 grams in 100 grams of water.[15] Several hydrates [16] and complex periodates [17] have been described, examples being $(NH_4)_2H_3IO_6$, prepared by Rammelsberg and Groth,[18] and $(NH_4)_3H_7(IO_6)_2,2\frac{1}{2}H_2O$.[19] The hydrated salt with the second formula is obtained in the form of rectangular crystals by agitating periodic acid with excess of 25 per cent. ammonia at 140° C. for several hours.

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[1] Girard and Laroche, *Mon. Scient.*, 1909, [4], 23, i., 217.

[2] Alvisi, *Gazzetta*, 1899, 29, i., 121.

[3] Maumené, *Compt. rend.*, 1870, 70, 147; Kraut, *Gmelin-Kraut's Handbuch der anorg. Chem.*, Heidelberg, 1872–1897, 2, i., 560; Foster, *Trans. Chem. Soc.*, 1886, 33, 470; Bosetti, *Arch. Pharm.*, 1889, [3], 27, 120.

[4] Rammelsberg, *Pogg. Annalen*, 1833, 52, 85; compare Retgers, *Zeitsch. physikal. Chem.*, 1890, 5, 436.

[5] Compare Gmelin-Kraut, *Handbuch der anorg. Chem.*, Heidelberg, 1872–1897, 2, i., 289, 495.

[6] Gmelin-Kraut, *ibid.*; Guyard, *Compt. rend.*, 1883, 97, 526; *Mon. Scient.*, 1883, [3], 13, 1011.

[7] Eakle, *Zeitsch. Kryst. Min.*, 1896, 26, 558; Ries, *ibid.*, 1905, 41, 243.

[8] Clarke, *Amer. J. Sci.*, 1877, [3], 14, 281.

[9] Meerburg, *Zeitsch. anorg. Chem.*, 1905, 45, 324.

[10] Rammelsberg, *Pogg. Annalen*, 1838, 44, 555.

[11] Ditte, *Ann. Chim. Phys.*, 1890, [6], 21, 146.

[12] Meerburg, *loc. cit.*; Blomstrand, *J. prakt. Chem.*, 1889, 40, 338.

[13] Barker, *Trans. Chem. Soc.*, 1908, 93, 15.

[14] Rammelsberg, *Pogg. Annalen*, 1868, 134, 368.

[15] Barker, *loc. cit.*

[16] Eakle, *Zeitsch. Kryst. Min.*, 1896, 26, 558; Ihre, *Ber.*, 1876, 9, 316; Langlois, *Ann. Chim. Phys.*, 1852, [3], 34, 257; *Annalen*, 1852, 83, 153.

[17] Ihre, *loc. cit.*; Rammelsberg and Groth, *Pogg. Annalen*, 1868, 134, 379.

[18] Rammelsberg and Groth, *loc. cit.*; compare Rosenheim and Loewenthal, *Kolloid Zeitsch.*, 1919, 25, 53.

[19] Rosenheim and Loewenthal, *loc. cit.*

Ammonium manganate and permanganate.—The modes of preparation and the properties of ammonium manganate and permanganate are given in Vol. VIII.

Ammonium oxide.—No oxide corresponding with ammonium hydroxide has been prepared with certainty (compare ammonium hydroxide).

Ammonium peroxides.—At −10° C. dry ammonia reacts with a solution of 98 per cent. hydrogen peroxide in absolute ether to form a crystalline precipitate of the formula NH_4O_2H or $(NH_4)_2O_2,H_2O_2$. It melts at 14° C., and is converted by the prolonged action of ammonia into an oil, $(NH_4)_2O_2$, which solidifies at −40° C., begins to decompose about −10° C., and melts at −2° C. It readily loses ammonia, regenerating the parent substance, NH_4O_2H.[1] A crystalline, hydrated form of the composition $(NH_4)_2O_2,2H_2O_2,10H_2O$, has been prepared. Potassium hydroxide decomposes it, with formation of ammonia and potassium peroxide.

Ammonium hydroxide, NH_4OH.—Ammonia dissolves readily in water to form a solution of weakly basic character (p. 9).[2] The heat of solution is 3·845 Cal., the maximum evolution of heat corresponding with 46 per cent. of ammonia, and the formation of a hydrate, $NH_3,1{\cdot}109H_2O$. The maximum contraction corresponds with 52 per cent. of ammonia, and with the formation of a hydrate, $NH_3,0{\cdot}9H_2O$. These facts point to the existence of a hydrate, NH_3,H_2O.[3] When a solution containing about 49 per cent. of ammonia is cooled, it solidifies at −79° C. to small colourless crystals of the monohydrate, NH_3,H_2O, the theoretical percentage of ammonia in a compound of this formula being 48·59. A solution containing 65 per cent. of ammonia freezes at the same temperature, yielding larger crystals of the formula $2NH_3,H_2O$, the theoretical percentage of ammonia being 65·4. It has been suggested that this substance is ammonium oxide, $(NH_4)_2O$. The monohydrate resembles the hydroxides of sodium and potassium.[4] The freezing-point curves of aqueous solutions of ammonia indicate the existence of both these hydrates.[5]

Electrochemical oxidation of a solution of ammonium hydroxide with a current of low density in presence of sodium chloride and glue yields hydrazine, N_2H_4.[6]

The action on sulphur of ammonium hydroxide solution of density 0·888 is similar to that of a concentrated aqueous solution of sodium or potassium hydroxide (pp. 111 and 171).

Ammonium sulphide, $(NH_4)_2S$.—At −18° C. hydrogen sulphide combines with twice its volume of ammonia to form colourless, strongly alkaline crystals of ammonium sulphide,[7] stable only at low temperature,

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[1] d'Ans and Wedig, *Ber.*, 1913, 46, 3075; compare Melikov and Pissarjewsky, *Ber.*, 1897, 30, 3144; 1898, 31, 152, 446; *J. Russ. Phys. Chem. Soc.*, 1898, 30, 475; *Zeitsch. anorg. Chem.*, 1898, 18, 89; Melikov, *Ber.*, 1913, 46, 3899.

[2] From the results of experiments on the dissociation-pressure of hydrated cupric alkali-metal (or ammonium) sulphates, Caven and Ferguson (*Trans. Chem. Soc.*, 1922, 121, 1413) consider the order of increasing basic strength of the following hydroxides to be $KOH < RbOH < NH_4OH < CsOH$; compare Tutton, *ibid.*, 1903, 83, 1049; Caven, *Chemistry and Industry*, 1923, 42, 164, 448; Moore, *ibid.*, 343.

[3] Baud and Gay, *Compt. rend.*, 1909, 148, 1327; *Ann. Chim. Phys.*, 1909, [8], 17, 398.

[4] Rupert, *J. Amer. Chem. Soc.*, 1909, 31, 866; 1910, 32, 748; compare Caven, *loc. cit.*

[5] Smits and Postma, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 186.

[6] Turrentine and Olin, *J. Amer. Chem. Soc.*, 1915, 37, 1114.

[7] Bineau, *Ann. Chim. Phys.*, 1838, 67, 230; 68, 435; 1839, 70, 261.

and readily decomposed into ammonia and ammonium hydrogen sulphide. Bloxam[1] regards the ordinary solution of ammonium sulphide as $(NH_4)_2S,2NH_4SH+2NH_4OH$. Several complex derivatives with ammonia have been described.[2] The heat of formation of the sulphide from ammonia and hydrogen sulphide in aqueous solution is given as 6·2 Cal.[3] and 6·3 Cal.[4]

Ammonium hydrogen sulphide, NH_4SH.—The primary sulphide is formed in white crystals by the interaction of ammonia and hydrogen sulphide in ethyl-acetate solution.[5] At or below 0° C. it undergoes only a slow decomposition into hydrogen sulphide and ammonia. Its melting-point in a closed vessel is 120° C.[6] Its heat of formation from sulphur-vapour, hydrogen, and nitrogen has been calculated[7] to be 42·4 Cal. In aqueous solution it undergoes extensive hydrolytic dissociation, and the strongly alkaline solution is oxidized by exposure to air, yielding a yellow solution containing polysulphides, and also sulphite and thiosulphate.[8] This liquid constitutes the ordinary solution of ammonium sulphide employed in analysis; it can also be prepared by dissolving sulphur in a solution of ammonium hydrogen sulphide, or by distilling a hot solution of sodium sulphide and ammonium chloride.[9]

The so-called "volatile liver of sulphur" is a mixture of ammonium hydrogen sulphide and polysulphides, and is obtained as a dark-red, fuming liquid by distilling ammonium chloride, sulphur, and lime.[10]

Ammonium polysulphides.—Various solid polysulphides have been described,[11] but there is no certainty that they are true compounds. Examples are the *tetrasulphide*, $(NH_4)_2S_4$, unstable yellow crystals prepared by cooling the mother-liquor of the pentasulphide after treatment with hydrogen sulphide and ammonia, and along with the pentasulphide by the action of these reagents on a solution of the enneasulphide; the *pentasulphide*, $(NH_4)_2S_5$, rhombic orange crystals obtained by dissolving sulphur in a warm solution containing hydrogen sulphide and ammonia in the ratio 1 : 2, or by addition of alcohol to a cold concentrated solution of ammonium sulphide saturated with sulphur[12]; the *heptasulphide*, $(NH_4)_2S_7$,[13] ruby-red crystals produced by dissolving the pentasulphide in its own mother-liquor and allowing the solution to crystallize, or as crystals of violet lustre and the formula $3(NH_4)_2S_7,4H_2O$ by saturating a concentrated solution of ammonia with hydrogen sulphide and sulphur; and the *enneasulphide*, $(NH_4)_2S_9,\frac{1}{2}H_2O$, deep-red crystals deposited from the mother-liquor of the pentasulphide after prolonged exposure to air.

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[1] Bloxam, *Zeitsch. anorg. Chem.*, 1908, 60, 113.

[2] Bloxam, *Chem. News*, 1893, 68, 97; Maumené, *Compt. rend.*, 1879, 89, 506.

[3] Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 187.

[4] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 1, 264.

[5] Naumann, *Ber.*, 1910, 43, 313; compare Troost, *Compt. rend.*, 1879, 88, 1267.

[6] Briner, *Compt. rend.*, 1906, 142, 1416.

[7] Berthelot, *ibid.*, 1880, 90, 779; *Ann. Chim. Phys.*, 1880, [5], 20, 255.

[8] Bloxam, *Chem. News*, 1893, 68, 97; *Trans. Chem. Soc.*, 1895, 67, 277.

[9] Donath, *Chem. Zeit.*, 1891, 15, 1021.

[10] Gay-Lussac, *Pogg. Annalen*, 1829, 15, 538; *Ann. Chim. Phys.*, 1829, 40, 302; Vauquelin, *ibid.*, 1817, 6, 42.

[11] Fritzsche, *J. prakt. Chem.*, 1841, 24, 460; 1844, 32, 313; Bloxam, *Trans. Chem. Soc.*, 1895, 67, 277.

[12] Byers, *Amer. Chem. J.*, 1902, 28, 490.

[13] Fritzsche's heptasulphide is regarded by Sabatier (*Ann. Chim. Phys.*, 1881, [5], 22, 73) as an *octasulphide*, $(NH_4)_3S_8$.

Ammonium sulphite, $(NH_4)_2SO_3,H_2O$.—Neutralization of sulphurous acid by ammonia yields a solution from which the normal sulphite can be obtained as monohydrate in the form of prismatic crystals.[1] At 120° C. the hydrated salt loses part of its water, and is partly converted into the pyrosulphite.[2] It can be sublimed at 150° C. in a current of nitrogen, but the vapour is decomposed into sulphur dioxide, ammonia, and water.[2] In the dry state the salt is more susceptible to oxidation than when moist.[3] The slow oxidation to ammonium sulphate is much accelerated by keeping the solution alkaline with ammonia, by the presence of oxygen-carriers, and by pressure.[4] Its heat of formation in the anhydrous form from its elements is 215·4 Cal.[5] At 12° C. it dissolves in its own weight of water, yielding a solution of alkaline reaction.

Ammonium pyrosulphite, $(NH_4)_2S_2O_5$.—Evaporation in vacuum of a solution of the normal salt saturated with sulphur dioxide yields the pyrosulphite in the form of very deliquescent, rhombic prisms.[6] On exposure to air it decomposes with evolution of sulphur dioxide. Its heat of formation is 300·0 Cal.[5] Its aqueous solution gradually decomposes, with formation of thiosulphate.[7]

A basic sulphite,[8] $2(NH_4)_2SO_3,2NH_3,3H_2O$, and several double sulphites [9] have been described.

Ammonium sulphate, $(NH_4)_2SO_4$.—The sulphate is found in volcanic districts as *mascagnite*. It is said to be formed in the soil by the action of organic ammonia on calcium sulphate,[10] and is one of the products of the combustion of coal-gas.[11]

Ammonium sulphate can be prepared by the general methods applicable to ammonium salts, and also by the action of sulphuric acid on ammonium chloride.[12] It is manufactured by neutralizing with sulphuric acid the ammonia of coal or peat,[13] and many other methods of manufacture have been worked and suggested.[14] Veevers has written a historical summary of the methods employed in its manufacture.[15]

The ammonia formed as a by-product in the manufacture of coal-gas,

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[1] Marignac, *Ann. Mines*, 1857, [5], 12, 25; Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 217; compare Muspratt, *Annalen*, 1844, 50, 269; Hartog, *Compt. rend.*, 1887, 104, 1793; Lachomette, *J. Gasbeleuchtung*, 1888, 31, 133; Carpenter and Linder, *J. Soc. Chem. Ind.*, 1904, 24, 63.

[2] Divers and Ogawa, *Trans. Chem. Soc.*, 1900, 77, 335.

[3] Hartog, *Compt. rend.*, 1887, 104, 1793.

[4] Badische Anilin- und Soda-Fabrik, *French Patent*, No. 463487.

[5] de Forcrand, *Compt. rend.*, 1885, 100, 244; *Ann. Chim. Phys.*, 1887, [6], 11, 277.

[6] Marignac, *loc. cit.*; compare Muspratt, *Phil. Mag.*, 1847, [3], 30, 414; Fock and Klüss, *Ber.*, 1890, 23, 3149.

[7] Rochleder, *Jahresbericht*, 1856, 291.

[8] Muspratt, *Phil. Mag.*, 1847, [3], 30, 414; compare Marignac, *loc. cit.*; Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 217.

[9] Marignac, *Ann. Mines*, 1857, [5], 12, 29; Tauber, *Ber.*, 1888, 21, 763; Schwicker, *Ber.*, 1889, 22, 1732; Hartog, *Amer. J. Pharm.*, 1890, 20, 3.

[10] Péchard, *Compt. rend.*, 1889, 109, 145.

[11] Přiwoznik, *Ber.*, 1892, 25, 2200.

[12] Mond, *Ber.*, 1884, 17, 390.

[13] Compare Martellière, *Chem. Zeit.*, 1881, 128; Lachomette, *J. Gasbeleuchtung*, 1888, 31, 133. See this series, Vol. V.

[14] Grouven, *J. Soc. Chem. Ind.*, 1878, 1, 398; Wolfrum, *Ber.*, 1887, 18, 406; Leybould, *Dingler's Polytech. J.*, 1888, 267, 31, 81, 125; 268, 136, 172, 586; 269, 268; Zimpell, *J. Gasbeleuchtung*, 1905, 48, 683; Berlin-Anhaltische Maschinenbau- A.-G., *German Patent*, 1905, No. 165308; Ost, *Zeitsch. angew. Chem.*, 1906, 19, 609; Frank, *ibid.*, 1908, 21, 1597.

[15] Veevers, *Dingler's Polytech. J.*, 1891, 280, 278.

and of coke in coke-ovens, furnishes the main bulk of the world's supply of ammonium sulphate. Most of the ammonia is dissolved in the condensed aqueous vapour obtained by cooling the gas, and the residual portion is extracted by washing with water. In coke-works the ammonia is sometimes absorbed from the hot gas by means of sulphuric acid, after the removal of the tar.

The free ammonia in the aqueous solution is expelled by heat, and absorbed by sulphuric acid in a lead saturator; and the fixed ammonia is then liberated by lime, and similarly absorbed.

In Woltereck's process for the manufacture of ammonia from peat,[1] carried on at Carnlough in the north of Ireland, the wet peat is burnt in air and steam at a low temperature. After the tar produced has been washed out by oils of high boiling-point, and the acetic acid removed by hot milk of lime, the ammonia is absorbed by sulphuric acid.

The sulphate crystallizes in transparent rhombic crystals,[2] isomorphous with those of potassium sulphate. The effect of various impurities on the colour of the salt has been investigated by Leo.[3] The literature contains many contradictory statements respecting the melting-point of ammonium sulphate and the behaviour of the substance under the influence of heat. According to Marchand,[4] the melting-point is 140° C., but Watson Smith[5] and Caspar[6] regard this temperature as the melting-point of the primary sulphate. Watson Smith[7] states that ammonium sulphate begins to evolve ammonia at 100° C., and at 300° C. is completely converted into the primary sulphate. According to Caspar,[6] in an open tube the normal sulphate softens at 310° C., melts at a temperature between 336° and 339° C., and decomposes with evolution of gas at 355° C.; in a closed tube it begins to soften about 360° C., and melts between 417° and 423° C. Jänecke[8] states that both the normal sulphate and the primary sulphate melt at 251° C., but in a later paper[9] gives 147° C. as the melting-point of the primary sulphate. The explanation of these very divergent values is to be found in the observation by Kendall and Davidson[10] of the impossibility of determining in an open tube the true melting-point of the normal sulphate, owing to loss of ammonia even at 200° C. When the salt is heated in a sealed tube almost filled, it softens at 490° C. and melts at $513° + 2°$ C., the value given representing the melting-point of the substance at an ammonia pressure of considerably more than one atmosphere. When the salt is heated in an open tube, decomposition is complete at 365° C.[11]

Jänecke's[8] value for the boiling-point of the normal sulphate, 357° C., does not accord with the work of Kendall and Davidson.[12] The

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[1] Woltereck, *British Patents*, 1904, No. 16504; 1906, Nos. 28963 and 28964.

[2] Mitscherlich, *Pogg. Annalen*, 1830, 18, 168; Tutton, *Trans. Chem. Soc.*, 1903, 83, 1049; *Zeitsch. Kryst. Min.*, 1905, 41, 525.

[3] Leo, *Stahl und Eisen*, 1914, 34, 439.

[4] Marchand, *Pogg. Annalen*, 1837, 42, 556.

[5] Watson Smith, *J. Soc. Chem. Ind.*, 1911, 30, 253; compare Reik, *Monatsh.*, 1902, 23, 1033.

[6] Caspar, *Ber.*, 1920, 53, [B], 821.

[7] Watson Smith, *loc. cit.*

[8] Jänecke, *Zeitsch. angew. Chem.*, 1920, 33, 278.

[9] Jänecke, *ibid.*, 1921, 34, 542.

[10] Kendall and Davidson, *J. Ind. Eng. Chem.*, 1921, 13, 303; compare Kendall and Landon, *J. Amer. Chem. Soc.*, 1920, 42, 2131; Kattwinkel, *Ber.*, 1922, 55, [B], 874.

[11] Kattwinkel, *loc. cit.*

[12] Kendall and Davidson, *loc. cit.*

density of this substance is 1·769[1] at 20° C. Its heat of formation from the elements is given as 281·9 Cal.[2] and 283·5 Cal.[3] It dissolves in water with absorption of heat.[4]

Solubility of Ammonium Sulphate.[5]

Temperature, °C. .	0	10	20	30	40	60	80	100	108·9
Grams of $(NH_4)_2SO_4$ in 100 g. of water	70·6	73·0	75·4	78·0	81·0	88·0	95·3	103·3	107·5

The density of the solution saturated at 15° C. is 1·248; and at 19° C., 1·241. Crystals of the composition $(NH_4)_2SO_4,H_2O_2$ have been prepared from aqueous solutions containing hydrogen peroxide.[6]

When heated with solid potassium nitrite, ammonium sulphate reacts very energetically, sufficient heat being generated to raise the temperature of the mass to incandescence.[7] When heated in solution, the two substances decompose, all the nitrogen being evolved in the free state.[8] Electrolytic oxidation of a dilute-acid solution of ammonium sulphate at a lead-peroxide anode produces hydroxylamine and hyponitrous acid, these substances decomposing with liberation of nitrogen and nitrous oxide:[9]

$$(HNO)_2=N_2O+H_2O\,;\quad 2NH_2OH+(HNO)_2=2N_2+4H_2O.$$

In alkaline solution only the reaction indicated in the second equation takes place. When heated in sulphuric-acid solution with platinum-black, sulphur dioxide and nitrogen are evolved:[10]

$$4H_2SO_4+Pt=Pt(SO_4)_2+2SO_2+4H_2O\,;$$
$$3Pt(SO_4)_2+2(NH_4)_2SO_4=8H_2SO_4+3Pt+2N_2.$$

Ammonium sulphate is employed in the fractional precipitation of proteins.[11] It also finds application as a fertilizer,[12] the nitrogen being assimilated by the plants either as ammonia, or after nitrification to nitrate.

A number of double salts have been described, including compounds with lithium,[13] sodium,[14] and copper.[15]

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[1] Tutton, *Trans. Chem. Soc.*, 1903, 83, 1049; *Zeitsch. Kryst. Min.*, 1905, 41, 525; compare Retgers, *Zeitsch. physikal. Chem.*, 1889, 3, 310.

[2] Thomsen, *J. prakt. Chem.*, 1880, [2], 21, 449.

[3] Berthelot, *Ann. Chim. Phys.*, 1873, [4], 29, 440, 448.

[4] Berthelot, *ibid.*, 1875, [5], 4, 106; Thomsen, *J. prakt. Chem.*, 1878, [2], 17, 178.

[5] Alluard, *Compt. rend.*, 1864, 59, 500.

[6] Willstätter, *Ber.*, 1903, 36, 1828.

[7] Tommasi, *Chem. News*, 1881, 43, 241.

[8] Emmerling, *Landw. Versuchs-Stat.*, 1886, 32, 440.

[9] Alexéeff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1155.

[10] Delépine, *Compt. rend.*, 1905, 141, 886.

[11] Heynsius, *Arch. ges. Physiol.*, 1884, 34, 330; Kander, *Arch. expt. Path. Pharm.*, 1886, 20, 411.

[12] Brown, *Chem. News*, 1886, 53, 217; Baxter, *ibid.*, 223; Pichard, *J. Soc. Chem. Ind.*, 1885, 4, 460; Dehérain, *Ann. agronomiques*, 1887, 13, 241; Gerlach and Vogel, *Centr. Bakt. Par.*, 1905, ii., 14, 124.

[13] Wyrouboff, *Bull. Soc. franç. Min.*, 1880, 3, 199; Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 60; Schreinemakers and Cocheret, *Chem. Weekblad*, 1905, 2, 771; Schreinemakers and Bornwater, *ibid.*, 1906, 3, 569.

[14] Mitscherlich, *Pogg. Annalen*, 1843, 58, 469; Schiff, *Annalen*, 1860, 114, 68; Lang, *Sitzungsber, K. Akad. Wiss. Wien*, 1862, 45, 108; Reinsch, *Zeitsch. Kryst. Min.*, 1884, 9, 561; Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 60.

[15] Schreinemakers, *Zeitsch. physikal. Chem.*, 1909, 66, 687.

Ammonium hydrogen sulphate, NH_4HSO_4.—On cooling a saturated solution of the normal sulphate in concentrated sulphuric acid, the primary sulphate is deposited in deliquescent, rhombic prisms.[1] It is also produced by heating the normal salt.[2] For the melting-point of the primary sulphate,[3] Watson Smith[4] gives 140° C., but more reliance can be placed on the value 146·9° ± 0·5° C. of Kendall and Landon[5] and on that (147° C.) of Jänecke.[6] For the boiling-point, Jänecke[7] gives 490° C. The density of the primary sulphate is given as 1·787[8] and 1·815.[9] It is soluble in an equal weight of water.[10] Several other acid sulphates have been described,[11] such as $(NH_4)_2SO_4,3H_2SO_4$, melting at 48° C.[12] An ammonia compound, $(NH_4)_2SO_4,2NH_3$, has also been prepared.[13]

Ammonium pyrosulphate, $(NH_4)_2S_2O_7$.—Sulphur trioxide combines with ammonium sulphate with evolution of heat, yielding the pyrosulphate as an amorphous, translucent, deliquescent substance, rendered crystalline by fusing and allowing to solidify. Its melting-point is given as 138° C.[13] The primary sulphate crystallizes from its solution.[14]

An *octasulphate*, $(NH_4)_2O,8SO_3$, has also been described.[15]

Ammonium persulphate, $(NH_4)_2S_2O_8$.—The persulphate is produced at the anode in the electrolysis of a cooled saturated solution of ammonium sulphate in dilute sulphuric acid, a high anodic current-density and a diaphragm being employed.[16] It can also be prepared technically without a diaphragm.[17] It forms monoclinic crystals,[18] its solubility at 0° C. being 58 grams in 100 grams of water,[19] and greater than that of any other persulphate.[20] If free from moisture and protected from sunlight, the dry salt scarcely undergoes any change during the lapse of years.[21] When warmed with nitric acid it evolves ozone in much larger amount than the corresponding salts of sodium and potassium, the reaction affording a method of preparing this gas.[22] It converts metallic oxides into persulphates, peroxides, or sesquioxides, with evolution of ammonia.[23]

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[1] Marignac, *Ann. Mines*, 1857, [5], 12, 38.

[2] Watson Smith, *J. Soc. Chem. Ind.*, 1911, 30, 253; compare Reik, *Monatsh.*, 1902, 23, 1033.

[3] Compare the section on normal ammonium sulphate.

[4] Watson Smith, *loc. cit.*

[5] Kendall and Landon, *J. Amer. Chem. Soc.*, 1920, 42, 2131; compare Kendall and Davidson, *J. Ind. Eng. Chem.*, 1921, 13, 303.

[6] Jänecke, *Zeitsch. angew. Chem.*, 1921, 34, 542; compare, however, Jänecke, *ibid.*, 1920, 33, 278.

[7] Jänecke, *ibid.*, 1920, 33, 278.

[8] Schiff, *Annalen*, 1858, 107, 83.

[9] Gossner, *Zeitsch. Kryst. Min.*, 1904, 39, 381.

[10] Link, *Crell's chem. Ann.*, 1796, i., 26.

[11] Mitscherlich, *Pogg. Annalen*, 1836, 39, 195; *Ann. Mines*, 1857, [5], 12, 38; (but compare Schiff, *Annalen*, 1858, 107, 83; Johnson and Chittenden, *Amer. J. Sci.*, 1878, [3], 15, 131); d'Ans, *Zeitsch. anorg. Chem.*, 1913, 80, 235.

[12] Kendall and Landon, *loc. cit.*; Jänecke, *Zeitsch. angew. Chem.*, 1921, 34, 542.

[13] Jänecke, *loc. cit.*

[14] Schulze, *Ber.*, 1884, 17, 2705.

[15] Weber, *ibid.*, 2497.

[16] Berthelot, *Compt. rend.*, 1892, 114, 876; Elbs, *J. prakt. Chem.*, 1893, [2], 48, 185.

[17] Müller and Friedberger, *Zeitsch. Elektrochem.*, 1902, 8, 230; Konsortium für elektrochemische Industrie, *German Patent*, 1908, No. 195811.

[18] Fock, *Zeitsch. Kryst. Min.*, 1893, 22, 29.

[19] Marshall, *Trans. Chem. Soc.*, 1891, 59, 777.

[20] Elbs and Schönherr, *Zeitsch. Elektrochem.*, 1894, 1, 417, 468; 1895, 2, 162, 245.

[21] Elbs and Neher, *Chem. Zeit.*, 1921, 45, 1113.

[22] Malaquin, *J. Pharm. Chim.*, 1911, [7], 3, 329.

[23] Seyewitz and Trawitz, *Compt. rend.*, 1903, 137, 130.

With sodium peroxide ammonium persulphate reacts energetically, with production of incandescence and smoke : [1]

$$(NH_4)_2S_2O_8+2Na_2O_2=2Na_2SO_4+4H_2O+N_2.$$

It is partially decomposed by exposure to ultraviolet rays.[2] It can be estimated by the aid of titanium trichloride.[3]

Ammonium thiosulphate, $(NH_4)_2S_2O_3$.—A hydrate of the formula $3(NH_4)_2S_2O_3,H_2O$ is produced by the interaction of ammonium carbonate and calcium thiosulphate in aqueous solution, and on concentration is deposited in the form of deliquescent needles or rhombic laminæ.[4] The anhydrous salt is formed by the action of sulphur dioxide on a solution of the sulphide,[5] and is a by-product in the reduction of *p*-dinitrobenzene to *p*-nitroaniline by means of ammonium sulphide.[6] It is also formed by the action of ammonium sulphate on ammonium polysulphides,[7] and by that of ammonia on sulphur trioxide[7] or sulphur.[8] The monoclinic[9] crystals decompose almost completely at 150° C., with production of ammonium sulphite, sulphur, ammonia, and hydrogen sulphide.[10] It is employed in iodometry.

Ammonium potassium thiosulphate, $NH_4KS_2O_3$.—Concentration of an aqueous solution containing equimolecular proportions of the thiosulphates of ammonium and potassium yields the double thiosulphate in monoclinic crystals.[11]

Ammonium dithionate, $(NH_4)_2S_2O_6$.—Aqueous solutions of barium dithionate and ammonium sulphate yield on concentration the *semihydrate* in hair-shaped crystals.[12] At 16° C. the solubility is 127 grams in 100 grams of water, the solution being accompanied by the absorption of much heat. Heat decomposes the dithionate into ammonium sulphate, water, and sulphur dioxide.[13] It combines with an equimolecular proportion of ammonium chloride, yielding rhombic crystals of the formula $(NH_4)_2S_2O_6,NH_4Cl$.[14]

Ammonium trithionate, $(NH_4)_2S_3O_6$.—An aqueous solution of potassium trithionate reacts with hydrofluosilicic acid and ammonia to form the trithionate, which is precipitated from its aqueous solution by alcohol as a very deliquescent, unstable salt.[15] It is also formed, along with the tetrathionate, by the action of sulphur dioxide on ammonium thiosulphate : [16]

$$4(NH_4)_2S_2O_3+6SO_2=2(NH_4)_2S_3O_6+2(NH_4)_2S_4O_6.$$

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[1] Kempf and Oehler, *Ber.*, 1908, 41, 2576.

[2] Thiele, *Zeitsch. angew. Chem.*, 1909, 22, 2472.

[3] Knecht and Hibbert, *Ber.*, 1905, 38, 3318.

[4] Rammelsberg, *Pogg. Annalen,* 1842, 56, 298.

[5] Fock and Klüss, *Ber.*, 1889, 22, 3099.

[6] Arppe, *Annalen,* 1855, 96, 113.

[7] Spring, *Ber.*, 1874, 7, 1157.

[8] Senderens, *Compt. rend.*, 1887, 104, 58.

[9] Fock and Klüss, *loc. cit.* ; Wyrouboff, *Bull. Soc. franç. Min.*, 1890, 13, 152.

[10] Divers and Ogawa, *Trans. Chem. Soc.*, 1900, 77, 335 ; compare Spring, *Ber.*, 1874, 7, 1157.

[11] Fock and Klüss, *Ber.*, 1890, 23, 534.

[12] Heeren, *Pogg. Annalen,* 1826, 7, 172 ; Klüss, *Annalen,* 1888, 246, 179 ; compare Ruppin, *Zeitsch. physikal. Chem.*, 1894, 14, 471.

[13] Heeren, *loc. cit.*

[14] Fock and Klüss, *Ber.*, 1891, 24, 3017.

[15] Divers and Ogawa, *Trans. Chem. Soc.*, 1900, 77, 335.

[16] Raschig, *Zeitsch. angew. Chem.*, 1920, 33, 260.

Ammonium tetrathionate, $(NH_4)_2S_4O_6$.—The tetrathionate is produced by the action of sulphur dioxide on an aqueous solution of ammonium sulphide :[1]

$$(NH_4)_2S+3SO_2=(NH_4)_2S_4O_6.$$

In aqueous solution it decomposes in accordance with the equation[2]

$$(NH_4)_2S_4O_6=(NH_4)_2SO_4+SO_2+2S.$$

Ammonium thiosulphate reacts with it, forming ammonium sulphate and liberating sulphur :

$$2(NH_4)_2S_2O_3+(NH_4)_2S_4O_6=3(NH_4)_2SO_4+5S.$$

Ammonium selenide, $(NH_4)_2Se$.—Excess of ammonia reacts with hydrogen selenide to form ammonium selenide as a white mass.[3] It is also produced in the form of black, orthorhombic crystals by concentrating in vacuum over sulphuric acid an aqueous solution of ammonium molybdate and ammonia saturated with hydrogen selenide, the dark colour being probably due to slight decomposition.[4] On exposure to air it gradually decomposes, with liberation of black selenium. It dissolves in water, forming a red solution from which metallic salts precipitate the corresponding selenide. Its heat of formation from its elements in dilute solution is 44·6 Cal.[5]

Ammonia unites with excess of hydrogen selenide to form *ammonium hydrogen selenide*, NH_4SeH, the heat of formation of the solid compound from its elements being 28·9 Cal.[5]

Ammonium selenite, $(NH_4)_2SeO_3$.—Concentration of an alcoholic or aqueous solution of selenious acid saturated with ammonia yields the selenite in four-sided columns or laminæ.[6] On heating, it decomposes with separation of selenium, and evolution of nitrogen.

Ammonium selenates.—On evaporation, a solution of selenic acid saturated with ammonia yields the *normal selenate*, $(NH_4)_2SeO_4$, in monoclinic[7] crystals. At 7° C. its solubility is 117 grams in 100 grams of water.[8] When gently heated, the normal salt is converted into *ammonium hydrogen selenate*, NH_4HSeO_4,[9] of density 2·162.[10]

Several complex selenate derivatives have been described.[11]

ISOMORPHISM OF THE ALKALI-METAL SULPHATES AND SELENATES.

The normal sulphates and selenates of the alkali-metals, $R_2S[Se]O_4$, where R represents potassium, rubidium, or cæsium, form excellent crystals belonging to the rhombic system ; and these salts furnish one

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[1] Hurdelbrink, *J. Gasbeleuchtung*, 1910, 53, 956.

[2] Paepe, *Bull. Soc. chim.*, 1912, 26, 244.

[3] Bineau, *Ann. Chim. Phys.*, 1838, 67, 230 ; 68, 435 ; 1839, 70, 261.

[4] Lenher and Smith, *J. Amer. Chem. Soc.*, 1898, 20, 277.

[5] Fabre, *Compt. rend.*, 1886, 103, 269.

[6] Muspratt, *Annalen*, 1849, 70, 275.

[7] Topsöe, *Sitzungsber. K. Akad. Wiss. Wien*, 1872, 66, 18 ; Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 6 ; Tutton, *Trans. Chem. Soc.*, 1906, 89, 1059 ; compare Lang, *Sitzungsber. K. Akad. Wiss. Wien*, 1862, 45, 108 ; Rammelsberg, *Handbuch der Krystallographisch-Physikalischen Chemie*, Leipsic, 1881–1882, 1, 497.

[8] Tutton, *loc. cit.*

[9] Cameron and Davy, *Chem. News*, 1878, 38, 133.

[10] Topsöe, *loc. cit.*

[11] Retgers, *loc. cit.* ; Weinland and Barttlingck, *Ber.*, 1903, 36, 1397. On *ammonium tellurite*, compare Lenher and Wolensky, *J. Amer. Chem. Soc.*, 1913, 35, 718.

of the best examples of an isomorphous series. They also combine with the sulphates and selenates of magnesium, zinc, nickel, cobalt, ferrous iron, manganese, copper, and cadmium to form another fine series of isomorphous double salts with six molecules of water of crystallization, most of them yielding excellent crystals belonging to the monoclinic system. The general formula of this group is $R_2M(S[Se]O_4)_2,6H_2O$, where M represents one of the dyad-acting metals named. The crystals of these two series of salts, as well as those of some analogous double chromates, and also the ammonium salts of both the rhombic and the monoclinic series—for ammonium readily replaces the alkali-metal,—have been studied in great detail by A. E. H. Tutton in a series of researches extending from the year 1890 over a period of thirty-two years, two papers communicated to the Royal Society in March, 1922, completing the work.[1] The primary object of the investigation was to study the influence on the crystal form, structure, and physical properties of interchanging the alkali-metals for one another, and the effect of replacing them by the radical ammonium, and for this purpose 75 salts were studied completely. The work involved the measurement of over 45000 crystal angles; the carrying out of over 500 density determinations; and the preparation of over 2000 section-plates, rectangular blocks, and 60° prisms, with which an immense number of optical, thermal, and other physical measurements were made.

The results have proved of even greater significance than was expected. They have not only provided a complete crystallographic description in detail of two of the most important series of isomorphous salts known, but have rendered perfectly clear the exact sense in which the term "isomorphism" is to be understood; and have proved finally and conclusively the truth of Haüy's generalization that every crystallizable individual chemical substance is endowed with its own peculiar and distinct crystalline form and physical properties, for even the members of these isomorphous series show differences amounting to a maximum of 2·5° in the interfacial angles of their similarly symmetrical crystals. The research has also revealed the important fact that these differences of angle and properties follow a definite law of progression, the crystallographic changes following the order of progression of the atomic numbers of the alkali-metals interchanged. This phenomenon has been shown to be due to the progressive differences in the structure and sizes of the atoms interchanged, and thus to be connected intimately and in full concordance with the results of recent researches on the structure of the atom, and with those derived from the X-ray analysis of crystals. In the laboratory of Sir William Bragg, Tutton's results for the simple sulphates of potassium, rubidium, and cæsium have been completely confirmed by the X-ray analysis of the same crystals as were used by him.

The three alkali-metals potassium, rubidium, and cæsium form numbers 4, 6, and 8 of the even series of the most strongly electropositive group of the periodic classification, and have the atomic-sequence numbers 19, 37, and 55, differing at each step by 18 units, the atomic number of rubidium being thus exactly the mean of the atomic numbers of potassium and cæsium. The increase by 18 units

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[1] Tutton, *Proc. Roy. Soc.*, 1922, [A], 101, 225, 245. At the conclusion of the second paper a complete list of the thirty-two memoirs is given, with references.

in atomic number in passing from potassium to rubidium and thence to cæsium means the addition of a complete shell of electrons to the structure of the atom of the alkali-metal according to the Lewis-Langmuir version of the atomic-structure theory, or of two complete shells according to the Bohr-Sommerfeld version. It has also been shown by W. L. Bragg that these three alkali-metals occupy the positions corresponding with the sharp maxima of the curve of atomic diameters, which expresses the size of the chemical atoms as revealed in the accumulated results of X-ray analyses of crystals; and that there is a considerable increase in the size of the atom from potassium to rubidium, and again from rubidium to cæsium, corresponding with this addition of electrons in one or two shells.

All Tutton's investigations fully confirm one another in the details of the measurements of both exterior angles and of interior physical constants. Their main results may be summarized in the statement that the progression in the atomic-sequence number, and its attendant progression in the size of the atom, is accompanied by a similarly definite progression in the characters, external or internal, of the crystals of these isomorphous rhombic and monoclinic series, when the potassium in the initial salt of the series is replaced by rubidium, and the rubidium in turn replaced by cæsium. This fact has been proved definitely for the interfacial angles; for the axial ratios; for the variable axial angle of the monoclinic series; for the relative volumes and edge-dimensions of the rhombic or monoclinic cells of the structural space-lattices; for the refractive indices and molecular refractions; for the amount of double refraction; for the orientation of the optical ellipsoid of the monoclinic series, which is free to rotate about the symmetry-axis, and does so progressively; for the thermal expansions of the rhombic sulphates, which alone were suitable for dilatation experiments; and finally, by the X-ray analysis of the sulphates by Sir William Bragg's X-ray spectrometer for the absolute dimensions of the space-lattice cells, Tutton's relative measures having been found correct to 1 in 1000.

Another result of Tutton's work has also proved to be of deeper significance than was at first appreciated. The ammonium salts are almost perfectly isostructural with the analogous rubidium salts, the replacement of rubidium atoms by ammonium ((NH_4)) radicals involving practically no change in the relative dimensions of the structural cell-edges. This result also has been confirmed fully by the absolute determinations by X-rays for rubidium and ammonium sulphates. It follows that the valency-volume theory of Pope and Barlow is incorrect, since according to that theory the relative volumes of rubidium sulphate and ammonium sulphate should be as 1 to 2, the valency volumes being 12 and 24 respectively. The subsequent discovery of the law of atomic diameters from the results of X-ray analyses has decided the matter by showing that size of atom is involved, but that the sizes are not proportional to the valencies and are those expressed in the curve and table of atomic diameters of W. L. Bragg.

Tutton's main law of progression of the crystallographic properties of the salts of these isomorphous series with the atomic number of the interchangeable alkali-metal is in complete agreement with this law of atomic diameters, and the two laws may be said mutually to support each other. To go even deeper, however, the law of progression of the crystal properties is the natural outcome of the operation of the law of Moseley, which gives us the basis of atomic structure. It states that the atom is composed of a positively electrified nucleus, its charge being equal to the atomic-sequence number; and that this mass-bearing nucleus is surrounded by this same atomic number of negative electrons, each of unit charge, the two modes of arrangement of these electrons being those associated with the Bohr-Sommerfeld and Lewis-Langmuir versions of the atomic-structure theory. This law is fundamental, and the progressive increase in size and complexity of the atomic structure affords in itself an adequate explanation of Tutton's law, which might be expected to follow as a natural consequence. It is very satisfactory that all these results of recent work confirm and substantiate one another, for the concordance renders it certain that they are very near the truth.

Ammonium chromates.—The modes of preparation and the properties of *ammonium chromate* and *dichromate* are considered in Vol. VII., Part III.

Ammonium hydrazoate, NH_4N_3.—The hydrazoate is formed by the interaction of ammonia and a dry, ethereal solution of hydrazoic acid.[1] It melts and decomposes violently at 160° C.

Ammonium nitrite, NH_4NO_2.—The nitrite is a product of the oxidation in the air of nitrogenous material, especially ammonia, its formation being much accelerated by the presence of catalysts such as ferric oxide and platinum.[2] It is also formed by the combustion of organic products such as coal-gas, and by the oxidation of atmospheric nitrogen under the influence of the electric discharge.[3] It is generated by the action of the silent electric discharge on a mixture of nitrous oxide and water-vapour.[4] It is one of the products of the combustion of ammonia in oxygen.[5] Its direct formation from nitrogen and oxygen has been observed when platinum-black has been introduced into a solution of sodium hydroxide, the gases being occluded in the metal [6]; and also during the combustion of hydrogen in air.[7] It is also produced by the interaction of ammonia, nitric oxide, and oxygen: [8]

$$2NH_3+2NO+H_2O+O=2NH_4NO_2.$$

The preparation of ammonium nitrite has been effected by various methods. Examples are the double decomposition of lead [9] or barium [8] nitrite and ammonium sulphate; the action of nitrogen peroxide on ammonium hydroxide, and purification of the nitrite by fractional crystallization [10]; passing a mixture of air and ammonia over heated platinized asbestos [11]; and heating a very concentrated solution of ammonium chloride and sodium nitrite in vacuum between 60° and 80° C., the ammonium nitrite subliming into the neck of the flask.[12] It

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[1] Browne and Houlehan, *J. Amer. Chem. Soc.*, 1911, 33, 1742; compare Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 261.

[2] Smith, *Trans. Chem. Soc.*, 1906, 89, 473.

[3] Berthelot, *Ann. Chim. Phys.*, 1877, [5], 12, 445; *Bull. Soc. chim.*, 1877, [2], 27, 338.

[4] Losanitsch and Jovitschitsch, *Ber.*, 1897, 30, 135.

[5] Hodgkinson and Lowndes, *Chem. News*, 1888, 58, 27.

[6] Löw, *Ber.*, 1890, 23, 1443.

[7] Hoppe-Seyler, *Zeitsch. physiol. Chem.*, 1878, 2, 1.

[8] Berthelot, *Bull. Soc. chim.*, 1874, [2], 21, 55.

[9] Berzelius, *Gilbert's Annalen*, 1812, 40, 206.

[10] Millon, *Ann. Chim. Phys.*, 1847, [3], 19, 255.

[11] Warren, *Chem. News*, 1891, 64, 290.

[12] Neogi and Adhicāry, *Trans. Chem. Soc.*, 1911, 99, 116.

can also be produced by the action of nitrogen peroxide on ammonium carbonate, extracting the product with absolute alcohol, and precipitating the nitrite with ether[1]; and by a similar precipitation-method from an aqueous alcoholic solution of sodium nitrite and ammonium sulphate.[2] The methods employed in its preparation have been summarized by Sörensen.[1]

Ammonium nitrite crystallizes in deliquescent, feather-like needles with a faint yellowish tinge. Its heat of formation from its elements is 64·8 Cal.[3] When heated, either in the solid state or in solution, it decomposes into nitrogen and water:

$$NH_4NO_2=N_2+2H_2O.$$

For the solid the decomposition takes place between 60° and 70° C., and readily develops an explosive character.[4] It is facilitated by acidifying the nitrite.[5] The pure salt is said to be non-explosive, but to be decomposed in accordance with the equation by heating at 100° C. in a Hofmann tube.[6] The salt is comparatively stable when kept beneath a layer of alcohol-free ether.

The decomposition of the nitrite in aqueous solution has been the subject of many investigations.[7] In vacuum at 37° to 40° C. the decomposition is very slight; at 70° C. it proceeds slowly in accordance with the equation, but most of the salt sublimes unchanged. When the sublimate is heated with a naked flame, it yields nitrogen and up to 6 per cent. of nitric oxide.[8]

The decomposition of the nitrite is much accelerated by the catalytic action of platinum-black.[9] Other catalysts are also said to facilitate the reaction.[10]

Ammonium nitrate, NH_4NO_3.—The nitrate can be prepared by the general methods applicable to the ammonium salts. It is also produced by heating the nitrate of an alkali-metal with ammonium sulphate at 160° to 200° C., the fused ammonium nitrate being separated from the solid alkali-metal sulphate by centrifuging.[11] Another method consists in cooling a concentrated solution of sodium nitrate and ammonium sulphate to —15° C., sodium sulphate being precipitated. On evaporation of the mother-liquor, most of the sodium sulphate is deposited; addition of nitric acid to the clear solution causes crystallization of the ammonium nitrate.[12] When sodium nitrate is

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[1] Sörensen, *Zeitsch. anorg. Chem.*, 1894, 7, 1.

[2] Biltz and Gahl, *Zeitsch. Elektrochem.*, 1905, 11, 409.

[3] Berthelot, *Ann. Chim. Phys.*, 1880, [5], 20, 255.

[4] Berthelot, *Compt. rend.*, 1874, 78, 102.

[5] Sörensen, *loc. cit.*

[6] Neogi and Adhicāry, *Trans. Chem. Soc.*, 1911, 99, 116.

[7] Berzelius, *Gilbert's Annalen*, 1812, 40, 206; Corenwinder, *Ann. Chim. Phys.*, 1849, [3], 26, 296; Millon, *ibid.*, 1847, [3], 19, 255; Bohlig, *Annalen*, 1863, 125, 21; Angeli and Boeris, *Atti R. Accad. Lincei*, 1892, [5], 1, ii., 70; *Gazzetta*, 1892, 22, ii., 349; Wegscheider, *Zeitsch. physikal. Chem.*, 1901, 36, 543; Arndt, *ibid.*, 1902, 39, 64; 1903, 45, 570; Blanchard, *ibid.*, 1902, 41, 681; 1905, 51, 117; Veley, *Trans. Chem. Soc.*, 1903, 83, 736; Berger, *Bull. Soc. chim.*, 1904, [3], 41, 682; Biltz and Gahl, *Zeitsch. Elektrochem.*, 1905, 11, 409.

[8] Rây, *Trans. Chem. Soc.*, 1909, 95, 345.

[9] Vondráček, *Zeitsch. anorg. Chem.*, 1904, 39, 37.

[10] Arndt, *loc. cit.*; Blanchard, *loc. cit.*; Veley, *Proc. Roy. Soc.*, 1888, 44, 239; *Phil. Trans.*, 1888, 179, 257; Löw, *Ber.*, 1890, 23, 3018.

[11] Roth, *German Patent*, *Ber.*, 1890, 23 (Referate), 714.

[12] Benker, *Chem. Zeit.*, 1892, 654; compare Groendahl and Landin, *Mon. Scient.*, 1893, [4], 7, ii., 257.

substituted for the chloride in the Solvay process, ammonium nitrate is obtained as a by-product.[1] In the electrolysis of water kept saturated with nitrogen at high pressure, nitric acid is produced at the positive electrode, and can be converted into the nitrate by the action of ammonia.[2] Another electrolytic process consists in electrolyzing dilute nitric acid with an aluminium cathode, and concentrating the solution as soon as neutralization is complete : [3]

$$2HNO_3+8H=NH_4NO_3+3H_2O.$$

References to other manufacturing methods are appended.[4]

The ozonization of air by moist phosphorus is said to produce ammonium nitrate,[5] and it is also formed by the combustion of ammonia in oxygen, and by that of hydrogen in nitric acid.[6] When ozone reacts with liquid ammonia cooled with ether and liquid carbon dioxide, the product consists of ammonium nitrate containing 2 per cent. of ammonium nitrite.[7]

Ammonium nitrate is a white salt, and in presence of certain impurities is very deliquescent. It is pentamorphous, crystallizing in five distinct modifications, a tetragonal (α), two rhombic (β and γ), a rhombohedral (δ), and a regular (ϵ) form. The transition-points [8] are:

α Tetragonal $\longrightarrow$ β rhombic, $-17°$ C.
β Rhombic $\longrightarrow$ γ rhombic, 32·1° C.[9]
γ Rhombic $\longrightarrow$ δ rhombohedral, 84·2° C.[10]
δ Rhombohedral $\longrightarrow$ ϵ regular, 125·2° C.[10]

It is not isomorphous with sodium nitrate.[11] The melting-point is given as 165° C.,[12] 165° to 166° C.,[13] and 166° to 167° C.[14]; but Saunders's determination,[15] 169° C., and Early and Lowry's determination,[16] 169·6° C., are the most reliable, as they were careful to eliminate the depression incidental to the presence of traces of moisture.

The effect of water on the freezing-point is made evident by the table : [17]

Percentage of water . .	0	1·05	2·01	3·20	4·39	6·24	8·76	10·04
Freezing-point, °C. . .	169	157	146	133	122	112	99	95
Change of freezing-point for 1 per cent. of water	11·4	11·4	10·9	—	5·4	5·2	—	

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[1] Compare Fairley, *J. Soc. Chem. Ind.*, 1897, 16, 211.

[2] Nithack, *German Patent*, 1896, No. 95532.

[3] Elektrochemische Werke, Berlin, *German Patent*, 1911, No. 233895.

[4] Wahlenberg, *British Patent*, 1889, No. 12451; Craig, *German Patent*, 1896, No. 92172; Roth, *ibid.*, 1904, No. 149026; compare Fairley, *ibid.*, 1896, No. 97400; Lennox, *ibid.*, 1896, No. 96689; Rudeloff, *ibid.*, 1905, No. 166427; Naumann, *ibid.*, No. 166746. A summary of the Patent literature on the preparation of ammonium nitrate is given by Oelker, *Zeitsch. ges. Schiess-Sprengstoffwesen*, 1916, 9, 81.

[5] Kingzett, *Chem. News*, 1881, 43, 97.

[6] Hodgkinson and Lowndes, *ibid.*, 1888, 58, 27.

[7] Strecker and Thienemann, *Ber.*, 1920, 53, [B], 2096.

[8] Early and Lowry, *Trans. Chem. Soc.*, 1919, 115, 1387.

[9] Compare Müller and Kaufmann, *Zeitsch. physikal. Chem.*, 1903, 42, 497.

[10] Compare Schwarz, *Beiträge zur Kenntniss der umkehrbahren Ummwandlungen polymorphen Körper*, Göttingen, 1894.

[11] Early and Lowry, *Trans. Chem. Soc.*, 1922, 121, 963.

[12] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[13] Pickering, *Chem. News*, 1878, 38, 267.

[14] Schiff and Monsacchi, *Zeitsch. physikal. Chem.*, 1896, 21, 277.

[15] Saunders, *Trans. Chem. Soc.*, 1922, 121, 698.

[16] Early and Lowry, *ibid.*, 1919, 115, 1387.

[17] Millican, Joseph, and Lowry, *ibid.*, 1922, 121, 959.

The density of ammonium nitrate is 1·709[1]: 1·6973[2] at 23° C., 1·725[3] at 15° C., and 1·725[4] at 20° C. Its heat of formation from its elements is given as 87·9 Cal.[5] and 88·1 Cal.[6]; and its specific heat as 0·407 between 0° and 31° C.[7] Its solubility in water is given in the table.[8]

SOLUBILITY OF AMMONIUM NITRATE.

Temperature, °C.	Density of Solution.	Grams of NH_4NO_3 in 100 grams of Water.	Solid Phase.
0	..	118·3	NH_4NO_3 rhombic β
12·2	1·2945	153·4	,, ,, ,,
20·2	1·3116	192·4	,, ,, ,,
30·0	1·3299	241·8	,, ,, ,,
32·1	1·3344	256·9	,, ,, $\alpha+\beta$
35·0	1·3394	265·8	,, ,, α
40	1·3464	297·0	,, ,, ,,
50	..	344	,, ,, ,,
60	..	421	,, ,, ,,
80	..	580	,, ,, ,,
100	..	871	,, rhombohedral ?

When heated, ammonium nitrate first melts, then dissociates in accordance with the scheme[9]

$$NH_4NO_3 \rightleftharpoons NH_3+HNO_3;$$

and commences to evolve a gas containing 98 per cent. of nitrous oxide,[9] the reaction beginning at 185° C.:[10]

$$NH_4NO_3=N_2O+2H_2O+29·5 \text{ Cal.}$$

This gas always contains free nitrogen, nearly 2 per cent. being present up to 260° C., and considerably more at higher temperatures:[9]

$$5NH_3+3HNO_3=4N_2+9H_2O.$$

Traces of nitrogen peroxide and of nitric oxide are always present, the proportion of each between 220° and 260° C. averaging 0·001 per cent. The evolution of gas increases with rise of temperature, and is steady up to 250° C. At higher temperatures it becomes spasmodic, and

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[1] Schiff, *Annalen*, 1858, 107, 59; 1859, 111, 80.

[2] Schiff and Monsacchi, *Zeitsch. physikal. Chem.*, 1896, 21, 277.

[3] Retgers, *ibid.*, 1889, 4, 592.

[4] Haigh, *J. Amer. Chem. Soc.*, 1912, 34, 1137.

[5] Berthelot, *Ann. Chim. Phys.*, 1880, [5], 20, 255; *Compt. rend.*, 1880, 90, 779; *Bull. Soc. chim.*, 1880, [2], 33, 509.

[6] Thomsen, *J. prakt. Chem.*, 1880, [2], 21, 449.

[7] Bellati and Romanese, *Ann. Physik Beibl.*, 1887, 11, 520; *Atti Inst. Ven.*, 1886, [6], 4, 1395.

[8] Müller and Kaufmann, *Zeitsch. physikal. Chem.*, 1903, 42, 497; taken from Seidell, *Solubilities of Inorganic and Organic Substances* (Crosby Lockwood & Son, 1911).

[9] Saunders, *Trans. Chem. Soc.*, 1922, 121, 698.

[10] Pickering, *Chem. News*, 1878, 38, 267; Veley, *Trans. Chem. Soc.*, 1883, 43, 370; compare Berthelot, *Compt. rend.*, 1876, 82, 932.

above 260° it is liable to develop a slightly explosive character. Traces of chlorides present produce chlorine, but sulphates and sodium nitrate do not affect the decomposition.[1] It is much accelerated by the presence of ammonia, and by that of graphite, powdered glass,[2] and spongy platinum.[3] With the catalyst last mentioned, nitrogen is evolved. In presence of oxidizable substances, such as charcoal, the decomposition is of an explosive character,[4] mercuric fulminate being specially suitable as a primer.[5] The nitrate is employed in the manufacture of explosives.

In the fused state ammonium nitrate oxidizes phosphorus to phosphoric acid,[6] and reacts with many metals, examples being lead, bismuth, cadmium, zinc, magnesium, nickel, and barium.[7] At 120° C. sulphuric acid generates nitric acid, and at 150° C. nitrogen and nitrogen peroxide are also liberated.[8] Ammonium nitrate reacts with fused sodium nitrite with explosive violence.[9] In aqueous solution it is reduced by certain metals,[10] evaporation in contact with iron causing loss of ammonia and corrosion of the iron. This effect is obviated by employing vessels of aluminium or of acid-resisting material.[11] Solutions of ammonium nitrate in ammonia and in ammonium thiocyanate also exert a very corrosive action on iron and steel.[12]

The solid nitrate absorbs dry ammonia, yielding a colourless mobile liquid, the composition varying with the temperature and pressure. The product is known as " Divers's liquid," and appears to consist of solutions of ammonium nitrate and ammonia in one another. In its chemical behaviour this liquid resembles liquid ammonia. It dissolves bromine with liberation of nitrogen, and is converted by iodine into a solid mass, possibly Millon's compound, $N_2H_6I_2$. It dissolves potassium, sodium, magnesium, zinc, and cadmium, the nitrate being reduced to nitrite.[13]

Nitric acid combines with ammonium nitrate to form *acid nitrates*. The *trinitrate*, $NH_4NO_3,2HNO_3$, forms prismatic needles, m.p. 29° to 30° C., and the *dinitrate*, NH_4NO_3,HNO_3, six-sided laminæ, m.p. about 12° C.[14] Fig. 12 gives Groschuff's solubility-curves of the nitrate and its acid salts in nitric acid, as well as those of the potassium salt and its acid salts in the same solvent, and those of the trinitrates in water.

Ammonium nitrate forms double salts, examples being those with silver nitrate [15] and ammonium sulphate.[16]

[1] Saunders, *Trans. Chem. Soc.*, 1922, 121, 698.

[2] Veley, *Proc. Roy. Soc.*, 1888, 44, 239.

[3] Reiset and Millon, *J. prakt. Chem.*, 1843, 29, 365.

[4] de Lome, *Compt. rend.*, 1878, 87, 1005.

[5] Lobry de Bruyn, *Rec. trav. chim.*, 1891, 10, 127.

[6] Marchand, *J. prakt. Chem.*, 1838, 13, 442.

[7] Hodgkinson and Coote, *Chem. News*, 1904, 90, 142.

[8] Pelouze, *Ann. Chim. Phys.*, 1841, [3], 2, 47.

[9] Tommasi, *Chem. News*, 1881, 43, 241.

[10] Compare Hodgkinson and Coote, *loc. cit.*; Ramann, *Ber.*, 1881, 14, 1430; Morin, *Compt. rend.*, 1885, 100, 1497.

[11] Prideaux and Caven, *J. Soc. Chem. Ind.*, 1919, 38, 353.

[12] Davis, Olmstead, and Lundstrum, *J. Amer. Chem. Soc.*, 1921, 43, 1580.

[13] Divers, *Proc. Roy. Soc.*, 1873, 21, 109; *Phil. Trans.*, 1873, 163, 359; *Compt. rend.*, 1885, 101, 847; *Zeitsch. physikal. Chem.*, 1898, 26, 107; Arth, *Compt. rend.*, 1885, 100, 1588; Bronn, *Verflüssigtes Ammoniak als Lösungsmittel*, Berlin, 1905, 33.

[14] Groschuff, *Ber.*, 1904, 37, 1486; compare Ditte, *Ann. Chim. Phys.*, 1879, [5], 18, 320; *Compt. rend.*, 1879, 89, 576; Engel, *ibid.*, 1887, 104, 911.

[15] Schreinemakers, *Zeitsch. physical. Chem.*, 1909, 65, 553; Schreinemakers and de Baat, *Chem. Weekblad*, 1910, 7, 259.

[16] Schreinemakers and Hoenen, *ibid.*, 1909, 6, 51.

Ammonium hypophosphite, $NH_4H_2PO_2$.—Evaporation of the solution obtained by mixing solutions of barium hypophosphite and ammonium sulphate yields a residue from which alcohol extracts ammonium hypophosphite, hexagonal[1] laminæ or rhombic[2] plates, melting at 100° C. When heated above its melting-point it is converted into spontaneously inflammable phosphine, ammonia, and water.

Ammonium phosphites.—Excess of ammonia reacts with phosphorous acid to form *secondary ammonium phosphite*, $(NH_4)_2HPO_3$, evaporation of the solution over sulphuric acid yielding the salt in four-sided columnar crystals of very deliquescent character.[3] It is also produced by the action of ammonia on the primary salt at 80° to 100° C.,[4] or on phosphorous oxide in presence of water. It readily loses ammonia and water, and strong heating produces phosphine and phosphoric acid.[3]

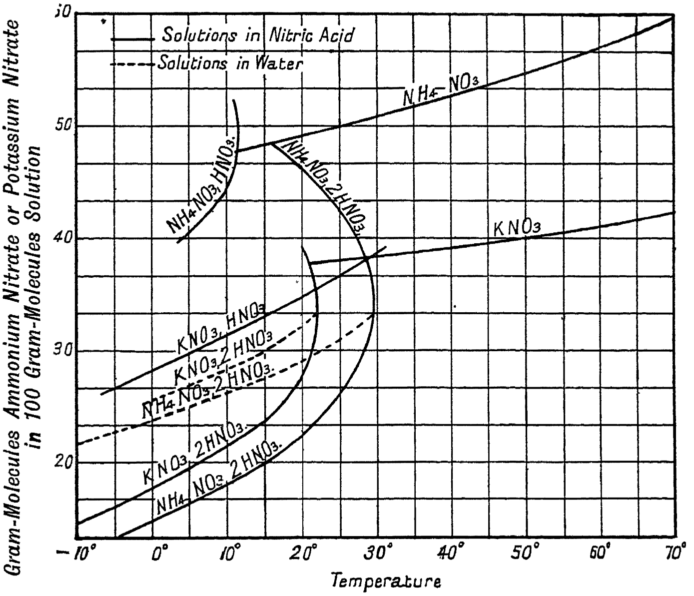

FIG. 12.—Solubility of ammonium nitrate, of potassium nitrate, and of their acid salts in nitric acid, and of the trinitrates in water.

Primary ammonium phosphite, $NH_4H_2PO_3$, can be prepared from phosphorous acid by addition of sufficient ammonia to change the colour of methyl-orange.[4] On concentrating the solution it separates in monoclinic prisms, melting at about 123° C. At 145° C. it evolves ammonia, and at higher temperatures phosphine. Its solubility at 14·5° C. is 190 grams in 100 grams of water.[4] At 100° C. it is decomposed by water, with liberation of ammonia.[5]

Ammonium hypophosphates.—Excess of ammonia converts hypophosphoric acid in solution into *normal ammonium hypophosphate*,

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[1] Wurtz, *Ann. Chim. Phys.*, 1843, [3], 7, 193.

[2] Beckenkamp, *Zeitsch. Kryst. Min.*, 1903, 37, 618.

[3] Rose, *Pogg. Annalen*, 1828, 12, 85.

[4] Amat, *Compt. rend.*, 1887, 105, 809.

[5] Dufet, *Bull. Soc. franç. Min.*, 1892, 14, 206.

$(NH_4)_4P_2O_6$, unstable tetragonal crystals probably containing one molecule of water of crystallization. On exposure to air the crystals evolve ammonia, and acquire a milk-like appearance. They dissolve in 30 times their weight of water, yielding a solution of very alkaline reaction. On heating, a spontaneously inflammable mixture of hydrogen and phosphine is liberated.[1]

When a solution of the normal salt is boiled until evolution of ammonia ceases, *secondary ammonium hypophosphate*, $(NH_4)_2H_2P_2O_6$, separates in very stable rhombic crystals,[2] melting at 170° C.[3] It dissolves in 14 times its weight of water at ordinary temperature.

On evaporation of a solution containing ammonia and hypophosphoric acid in equimolecular proportions, *primary ammonium hypophosphate*, $NH_4H_3P_2O_6$, crystallizes out.[4]

Ammonium orthophosphates.—Evaporation of a solution of phosphoric acid neutralized with excess of ammonia yields the trihydrate of the *normal phosphate*, $(NH_4)_3PO_4,3H_2O$, in the form of transparent prisms.[5] A pentahydrate has also been described.[6] When the ammoniacal solution is heated with aluminium, the phosphate of this metal is formed ; zinc liberates hydrogen.[7]

The ordinary salt, *secondary ammonium phosphate*, $(NH_4)_2HPO_4$, is prepared by concentrating a solution of phosphoric acid with addition of sufficient ammonia to prevent the development of an acidic reaction. It forms monoclinic crystals,[8] of density 1·619 [9] or 1·678.[10] It readily loses ammonia, with formation of the primary phosphate, the decomposition being rapid at 166° C.[11] Above this temperature the primary phosphate is transformed into pyrophosphate. The aqueous solution of the secondary phosphate has a strongly alkaline reaction, and is decomposed by boiling, with evolution of ammonia and formation of the primary salt.

The *primary ammonium phosphate*, $NH_4H_2PO_4$, forms tetragonal crystals.[12] Its density is given as 1·758,[13] 1·779,[14] and 1·803 [15] at 19° C.

The ammonium phosphates are employed for soil fertilization.[16]

The most important of the double salts of phosphoric acid with ammonium and the alkali-metals is *sodium ammonium hydrogen phosphate* or "microcosmic salt," $NaNH_4HPO_4,4H_2O$, a constituent of putrefying urine, and also present in guano under the name *stercorite*.[17] It can be prepared by the interaction of secondary sodium phosphate and ammonium chloride, or that of secondary ammonium phosphate and sodium chloride. It forms colourless columnar crystals belonging

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[1] Salzer, *Annalen*, 1878, 194, 28.
[2] Salzer, *loc. cit.*; *Annalen*, 1882, 211, 1.
[3] Sabanéeff, *Zeitsch. anorg. Chem.*, 1898, 176, 480.
[4] Salzer, *Annalen*, 1882, 211, 1.
[5] Schottländer, *Zeitsch. anorg. Chem.*, 1894, 7, 343 ; compare Kraut, *ibid.*, 392.
[6] Sestini, *Gazzetta*, 1879, 9, 298.
[7] Smith, *J. Soc. Chem. Ind.*, 1904, 23, 475.
[8] Mitscherlich, *Ann. Chim. Phys.*, 1821, 19, 385; Rammelsberg, *Ber.*, 1869, 3, 278.
[9] Schiff, *Annalen*, 1859, 112, 88.
[10] Buignet, *Jahresbericht*, 1861, 15.
[11] Knorre, *Zeitsch. anorg. Chem.*, 1900, 24, 369.
[12] Krickmeyer, *Zeitsch. physikal. Chem.*, 1896, 21, 53.
[13] Schiff, *Annalen*, 1859, 112, 88.
[14] Schröder, *Ber.*, 1874, 7, 677; *Dichtigkeitsmessungen*, Heidelberg, 1873.
[15] Krickmeyer, *loc. cit.*
[16] Compare Vogel, *Zeitsch. angew. Chem.*, 1891, 4, 568.
[17] Herapath, *J. Chem. Soc.*, 1849, 2, 70.

to the monoclinic system,[1] with a saline, ammoniacal taste, and density 1·554.[2] It loses ammonia readily, and is converted by heat into secondary sodium phosphate. When heated with metallic salts it forms vitreous "microcosmic beads" of characteristic colour, and is employed in qualitative analysis.

Potassium diammonium phosphate, $K(NH_4)_2PO_4,4H_2O$, is obtained by passing ammonia into a cooled solution of potassium dihydrogen phosphate, and filtering rapidly in an atmosphere of ammonia. On exposure to air, the deliquescent salt evolves ammonia, but it can be preserved in sealed tubes.[3] Other double salts with sodium,[4] and with lithium[5] and potassium,[6] have been prepared.

Ammonium pyrophosphates.—Excess of ammonia reacts with pyrophosphoric acid to form *normal ammonium pyrophosphate*, $(NH_4)_4P_2O_7$, precipitated from aqueous solution by addition of alcohol. It forms crystalline laminæ, dissolving very readily in water to a solution of alkaline reaction.[7] When boiled, this solution evolves ammonia, yielding an acid solution of *secondary ammonium pyrophosphate*, $(NH_4)_2H_2P_2O_7$.

Double pyrophosphates with sodium[8] and with potassium[9] have also been described.

Ammonium metaphosphates.—Several metaphosphates are known,[10] among them *ammonium monometaphosphate*, NH_4PO_3, formed from the dimetaphosphate by prolonged heating at 200° C.[11] It is only slightly soluble in water.

Ammonium arsenites.—Between 70° and 80° C. ammonia reacts with a solution of arsenious oxide to form acicular crystals of *ammonium meta-arsenite*, NH_4AsO_2.[12] With concentrated ammonia arsenious oxide yields the crystalline *ammonium pyroarsenite*, $(NH_4)_4As_2O_5$, an unstable substance decomposed with evolution of ammonia on exposure to air.[13]

Ammonium arsenates.—Excess of ammonia precipitates *normal ammonium arsenate*, $(NH_4)_3AsO_4$, from concentrated solutions of the primary and secondary salts. It yields a very alkaline solution, decomposed by zinc and by aluminium with evolution of hydrogen and arsine.[14] *Secondary ammonium arsenate*, $(NH_4)_2HAsO_4$, is gradually deposited from a concentrated solution of arsenic acid and ammonium hydroxide.[15] Loss of ammonia, or addition of arsenic acid to its solution, converts it into *primary ammonium arsenate*, $NH_4H_2AsO_4$, crystals of density 2·307[16] or 2·3105.[17]

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[1] Thomson and Bloxam, *Trans. Chem. Soc.*, 1882, 41, 379.
[2] Schiff, *Annalen*, 1859, 112, 88.
[3] Corelli, *Gazzetta*, 1921, 51, ii., 380.
[4] Uelsmann, *Arch. Pharm.*, 1859, [2], 99, 138; Herzfeld and Feuerlein, *Zeitsch. anal. Chem.*, 1881, 20, 191; Meslin, *Compt. rend.*, 1905, 140, 782.
[5] Berzelius, *Lehrbuch der Chemie*, 3rd ed., Dresden, 1833–1841, 4, 213.
[6] Filhol and Senderens, *Compt. rend.*, 1882, 94, 649.
[7] Schwarzenberg, *Annalen*, 1848, 65, 141.
[8] Schwarzenberg, *loc. cit.*; Rammelsberg, *Ann. Physik*, 1883, [2], 20, 943.
[9] Schwarzenberg, *loc. cit.*; Retgers, *Zeitsch. physikal. Chem.*, 1894, 15, 529.
[10] Compare metaphosphoric acid, this series, Vol. VI.
[11] Fleitmann, *Pogg. Annalen*, 1849, 78, 233, 238.
[12] Luynes, *J. prakt. Chem.*, 1857, 72, 80.
[13] Pasteur, *Annalen*, 1848, 68, 308; Stein, *ibid.*, 1850, 74, 218.
[14] Smith, *J. Soc. Chem. Ind.*, 1904, 23, 475; 1911, 30, 253.
[15] Salkowsky, *J. prakt. Chem.*, 1868, 104, 129.
[16] Schröder, *ibid.*, 1879, [2], 19, 266.
[17] Muthmann, *Zeitsch. Kryst. Min.*, 1894, 22, 497.

Several double arsenates of ammonium and sodium have been described.[1]

Ammonium antimonates.—On heating antimonic acid with ammonium hydroxide, *ammonium meta-antimonate*, $NH_4SbO_3,2H_2O$, is precipitated in the form of a powder.[2] *Secondary ammonium pyro-antimonate*, $(NH_4)_2H_2Sb_2O_7$, is also said to have been prepared.[3]

Ammonium carbonates.[4]—The *normal carbonate*, $(NH_4)_2CO_3,H_2O$, is produced by the action of ammonia on the solid commercial carbonate (p. 239) or its aqueous solution, and also by a similar process from ammonium carbamate.[5] On account of its insolubility in concentrated ammonia solution, the salt crystallizes out. It can also be prepared by dry distillation of the commercial product, or by crystallization from a solution in dilute alcohol.[5] It is also produced by heating barium or strontium carbonate with ammonium chloride or nitrate,[6] and is stated to be formed by heating a mixture of nitric oxide and acetylene in presence of spongy platinum.[7]

Ammonium carbonate crystallizes in plates or prisms, which at 58° C. decompose rapidly into ammonia, carbon dioxide, and water. It dissolves in less than its own weight of water at 15° C.[8] Its heat of formation from ammonia and carbon dioxide is 39·3 Cal.[9]

Electrolysis of an aqueous solution of ammonium carbonate yields oxygen and ammonium nitrate at the anode.[10]

The normal carbonate is a decomposition-product of urine,[11] and plays an important part in the nitrification of ammonia and ammonium salts in the soil.[12]

Ammonium hydrogen carbonate, NH_4HCO_3, is formed by the interaction at ordinary temperature of ammonia, water-vapour, and excess of carbon dioxide.[13] In nature it is often produced by the decay of nitrogenous material, and it is a constituent of guano.[14] It has been prepared by passing air and water-vapour alternately over red-hot coke, the gaseous product being then led through tubes filled with porous material:[15]

$$N+3H+CO_2+H_2O=NH_4HCO_3.$$

The primary carbonate is known, in the form of powder, as rhombic crystals,[16] and in a monoclinic modification.[17] Its density is given as

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[1] Uelsmann, *Arch. Pharm.*, 1859, [2], 99, 138; Filhol and Senderens, *Compt. rend.*, 1882, 94, 649; 95, 343.

[2] Frémy, *J. prakt. Chem.*, 1848, 45, 215.

[3] Frémy, *loc. cit.*; Raschig, *Ber.*, 1885, 18, 2743.

[4] For a summary of the older literature, see Divers, *J. Chem. Soc.*, 1870, 23, 171, 359, 364.

[5] Divers, *loc. cit.*

[6] Selvatici, *Bull. Assoc. chim. Sucr. Dist.*, 1910, 27, 669.

[7] Angelucci, *Gazzetta*, 1906, 36, ii., 517.

[8] Divers, *loc. cit.*

[9] Raabe, *Rec. trav. chim.*, 1882, 1, 158.

[10] Fichter and Kappeler, *Zeitsch. Elektrochem.*, 1909, 15, 937.

[11] Ladureau, *Compt. rend.*, 1884, 99, 877; Miquel, *ibid.*, 1890, 111, 501.

[12] Warington, *Trans. Chem. Soc.*, 1884, 45, 637; *Mon. Scient.*, 1885, [3], 15, 115; Schloesing, *Compt. rend.*, 1889, 109, 883.

[13] Berthelot and André, *ibid.*, 1886, 103, 665.

[14] Teschenmacher, *Phil. Mag.*, 1846, [3], 28, 548; Ulex, *Annalen*, 1847, 61, 392; Phipson, *J. Chem. Soc.*, 1863, 16, 74.

[15] Kraut, *Arch. Pharm.*, 1886, [3], 24, 21.

[16] Miller, *Pogg. Annalen*, 1831, 23, 558; Rose, *ibid.*, 1839, 46, 400; Deville, *Ann. Chim. Phys.*, 1854, [3], 40, 87; *J. prakt. Chem.*, 1854, 62, 22; Rammelsberg, *Handbuch der Krystallographisch-Physikalischen Chemie*, Leipsic, 1881–1882, 1, 545.

[17] Landolt, *Beziehungen zwischen physikal. Eigensch. und chem. Zus.*, Brunswick, 1898, 46.

1·573[1] and 1·544[2] at 15° C. Its solubility at 17·1° C. is 19·35 grams in 100 grams of water,[2] the salt crystallizing well from aqueous solution. It is a product of the decomposition of the normal carbonate at ordinary temperature.[3]

A *tetra-ammonium dihydrogen carbonate*, $(NH_4)_4H_2(CO_3)_3,H_2O$, can be prepared by heating the commercial salt to fusion, and allowing the liquid to solidify[4]; by crystallizing the commercial salt from warm ammonium hydroxide[5]; and by the action of alcohol on the normal salt.[6] It forms rhombic plates and prisms, soluble in 5 times their weight of water at 15° C. Its properties are intermediate between those of the normal carbonate and the primary carbonate, and it is doubtful whether it is a definite compound or a mixture of these two salts.

Commercial ammonium carbonate is a mixture of ammonium hydrogen carbonate and *ammonium carbamate*, $NH_2{\cdot}CO{\cdot}ONH_4$, and is probably a definite compound of the two salts.[7] It is formed by distillation of a mixture of ammonium chloride with carbonate of potassium, sodium, or calcium, and was formerly manufactured by the dry distillation of animal excrement, horn, and other substances. It is now obtained as a by-product of the gas-manufacture, and after sublimation condenses in hard lumps.

Ammonium cyanide, NH_4CN.—The cyanide is manufactured by passing ammonia alone or mixed with hydrocarbons[8] over red-hot coke ; or by heating ammonia with carbon monoxide :

$$2NH_3+C=NH_4CN+H_2\ ;\quad CO+2NH_3=NH_4CN+H_2O\ ;$$

or by passing a mixture of ammonia, hydrogen, and nitrogen over coke at 1100° C.[9] It is also a by-product in the manufacture of coal-gas,[10] and is formed by the interaction of ammonia and calcium carbide at 650° C.[11] Other methods of formation are the combination of methane and nitrogen under the influence of the silent electric discharge,[12] and the distillation of ammonium chloride with anhydrous cyanides.[13]

Ammonium cyanide forms colourless cubes, readily volatilized and completely dissociated at comparatively low temperatures.[14] Its heat of formation from diamond, hydrogen, and nitrogen is 3·2 Cal.[15] It dissolves readily in both water and alcohol, the salt being extensively dissociated in aqueous solution. It is extremely poisonous.

Ammonium thiocyanate, NH_4CNS.—The thiocyanate is manu-

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[1] Schiff, *Annalen*, 1858, 107, 64.

[2] Dibbits, *J. prakt. Chem.*, 1874, [2], 10, 434.

[3] Divers, *J. Chem. Soc.*, 1870, 23, 171, 359, 364 ; Deville, *Ann. Chim. Phys.*, 1854, [3], 40, 87 ; *J. prakt. Chem.*, 1854, 62, 22 ; Vogler, *Zeitsch. anal. Chem.*, 1878, 17, 451.

[4] Rose, *Pogg. Annalen*, 1839, 46, 400.

[5] Deville, *loc. cit.*

[6] Divers, *loc. cit.*

[7] Compare Dibbits, *loc. cit.*

[8] Langlois, *Berzelius's Jahresbericht*, 1822, 84 ; compare Bergmann, *J. Gasbeleuchtung*, 1896, 39, 117, 140.

[9] Lance, *Compt. rend.*, 1897, 124, 819.

[10] Pendrié, *J. Gasbeleuchtung*, 1888, 31, 1006.

[11] Salvadori, *Gazzetta*, 1905, 35, i., 236.

[12] Figuier, *Compt. rend.*, 1886, 102, 694.

[13] Bineau, *Annalen*, 1839, 32, 230.

[14] Bineau, *loc. cit.* ; Ostwald, *Lehrbuch der allgemeinen Chemie*, 1st ed., Leipsic, 1885–1887, 2, 687 ; Deville and Troost, *Compt. rend.*, 1859, 49, 239 ; 1863, 56, 891 ; *Annalen*, 1860, 113, 42 ; 1863, 127, 274.

[15] Berthelot, *Compt. rend.*, 1880, 91, 79.

factured by heating a mixture of carbon disulphide and alcoholic ammonia:[1]

$$CS_2+4NH_3=NH_4CNS+(NH_4)_2S.$$

It is also formed by the action of hydrogen cyanide on ammonium polysulphides:[2]

$$HCN+(NH_4)_2S_2=NH_4CNS+NH_4SH.$$

It is a constituent of the ammoniacal liquor of the gasworks, and can be prepared from it,[3] and also by other methods.[4]

Ammonium thiocyanate forms colourless, monoclinic[5] plates or laminæ, of density 1·31[6] at 13° C. Its melting-point is given as 149° C.,[7] 159° C.,[8] and 169° C.,[9] but an exact determination of this constant is precluded by the ready transformation of the salt into the isomeric thiourea, $CS(NH_2)_2$.[10] The heat of formation of ammonium thiocyanate from its elements is given as 21·8 Cal.[11] and 28·4 Cal.[12] It is very soluble in water, 162 grams dissolving in 100 grams of water at 20° C.[13] It is employed in quantitative analysis,[14] in the manufacture of explosives,[15] and in photography.

Ammonium ferrocyanide and ferricyanide.—The modes of preparation and the properties of ammonium ferrocyanide and ferricyanide are described in Vol. IX., Part II.

Ammonium silicate.—No ammonium salt of silicic acid has been isolated.[16] Experiments on the electrical conductivity of solutions of silicic acid in aqueous ammonia indicate the probability of the formation of a true ammonium silicate in solution.[17]

Ammonium borates.—Many borates of ammonium have been described, but their existence as definite chemical individuals is in most instances doubtful.[18] *Ammonium tetraborate*, $(NH_4)_2B_4O_7,4H_2O$, is prepared by cooling a warm solution of boric acid in excess of ammonium hydroxide. It forms tetragonal crystals,[19] soluble in 12 times their weight of water at the ordinary temperature.

Excess of boric acid and warm ammonium hydroxide yield rhombic

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[1] Zeise, *Annalen*, 1843, 47, 36; Millon, *Jahresbericht*, 1860, 237; Gries, *ibid.*, 1861, 340; Claus, *Annalen*, 1875, 179, 112; Tscherniak and Günsburg, *Ber.*, 1879, 12, 140, 2024; 1882, 15, 98; Schulze, *J. prakt. Chem.*, 1883, [2], 27, 518.

[2] Liebig, *Annalen*, 1847, 61, 126.

[3] Dyson, *Dingler's Polytech. J.*, 1884, 251, 457; Gorke, *Dissertation*, Leipsic, 1905.

[4] Compare Arnu, *Ber.*, 1883, 16, 418.

[5] Gossner, *Zeitsch. Kryst. Min.*, 1903, 38, 110.

[6] Clarke, *Amer. J. Sci.*, 1877, [3], 14, 281; compare Schröder, *Ber.*, 1878, 11, 2215.

[7] Findlay, *Trans. Chem. Soc.*, 1904, 85, 403.

[8] Reynolds, *Annalen*, 1869, 150, 255.

[9] Gossner, *loc. cit.*

[10] Volhard, *J. prakt. Chem.*, 1874, [2], 9, 11; Waddel, *J. Physical Chem.*, 1899, 2, 525; Reynolds and Werner, *Trans. Chem. Soc.*, 1903, 83, 1; Findlay, *ibid.*, 1904, 85, 403.

[11] Joannis, *Ann. Chim. Phys.*, 1882, [5], 26, 482.

[12] Matignon, *ibid.*, 1893, [6], 28, 527.

[13] Rüdorff, *Ber.*, 1869, 2, 68.

[14] Volhard, *Annalen*, 1877, 190, 1.

[15] Rheinische Dynamitfabrik, *German Patent*, 1904, No. 148203.

[16] Struckmann, *Annalen*, 1855, 94, 345.

[17] Schwarz, *Ber.*, 1916, 49, 2358; 1919, 52, [B], 601; Schwarz and Souard, *Ber.*, 1920, 53, [B], 1.

[18] Compare Sborgi, *Atti R. Accad. Lincei*, 1912, [5], 21, ii., 855; 1913, [5], 22, i., 90.

[19] Rammelsberg, *Pogg. Annalen*, 1853, 90, 21.

crystals[1] of the *pentaborate*, $(NH_4)_2O,5B_2O_3,8H_2O$, soluble in 8 times their weight of cold water.

The mineral *larderellite*, $(NH_4)_2O,4B_2O_3,5H_2O$, is found in nature in association with boric acid in the lagoons of Tuscany.

Ammono-salts of the Alkali-metals.—The interaction of metallic amides in ammonia solution produces the so-called *ammono-salts*.[2]

Dipotassium ammonosodiate, $(Na[NH_2]_3)K_2$, is formed by the action of potassamide on sodamide in solution in liquid ammonia, by bringing sodium iodide into contact with excess of potassamide dissolved in liquid ammonia, and by the interaction in presence of a small proportion of platinum-black of sodium and a solution of potassamide in liquid ammonia. This substance forms well-developed crystals, and is stable *in vacuo* at 100° C., but at higher temperatures it melts with evolution of ammonia, and attacks glass.

Monorubidium ammonosodiate, $(Na[NH_2]_2)Rb$, is the product of the simultaneous action of sodium and rubidium on liquid ammonia. It is soluble in this solvent, and is energetically decomposed by water with formation of sodium and rubidium hydroxides. Its solution in liquid ammonia is converted by a large excess of rubidium into *dirubidium* ammonosodiate, $(Na[NH_2]_3)Rb_2$, a substance much more soluble in liquid ammonia than its parent compound.

Dipotassium ammonolithiate, $(Li[NH_2]_3)K_2$, is formed from potassamide and lithium iodide in solution in liquid ammonia, and under the influence of platinum-black by the simultaneous action of potassium and lithium on liquid ammonia. The very small, colourless crystals are almost insoluble in liquid ammonia. With acid amides, ammonium halides, and ammonium salts of oxy-acids it yields the corresponding salts of lithium, potassium, and ammonium.

Monorubidium ammonolithiate, $(Li[NH_2]_2)Rb$, is prepared by the action in presence of platinum-black of lithium on rubidamide dissolved in liquid ammonia. The white crystals are sparingly soluble in liquid ammonia, and are decomposed analogously to those of the dipotassium derivative.

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[1] Atterberg, *Zeitsch. anorg. Chem.*, 1906, 48, 371.

[2] Franklin, *J. Physical Chem.*, 1919, 23, 36.

CHAPTER IX.

COPPER.

Symbol, Cu. Atomic weight, 63·57 (O=16).

Occurrence.—There are large quantities of *native copper* in the neighbourhood of Lake Superior, where masses of the metal weighing several tons have frequently been found; and at Santa Rita in New Mexico. Gowland [1] mentions one specimen from the Lake Superior district measuring 10 feet by 3 feet by 2 feet, and weighing over 6 tons. In Chile there are large quantities of sand containing between 60 and 90 per cent. of copper. The metal is also found in Cornwall, Sweden, Norway, Hungary, the Ural Mountains, and other places. Native copper is characterized by a high degree of purity.[2]

Great quantities of minerals with a large proportion of combined copper are widely distributed over the earth's surface. Examples are *cuprite* or *ruby copper*, Cu_2O (United States and Australia); *melaconite* or *tenorite*, CuO (United States); *malachite*, $CuCO_3,Cu(OH)_2$ (North and South America, Australia, and the Urals); *azurite* or *chessylite*, $2CuCO_3,Cu(OH)_2$ (Chessy in France, the Urals, Siberia, and North America); *chalcopyrite* or *copper pyrites*, $Cu_2Fe_2S_4$ (Cornwall, Devonshire, Wales, Ireland, Canada, Newfoundland, Australia, United States, France, Germany, Austria, Hungary, Sweden, Norway, and South America); *bornite*, *horse-flesh ore*, or *peacock ore*, Cu_3FeS_3 (Cornwall, Montana, Saxony, and Chile); *chalcocite* or *copper glance*, Cu_2S (United States); *covellite* or *indigo copper*, CuS (Serbia and Chile); *atacamite*, $CuCl_2,3Cu(OH)_2$ (Chile and Peru); *chrysocolla*, $CuSiO_3,2H_2O$ (Chile and the Urals).

The metal is also present in small proportion in plants and animals.

History.—Pure copper, or an alloy with tin in the form of bronze, appears to have been known for at least 7000 years. The metal was probably familiar to the Chaldeans before the year 5000 B.C.,[3] and seems to have been worked by the Egyptians about the same period, since Egyptian copper tools supposed to date from about the year 4400 B.C. have been discovered. The copper mines of the Sinai Peninsula were extensively worked by the Egyptians about the year 3700 B.C.[4]

About the year 1500 B.C. bronze containing between 5 and 16 per cent. of tin was without doubt extensively employed in Egypt. Copper

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[1] Gowland, *The Huxley Memorial Lecture for 1912*: published by the Royal Anthropological Institute of Great Britain and Ireland.

[2] Gowland, *Chem. News*, 1893, 68, 307.

[3] Gowland, *loc. cit.*

[4] Petrie, *Ancient Egypt*, 1915, Part I., 121; compare Berthelot, *Compt. rend.*, 1896, 123, 365.

vases of Cyprian origin dating from the same period have been found in Egypt. The metal employed in their manufacture was free from tin. The great metallurgical skill possessed by the makers of these vessels proves that copper must have been known in Cyprus for many centuries previous to their production.

Copper daggers found in Northern Italy probably date from about the year 2100 B.C.[1] Keith[2] gives the date 2000 B.C. for the beginning of the Bronze Age in Britain, five centuries later than the date suggested by Montelius.[3] Copper was probably known in China about the year 3000 B.C. There is evidence of its having been worked in India at an early period.

The association of the ores of copper with those of other metals is probably the cause of the production of alloys of varying composition by the prehistoric smelters. The earliest copper tools of Britain contain tin; those of Hungary up to 4·5 per cent. of antimony.[4]

Chinese and Japanese bronze mirrors dating from the first, fifth, seventh, eleventh, and twelfth centuries have been found to contain between 62 and 74 per cent. of copper associated with other metals. A Corean mirror of the tenth century contains 73 per cent. of copper, and considerable proportions have been found in ancient coins, arrow-heads, and water-pots from these lands.[5]

Copper deposits in Britain are said to have been known to the Phœnicians about the year 1000 B.C. In 1581 mining was being carried on at Keswick, in Cumberland, the ore being probably a sulphide. The Mines Royal Society established a works for copper-smelting at Neath, in Wales, in 1584. Various other works were started in Wales at different times, notably those erected by Lane and Pollard at Swansea in 1717.

The production of copper in Cornwall and Devon continued from the time of Queen Elizabeth to the end of the nineteenth century. In Ireland the industry was carried on from the beginning of the eighteenth century until 1880. The copper of Anglesey was known to the Romans, and the mines of the island were worked during the eighteenth and nineteenth centuries.

Reverberatory furnaces were constructed by Lambert in Chile in 1842, and the first blast furnace was erected by him in that country in 1857. So successful was the development of this enterprise, that Chile became the world's largest producer in the years 1861 to 1870, and furnished about half the total output. The decline of the Welsh industry dates from this period, and also the development of the manufacture in the United States of America, Calumet, in the Lake Superior district, becoming an important centre. The next decade is noted for the inception of copper-mining in Spain and Portugal, the chief centres being the Andalusian, San Domingo, Tharsis, and Rio Tinto mines.

Between 1881 and 1890 the United States of America became the greatest producer, manufacturing one-third of the world's output. In addition to the Lake mines, works were begun in Montana and Arizona.

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[1] Montelius, *J. Anthropol. Inst.*, 1897, 26, 258.

[2] Keith, Presidential Address to the Royal Anthropological Institute, January 26, 1915.

[3] Montelius, *Archeologia*, 1909, 61, 162.

[4] Compare Berthelot, *Compt. rend.*, 1893, 116, 161; 1894, 118, 764; 1897, 124, 328; *Ann. Chim. Phys.*, 1889, [6], 17, 508; Coffey, *J. Anthropol. Inst.*, 1901, 31, 265.

[5] Chikashige, *Trans. Chem. Soc.*, 1920, 117, 917.

Spain and Portugal continued to prosper, and under Gowland's influence Japan also entered the field of competition. Simultaneously, the Chilean output began to decline.

In 1800, 75 per cent. of the world's production of copper came from Great Britain. In 1913 the British output had fallen to 6 per cent., and that of the United States of America had risen to 55 per cent. During the same period the total annual production increased a hundredfold, from 10,000 to 1,000,000 tons.[1]

The last ten years of the nineteenth century witnessed the establishment of complete supremacy by the United States of America, more than half the total output being produced there. During the present century that country has further improved its position, the production for the year 1916 being estimated at 865,000 long tons.

The name of the metal is derived from the Latin *cyprium*, Cyprus, that island having constituted the chief source of the copper employed by the Romans. Later, the name changed to *cuprum*, from which the word copper is derived.

Preparation.[2]—The methods employed in the manufacture of copper from its ores may be classified in three main divisions: (1) *dry methods*, for ores with more than 4 per cent. of copper; (2) *wet methods*, for ores with less than 4 per cent. of copper; (3) *electrometallurgical methods.*

(1) Dry Methods.

The ore is first calcined or roasted,[3] a part of the arsenic and antimony present being eliminated as oxide or sulphide, and part remaining as arsenate or antimonate. Simultaneously, a considerable proportion of the sulphur is removed, the roasted ore consisting chiefly of sulphides, sulphates, and oxides. It is then smelted to a mixture of copper and iron sulphides, known as *copper-matte* or *coarse-metal*, the process being carried out either in a blast furnace (German or Swedish process) or in a reverberatory furnace (English process). The matte is then smelted with coke and siliceous fluxes to slag off the iron, the operation being performed in a blast furnace (German process), a reverberatory furnace (English process), or a converter (Bessemer process). The product is an impure copper sulphide, called *blue-metal* when it contains iron, *pimple-metal* when free copper and copper oxide are present, and *fine-metal* or *white-metal* when it consists of a fairly pure copper sulphide with about 75 per cent. of the metal. This product is again smelted to form *coarse-copper*, containing about 95 per cent. of the metal. The coarse-copper is then refined. In the American or pyritic smelting process the raw ore is smelted directly to matte in a blast furnace. The various processes are named after the countries in which they have been most developed, but no individual process is limited to the country of its origin.

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[1] Compare Carpenter, *Cantor Lectures on Progress in the Metallurgy of Copper*, Royal Society of Arts, December, 1917.

[2] For full metallurgical details reference should be made to *Modern Copper Smelting*, by D. M. Levy (Griffin & Co.); and to the *Cantor Lectures on Progress in the Metallurgy of Copper*, by H. C. H. Carpenter (Royal Society of Arts, December 1917).

[3] An attempt has been made to elucidate the mechanism of the roasting process (Reinders and Goudriaan, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, 18, 150) by determining the pressure of the sulphur dioxide in equilibrium with various combinations of intermediate products.

The German or Swedish process involves five steps : (1) roasting the ore ; (2) smelting the roasted ore to *matte* in a blast furnace ; (3) roasting the matte ; (4) smelting the matte in a blast furnace with coke and fluxes to *black-metal* or *coarse-metal ;* (5) refining the coarse-metal. During the process the siliceous material and part of the iron are converted into a fused silicate-slag, floating on a heavier layer of copper matte consisting of a fused mixture of cuprous sulphide and ferrous sulphide. The reduction to copper is effected chiefly by carbon monoxide or carbon, and not by the sulphur present. To concentrate the matte, the cycle of oxidation by roasting and reduction by smelting is repeated several times, the iron being gradually removed as a fused slag of ferrous silicate.

The English process comprises six operations : (1) calcination ; (2) smelting to *matte* in a reverberatory furnace ; (3) roasting the matte ; (4) smelting the matte in a reverberatory furnace to *white-metal* or *fine-metal ;* (5) conversion of the fine-metal into *coarse-copper* or *blister-copper*, sometimes after a preliminary calcination ; (6) refining the coarse-copper. In this process the calcined ore is smelted in a reverberatory furnace, the reduction being effected by the interaction of the sulphides and oxides or sulphates, with evolution of sulphur dioxide, thus yielding a more concentrated matte than the blast-furnace process :

$$Cu_2S+2Cu_2O=6Cu+SO_2;$$
$$Cu_2S+2CuO=4Cu+SO_2;$$
$$Cu_2S+CuSO_4=3Cu+2SO_2.$$

The siliceous lining of the hearth converts the ferrous oxide into a slag of ferrous silicate. By altering the air-supply to the furnace, the matte is subjected to alternate oxidation and reduction. Both the German process and the English process depend on the fact that copper has a greater affinity for sulphur than for oxygen, and iron a greater affinity for oxygen than for sulphur.

The Welsh process differs from the English method in the enrichment of the matte by smelting with copper slags formed in subsequent operations.

The Anglo-German process is a combination of the English and German methods. After calcination the ore is smelted in a shaft furnace, and the matte is concentrated in a reverberatory furnace. The subsequent smelting to coarse-metal can be effected in either type of furnace.

The concentration of the matte and its subsequent smelting to coarse-copper are also effected by the Bessemer process, a modified type of Bessemer converter with the side tuyeres raised about 10 inches above the bottom lining being employed. The process finds extensive application, a large proportion of the arsenic and antimony being eliminated. A serious item of expense is the renewal of the siliceous lining of the converter, the silica required for slagging the iron being provided from this source.

In localities where fuel is expensive, *pyritic smelting*[1] has been considerably developed. It was devised by John Holway[2] in 1878.

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[1] Schiffner, *Rep. 5th Internat. Congress Appl. Chem.*, 1903, 2, 102 ; Lodin, *ibid.*, 251.

[2] Holway, *A New Application of Bessemer's Method of Rapid Oxidation by which Sulphides are utilized as Fuel*, Royal Society of Arts, February 1879.

The ore is roasted in an oxidizing atmosphere in the upper part of the blast furnace, two types of procedure being in vogue. The heat can be maintained by the combustion of the sulphur in the ore, no external fuel or hot blast being employed; or the process is facilitated by addition of fuel, or by a hot blast, or by both modifications simultaneously.

Ores not containing sulphur, such as the oxide and carbonate, are reduced with coke in a blast furnace. The impurities associated with native copper are removed by slagging in a reverberatory furnace.

The reduction of copper ores in the electric furnace has been studied by Juschkewitsch.[1] Stephan[2] has given an account of its application to the extraction of copper from its ores.

The unchallenged supremacy of the United States of America in copper production is attributed by Carpenter[3] to two causes:—

"A. Improvements effected in that country since 1880 in the technique of copper smelting and refining, enabling ores of very low grade to be worked economically.

B. The enormous reserves of ore existing in Arizona, Montana, Michigan, Utah, Tennessee, Mexico, and Chile.

The developments in manufacture are summarized by Carpenter as follows:—

1. Great improvements in mining and ore-dressing operations (mechanical concentration).
2. The use of mechanically rabbled roaster furnaces.
3. The manufacture of sulphuric acid both from blast-furnace and roaster gases.
4. The blast-roasting and sintering of sulphide fines.
5. The practical application of the pyritic smelting principle to suitable raw ores, and to practically all copper mattes.
6. An enormous increase in the capacity and output both of blast and reverberatory furnaces.
7. The recovery of metal values from the furnace waste-gases.
8. The adoption of electrolytic refining, followed in many cases by furnace refining with the recovery of precious-metal values in the copper which more than suffice to pay for their extraction.

And, most recently of all,

9. The application of either leaching or flotation processes or both to low-grade ores, tailings, etc."

The chief impurities present in coarse-copper are iron, lead, zinc, nickel, cobalt, bismuth, arsenic, antimony, sulphur, selenium, and tellurium. The *dry refining process* involves an oxidizing fusion in a reverberatory furnace, the impurities being either volatilized or slagged. Part of the cuprous oxide formed by oxidation dissolves in the metal, rendering it hard and brittle. This oxide is partly reduced by interaction with the cuprous sulphide still present. The molten mass is *poled* with a pole of green wood, the evolved gases facilitating the elimination of the sulphur dioxide, and partially reducing the cuprous oxide to copper. To finish the reduction, the copper is covered with a layer of wood-charcoal or anthracite, and again poled. Excessive

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[1] Juschkewitsch, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 469.

[2] Stephan, *Metall und Erz*, 1912, 10, 11.

[3] Carpenter, *Cantor Lectures on Progress in the Metallurgy of Copper*, Royal Society of Arts, December 1917.

poling is deleterious, causing the reduction of arsenates and antimonates to the corresponding elements, and thus deteriorating the quality of the copper. The soft, malleable metal is known as *tough-pitch* copper, and displays a lustrous, silky fracture. Several varieties of copper are recognized in the trade: *bean-shot* copper is formed by pouring the metal into hot water; *feathered-shot* copper by pouring into cold water; *rosette* copper by cooling the surface of the fused metal with water, and removing the thin, dark red crust formed; *japan* copper by casting into ingots, and cooling rapidly with water, its colour being purple-red; *tile* copper, an impure form produced by refining the first tappings; *best-selected* copper, a purer type.

(2) Wet Methods.

Wet methods of extraction are applied to low-grade ores containing not less than 0·25 to 1 per cent. of copper, or to products containing copper associated with gold and silver. For ores containing copper as oxide or carbonate, the solvents employed are sulphuric acid, hydrochloric acid, and ferrous chloride.

The original Hunt-Douglas process [1] involves treatment of the ore at 70° C. with a solution of ferrous chloride produced by the interaction of sodium chloride and ferrous sulphate. The ferrous chloride converts copper oxide and carbonate into a solution of cuprous and cupric chlorides, ferric hydroxide being precipitated and carbon dioxide evolved. After filtration to remove ferric hydroxide the copper is precipitated by addition of scrap iron, the ferrous chloride thus regenerated being available for further use in the first stage of the process. The amount of iron required is small, but the method is handicapped by difficulty in filtering the ferric hydroxide, by the tendency of the copper solution to undergo atmospheric oxidation, and by the fact that any silver present is dissolved.

In the modern Hunt-Douglas process the ore is leached with dilute sulphuric acid, and the copper converted into cupric chloride by addition of ferrous chloride or calcium chloride. The use of the calcium salt entails removal of the calcium sulphate by filtration. The cupric salt is precipitated as cuprous chloride by reduction with sulphur dioxide, and the precipitate is converted into metallic copper by treatment with iron, or into cuprous oxide by the action of milk of lime. In this process the amount of iron needed is proportionately small, ferric hydroxide is not precipitated, and silver is not dissolved.

When the ore contains cuprous sulphide this salt is converted into a soluble form: cupric sulphate, soluble in water; cupric oxide, soluble in hydrochloric or sulphuric acid; cupric chloride, soluble in water; or cuprous chloride, soluble in solutions of metallic chlorides.

Conversion into the sulphate is effected by weathering, a slow and expensive process; by calcination, for ores containing a high percentage of iron pyrites; by calcination with ferrous or aluminium sulphate; or by calcination with ferric sulphate as an adjunct to the weathering process.

The transformation into oxide is carried out by calcination in a reverberatory furnace, or, if the sulphur is to be recovered, in a muffle

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[1] Hunt, *Compt. rend.*, 1869, 69, 1357; A. Meyer, *Berg- und Hütten-männische Zeit.*, 1862, 21, 182.

furnace. Its economical working is contingent on the availability of a cheap supply of hydrochloric or sulphuric acid.

The formation of the chlorides is effected in the *dry way* by calcination with sodium chloride; or in the *wet way* by interaction with ferrous chloride and hydrochloric acid or with ferric chloride. The wet way is only adopted if fuel is scarce, or the escape of noxious vapours into the atmosphere is not permissible. In the dry method the ore is oxidized by a preliminary roasting, and then chloridized by calcination with sodium chloride or *Abraum* salts in a furnace of the reverberatory or muffle type, the principal product being cupric chloride. The Dötsch modification of the wet process, worked at Rio Tinto, depends on the action of ferric-chloride solution on a mixture of the ore with sodium sulphate and ferric chloride. The liquid drawn off from the bottom of the heaps of ore contains cuprous chloride in solution as a complex salt. The copper is liberated by the action of iron, the ferrous chloride simultaneously formed being chlorinated in towers to ferric chloride, and the product employed for moistening the heaps of ore.

After lixiviation of the sulphate, oxide, or chlorides obtained by these methods, the copper is precipitated by the process already described. If the *cement copper* thus obtained contains over 55 per cent. of the metal, it is refined directly; if the percentage is lower, it is first smelted with matte or calcined copper pyrites.

References to other wet processes of copper extraction are appended.[1]

(3) ELECTROMETALLURGICAL METHODS.

Several processes for the extraction of copper by electrometallurgical methods have been devised. The Marchese patent[2] aimed at the decomposition of copper matte and deposition of the copper simultaneously in a sulphuric-acid electrolyte with a copper-matte anode and a copper cathode. In Siemens and Halske's patent[3] the copper of the ore was oxidized to the cupric state by an acid solution of ferric sulphate, and the copper deposited electrolytically in a second vessel with a diaphragm separating the cathode and the anode. Neither process has been commercially successful.

Höpfner's patent[4] is worked on a small scale. The ore is extracted with a solution of cupric chloride and calcium or sodium chloride, the copper of the cupric salt and that of the cuprous sulphide being converted into cuprous chloride, with precipitation of sulphur. The copper is deposited from the cuprous-chloride solution in a cell fitted with a diaphragm, a copper cathode, and a carbon anode, the extracting liquid being regenerated at the anode, and being thus available for further extraction of the ore.

Processes devised by Carmichael[5] and by Browne[6] have been employed in Canada for the extraction of copper.

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[1] Neill, *Mineral Industry*, 1902, 10, 216; Gin, *Rep. 5th Internat. Congress Appl. Chem.*, 1903, 2, 116; Arsdale, *Engin. Mining J.*, 1903, 75, 853.

[2] *German Patent*, 1882, No. 22429.

[3] *German Patent*, 1886, No. 42243; compare Borchers, *Berg- und Hütten-männische Zeit.*, 1893, 52, 251, 269; Cohen, *Zeitsch. Elektrochem.*, 1894, 1, 50.

[4] *German Patent*, 1888, No. 53782.

[5] *U.S.A. Patent*, 1903, No. 719132.

[6] Compare Haber, *Zeitsch. Elektrochem.*, 1903, 9, 392.

The process patented by Jumau[1] involves the extraction of the roasted ore with an ammoniacal solution of ammonium sulphate or sulphite. Sulphurous acid reacts with the solution thus formed, precipitating either cuprous sulphite or cupro-cupric sulphite :

$$3Cu(OH)_2+3SO_2=CuSO_3,Cu_2SO_3+H_2SO_4+2H_2O.$$

The precipitated sulphite is redissolved in an ammoniacal solution of ammonium sulphate or sulphite, and the solution electrolyzed.

Electrolytic Refining.[2]—In 1865 Elkington patented a process for the electrolytic refining of copper, similar in principle to the method employed at the present day. In the modern process the bath is a solution containing 12 to 20 per cent. of copper sulphate and 4 to 10 per cent. of sulphuric acid. A fairly pure anode of copper containing small amounts of silver, gold, arsenic, antimony, iron, and other impurities is employed, the metal being deposited on a copper cathode. A pure and coherent deposit of copper is obtained with a low current-density of 0·0043 to 0·0484 ampère per sq. cm., the noble metals being deposited in the anode mud, and the other impurities remaining partly in this mud, and partly entering into solution. If the current-density be too low, the deposited copper is pale and brittle ; if too high, it is dark-brown and spongy. Constant attention must be paid to the composition and degree of acidity of the electrolyte, both important factors influencing the nature of the deposit. With rotating cathodes a good deposit is obtained with currents of high density, but in practice this modification is precluded by the disturbance of the anode mud, the solid particles in the electrolyte causing the formation of nodular growths on the deposited copper. The yield of copper obtained by the electrolytic method usually corresponds with a current-efficiency of 94 to 96 per cent., although it is possible to attain an efficiency of 98 per cent. The bath is usually maintained at a temperature of 40° to 50° C.

Jumau's process (*ut supra*) for the electrolytic extraction of copper from its ores is also applicable to the production of pure copper from solutions of its compounds.[3] The cupric sulphite or cupro-cupric sulphite precipitated from the copper solution by the action of sulphurous acid or a sulphide is decomposed by sulphuric acid into cupric sulphate and metallic copper. The metal thus liberated is pressed into a form suitable for an anode, and refined electrolytically.

Refining by other Methods.—Various other methods are available for the purification of copper. An example is the ready reduction of cuprous chloride by soft iron, a substance without action on cupric chloride. Aluminium slowly reduces a warm solution of cupric sulphate. Vigoroux[4] recommends a method depending on the action of aluminium on a solution of copper in concentrated hydrochloric acid.

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[1] *German Patents*, 1907, Nos. 189643 and 191566.

[2] Compare Ulke, *Elektrolytische Raffination des Kupfers*, Halle, 1904 ; Borchers, *Elektrometallurgie*, 3rd ed., Leipsic, 1903, 185 ; Haber, *Zeitsch. Elektrochem.*, 1903, 9, 384 ; Addicks, *Trans. Amer. Electrochem. Soc.*, 1904, 5, 120 ; Förster and Seidel, *Zeitsch. anorg. Chem.*, 1897, 14, 106 ; Förster and Coffetti, *Ber.*, 1905, 38, 2934 ; Ullmann, *Zeitsch. Elektrochem.*, 1897, 3, 516 ; Sand, *Zeitsch. physikal. Chem.*, 1901, 35, 641 ; Schwab and Baum, *J. Physical Chem.*, 1903, 7, 514 ; *Trans. Amer. Electrochem. Soc.*, 1903, 4, 55 ; von Hübl, *Mittheil. militär-geograph. Inst.*, 1886, 6, 51 ; Swan, *J. Soc. Chem. Ind.*, 1901, 20, 663 ; Kiliani, *Berg- und Hütten-männische Zeit.*, 1885, 44, 249 ; McJohnson, *Trans. Amer. Electrochem. Soc.*, 1901, 2, 171.

[3] *German Patent*, 1907, No. 189974 ; 1908, No. 204673.

[4] Vigoroux, *Bull. Soc. chim.*, 1907, [4], 1, 7.

Copper-plating is effected by the electrolytic deposition of the metal from a bath of the cyanides of copper and potassium, and is an important industry.

Physical Properties.—Copper is a metal of characteristic reddish colour, freshly fractured surfaces having a pinkish or yellowish tinge. When cuprous oxide is present, the colour of the fracture is purple-red. The metal crystallizes in octahedra belonging to the cubic system. Meunier[1] observed that the introduction of a red-hot copper wire into the Bunsen gas-mixture does not ignite the gas, but causes the wire to glow, the copper becoming very brittle and apparently crystalline. The density of the pure electrolytic metal is $D_4^0=8{\cdot}945$,[2] $D_4^{15}=8{\cdot}9587$,[3] $D^{1083}=8{\cdot}40$,[4] $D^{1200}=8{\cdot}35$[4]; that of pure distilled copper after compression is $D_4^{20}=8{\cdot}9326$ to 8·9376.[5] Owing to its porous nature commercial copper has a lower density, 8·2 to 8·5. The melting-point is given as 1081° C.,[6] 1082·6° C.,[7] 1083° C.,[8] 1084° C.,[9] 1085° C.,[10] and 1103° C.[11] The freezing-point is depressed by the addition of cuprous oxide, the eutectic being reached with 4·7 per cent. of oxide, and at 1065° C.[10] The values stated for the boiling-point[12] are 2310° C., 2180° C. at 257 mm., and 1980° C. at 100 mm. At white heat the molten metal emits a bluish-green light.

Copper is very tenacious, malleable, and ductile, and can be drawn into wire, or beaten out into thin leaves. When heated on glass, thin copper-leaf becomes transparent.[13] According to Kahlbaum,[14] the mean specific heat between 0° and 100° C. is 0·09272 (uncompressed) or 0·09266 (compressed). Magnus[15] gives the value 0·0951 for the temperature-interval 15° to 238° C. As the result of twenty-seven determinations, Harper[16] found that the expression

$$0{\cdot}0917+0{\cdot}000048(t-25)\text{ cal.}$$

furnishes a basis for the calculation of the specific heat of copper at temperatures between 15° and 50° C.[17] The electric conductivity of

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[1] Meunier, *Compt. rend.*, 1911, 152, 194.

[2] Hampe, *Zeitsch. Berg-, Hütten-, und Salinen-wesen*, 1873, 21, 218.

[3] Swan and Rhodin, *Proc. Roy. Soc.*, 1894, 56, 64.

[4] Pascal and Jouniaux, *Compt. rend.*, 1914, 158, 414.

[5] Kahlbaum, Roth, and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 271.

[6] Heycock and Neville, *Trans. Chem. Soc.*, 1895, 67, 190; Day and Clement, *Amer. J. Sci.*, 1908, [4], 26, 405.

[7] Day and Sosman, *ibid.*, 1910, [4], 29, 93.

[8] Waidner and Burgess, *Bull. Bureau Standards*, 1909, 6, 149; Pascal and Jouniaux, *Compt. rend.*, 1914, 158, 414; Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186.

[9] Holborn and Wien, *Wied. Annalen*, 1892, 47, 107; 1895, 56, 360; Holborn and Day, *Ann. Physik*, 1900, [4], 2, 523; 1901, [4], 4, 99; Glaser, *Metallurgie*, 1904, 1, 103, 121; Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1; compare Curry, *J. Physical Chem.*, 1907, 11, 425.

[10] Dejean, *Rev. de Métallurgie*, 1906, 3, 233.

[11] Heyn, *Zeitsch. anorg. Chem.*, 1904, 39, 1.

[12] Greenwood, *Proc. Roy. Soc.*, 1909, [A], 82, 396; 1910, [A], 83, 483; *Zeitsch. Elektrochem.*, 1912, 18, 319; compare Féry, *Ann. Chim. Phys.*, 1903, [7], 28, 428; von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, 56, 331.

[13] Turner, *Proc. Roy. Soc.*, 1908, [A], 81, 301.

[14] Kahlbaum, Roth, and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 271.

[15] Magnus, *Ann. Physik.* 1910, [4], 31, 597.

[16] Harper, *J. Washington Acad. Sci.*, 1914, 4, 489.

[17] Compare Nernst and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247; Schimpff, *Zeitsch. physikal. Chem.*, 1910, 71, 257; Richards and Jackson, *ibid.*, 1910, 70, 414.

copper is almost as great as that of silver,[1] the ratio at 13° C. being 100 : 96·4. It has been suggested that copper can dissolve to a minute extent in water.[2]

The possibility of the existence of a metastable form of copper has been discussed by Cohen and Inouye.[3]

The molecular weight of the vapour has not been determined, but in solution in mercury,[4] molten tin,[5] and molten lead [6] the molecule is monatomic.

Occlusion of Gases.

Solid copper occludes hydrogen (p. 23), but not nitrogen, carbon monoxide, or sulphur dioxide.[7] Merton [8] found that precipitated copper readily absorbs gases, which are expelled at high temperature. After a few weeks its power of absorption vanishes.

Molten copper absorbs hydrogen [9] and sulphur dioxide,[10] the occluded gases being eliminated on cooling. The liquid metal does not absorb nitrogen. It combines with oxygen to form cuprous oxide, so that fall of temperature is not attended by evolution of the gas. It decomposes hydrocarbons such as methane and ethane, with occlusion of hydrogen and separation of carbon.

According to Stahl,[11] the absorption of gases by molten copper generally becomes greater with the temperature up to a certain point, with increase in the purity of the metal, and with the partial pressure of the gas. At 650° C. 100 grams of copper dissolve 0·1 milligram of hydrogen, and at 1500° C. 1·4 milligram, the solubility of the gas in both solid and liquid copper increasing as the square root of the pressure. The absorbed hydrogen has no influence on the conductivity of the metal. At 1420° C. 61 grams of copper absorb 0·15 c.c. of carbon monoxide, the physical properties of the metal undergoing a marked change.

At 800° C. and higher temperatures the ductility of copper is considerably increased by the presence of oxygen, but above 720° C. hydrogen has a weakening effect.[12]

Electrolysis of a neutral or slightly alkaline solution of cupric acetate with a copper anode and a platinum cathode yields a deposit regarded by Schützenberger [13] as an allotropic form of copper. It is a very brittle, bronze-coloured substance of low specific gravity and high electric resistance. It readily undergoes atmospheric oxidation, and decomposes nitric acid with evolution of nitrous oxide. Schützenberger's original product contained cuprous oxide, and Wiedemann [14] attributed its properties to the presence of this substance. It is possible, however,

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[1] Compare Niccolai, *Atti R. Accad. Lincei,* 1907, [5], 16, i., 906.

[2] Traube, Mangarini, and Scala, *ibid.*, 1909, [5], 18, i., 542.

[3] Cohen and Inouye, *Chem. Weekblad,* 1909, 6, 881.

[4] G. Meyer, *Zeitsch. physikal. Chem.*, 1891, 7, 477.

[5] Heycock and Neville, *Trans. Chem. Soc.*, 1890, 57, 376.

[6] Heycock and Neville, *ibid.*, 1892, 61, 888.

[7] Sieverts, *Zeitsch. Elektrochem.*, 1910, 16, 707 ; Sieverts and Krumbhaar, *Zeitsch. physikal. Chem.*, 1910, 74, 277 ; Stubbs, *Trans. Chem. Soc.*, 1913, 103, 1445.

[8] Merton, *Trans. Chem. Soc.*, 1914, 105, 645.

[9] Sieverts, *Zeitsch. physikal. Chem.*, 1907, 60, 129.

[10] Sieverts, *Zeitsch. Elektrochem.*, 1910, 16, 707 ; Sieverts and Krumbhaar, *loc. cit.*

[11] Stahl, *Metall und Erz,* 1914, 11, 470.

[12] Bengough and Hanson, *J. Inst. Metals,* 1914, 12, 56.

[13] Schützenberger, *Compt. rend.*, 1878, 86, 1265.

[14] Wiedemann, *Pogg. Annalen,* 1879, [2], 6, 81 ; compare Schützenberger, *Bull. Soc. chim.*, 1879, [2], 31, 291.

to prepare the product free from the oxide, although it always contains carbon and hydrogen. Benedicks[1] regards it as a solid solution of acetic acid in copper.

Colloidal Copper.

An impure *hydrosol* of copper was first prepared by Lottermoser[2] as an adsorption-compound with stannic oxide by heating a slightly alkaline solution of a cupric salt with a similar solution of stannous chloride in presence of an alkali-metal citrate or tartrate. With water the black precipitate yields a reddish-brown liquid, rapidly oxidized by atmospheric oxygen, with production of a greenish coloration which soon becomes yellow.

In dilute solution ammoniacal cupric sulphate is reduced by hydrazine hydrate, and cupric sulphate by hypophosphorous acid, the product of each reaction being an unstable hydrosol, which has a blue colour by transmitted light, and a reddish-brown colour by reflected light.[3] The hydrosol is coagulated by prolonged heating, and is rapidly oxidized by exposure to air, with development of a green to yellowish-green coloration. Admixture with a solution of gum considerably increases the stability of the hydrosol.

Reduction of colloidal copper oxide in concentrated solution by hydrazine hydrate produces the unstable, blue liquid hydrosol, but in dilute solution in presence of ammonia the product is a stable, red liquid hydrosol. Evaporation of the red solution in presence of hydrazine hydrate yields a stable, solid red hydrosol. Other colloidal forms of copper combined with sodium lysalbate or protalbate have been prepared.[4]

By Bredig's pulverization-method Billitzer[5] has prepared a brown hydrosol, and Ehrenhaft[6] a moderately stable olive-green to brownish-green hydrosol.

Organosols of copper have been prepared by several investigators.[7]

Chemical Properties.—At ordinary temperatures copper is not attacked by dry air, but in presence of moisture and carbon dioxide it becomes coated with a green basic carbonate. When heated in oxygen it is converted into cuprous and cupric oxides. At temperatures above 200° to 250° C. nitrous oxide[8] and nitric oxide[9] convert it into cuprous oxide, and nitrogen peroxide[10] into cupric oxide and possibly a substance Cu_2NO_2, although more recent work[11] has failed to confirm the formation of the compound last mentioned. The action of air begins at 145° C., and is more energetic than that of oxygen, which begins above 60° to 80° C., a phenomenon probably originating in the formation of oxides of nitrogen.[12] At temperatures below 200° C. dry

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[1] Benedicks, *Metallurgie*, 1907, 4, 1; compare Schützenberger, *Compt. rend.*, 1878, 86, 1397.

[2] Lottermoser, *J. prakt. Chem.*, 1899, [2], 59, 492.

[3] Gutbier and Hofmeier, *Zeitsch. anorg. Chem.*, 1902, 32, 355; 1905, 44, 227.

[4] Paal and Leuze, *Ber.*, 1906, 39, 1545, 1550.

[5] Billitzer, *Ber.*, 1902, 35, 1929.

[6] Ehrenhaft, *Wien Anz.*, 1902, 39, 241.

[7] Svedberg, *Ber.*, 1905, 38, 3616; 1906, 39, 1705; Rassenfosse, *Bull. Acad. roy. Belg.*, 1910, 738; Pieroni, *Gazzetta*, 1913, 43, i., 197.

[8] Sabatier and Senderens, *Compt. rend.*, 1895, 120, 618.

[9] Sabatier and Senderens, *ibid.*, 1892, 114, 1429.

[10] Sabatier and Senderens, *ibid.*, 1892, 115, 236.

[11] Tartar and Semon, *J. Amer. Chem. Soc.*, 1921, 43, 494.

[12] Jordis and Rosenhaupt, *Zeitsch. angew. Chem.*, 1908, 21, 50; Jordis, *Chem. Zeit.*, 1908, 32, 19.

oxygen is absorbed slightly more rapidly than the moist gas. At ordinary pressure and temperature chlorine combines with the metal to form cupric chloride and a small proportion of the cuprous salt; at a high temperature cuprous chloride is the sole product. When copper is heated in gaseous hydrogen chloride, cuprous chloride is produced, and hydrogen evolved.[1] At 1200° C. the metal reacts slowly with carbon dioxide, forming cuprous oxide and carbon monoxide.[2] An arc between copper poles burns in carbon dioxide almost as well as in air, but very imperfectly in coal-gas or steam.[3]

Copper is not attacked by water at ordinary temperatures, or at 100° C., and only slightly at white heat; but very prolonged immersion in sea-water produces a superficial coating of cuprous oxide.[4] It is insoluble in dilute sulphuric acid of 5 to 10 per cent. strength,[5] but reacts with the concentrated acid in accordance with the equations [6]

$$(1)\ Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O,$$

this reaction probably taking place in the two stages

$$(a)\ Cu+H_2SO_4=CuSO_4+2H,$$
$$(b)\ H_2SO_4+2H=SO_2+2H_2O;$$

and

$$(2)\ 5Cu+4H_2SO_4=Cu_2S+3CuSO_4+4H_2O.$$

The first reaction proceeds between 0° and 270° C., the second accompanying it between 0° and 100° C. When the copper is exhausted, the cuprous sulphide is then decomposed in accordance with the equations

$$Cu_2S+2H_2SO_4=CuS+CuSO_4+SO_2+2H_2O,$$
$$CuS+2H_2SO_4=CuSO_4+SO_2+S+2H_2O.$$

The black residue formed in the reaction appears to be mainly cuprous sulphide.

Nitric acid dissolves copper, forming cupric nitrate and oxides of nitrogen. The primary process corresponds with the equation

$$Cu+2HNO_3=Cu(NO_3)_2+2H,$$

but hydrogen is not evolved, being oxidized to water by the nitric acid. The action is conditioned by the presence of nitrous acid as a catalyst, since in absence of this acid the velocity of solution of copper in nitric acid of moderate concentration is very small. A similar retardation is produced by addition of substances capable of reacting with nitrous acid, such as perchlorates, permanganates, hydrogen peroxide, or urea.[7] The velocity of the reaction

$$HNO_3+2H=HNO_2+H_2O$$

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[1] Wöhler, *Annalen*, 1858, 105, 360.

[2] von Bacho, *Monatsh.*, 1916, 37, 119.

[3] Hagenbach, *Physikal. Zeitsch.*, 1909, 10, 649.

[4] Jorissen, *Chem. Weekblad*, 1909, 6, 150.

[5] Gannon, *Proc. Roy. Soc.*, 1893, 55, 66; Schuster, *ibid.*, 84.

[6] Lunge, *Chem. Industrie*, 1886, 9, 47; Pickering, *Trans. Chem. Soc.*, 1878, 33, 112; Baskerville, *J. Amer. Chem. Soc.*, 1895, 17, 904; 1896, 18, 942; van Deventer, *Chem. Weekblad*, 1905, 2, 137; 1906, 3, 515; Sluiter, *ibid.*, 1906, 3, 63.

[7] Millon, *Ann. Chim. Phys.*, 1842, [3], 6, 95; *J. prakt. Chem.*, 1843, 29, 338; Veley, *Chem. News*, 1889, 59, 303; 1891, 63, 3; *Proc. Roy. Soc.*, 1890, 48, 458; Ihle, *Zeitsch. physikal. Chem.*, 1895, 19, 577.

is much accelerated by the presence of nitrous acid, an example of *autocatalysis*.

The formation of the oxides of nitrogen must be regarded as a secondary process, due to the interaction of some of the initial products. The nature of the substances formed depends on the experimental conditions, such as the quantity, concentration, and temperature of the nitric acid, and the concentration of the cupric nitrate generated. An example of this influence is afforded by the observation of Ackworth and Armstrong [1] that the proportion of nitrous oxide formed increases with the dilution of the acid, and with the concentration of the cupric nitrate.

By employing 5N-nitric acid, Bagster [2] obtained a gas completely soluble in sodium hydroxide and free from nitric oxide. His explanation of the mechanism of the reaction involves the assumption that nitrous acid oxidizes the hydrogen film on the copper to unimolecular hyponitrous acid, HNO, being itself reduced to the same acid. Simultaneously, copper dissolves to replace the hydrogen. The unimolecular hyponitrous acid formed is assumed to undergo oxidation by nitric acid to nitrous acid, the oxidizer being also reduced to the same acid. Hyponitrous acid has been proved by Divers [3] to have the double molecule $H_2N_2O_2$, and can therefore be assumed to be readily oxidizable on liberation in the nascent state as HNO.

The products formed by the action of nitric acid on copper, and their relative proportions, have been investigated by Montemartini,[4] Freer and Higley,[5] Higley,[6] and Stansbie.[7] The table on p. 255 is given by Higley,[6] each observation being based on the solution of 0·3 gram of copper in not less than ten times the theoretical weight of nitric acid.

Normally, copper does not react with hot concentrated hydrochloric acid, but the periodic addition to the boiling liquid of some drops of nitric acid, or a few crystals of potassium chlorate, induces the ready formation of a clear solution of cuprous chloride (p. 262). As a result of electrolytic action, the presence of platinum also facilitates the solution of copper in hydrochloric acid, the platinum being the cathode and the copper the anode.

Watts and Whipple [8] have observed the corrosion of copper by acids to be promoted by contact with oxidizers.

In presence of oxygen the metal is rapidly dissolved by solutions containing free ammonia, with formation of complex cupric ammonium derivatives, the ammonia being oxidized to nitrite (p. 256). At 568° C. sodium hydroxide begins to attack copper.[9] The action of alkali-metal persulphates on copper and its alloys has been investigated by Groschuff.[10]

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[1] Ackworth and Armstrong, *Trans. Chem. Soc.*, 1877, 32, 54.

[2] Bagster, *ibid.*, 1921, 119, 82; compare Ackworth and Armstrong, *loc. cit.*; Divers, *Trans. Chem. Soc.*, 1889, 75, 112; Veley, *Phil. Trans.*, 1891, 182, 279; Ihle, *Zeitsch. physikal. Chem.*, 1895, 19, 577; Higley, *Amer. Chem. J.*, 1895, 17, 18; Lewis and Edgar, *J. Amer. Chem. Soc.*, 1911, 33, 292; Peters, *Zeitsch. anorg. Chem.*, 1919, 107, 313.

[3] Divers, *loc. cit.*

[4] Montemartini, *Gazzetta*, 1892, 22, i., 397.

[5] Freer and Higley, *Amer. Chem. J.*, 1893, 15, 71.

[6] Higley, *ibid.*, 1895, 17, 18.

[7] Stansbie, *J. Soc. Chem. Ind.*, 1908, 27, 365.

[8] Watts and Whipple, *Trans. Amer. Electrochem. Soc.*, 1917, 32, 257.

[9] Le Blanc and Bergmann, *Ber.*, 1909, 42, 4728.

[10] Groschuff, *Deutsch. Mechan. Zeit.*, 1908, 133, 142; 1910, 134.

TABLE OF PRODUCTS FORMED BY ACTION OF EXCESS OF A SOLUTION OF NITRIC ACID ON COPPER.

Temperature, °C.	Density of Acid.	NO_2 (mg.).	N_2O_3 (mg.) (HNO_2).	NO (c.c.).	N_2O (c.c.).
65	1·05	..	6·45	58·5	2·61
65	1·10	..	16·02	54·3	3·36
60	1·10	..	23·4	52·26	4·03
25	1·15	..	34·15	51·57	1·35
20	1·20	..	60·49	45·9	
20	1·25	..	74·16	39·0	
20	1·30	76·7	141·4		
17	1·35	177·9	104·03		
0	1·40	340·5	40·0		
15	1·40	329·9	42·3		
50	1·40	327·9	44·7		

Copper and its salts do not exhibit radioactivity, and have no action on the photographic plate.[1]

The suggested possibility of transmuting copper into lithium and sodium has already been mentioned (pp. 55 and 87).

Valency and Ions.—Copper is usually considered to exhibit univalency in the *cuprous* compounds and bivalency in the *cupric* compounds. Its univalency in the cuprous compounds accords with the position of the metal in the periodic system, and is exemplified by the resemblance of the cuprous halides to the halides of silver and univalent gold, and also by the isomorphism of cuprous sulphide and silver sulphide. The bivalency of the atom in the cupric compounds is in agreement with the properties of many of its derivatives, a typical example being the isomorphism of cupric sulphate with the sulphates of ferrous iron, zinc, magnesium, and manganese.

Besides these two main classes of copper compounds, there appear to be other types of copper derivatives, among them oxides of the formulæ Cu_4O, Cu_3O, Cu_2O_3, and CuO_2. The *cuprous ion,* $Cu^{\cdot}$, corresponds with the cuprous compounds, which are colourless in aqueous solution. The *cupric ion,* $Cu^{\cdot\cdot}$, corresponds with the cupric compounds, which have a blue, green, violet, yellow, or brown colour in solution.

The cupric ion displays a characteristic power of forming complex derivatives with ammonia [2] and substituted ammonias, an example being the cupric ammonium hydroxides mentioned on p. 254. A great number of other complex derivatives are derived from cuprous or cupric ions. In certain of these compounds both kinds of copper ions are present simultaneously, examples being the complex cupric-cuprous

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[1] Perman, *Trans. Chem. Soc.*, 1908, 93, 1775.

[2] Compare Hantzsch and Robertson, *Ber.*, 1908, 41, 4328; 1909, 42, 2135; Dawson, *Ber.*, 1909, 42, 720; *Trans. Chem. Soc.*, 1909, 95, 370; Biltz, *Zeitsch. physikal. Chem.*, 1909, 67, 561; Poma, *Atti R. Accad. Lincei*, 1910, [5], 19, i., 223.

cyanides and sulphites. The cupric ion is characterized by a tendency to form basic salts, a great number having been described.[1]

Both cupric and cuprous salts act as oxidizers, the cupric derivatives being reduced to the cuprous or metallic condition, and the cuprous compounds to metallic copper. Alkaline solutions of cupric salts are employed in oxidation-processes in organic chemistry.[2]

Autoxidation.—The phenomenon of *autoxidation* is sometimes displayed in the oxidation of copper or cuprous salts. During the spontaneous oxidation of certain substances, oxygen is rendered "active," and can then oxidize other compounds normally indifferent to its action in absence of an autoxidizer. The process probably depends on the intermediate formation of a peroxide rich in oxygen, this product decomposing readily, and serving as an oxygen-carrier. Examples are the oxidation of ammonia to ammonium nitrite during the interaction of copper and oxygen in presence of ammonia[3]; the simultaneous oxidation of cuprous ammonium sulphate and a sulphite by atmospheric oxygen[4]; and the formation of nitrite during the absorption of oxygen from the air by cupric ammonium hydroxide.[5]

Catalysis.[6]—Many oxidations are accelerated by the presence of small quantities of cupric salts. The production of chlorine in the Deacon process by the oxidation of hydrogen chloride by atmospheric oxygen in presence of cupric chloride is generally regarded as illustrating the catalytic action of the copper salt.[7] Other oxidations are accelerated by the presence of the metal itself, among them that of ammonia to nitrogen, nitrogen oxides, and water. A similar effect has been observed with hydrogen, and with methane[8] and other organic compounds.

An interesting observation has been made by Palmer[9] in connexion with the catalytic action on ethyl alcohol and *iso*propyl alcohol of metallic copper. When produced by the reduction of copper oxide, the metal was found to be active in promoting catalysis of ethyl alcohol to acetaldehyde; but electrolytic copper was without effect on either alcohol.

Finely divided copper can also act as a catalyst in reductions,[10] and is employed as a catalyst in organic chemistry in the Sandmeyer reaction[11] and in other processes.

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[1] Compare Brun, *Compt. rend.*, 1889, 109, 66; Richards, *Proc. Amer. Acad. Sci.*, 1891, 25, 215; Sabatier, *Compt. rend.*, 1897, 125, 101, 175; 1899, 129, 211; Mailhe, *ibid.*, 1901, 133, 226; 1902, 134, 42, 233; Recoura, *ibid.*, 1901, 132, 1414; André, *ibid.*, 1563.

[2] Compare Breuer and Zincke, *Ber.*, 1880, 13, 639; Bösler, *Ber.*, 1881, 14, 327; Gattermann, Hölzle, and Johnson, *Ber.*, 1892, 25, 1075; Fischer, *Annalen*, 1882, 211, 229; Habermann and Hönig, *Monatsh.*, 1884, 5, 208.

[3] Schönbein, *Sitzungsber. K. Akad. Wiss. Berlin*, 1856, 580; Berthelot, *Compt. rend.*, 1863, 56, 1170.

[4] Julius Meyer, *Ber.*, 1902, 35, 3952.

[5] Loew, *J. prakt. Chem.*, 1878, [2], 18, 298.

[6] On the preparation of catalytic copper, see Piccard, *Helv. Chim. Acta*, 1922, 5, 147; compare Piccard and Larsen, *J. Amer. Chem. Soc.*, 1917, 39, 2006. On the influence of impurities on the catalytic activity, see Palmer, *Proc. Roy. Soc.*, 1922, [A], 101, 175; compare Palmer, *ibid.*, 1920, [A], 98, 13; 1921, [A], 99, 412.

[7] Levi and Bettoni, *Gazzetta*, 1905, 35, i., 320; see this series, Vol. VIII.

[8] Morel, *J. Pharm. Chim.*, 1905, [6], 21, 177.

[9] Palmer, *Proc. Roy. Soc.*, 1920, [A], 98, 13.

[10] Sabatier and Senderens, *Compt. rend.*, 1900, 130, 250, 1559; 1901, 133, 321; 1902, 134, 689; 1903, 135, 225; 1903, 136, 738, 921, 983; 1903, 137, 301.

[11] Hantzsch and Blagden, *Ber.*, 1900, 33, 2544.

Applications.—Copper is employed in large quantities in the manufacture of electric conductors and apparatus, and for many other purposes. Its alloys are of the highest importance in the arts, examples being the so-called bronzing powders,[1] brass, gun-metal, coins, and so on.

The effect of copper salts on the growth of wheat has been investigated by Voelcker[2] for the sulphate and carbonate. Quantities between 0·01 and 0·02 per cent. were found to have a stimulating effect. In smaller proportion the salts were without influence, and in larger amount they exerted a toxic action.

Atomic Weight.—The accepted value for the atomic weight of copper, 63·57, is in good accord with the periodic system, the properties of the metal and its compounds being functions of an atomic weight of this order belonging to an element of the fifth horizontal row of Group I. of this system. The atomic heat of copper at ordinary temperatures is 5·9 to 6·0, slightly less than the mean value 6·4 for the solid elements, but sufficiently in harmony with the law of Dulong and Petit. The isomorphism of the element with silver and gold, and that of the cuprous compounds with the derivatives of univalent silver, furnish additional evidence in favour of the atomic weight adopted.

Cryoscopic determinations of the molecular weight of copper in solution in other molten metals indicate the monatomic nature of its molecule.

Both chemical and physico-chemical methods have been employed in determining the atomic weight of copper. A summary is appended of the values obtained by both types of process, expressed in terms of the modern notation O=16. The antecedent data employed in the recalculation from the experimental results are:

Ag=107·880.
Ba=137·37.
Br= 79·916.
C=12·003.
H= 1·00762.
Na=22·996.
S=32·065.

A. *Chemical Methods.*—In 1814 Wollaston[3] calculated the equivalent of copper to be four times that of oxygen, or Cu=64.

The early researches of Berzelius,[4] Erdmann and Marchand,[5] Dumas,[6] and Millon and Commaille,[7] involved either syntheses or analyses of cupric oxide, the values found for the atomic weight of copper being 63·30, 63·46, 63·5, and 63·13. Dumas also made syntheses of cuprous sulphide, but gave no details concerning his experiments. His result did not differ much from the modern value, and was adopted for many years.

Hampe[8] made two series of experiments in 1874. In the first, copper was converted into the basic nitrate, and ignited in a current of

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[1] Compare Groschuff, *Deut. Mech. Zeit.*, 1912, 145, 153.

[2] Voelcker, *J. Roy. Agric. Soc. Engl.*, 1913, 74, 411.

[3] Wollaston, *Phil. Trans.*, 1814, 104, 21.

[4] Berzelius, *Afhandlingar i Fysik, Kemi, etc.*, Stockholm, 1806–1818, 3, 191; 6, 1; *Gilbert's Annalen*, 1811, 37, 284; *Schweigger's J.*, 1820, 30, 384; *Pogg. Annalen*, 1826, 8, 182.

[5] Erdmann and Marchand, *J. prakt. Chem.*, 1844, 31, 380.

[6] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 129.

[7] Millon and Commaille, *Compt. rend.*, 1863, 57, 145.

[8] Hampe, *Zeitsch. Berg-, Hütten-, und Salinen-wesen*, 1874, 21, 218; *Zeitsch. anal. Chem.*, 1874, 13, 354.

oxygen; in the second, cupric sulphate was dehydrated at 250° to 260° C., and the copper estimated electrolytically. His results were:

$\text{Cu} : \text{O} = 79{\cdot}8347 : 20{\cdot}1653$, whence $\text{Cu} = 63{\cdot}34$;
$\text{CuSO}_4 : \text{Cu} = 100 : 39{\cdot}725$, ,, ,, $= 63{\cdot}31$.

In 1883 Baubigny[1] dehydrated cupric sulphate by heating it to 440° C., ignited weighed portions of the salt at a temperature corresponding with the melting-point of gold, and weighed the residual cupric oxide. He found the ratio

$\text{CuO} : \text{SO}_3 = 49{\cdot}810 : 50{\cdot}190$, whence $\text{Cu} = 63{\cdot}46$.

The researches of Richards[2] on the atomic weight of copper, based on chemical methods only, were carried out between 1887 and 1891. In his first experiments, silver was precipitated by addition of electrolytic copper to excess of an ice-cold solution of silver nitrate. The results were:

1. (6 experiments) $\text{Cu} : 2\text{Ag} = 100 : 339{\cdot}408$, whence $\mathbf{Cu = 63{\cdot}569^{**}}$.
2. (5 experiments) $\text{Cu} : 2\text{Ag} = 100 : 339{\cdot}404$, ,, ,, $\mathbf{= 63{\cdot}570^{**}}$.

In the first series, the silver was dried at 150° C., and a correction was applied for the trace of moisture retained; in the second series, the silver was dried at incipient red heat.

The composition of cupric bromide was next investigated, the salt being prepared by oxidizing electrolytic copper and dissolving the oxide in hydrobromic acid. Weighed portions of the solution were electrolyzed to determine the copper, and other portions were precipitated with silver nitrate to estimate the bromine. Four series of determinations of the ratio 2AgBr : Cu were made, the first three being of a preliminary character. In the more accurate fourth series, the cupric bromide was titrated against silver, and the silver bromide collected and weighed. The results obtained were:

1. $2\text{AgBr} : \text{Cu} = 100 : 16{\cdot}927$, whence $\mathit{Cu = 63{\cdot}576^{*}}$.
2. $2\text{AgBr} : \text{Cu} = 100 : 16{\cdot}919$, ,, ,, $\mathit{= 63{\cdot}546^{*}}$.
3. $2\text{AgBr} : \text{Cu} = 100 : 16{\cdot}922$, ,, ,, $\mathit{= 63{\cdot}558^{*}}$.
4. $\left\{\begin{array}{l} 2\text{AgBr} : \text{Cu} = 100 : 16{\cdot}927, \text{ ,, ,, } \mathbf{= 63{\cdot}576^{**}}. \\ \text{Cu} : 2\text{Ag} = 100 : 339{\cdot}392, \text{ ,, ,, } \mathbf{= 63{\cdot}573^{**}}. \end{array}\right.$

The remainder of Richards's work on copper by chemical methods concerned the composition of cupric oxide and cupric sulphate, and was undertaken principally with the object of investigating the nature and magnitude of the errors of earlier workers. Cupric oxide prepared from the nitrate by ignition was found to contain occluded gases, mainly nitrogen. The impossibility of avoiding partial decomposition in the preparation of cupric sulphate free from water by dehydration of the pentahydrate was also demonstrated. At 260° C. the salt retains more than 0·1 per cent. of water, and at 400° C. 0·042 per cent. These errors vitiated the results of most of the early workers on the atomic weight of copper, and explain the low values found by Hampe.

In the investigation of Richards they were evaluated, and the

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[1] Baubigny, *Compt. rend.*, 1883, 97, 906.

[2] Richards, *Proc. Amer. Acad.*, 1887, 22, 342; 23, 177; 1890, 25, 195; 1891, 26, 240, 276; *Chem. News*, 1888, 58, 55, 68; 1891, 63, 20, etc.; 1892, 65, 236, etc.

necessary corrections applied. Both the water of crystallization and the copper in the pentahydrate of pure copper sulphate were determined. In some of the experiments, after electrolytic deposition of the copper, the sulphuric acid produced in the electrolysis was titrated with pure sodium carbonate, and the sodium sulphate formed was fused and weighed. The results were:

$CuSO_4,5H_2O$: Cu=100 : 25·451, whence *Cu=63·548**.
$CuSO_4$: Cu=100 : 39·832, ,, ,, =63·597.
Cu : Na_2CO_3 =100 : 166·838, ,, ,, *=63·532**.
Cu : Na_2SO_4 =100 : 223·525, ,, ,, *=63·553**.

In one experiment the sulphate was precipitated with barium chloride, and the barium sulphate weighed; but the result is of little value.

Richards also carried out three syntheses of cupric sulphate from the oxide, and two from the metal, deriving the ratios

$CuSO_4$: CuO=100 : 49·838, whence *Cu=63·548**.
$CuSO_4$: Cu =100 : 39·7835, ,, ,, *=63·468**.

Five analyses of cupric oxide by reduction in hydrogen furnished the ratio

Cu : O=79·900 : 20·100, whence Cu=63·602.

In 1906 Murmann[1] examined the composition of cupric oxide, but his results are of doubtful value. Copper oxide formed by heating the metal in oxygen was reduced by hydrogen, and values for the atomic weight varying between 63·513 and 64·397 were obtained. Brauner[2] regards the reduction-method as conducive of high values, but from the results of three oxidations he has calculated that Cu=63·53.

In 1913 de Coninck and Ducelliez[3] converted metallic copper into the nitrate, and ignited the salt to oxide, their value being *Cu=63·55*.

B. *Physico-chemical Method.*—This method consists in determining the electrochemical equivalent of copper with respect to that of silver. It involves passing the same quantity of electricity through solutions of cupric sulphate and silver nitrate, and weighing the metal deposited on the cathodes. The early researches of (1) Rayleigh and Mrs. Sidgwick,[4] (2) Gray,[5] (3) Shaw,[6] and (4) Vanni[7] gave the results:

1. Cu : 2Ag=100 : 340·561, whence Cu=63·354.
2. Cu : 2Ag=100 : 340·935, ,, ,, =63·285.
3. { Cu : 2Ag=100 : 339·953, ,, ,, =63·468.
   { Cu : 2Ag=100 : 339·983, ,, ,, =63·462.
4. Cu : 2Ag=100 : 340·406, ,, ,, =63·383.

During an elaborate investigation of the electrochemical equivalent

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[1] Murmann, *Monatsh.*, 1906, 27, 351.

[2] Brauner, *Abegg and Auerbach's Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i., 462.

[3] De Coninck and Ducelliez, *Rev. gén. Chim.*, 1913, 16, 122.

[4] Rayleigh and Mrs. Sidgwick, *Phil. Trans.*, 1884, 175, 470.

[5] Gray, *Phil. Mag.*, 1886, [5], 22, 389; 1888, [5], 25, 179.

[6] Shaw, *ibid.*, 1886, [5], 23, 138.

[7] Vanni, *Wied. Annalen*, 1891, [2], 44, 214.

of copper between the years 1899 and 1902, Richards, Collins, and Heimrod [1] identified two sources of error :

(1) Metallic copper slowly dissolves in an acid solution of cupric sulphate, the losses in weights of the electrodes when immersed in relatively large volumes of solution being approximately proportional to their surface-areas.

(2) Plates of copper covered by neutral solutions of cupric sulphate always gain weight, becoming coated with a film of cuprous oxide.

The influence of the first factor was diminished by working at a low temperature in an atmosphere of hydrogen. The employment of two copper coulometers in series fitted with cathodes of different surface-areas, and the determination of the slight difference between the weights of the copper deposits, made it possible to extrapolate for the increase in weight of a cathode of zero-area, and thus to eliminate the solution-error.

The second difficulty was avoided by electrolyzing slightly acidic solutions of cupric sulphate.

A series of seventeen experiments gave the ratio

$$\text{Cu} : 2\text{Ag} = 100 : 339{\cdot}615.$$

Subsequent investigation by Richards and Heimrod [2] of the silver coulometer employed, proved the " silver " in the deposits to be too heavy by 0·059 per cent. The corrected ratio is

$$\text{Cu} : 2\text{Ag} = 100 : 339{\cdot}415, \text{ whence } \mathbf{Cu = 63{\cdot}568^{**}}.$$

The mean of four somewhat discordant results obtained by Gallo [3] in 1905 gave the ratio

$$\text{Cu} : 2\text{Ag} = 100 : 339{\cdot}483, \text{ whence } Cu = 63{\cdot}555.$$

In 1912 Pécheux [4] found Cu=63·43.

In a very careful redetermination of the electrochemical equivalent of copper by Shrimpton [5] in 1914, the errors indicated by Richards, Collins, and Heimrod were determined, and due allowance made. The resulting ratio was

$$\text{Cu} : 2\text{Ag} = 100 : 339{\cdot}443, \text{ whence } \mathbf{Cu = 63{\cdot}563}.$$

C. *Summary.*—The numerous ratios established by Richards and his collaborators leave little doubt as to the atomic weight of copper. The five ratios considered most reliable by Richards are indicated by two asterisks (**), other ratios of a confirmatory nature being denoted by a single asterisk (*). Since the results with two asterisks vary only between Cu=63·568 and Cu=63·576, the atomic weight of copper must approximate closely to

$$\mathbf{Cu = 63{\cdot}57},$$

the value given in the current table of the International Committee on

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[1] Richards, Collins, and Heimrod, *Proc. Amer. Acad.*, 1899, 35, 123 ; *Zeitsch. physikal. Chem.*, 1900, 32, 321.

[2] Richards and Heimrod, *Proc. Amer. Acad.*, 1902, 37, 415 ; *Zeitsch. physikal. Chem.* 1902, 41, 302.

[3] Gallo, *Atti R. Accad. Lincei*, 1905, [5], 14, i., 23.

[4] Pécheux, *Compt. rend.*, 1912, 154, 1419.

[5] Shrimpton, *Proc. Physical Soc. London*, 1914, 26, 292.

Atomic Weights. The results obtained by Gallo, and by de Coninck and Ducelliez, accord reasonably with this number; and those of Shrimpton are in good agreement.

Calculating the foregoing results on the basis Ag=107·883, Brauner[1] has arrived at the value **Cu=63·56** from ratios considered by him most trustworthy.

CUPROUS COMPOUNDS.[2]

Cuprous hydride, CuH.—Addition of a concentrated solution of cupric sulphate to a solution of hypophosphorous acid[3] or of zinc hypophosphite[4] yields a powder containing 1·22 per cent. of hydrogen, but the chemical individuality of the product is open to question. Berthelot[5] doubted the possibility of the existence of cuprous hydride, but more recent work has proved his views to be erroneous.[6] The pure hydride can be prepared by the action of sodium hypophosphite on a moderately dilute solution of cupric sulphate at 70° C., but the product formed at ordinary temperature is contaminated with cuprous oxide and cupric phosphate.[7] It is a very unstable, reddish-brown substance, takes fire in chlorine, and is converted by hydrogen chloride into hydrogen, copper, and cuprous chloride. The dry substance cannot be kept for more than twenty-four hours, and at 60° C. decomposes suddenly, leaving a sponge of metallic copper.

A very unstable copper hydride of unknown composition has been prepared in the form of a dark-brown powder by Stock and Kuss[8] by the interaction of cupric sulphate and potassium hypoborate, KH_3OB. It decomposes readily, evolving hydrogen, and leaving a brown residue of metallic copper.

Cuprous fluoride, CuF.—The fluoride has been prepared by the interaction of hydrogen fluoride and cuprous chloride, and also by the dissociation of cupric fluoride, both processes taking place at a high temperature.[9] The product of the action of hydrogen-fluoride solution on cuprous oxide[10] appears to be impure copper only.[11] The fluoride is a ruby-red solid.

Cuprous chloride, CuCl.—The pure chloride is more readily prepared than any other cuprous compound. A summary of the more important methods is appended.

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[1] Brauner, *Abegg and Auerbach's Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i., 467.

[2] Alloys of copper with silver are mentioned on pp. 297 and 301, and with gold on pp. 333 and 336. Additional alloys are described in the other volumes of this series. An interesting example of cementation by ferro-manganese is given by Sirovich and Cartoceti (*Gazzetta*, 1921, 51, ii., 245). On heating a copper bar at 900° C. with powdered ferro-manganese and 5 per cent. of wood-charcoal for some hours, a considerable proportion of manganese was found to have penetrated the copper.

[3] Wurtz, *Compt. rend.*, 1844, 18, 702; 1879, 89, 1066; 1880, 90, 22; *Ann. Chim. Phys.*, 1844, [3], 11, 250.

[4] Schützenberger, *Compt. rend.*, 1869, 69, 196.

[5] Berthelot, *Compt. rend.*, 1879, 89, 1005.

[6] Mylius and Fromm, *Ber.*, 1894, 27, 647; Bartlett and Merrill, *Amer. Chem. J.*, 1912, 17, 185; Sieverts and Loessner, *Zeitsch. anorg. Chem.*, 1912, 76, 1.

[7] Firth and Myers, *Trans. Chem. Soc.*, 1911, 99, 1329; *Zeitsch. anorg. Chem.*, 1913, 80, 93.

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

[9] Poulenc, *Compt. rend.*, 1893, 116, 1446.

[10] Berzelius, *Pogg. Annalen*, 1824, 1, 28.

[11] Mauro, *Zeitsch. anorg. Chem.*, 1892, 2, 25; Poulenc, *loc. cit.*

(1) The chloride is precipitated by addition of excess of water to the solution obtained by the interaction of cuprous oxide and hydrochloric acid in absence of air.[1]

(2) In a neutral atmosphere at red heat, cupric chloride decomposes with formation of cuprous chloride and evolution of chlorine.[2]

(3) In presence of a small proportion of potassium chlorate to facilitate solution, copper dissolves in hydrochloric acid, with production of cuprous chloride[3] (*cf.* p. 254).

(4) Sulphur dioxide precipitates the chloride from an aqueous solution of cupric sulphate and sodium chloride. After being washed with dilute sulphurous acid, and then glacial acetic acid, the salt can be dried by the aid of heat.[4] The reduction of a solution of cupric chloride, with formation of cuprous chloride, can also be effected by means of phosphorous acid.[5]

(5) Excess of water precipitates cuprous chloride from the colourless solution produced by heating cupric sulphate with an equal weight of copper-turnings, twice the weight of sodium chloride, and ten times the weight of water.[6]

(6) Erdmann[7] recommends boiling until colourless the mixture prepared by adding concentrated hydrochloric acid (200 c.c.) and metallic copper (32 grams) to a solution of cupric chloride (42 grams) in hot water (100 c.c.), fuming hydrochloric acid being added towards the close of the operation. The chloride is precipitated by diluting the solution with excess of water.

(7) A very convenient method[8] involves boiling copper-turnings with concentrated hydrochloric acid in a flask with a vertical air-condenser until the solution becomes clear, a few drops of concentrated nitric acid being added periodically. The solution is filtered through asbestos into a large excess of distilled water covered with a layer of ether to prevent the absorption of air. After the precipitate has settled, the supernatant liquid is syphoned off, the cuprous chloride washed quickly on a filter with water, alcohol, and ether, and dried in vacuum over sulphuric acid.

References to other methods of preparation are appended.[9]

The pure salt prepared by Manchot and Friend's method is a perfectly white, crystalline powder, and in absence of moisture is unaffected by light or air. It crystallizes from hot hydrochloric acid in white tetrahedra of density[10] 3·53. For its melting-point in absence of air Mönkemeyer[11] gives 419° C., Korreng[12] and also Hachmeister[13] give 425° C.,

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[1] Proust, *Ann. Chim.*, 1800, 32, 26.

[2] Rose, *Pogg. Annalen*, 1836, 38, 121.

[3] Lupton, *Chem. News*, 1874, 30, 233.

[4] Wöhler, *Annalen*, 1864, 130, 373; Péan de Saint-Gilles, *Ann. Chim. Phys.*, 1854, [3], 42, 38; Rosenfeld, *Ber.*, 1879, 12, 954.

[5] Sieverts and Major, *Zeitsch. anorg. Chem.*, 1909, 64, 29.

[6] Denigès, *Compt. rend.*, 1889, 108, 567.

[7] Erdmann, *Chemical Preparations* (Wiley, 1900), 14.

[8] Manchot and Friend, *Annalen*, 1908, 359, 100.

[9] Jones, *Amer. Chem. J.*, 1899, 22, 287; Rybalkim, *J. Russ. Phys. Chem. Soc.*, 1889, 21, 155; Cavazzi, *Gazzetta*, 1886, 16, 167; Wöhler, *Annalen*, 1858, 105, 360; Proust, *J. de Physique*, 1804, 59, 350; *Neues allgemeines Journal der Chemie* (Gehlen), 1806, 6, 573.

[10] Playfair and Joule, *Mem. Chem. Soc.*, 1845, 2, 401; 1848, 3, 57.

[11] Mönkemeyer, *Jahrb. Min. Beil.-Bd.*, 1909, 22, 1.

[12] Korreng, *ibid.*, 1914, 37, 51.

[13] Hachmeister, *Zeitsch. anorg. Chem.*, 1919, 109, 145.

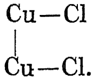
and Carnelley[1] gives 434° C. Carnelley and Williams[2] give the boiling-point as 954° to 1052° C. For the specific heat Regnault[3] found the value 0·1383.

On exposure to light and moisture, cuprous chloride develops a violet or dark-blue tint. It also exhibits phototropy when immersed in water slightly acidified with sulphurous acid and subjected to the action of direct sunlight, the colour changing through greyish blue and dark blue to a dark-copper colour, with development of a metallic lustre after a few minutes. In the dark the original white colour is restored in about 48 hours. In absence of moisture the chloride is not sensitive to light, the phenomenon being possibly due to the light inducing the formation of a hydrate unstable in the dark.[4] In contact with damp air cuprous chloride is converted into a dark-green mixture of cupric chloride and basic cupric chloride. Water transforms it into a mixture of copper, cuprous oxide, and cupric chloride.[5]

Assuming the valency of copper to be unity, the formula for cuprous chloride becomes

$$\mathrm{Cu{-}Cl.}$$

Without postulating the univalency of copper, the constitution of the salt can be represented by a double formula



$$\begin{array}{l}\mathrm{Cu{-}Cl}\\ \;|\\ \mathrm{Cu{-}Cl.}\end{array}$$

Determinations by Victor Meyer and his collaborators[6] of the density of gaseous cuprous chloride at 1600° to 1700° C. gave values approximately 6·5 times that of the atmosphere. Taking air as unity, the vapour-density calculated from the formula Cu_2Cl_2 is 6·83. The close agreement between the two values supports the adoption of the double formula to represent the molecular constitution of gaseous cuprous chloride.

Cryoscopic determinations in dilute solution with pyridine,[7] quinoline,[8] and fused bismuth chloride[9] as solvents have proved the constitution of the salt under these conditions to correspond with the simpler formula Cu—Cl. Solutions in mercuric chloride consist of a mixture of single and double molecules.[10]

The conflict of evidence as to the molecular formula of cuprous chloride precludes dogmatic generalization regarding the valency of copper in the cuprous compounds. As a matter of expediency, it seems desirable to assume the univalency of the metal in these derivatives, a view supported by other arguments previously cited (p. 255). To explain the formation of double molecules, an interesting assumption

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[1] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[2] Carnelley and Williams, *ibid.*, 1880, 37, 125.

[3] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129.

[4] Singh, *Trans. Chem. Soc.*, 1922, 121, 782.

[5] Lescœur, *Ann. Chim. Phys.*, 1894, [7], 2, 97; Haywood, *J. Physical Chem.*, 1897, 1, 411; Bodländer and Storbeck, *Zeitsch. anorg. Chem.*, 1902, 31, 1, 458.

[6] Biltz and Victor Meyer, *Ber.*, 1889, 22, 725; Victor Meyer and Carl Meyer, *Ber.*, 1879, 12, 609, 1112, 1185, 1292.

[7] Werner, *Zeitsch. anorg. Chem.*, 1897, 15, 565.

[8] Riban, *Bull. Soc. chim.*, 1879, [2], 31, 385.

[9] Beckmann and Gabel, *Zeitsch. anorg. Chem.*, 1906, 51, 236.

[10] Beckmann, *ibid.*, 1907, 55, 175.

has been made by Friend[1] as to the tervalency of the chlorine atom in cuprous chloride. This view finds expression in the molecular formula $Cu-Cl=Cl-Cu$.

The heat of formation of the simple molecule CuCl from solid copper and gaseous chlorine is given as 32·9 Cal.[2] and 35·4 Cal.[3]

Cuprous chloride is characterized by its power of absorbing carbon monoxide, its solution in either hydrochloric acid or ammonia being extensively employed for this purpose in gas-analysis. Contact of a concentrated solution of cuprous chloride in hydrochloric acid with carbon monoxide causes precipitation of the carbonyl-compound in white, crystalline flakes. The ready oxidation of the crystals by atmospheric oxygen renders direct analysis difficult, the first correct results being obtained by Jones[4] in the year 1899. He proved the composition to correspond with the formula $CuCl,CO,2H_2O$, and his view has been confirmed by the work of Manchot and Friend.[5]

Carbon monoxide is also absorbed by solutions of cuprous chloride in ammonium hydroxide, aniline, *o*-toluidine, pyridine, and piperidine, the maximum absorption corresponding with one molecule of the monoxide to each atom of copper. Carbon monoxide is not absorbed by mixtures of either alcohol and cuprous chloride, or alcoholic hydrogen chloride and cuprous chloride.[5]

In contact with dilute hydrochloric acid, sulphur reacts with cuprous chloride to form cuprous sulphide, possibly in accordance with the equation

$$2Cu_2Cl_2+S=Cu_2S+2CuCl_2.$$

The coating of cuprous sulphide formed soon inhibits further action.[6]

In presence of concentrated hydrochloric acid sulphur dioxide oxidizes cuprous chloride to cupric chloride, with deposition of sulphur :

$$2Cu_2Cl_2+SO_2+4HCl=4CuCl_2+2H_2O+S.$$

The formation of sulphuric acid in this reaction has not been detected, although in presence of concentrated, but not of dilute, hydrochloric acid sulphur can reduce cupric chloride in accordance with the equation[7]

$$6CuCl_2+S+4H_2O=3Cu_2Cl_2+6HCl+H_2SO_4.$$

At the boiling-point an aqueous solution of ammonium chloride reacts with finely divided copper, ammonia being evolved. On cooling, crystals of the formula $CuCl,NH_3$ are deposited from the solution.[8] According to Dehérain,[9] an amorphous, black substance of similar composition is produced by the interaction of gaseous ammonia and heated cuprous chloride. The phosphorus analogue of Ritthausen's ammonia compound is formed by the absorption of phosphine by a hydrochloric-acid solution of cuprous chloride,[10] its formula being $CuCl,PH_3$.

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[1] Friend, *Theory of Valency* (Longmans, 1909), 61.
[2] Thomsen, *Thermochemistry* (Longmans, 1908), 270.
[3] Berthelot, *Thermochimie*, Paris, 1897, 2, 318.
[4] Jones, *Amer. Chem. J.*, 1899, 22, 287.
[5] Manchot and Friend, *Annalen*, 1908, 359, 100.
[6] Pinkard and Wardlaw, *Trans. Chem. Soc.*, 1922, 121, 1300.
[7] Wardlaw and Pinkard, *ibid.*, 210.
[8] Ritthausen, *J. prakt. Chem.*, 1853, 59, 369.
[9] Dehérain, *Compt. rend.*, 1862, 55, 807.
[10] Riban, *Bull. Soc. chim.*, 1879, [2], 31, 385.

Other compounds of cuprous chloride include 2CuCl,LiCl,[1] m.p. 415° C.; CuCl,2KCl[2]; 2CuCl,Ag_2S[3]; CuCl,HgS[4]; CuCl,$C_6H_5{\cdot}NH_2$, analogous to the ammonia compound cited in the preceding paragraph, and its hydrochloride, CuCl,$C_6H_5{\cdot}NH_2$,HCl[5]; CuCl,$2C_5H_5N$ and CuCl,$3C_5H_5N$[6]; and CuCl,2HCl.[7]

Cuprous bromide, CuBr.—Several methods are available for the preparation of cuprous bromide, examples being the interaction of copper-turnings and an aqueous solution of cupric bromide at its boiling-point,[8] and the direct synthesis from bromine and excess of copper.[9] The most convenient process is that of Sandmeyer.[10] A solution of cupric sulphate (12·5 grams), potassium bromide (36 grams), and concentrated sulphuric acid (6 c.c.) in water (80 c.c.) is boiled under reflux with copper-turnings until the solution has become colourless. After precipitation by filtration through asbestos into a large excess of water covered with a layer of ether, the cuprous bromide is allowed to settle. The mother-liquor is then syphoned off, and the salt is washed on a filter with water, alcohol, and ether, and dried in a vacuum-desiccator over sulphuric acid.

The pure bromide is a white substance, but gradually develops a yellow tint, and on exposure to sunlight it acquires a bluish colour.[8] In phototropic character it resembles cuprous chloride, exposure to light changing its colour through dark green to dark copper. If the duration of the action of the light has been limited to a few minutes, keeping in the dark for 30 hours reverses the colour changes.[11] The melting-point of the bromide is given by Mönkemeyer[12] as 480° C., and by Carnelley and Williams[13] as 504° C. The boiling-point[13] is between 861° and 954° C., and the density is given by Bödeker[14] as 4·72.

Cuprous bromide is insoluble in water. Its solutions in hydrochloric acid, hydrobromic acid, and ammonium hydroxide readily absorb carbon monoxide. The maximum absorption for the ammoniacal solution corresponds with one molecule of carbon monoxide to each atom of copper.[15] When prepared in absence of air, the solution in ammonium hydroxide is colourless, but on contact with oxygen it develops a blue colour. The liquid obtained by dissolving cuprous bromide in an aqueous solution of sodium chloride or of sodium thiosulphate does not absorb carbon monoxide.

The heat of formation of the simple molecular compound CuBr from solid copper and liquid bromine is 24·985 Cal.[16]

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[1] Korreng, *Jahrb. Min. Beil.-Bd.*, 1914, 37, 51; compare Sandonnini, *Gazzetta*, 1914, 41, i., 290.

[2] Korreng, *loc. cit.*

[3] Huntingdon, *Chem. News*, 1882, 46, 177.

[4] Raschig, *Ber.*, 1884, 17, 679; Heumann, *ibid.*, 1874, 7, 1390.

[5] Saglier, *Compt. rend.*, 1888, 106, 1422.

[6] Lang, *Ber.*, 1892, 21, 1584.

[7] Neumann, *Monatsh.*, 1894, 15, 492.

[8] Renault, *Compt. rend.*, 1864, 59, 329.

[9] Berthemot, *Ann. Chim. Phys.*, 1830, [2], 44, 224, 385; Colson, *Compt. rend.*, 1899, 128, 1458; Rammelsberg, *Pogg. Annalen*, 1842, 55, 246.

[10] Sandmeyer, *Ber.*, 1884, 17, 2650; compare Denigès, *Compt. rend.*, 1889, 108, 567.

[11] Singh, *Trans. Chem. Soc.*, 1922, 121, 782.

[12] Mönkemeyer, *Jahrb. Min. Beil.-Bd.*, 1909, 22, 1.

[13] Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 125.

[14] Bödeker, *Die Beziehungen zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen*, Leipsic, 1860.

[15] Manchot and Friend, *Annalen*, 1908, 359, 100.

[16] Thomsen, *Thermochemistry* (Longmans, 1908), 270.

The complex derivatives of cuprous bromide include $CuBr,NH_3$ (Richards and Merigold)[1]; $CuBr,2NH_3$ (Saglier)[2]; and $CuBr,3NH_3$ (Richards and Merigold).[1]

Cuprous iodide, CuI.—The preparation of cuprous iodide can be effected by methods analogous to those adopted for cuprous bromide. Among them are the interaction of finely divided copper and either iodine[3] or concentrated hydriodic acid[4] under the influence of heat.

The iodide is also produced by the action of sulphur dioxide on an aqueous solution of cupric sulphate and potassium iodide:[5]

$$2CuSO_4+4KI=2CuI+2K_2SO_4+I_2;$$
$$SO_2+2H_2O+I_2=H_2SO_4+2HI.$$

The hydrogen iodide produced reacts with another portion of the cupric sulphate, the whole reaction corresponding with the equation

$$4CuSO_4+4KI+2SO_2+4H_2O=4CuI+2K_2SO_4+4H_2SO_4.$$

Ferrous sulphate can also be employed as reducer:[6]

$$2CuSO_4+2KI+2FeSO_4=2CuI+Fe_2(SO_4)_3+K_2SO_4.$$

The iodide can also be prepared from aqueous solutions of cupric sulphate and potassium iodide without subsequent reduction, the liberated iodine being removed by agitation with alcohol.[7]

The best method of preparing cuprous iodide depends on the interaction of cold solutions of cupric sulphate (30 grams), potassium iodide (16 grams), and sodium thiosulphate (25 grams):

$$2CuSO_4+2KI+2Na_2S_2O_3=2CuI+K_2SO_4+Na_2S_4O_6+Na_2SO_4.$$

After repeated washing with water and with alcohol, the precipitated iodide is dried in a vacuum-desiccator over sulphuric acid.

The white powder obtained by the last process gradually acquires a slight brown tint, but the salt does not exhibit phototropy.[8] Cuprous iodide crystallizes in white tetrahedra, melting at 590° C. according to Mönkemeyer,[9] or 628° C. according to Carnelley and O'Shea.[10] Carnelley and Williams[11] give the boiling-point as between 759° and 772° C. Its density is $D_4^{14 \cdot 5}=5 \cdot 672$.[12] The heat of formation of the simple molecule CuI from solid copper and solid iodine is 16·26 Cal.[13]

Solutions of cuprous iodide in hydrochloric acid and in ammonia readily absorb carbon monoxide, the maximum absorption corresponding with one molecule of the gas to each atom of copper.[14] The salt also dissolves in solutions of sodium sulphate and potassium cyanide, but the liquids produced do not absorb carbon monoxide.

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[1] Richards and Merigold, *Zeitsch. anorg. Chem.*, 1898, 17, 245.
[2] Saglier, *Compt. rend.*, 1886, 102, 1552.
[3] Renault, *ibid.*, 1864, 59, 329.
[4] Rose, *Pogg. Annalen*, 1825, 4, 10; Meusel, *Ber.*, 1870, 3, 123.
[5] Duflos, *Annalen*, 1841, 39, 253.
[6] Soubeiran, *J. Physique*, 1884, 13, 427.
[7] Berthemot, *J. Pharm. Chem.*, 1878, 14, 614.
[8] Singh, *Trans. Chem. Soc.*, 1922, 121, 782.
[9] Mönkemeyer, *Jahrb. Min. Beil.-Bd.*, 1909, 22, 1.
[10] Carnelley and O'Shea, *Trans. Chem. Soc.*, 1884, 45, 409.
[11] Carnelley and Williams, *ibid.*, 1880, 37, 125.
[12] Spring, *Zeitsch. anorg. Chem.*, 1901, 27, 308.
[13] Thomsen, *Thermochemistry* (Longmans, 1908), 270.
[14] Manchot and Friend, *Annalen*, 1908, 359, 100.

Several complex derivatives of cuprous iodide have been prepared, including $CuI,2NH_3$[1]; $2CuI,2NH_4I,H_2O$[2]; $CuI,NH_4I,4(NH_4)_2S_2O_3$[3]; $2CuI,(NH_4)_2S_2O_3,H_2O$[3]; $2CuI,K_2S_2O_3,H_2O$[3]; and $2CuI,Na_2S_2O_3,H_2O$.[3]

Copper suboxide, Cu_4O.—The olive-green precipitate produced by the interaction of solutions of potassium stannite and cupric sulphate[4] appears not to be the suboxide or quadrantoxide, Cu_4O, but a mixture of cuprous oxide and copper.[5]

Cuprous oxide, Cu_2O.—This oxide occurs as the mineral *cuprite* or *ruby copper.* It is formed by reduction of alkaline solutions of complex cupric salts with a reducing sugar, such as dextrose, an example being the reduction of Fehling's solution,[6] the oxide being deposited as a red, crystalline powder.

Cuprous oxide is produced in the form of an orange-yellow, amorphous gel containing water by the reduction of an alkaline cupric solution with sodium hyposulphite:[7]

$$2CuO+Na_2S_2O_4+2NaOH=Cu_2O+2Na_2SO_3+H_2O.$$

A better method is the action of hydroxylamine on a cupric salt in presence of alkali.[8] The initial light-yellow product is probably a hydroxide. In absence of air, the colour quickly changes to orange or brick-red, the phenomenon being probably due to elimination of water. The dry product contains 2 to 3 per cent. of water, but above low red heat this water is expelled, the metastable, yellow, amorphous oxide becoming transformed into the stable, red, crystalline variety.

Other methods of formation are the addition of sodium carbonate to a solution of cupric sulphate and sodium chloride reduced with sulphurous acid,[9] and that of an alkaline solution of sodium potassium tartrate to a solution of cuprous chloride and sodium chloride.[10] At temperatures below 350° C. copper reacts with nitrous oxide to form cuprous oxide; above this temperature the product is cupric oxide.[11] Cuprous oxide is also formed at the anode in the electrolysis of a solution of cupric sulphate,[12] and by heating cupric oxide in steam.

The oxide crystallizes in cubic octahedra, melting above 1230° C. according to Truthe,[13] and at 1235° C. under a pressure of 0·6 mm. according to Roberts and Hastings Smyth,[14] and of density 5·75 to 6·09.[15] Its solubility in water is very slight, but it dissolves readily in aqueous solutions of ammonia, less readily in potassium hydroxide,[16] and easily in hydrogen halides, with formation of complex derivatives. The

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[1] Rammelsberg, *Pogg. Annalen*, 1839, 48, 162.

[2] Saglier, *Compt. rend.*, 1887, 104, 1440.

[3] Brun, *ibid.*, 1892, 114, 667.

[4] Rose, *Pogg. Annalen*, 1863, [4], 30, 1.

[5] Moser, *Zeitsch. anorg. Chem.*, 1909, 64, 200; compare Recoura, *Compt. rend.*, 1909, 148, 1105.

[6] Mitscherlich, *J. prakt. Chem.*, 1840, 19, 450; Böttger, *Annalen*, 1841, 39, 176; *J. prakt. Chem.*, 1863, 90, 163.

[7] Moser, *loc. cit.*

[8] Moser, *Zeitsch. anorg. Chem.*, 1919, 105, 112; compare Paal and Dexheimer, *Ber.*, 1914, 47, 2195; Sarma, *Chem. News*, 1921, 122, 99.

[9] Russell, *Chem. News*, 1894, 68, 308.

[10] Gröger, *Zeitsch. anorg. Chem.*, 1902, 31, 326.

[11] Sabatier and Senderens, *Compt. rend.*, 1895, 120, 618.

[12] Meyer, *Bull. Soc. chim. Belg.*, 1908, 22, 259.

[13] Truthe, *Zeitsch. anorg. Chem.*, 1912, 76, 161.

[14] Roberts and Hastings Smyth, *J. Amer. Chem. Soc.*, 1921, 43, 1061.

[15] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 54, 55.

[16] Guntz and Bassett, *Bull. Soc. chim.*, 1906, [3], 35, 201.

ammoniacal solutions absorb oxygen, yielding cupric compounds.[1] When heated in air, the oxide is stable only between 1025° and 1070° C.[2] At 155° C. reduction of the oxide to metallic copper by hydrogen becomes perceptible, the velocity of the reaction increasing rapidly with rise of temperature.[3] It is much accelerated by the presence of a dehydrating agent, such as barium monoxide.[4] At 250° C. the oxide is converted by a solution of chlorine in carbon tetrachloride into a dark-brown, amorphous compound of the formula Cu_2OCl_2.[5] At 1250° C. in an atmosphere of nitrogen it combines with ferric oxide to the crystalline, slightly magnetic *cuprous ferrite*, Cu_2O,Fe_2O_3.[6]

Cuprous hydroxide, $CuOH$.—The formation of the hydroxide by the interaction of alkalies and solutions of cuprous chloride has been described,[7] but it is doubtful whether a definite compound has ever been isolated.

Cuprous sulphide, Cu_2S.—The sulphide occurs in nature as the mineral *chalcocite* or *copper glance*. It is synthesized by heating copper with sulphur, and fusing the product to decompose the cupric sulphide simultaneously produced.[8] It can also be prepared from cupric sulphide by heating with hydrogen at 265° C., or with carbon dioxide at 130° to 150° C.[9]; and from copper by the action of sulphuric acid at 124° C.,[10] or of a solution of ammonium sulphide in absence of air.[11] It is also formed by heating cupric sulphide with sodium arsenite, sodium monothioarsenate being produced simultaneously :[12]

$$2CuS+Na_3AsO_3=Cu_2S+Na_3AsSO_3.$$

The mineral crystallizes in the rhombic system, its density being 5·7 to 5·8. The artificial substance forms dark-grey octahedra belonging to the cubic system, its density being given as 5·52 to 5·58,[13] and 5·785 (20° C.).[14] An evolution of 0·9 Cal. per gram-molecule attends the transformation of the rhombic into the cubic form, the transition-point being 103° C.[15] Its melting-point is given as 1057° C. (in sulphur-vapour),[14] 1091° C.,[16] 1096° C. (in an atmosphere of hydrogen sulphide),[14] 1114° C.,[17] and 1135° C.,[18] and its mean specific heat as 0·1212 between 9° and 97° C.[19] It is very slightly soluble in water, but is soluble in concentrated nitric

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[1] Julius Meyer, *Ber.*, 1902, 35, 3952.

[2] Foote and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1344 ; compare Walden, *ibid.*, 1350.

[3] Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 1.

[4] Berger, *Compt. rend.*, 1914, 158, 1798.

[5] Michael and Murphy, *Amer. Chem. J.*, 1910, 44, 365.

[6] Hilpert, *Ber.*, 1909, 42, 2248 ; *Verh. Deut. physikal. Ges.*, 1909, 11, 293.

[7] Frémy, *Ann. Chim. Phys.*, 1848, [3], 23, 391 ; Mitscherlich, *J. prakt. Chem.*, 1840, 19, 450.

[8] Winkelblech, *Annalen*, 1837, 21, 34 ; Rose, *Pogg. Annalen*, 1836, 28, 157 ; Hittorff *ibid.*, 1851, 84, 1 ; Bodländer and Idaszewski, *Zeitsch. Elektrochem.*, 1905, 11, 161.

[9] Pickering, *Trans. Chem. Soc.*, 1881, 39, 401.

[10] Pickering, *loc. cit.* ; compare Cundall, *ibid.*, 1914, 105, 60.

[11] Neumann, *Ber.*, 1873, 6, 748.

[12] Weinland and Storz, *Ber. Deut. Pharm. Ges.*, 1907, 17, 272.

[13] Schröder, *Neues Jahrbuch für Mineralogie*, 1875, 473.

[14] Posnjak, Allen, and Merwin, *Economic Geology*, 1915, 10, 491.

[15] Bellati and Lussana, *Atti Inst. Venet.*, 1889, [6], 7, 9.

[16] Bodländer and Idaszewski, *Zeitsch. Elektrochem.*, 1905, 11, 161.

[17] Truthe, *Zeitsch. anorg. Chem.*, 1912, 76, 161.

[18] Friedrich, *Metallurgie*, 1908, 5, 23.

[19] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129.

acid and sulphuric acid with decomposition.[1] The heat of formation evolved in the direct combination of the elements is 19·0 Cal.[2]

When suspended in a solution containing both ammonia and ammonium (or other) salts, air at atmospheric pressure oxidizes cuprous sulphide to cupric sulphate and thiosulphate, the reaction being slower than with cupric sulphide. In suspension in neutral or acidic solutions, cupric sulphate is produced, the reaction being less energetic than in presence of ammonia, and up to 160° C. requiring compressed air.[3]

With sodium monosulphide cuprous sulphide forms a double salt of the formula Na_2S,Cu_2S.[4] This compound melts at 700° C.

Cuprous sulphite, Cu_2SO_3.—Sulphur dioxide reacts with a solution of cupric acetate in acetic acid to form colourless, hexagonal leaflets, $Cu_2SO_3,\frac{1}{2}H_2O$.[5] In aqueous solution sulphur dioxide converts this substance into a red, prismatic form, Cu_2SO_3,H_2O, also formed by the action of this gas on alkali cuprous sulphites in presence of water.[6] The sulphite is capable of forming complex ammonium derivatives of the type $Cu_2SO_3,(NH_4)_2SO_3$.[5]

Cuprous sulphate, Cu_2SO_4.—Cuprous sulphate cannot be isolated by methods analogous to those employed for the preparation of the cuprous halides. Metallic copper dissolves in solutions of cupric sulphate containing free sulphuric acid, an equilibrium corresponding with the scheme

$$2Cu^{\cdot} \rightleftharpoons Cu^{\cdot\cdot}+Cu$$

being attained. At ordinary temperatures the proportion of cuprous sulphate formed is small, but it is increased by rise of temperature.[7]

Cuprous sulphate was first isolated by Recoura[8] by the interaction of molecular proportions of cuprous oxide and methyl or ethyl sulphate at 160° C. in absence of moisture. The presence of excess of the alkyl sulphate induces decomposition of the product with formation of cupric sulphate:

$$Cu_2O+(CH_3)_2SO_4=Cu_2SO_4+(CH_3)_2O.$$

The salt is dried by washing with ether and placing in a vacuum-desiccator over sulphuric acid.

The sulphate is a light-grey powder, instantly decomposed by water in accordance with the equation[9]

$$[Cu_2SO_4]+Aq.=CuSO_4\,(\text{dissolved})+[Cu]+21\text{ Cal.}$$

Since the heat of solution of anhydrous cupric sulphate in water is 15·8 Cal., the transformation of a gram-molecule of cuprous sulphate into cupric sulphate and copper is attended by the evolution of 5·2 Cal., the reaction being exothermic. The formation of cuprous sulphate is an endothermic reaction, although that of each of the other cuprous salts is accompanied by evolution of heat. At ordinary temperatures, in presence of dry air, cuprous sulphate is stable, but contact with moist air induces a very slow decomposition. The presence of ether renders

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[1] Compare Warlimont, *Metallurgie*, 1909, 6, 83.

[2] Wartenberg, *Zeitsch. physikal. Chem.*, 1909, 67, 446.

[3] Gluud, *Ber.*, 1922, 55, [B], 952.

[4] Friedrich, *Metall und Erz*, 1914, 11, 79.

[5] Ramberg, *Zeitsch. physikal. Chem.*, 1909, 69, 512.

[6] Rogojsky, *Annalen*, 1851, 80, 255; Étard, *Compt. rend.*, 1882, 95, 36.

[7] Foerster and Blankenberg, *Ber.*, 1906, 39, 4428.

[8] Recoura, *Compt. rend.*, 1909, 148, 1105.

[9] Compare Cundall, *Trans. Chem. Soc.*, 1914, 105, 60.

the action of moist air very rapid, the black mass formed being converted by water into a solution of cupric sulphate and a black oxide with properties similar to those of the product assumed by Rose to be a suboxide, Cu_4O (p. 267). Heating at 200° C. in air oxidizes cuprous sulphate to a brownish-black mixture of cupric oxide and cupric sulphate.

Cuprous sulphate dissolves in concentrated hydrochloric acid and in concentrated ammonium hydroxide. The ammoniacal solution yields a colourless, crystalline compound, $Cu_2SO_4,4NH_3,H_2O$, decomposed by water into metallic copper and an ammoniacal cupric compound.[1] Cuprous sulphate is also dissolved to a slight extent by glacial acetic acid. The deep-violet solution thus produced is rapidly oxidized by air to a blue liquid, from which crystals of an acid cupric acetate are deposited.[2]

Cuprous selenide, Cu_2Se.—The selenide occurs as the mineral *berzelianite.* It is produced by direct combination of copper and selenium-vapour, and is a dimorphous substance of steel-grey colour, the transition-point for the two forms being 110° C. At 20° C. its specific heat is 0·1047,[3] and its heat of formation 20·8 Cal.[4]

Cuprous telluride, Cu_2Te.—The telluride is formed by the interaction of tellurium-vapour and copper,[5] its heat of formation by this process being 14·3 Cal.[6]

Cuprous nitride, Cu_3N.—A dark olive-green substance containing 80 to 90 per cent. of cuprous nitride is produced by the action of dry ammonia on cuprous or cupric oxide at 250° to 260° C.[7] It is decomposed by concentrated acids. Potassamide reacts with a solution of cupric nitrate in liquid ammonia to form an olive-green substance, Cu_3N,nNH_3, which at ordinary temperature in vacuum changes to dark-brown *cuprous imide,* Cu_2NH, and is converted by heating at 160° C. in vacuum into cuprous nitride.[8] When heated in the air, the product formed explodes readily.[9] It is a black, amorphous mass, decomposed by water with evolution of heat.

Cuprous phosphide, Cu_3P.—Phosphine reacts with heated copper cuprous oxide,[10] chloride, or sulphide,[11] forming a black powder, Cu_3P density 6·59 to 6·75, also produced by reducing cupric phosphide with hydrogen. Other phosphides of the formulæ CuP [12], Cu_2P [13], Cu_5P, and Cu_6P [14] have been described, but their existence is doubtful.

Cuprous arsenides.—The arsenic compounds *domeykite,* Cu_3As ; *algodonite,* Cu_6As ; and *whitneyite* or *darwinite,* Cu_9As, occur as minerals.

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[1] Foerster and Blankenberg, *Ber.*, 1906, 39, 4428.

[2] Recoura, *Compt. rend.*, 1909, 148, 1105.

[3] Bellati and Lussana, *Atti Inst. Ven.*, 1889, [6], 7, 9, 1051.

[4] Fabre, *Ann. Chim. Phys.*, 1887, [6], 10, 505.

[5] Margottet, *Compt. rend.*, 1877, 85, 1142; *Thesis*, Paris, 1879; Brauner, *Monatsh.*, 1889, 10, 411.

[6] Fabre, *Bull. Soc. chim.*, 1883, [2], 40, 99; *Ann. Chim. Phys.*, 1888, [6], 14, 104.

[7] Schrötter, *Annalen*, 1841, 37, 136; Warren, *Chem. News*, 1887, 55, 155; Guntz and Bassett, *Bull. Soc. chim.*, 1906, [3], 35, 201.

[8] Franklin, *J. Amer. Chem. Soc.*, 1912, 34, 1501.

[9] Fitzgerald, *ibid.*, 1907, 29, 656.

[10] Rubenovitch, *Compt. rend.*, 1899, 128, 1398.

[11] Rose, *Pogg. Annalen*, 1826, 6, 206; 1832, 24, 295.

[12] Rose, *loc. cit.*; Granger, *Compt. rend.*, 1893, 117, 231; Cross and Higgins, *Trans. Chem. Soc.*, 1879, 35, 249.

[13] Hvoslef, *Annalen*, 1856, 100, 100; Schrötter, *Sitzungsber. K. Akad. Wiss. Wien*, 1849, 2, 304; Maronneau, *Compt. rend.*, 1899, 128, 936.

[14] Granger, *Compt. rend.*, 1891, 113, 1041.

Cuprous carbide or acetylide, Cu_2C_2.—The acetylide is formed by the action of acetylene on an ammoniacal solution of cuprous chloride,[1] or on a suspension of cuprous oxide in water.[2] It is a brownish-red, amorphous substance, and explosive in the dry state.[3] Prepared by the first method, it is associated with a molecule of water,[4] which can be removed by drying over sulphuric acid. The presence of this water has been attributed to adsorption,[5] and another explanation assumes the compound to have the formula $CH{\equiv}CCu,CuOH$.[6] Cuprous acetylide forms complex derivatives with solutions of cuprous chloride and potassium chloride in hydrochloric acid.[7] Among the examples of those described are the colourless $2CuCl,C_2H_2$ and $4CuCl,KCl,C_2H_2$; the yellow $8CuCl,2KCl,C_2H_2$; and the violet $2CuCl,Cu_2O,C_2H_2$. Manchot[8] found that excess of acetylene combines with cuprous chloride to form white crystals of the formula $CuCl,C_2H_2$. In presence of hydrochloric acid a dark-violet powder of the composition $CuCl,C_2Cu_2,H_2O$ is precipitated. In the dry state this substance is moderately stable. Acetylene combines with excess of cuprous chloride to form white prisms of the composition $2CuCl,C_2H_2$.

Cuprous carbonate.—Carles[9] claims to have prepared cuprous carbonate as a glaucous green powder, insoluble in water, by the action of copper on copper carbonate in presence of liquefied ammonia.

Cuprous cyanide, $CuCN$.—Addition of potassium cyanide to a solution of cuprous chloride in hydrochloric acid precipitates cuprous cyanide.[10] The best method for its preparation is to mix cold aqueous solutions of potassium cyanide (65 grams) and cupric sulphate (130 grams), and expel cyanogen by warming the mixture under an efficient air-extractor. After settling, the cuprous cyanide is decanted, and washed with water, alcohol, and ether.[11] References to other methods of preparation, and to Sandmeyer's process for aromatic nitriles, are appended.[12]

Cuprous cyanide is a white solid, and is soluble with difficulty in water. It is dissolved readily by cold, concentrated hydrochloric acid, and is reprecipitated from this solvent by addition of an aqueous solution of potassium hydroxide. In contact with air, its colourless solution in ammonium hydroxide develops a blue tint. The salt is also dissolved by aqueous solutions of ammonium chloride, sulphate, and nitrate, and by warm, dilute sulphuric acid. None of its solutions has the power of absorbing carbon monoxide.[13] The heat of formation of

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[1] Berthelot, *Ann. Chim. Phys.*, 1866, [4], 9, 385.

[2] Keiser, *Amer. Chem. J.*, 1892, 14, 285.

[3] Berthelot, *loc. cit.* With hydrochloric acid cuprous acetylide yields impure acetylene, probably contaminated with diacetylene, $HC{\equiv}C-C{\equiv}CH$ (Noyes and Tucker, *Amer. Chem. J.*, 1897, 19, 123).

[4] Blochmann, *Annalen*, 1874, 173, 174.

[5] Liebermann and Damerow, *Ber.*, 1892, 25, 1096.

[6] Scheiber, *Ber.*, 1908, 41, 3816; compare Makowka, *ibid.*, 824.

[7] Chavastelon, *Compt. rend.*, 1898, 126, 1810; 127, 68; 1900, 130, 1634, 1764; 131, 48; 1901, 132, 1489.

[8] Manchot, *Annalen*, 1912, 387, 257.

[9] Carles, *Bull. Soc. chim.*, 1915, [4], 17, 163.

[10] Proust, *J. de Physique*, 1804, 59, 350; *Neues allgemeines Journal der Chemie* (Gehlen), 1806, 6, 573.

[11] Jacquemin, *Bull. Soc. chim.*, 1885, [2], 43, 556; Varet, *Compt. rend.*, 1890, 110, 147.

[12] Vauquelin, *Ann. Chim. Phys.*, 1818, 9, 120; Wöhler, *Annalen*, 1851, 78, 370; Rammelsberg, *Pogg. Annalen*, 1837, 42, 124; Sandmeyer, *Ber.*, 1884, 17, 2650.

[13] Manchot and Friend, *Annalen*, 1908, 359, 100.

cuprous cyanide in the simple molecular form CuCN from carbon, solid copper, and gaseous nitrogen is 14·9 Cal.[1]

Cuprous thiocyanate, CuCNS.—The thiocyanate is produced by dissolving cuprous oxide or carbonate in thiocyanic acid, and by the interaction of solutions of potassium thiocyanate and a cupric salt in presence of a reducer, such as ferrous sulphate or sulphurous acid.[2] It is a white substance, its solubility at 18° C. being 0·23 mg. in 1 litre of water.[3] It dissolves in ammonium hydroxide and concentrated hydrochloric acid, and also in concentrated nitric acid with formation of cupric sulphate. It is employed in the preparation of aromatic thiocyanates.[4]

Cuprous silicide, Cu_4Si.—The fusion of copper and silicon has been stated[5] to produce a substance of this formula, but the existence of such a compound is doubtful.[6]

Cuprous silicofluoride, Cu_2SiF_6.—The silicofluoride has a copper-red colour, and melts at a high temperature with evolution of silicon tetrafluoride.[7]

Ammonio-cuprous Derivatives.[8]—A number of complex cuprous derivatives containing ammonia are known. Examples are *ammonio-cuprous hydroxide,*[9] $Cu(NH_3)OH$, and *ammonio-cuprous sulphate,* $Cu_2SO_4,4NH_3$, obtained as a pale green solution by dissolving cuprous oxide in an ammoniacal solution of an ammonium salt.[10] At 50° C., in an atmosphere of hydrogen, this sulphate is precipitated as a white crystalline powder by mixing alcohol and an aqueous solution containing cuprous oxide, ammonium sulphate, and ammonia, proving the basic character of ammoniacal cuprous oxide to be strong enough to displace ammonium from its salts. *Ammonio-cuprous nitrate,* $CuNO_3,2NH_3$, is a colourless, readily oxidized substance, formed by the action of liquid ammonia on ammonio-cupric nitrate, $Cu(NO_3)_2,4NH_3$.[11]

Carbonyl cuprous sulphate.—On decolorizing an aqueous solution of cupric sulphate with carbon monoxide, and evaporating in an atmosphere of this gas, a solid complex salt was obtained by Joannis.[12] He ascribed to it the formula $(Cu{\cdot}CO)_2SO_4,H_2O$. The great instability of the product is indicated by its decomposition by water into copper and cupric sulphate. In its constitution this compound resembles the carbonyl derivatives of the copper halides, the proportion of carbon monoxide to copper in its molecule being in the ratio of one molecule to one atom.

CUPRIC COMPOUNDS.

Cupric hydride.—Attempts to prepare cupric hydride have not led to the isolation of any definite compound.[13]

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[1] Varet, *Compt. rend.*, 1895, 121, 598.

[2] Meitzendorff, *Pogg. Annalen*, 1842, 56, 63.

[3] Prud'homme, *J. Chim. phys.*, 1911, 9, 519.

[4] Gattermann and Hausknecht, *Ber.*, 1890, 23, 738.

[5] Lebeau, *Compt. rend.*, 1905, 141, 889; 1906, 142, 154; Vigouroux, *ibid.*, 1906, 142, 87; 1907, 144, 917, 1214.

[6] Rudolfi, *Zeitsch. anorg. Chem.*, 1907, 53, 216; *Metallürgie*, 1908, 5, 257; Guertler, *ibid.*, 184.

[7] Berzelius, *Pogg. Annalen*, 1824, 1, 199; Stolba, *J. prakt. Chem.*, 1867, 102, 7.

[8] On the reducing action of carbon monoxide on ammonio-copper carbonates, compare Hainsworth and Titus, *J. Amer. Chem. Soc.*, 1921, 43, 1.

[9] Donnan and Thomas, *Trans. Chem. Soc.*, 1911, 99, 1788.

[10] Bouzat, *Bull. Soc. chim.*, 1909, [4], 5, 355; *Compt. rend.*, 1908, 146, 75.

[11] Sloan, *J. Amer. Chem. Soc.*, 1910, 32, 972.

[12] Joannis, *Compt. rend.*, 1897, 125, 948; 1903, 136, 615.

[13] Bartlett and Merrill, *Amer. Chem. J.*, 1895, 17, 185.

Cupric fluoride, CuF_2.—Evaporation[1] or precipitation with alcohol[2] of a solution of cupric oxide or carbonate in excess of hydrofluoric acid yields the fluoride in the form of dihydrate. It crystallizes in small, blue needles, slightly soluble in cold water, and converted by heat into the anhydrous salt. The interaction of gaseous hydrogen fluoride and cupric oxide also produces the anhydrous form as a white solid. It is soluble in mineral acids, is reduced by hydrogen, and is converted into cupric oxide by heating in air. Hot water transforms it into a pale green, slightly soluble *basic fluoride,* $Cu(OH)_2,CuF_2$,[1] a substance also produced by interaction of solutions of cupric sulphate and potassium fluoride.[2] An *acid salt,* $CuF_2,5HF,5H_2O$, has also been described.[3]

Cupric chloride, $CuCl_2$.—The anhydrous chloride is produced by heating copper or cuprous chloride in chlorine, or by dehydrating the dihydrate by heating at 150° C. in an atmosphere of hydrogen chloride,[4] or by addition of concentrated sulphuric acid to its aqueous solution.[5] It is a brownish-yellow, hygroscopic solid, melting at 498° C.,[6] of density 3·054.[7] It is readily soluble in water and organic solvents. Its heat of formation from its elements, calculated from the interaction of cupric oxide and hydrochloric acid, is given as 51·63 Cal.[8] and 51·4 Cal.[9] It is decomposed by heat into the cuprous salt and chlorine.[10]

The *dihydrate,* $CuCl_2,2H_2O$, is prepared by evaporating a solution of cupric oxide or carbonate in hydrochloric acid; or by evaporating a solution of cupric sulphate and sodium chloride, the dihydrate crystallizing out after sodium sulphate and chloride; or by addition of barium chloride to a solution of cupric sulphate, filtering, and concentrating. It crystallizes in green, deliquescent, rhombic prisms, but a blue, non-deliquescent form has also been described.[11] The density of the dihydrate is 2·47 to 2·535.[12] Its solubility at 17° C. is 43·06 grams in 100 grams of water.[13] A *trihydrate,* $CuCl_2,3H_2O$, exists at low temperatures.[14]

Numerous basic cupric chlorides have been described, although some of them may not be true chemical compounds.[15] As examples of these substances may be cited the green, rhombic crystals of the mineral atacamite, $CuCl_2,3Cu(OH)_2,nH_2O$, containing a varying proportion of water; the crystalline compound $CuCl_2,3Cu(OH)_2$, formed from brown cupric hydroxide and cupric-chloride solution[16]; and the compound $CuCl_2,3CuO,2H_2O$,[17] formed by the interaction of solutions of potassium hydroxide and cupric chloride.

Among the double salts of cupric chloride with other metallic salts

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[1] Berzelius, *Gmelin-Kraut's Handbuch der anorg. Chem.*, 6th ed., Heidelberg, 1872–1897, 3, 648.

[2] Balbiano, *Gazzetta*, 1884, 14, 74.

[3] Böhm, *Zeitsch. anorg. Chem.*, 1905, 43, 326.

[4] Sabatier, *Bull. Soc. chim.*, 1895, [3], 13, 598.

[5] Viard, *Compt. rend.*, 1902, 135, 168.

[6] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[7] Playfair and Joule, *Mem. Chem. Soc.*, 1845, 2, 401; 1848, 3, 57; Favre and Valson, *Compt. rend.*, 1874, 79, 968.

[8] Thomsen, *Thermochemistry* (Longmans, 1908), 269.

[9] Berthelot, *Thermochimie*, Paris, 1897, 2, 319.

[10] Rose, *Pogg. Annalen*, 1836, 38, 121.

[11] Stanford, *Chem. News*, 1863, 7, 81.

[12] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 24.

[13] Reicher and van Deventer, *Zeitsch. physikal. Chem.*, 1890, 5, 559.

[14] Chuard, *Archives Genève*, 1888, [3], 19, 477.

[15] Compare Dammer, *Handbuch der anorg. Chem.*, Stuttgart, 1892–1903, 2, ii., 668.

[16] Sabatier, *Compt. rend.*, 1897, 125, 101.

[17] Miller and Kenrick, *Trans. Roy. Soc. Canada*, 1901–1902, [2], 8, iii., 35.

may be mentioned $CuCl_2,LiCl,2H_2O$, a red compound[1]; other examples are $CuCl_2,2KCl,2H_2O$; $CuCl_2,KCl$[2]; and $CuCl_2,2NH_4Cl,2H_2O$.[3] References to the literature of other double salts are appended.[4]

In alcoholic solution cupric chloride combines with nitric oxide to form a double compound of the formula $CuCl_2,NO$.[5]

Cupric bromide, $CuBr_2$.—The anhydrous bromide is obtained by evaporating at low temperature a solution of cupric oxide or carbonate in hydrobromic acid.[6] It forms deliquescent crystals, similar in appearance to those of iodine. At red heat it is converted into cuprous bromide and bromine. Its heat of formation from its elements is 32·58 Cal.[7] A *basic bromide,* $CuBr_2,3Cu(OH)_2$, is known,[8] and also a number of double salts with other metallic bromides. These double salts are exemplified by the black $2LiBr,CuBr_2,6H_2O$[9]; $KBr,CuBr_2$, lustrous, dark-coloured prisms[9]; and the green $2NH_4Br,CuBr_2,2H_2O$.[10] Nitric oxide dissolves in an alcoholic solution of cupric bromide, forming a double compound of the formula $CuBr_2,NO$.[11]

Cupric iodide.—The iodide is formed in solution by the interaction of cuprous iodide and iodine solution, but it has not been isolated in the solid state, as it decomposes readily into cuprous iodide and iodine.[12] The solution is greenish-blue. Ammonia converts cupric iodide into a stable cuprammonium salt, $CuI_2,4NH_3,H_2O$, prepared more readily by exposure of ammoniacal cuprous iodide to air. A compound of the formula $2CuI,CuI_2,4NH_3$ is also known, and crystallizes in brilliant-green needles, insoluble in water, but soluble in an aqueous solution of ammonia.

Cupric chlorate, $Cu(ClO_3)_2$.—The chlorate is prepared by dissolving cupric hydroxide or carbonate in chloric acid, or by the interaction of cupric sulphate and barium chlorate. On evaporation of the solution it separates in the form of the tetrahydrate, which melts and decomposes at 73° C.[13]

Cupric perchlorate $Cu(ClO_4)_2$.—The perchlorate has also been described.[14]

Cupric bromate, $Cu(BrO_3)_2$.—Slow concentration of a solution of cupric carbonate in bromic acid yields the hexahydrate,[15] with density 2·583.[16]

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[1] Meyerhoffer, *Monatsh.*, 1892, 13, 716; *Sitzungsber. K. Akad. Wiss. Wien,* 1892, 101, ii.*b*, 599; compare Chassevant, *Compt. rend.*, 1891, 113, 646.

[2] Meyerhoffer, *Zeitsch. physikal. Chem.*, 1889, 3, 339; 1890, 5, 98.

[3] Meerburg, *Zeitsch. anorg. Chem.*, 1905, 45, 1.

[4] Schreinemakers and de Baat, *Zeitsch. physikal. Chem.*, 1909, 65, 586; Schreinemakers, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 615; *Zeitsch. physikal. Chem.*, 1910, 69, 557; 1909, 66, 687; Cambi, *Gazzetta*, 1909, 39, i., 361; Naumann, *Ber.*, 1909, 42, 3789.

[5] Manchot, *Ber.*, 1914, 47, 1601.

[6] Rammelsberg, *Pogg. Annalen*, 1842, 55, 246.

[7] Thomsen, *Thermochemistry* (Longmans, 1908), 318.

[8] Sabatier, *Compt. rend.*, 1897, 125, 101.

[9] Kurnakoff and Sementschenko, *Zeitsch. anorg. Chem.*, 1899, 19, 335.

[10] de Koninck, *Zeitsch. angew. Chem.*, 1888, 1, 507.

[11] Manchot, *Ber.*, 1914, 47, 1601.

[12] Traube, *Ber.*, 1884, 17, 1064; Carnegie, *Chem. News*, 1889, 59, 57; Jörgensen, *J. prakt. Chem.*, 1870, [2], 2, 347.

[13] Meusser, *Ber.*, 1902, 35, 1420; compare Wächter, *J. prakt. Chem.*, 1843, 30, 328; Bourgeois, *Bull. Soc. chim.*, 1898, [3], 19, 950.

[14] Serullas, *Ann. Chim. Phys.*, 1831, 46, 306.

[15] Rammelsberg, *Pogg. Annalen*, 1841, 52, 92.

[16] Topsöe, *Gmelin-Kraut's Handbuch der anorg. Chem.*, 6th ed., Heidelberg, 1872–1897, 3, 639.

Cupric iodate, $Cu(IO_3)_2$.—Solution of cupric hydroxide or carbonate in a solution of iodic acid yields the iodate, which is known in the anhydrous form,[1] and as monohydrate,[2] and dihydrate.[3] From excess of a solution of potassium iodate, cupric nitrate precipitates the pale-blue monohydrate. At 25° C. its solubility is $3{\cdot}3 \times 10^{-3}$ gram-molecules per litre of water.[4] A *basic iodate*, $Cu(IO_3)_2,Cu(OH)_2$, has also been prepared.[5]

Cupric periodates.—A number of periodates has been obtained by dissolving cupric hydroxide or carbonate in a solution of periodic acid, and also by the interaction of sodium periodate, $NaIO_4$, and solutions of cupric salts.[6] They have the formulæ $2CuO,I_2O_7,6H_2O$; $4CuO,I_2O_7,H_2O$; $4CuO,I_2O_7,7H_2O$; and $5CuO,I_2O_7,5H_2O$.

Cupric oxide, CuO.—This oxide is obtained as a black, amorphous powder by igniting cupric hydroxide, carbonate, or nitrate.[7] It is also formed on copper anodes in electrolytic oxidation.[8] The amorphous oxide can be converted into lustrous, cubic tetrahedra by heating with potassium hydroxide,[9] the crystalline variety being also produced by ignition to redness in a platinum crucible of a small amount of cuprous chloride.[10]

A blue variety of cupric oxide is said to have been prepared by precipitating cupric sulphate with sodium hydroxide in presence of dissolved aluminium.[11] On heating strongly, it blackens, the change being probably due to an agglomeration of the particles. On the other hand, Müller and Ernst[12] state that agitation of cupric oxide or hydroxide with sodium hydroxide produces a blue precipitate of sodium cuprite. On warming the mixture, this substance dissolves, and on cooling separates in crystals. In contact with excess of water, these crystals decompose to form the black oxide.

Cupric oxide occurs as the hexagonal *tenorite*, and also as the rhombic or monoclinic *melaconite*. According to Slade and Farrow,[13] the oxide melts above 1148° C., with partial decomposition into cuprous oxide; but Smyth and Roberts[14] state that it does not melt with dissociation below 1233° C. Its density is 6·32 to 6·43.[15] Its mean specific heat is 0·1420 between 12° and 98° C.,[16] and its heat of formation 37·16 Cal.[17]

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[1] Ditte, *Ann. Chim. Phys.*, 1890, [6], 21, 173; Granger and de Schulten, *Compt. rend.*, 1904, 139, 201.

[2] Rammelsberg, *Pogg. Annalen*, 1838, 44, 569.

[3] Millon, *Ann. Chim. Phys.*, 1843, [3], 9, 400.

[4] Spencer, *Zeitsch. physikal. Chem.*, 1913, 83, 290.

[5] Granger and de Schulten, *Compt. rend.*, 1904, 139, 201.

[6] Bengieser, *Annalen*, 1836, 17, 254; Langlois, *Ann. Chim. Phys.*, 1852, [3], 34, 257; Lautsch, *J. prakt. Chem.*, 1867, 100, 85; Rammelsberg, *Pogg. Annalen*, 1868, 134, 519.

[7] Vogel and Reischauer, *Dingler's Polytech. J.*, 1859, 153, 197; *Jahresb.*, 1863, 274; Erdmann and Marchand, *J. prakt. Chem.*, 1844, 31, 389.

[8] Müller and Spitzer, *Zeitsch. anorg. Chem.*, 1906, 50, 321; Schmiedt, *Zeitsch. Elektrochem.*, 1908, 15, 53.

[9] Becquerel, *Ann. Chim. Phys.*, 1832, 51, 101.

[10] Schulze, *J. prakt. Chem.*, 1880, [2], 21, 413.

[11] Schenck, *J. Physical Chem.*, 1919, 23, 283.

[12] Müller and Ernst, *Zeitsch. angew. Chem.*, 1921, 34, 371.

[13] Slade and Farrow, *Zeitsch. Elektrochem.*, 1912, 18, 817; compare Wöhler and Foss, *ibid.*, 1906, 12, 781.

[14] Hastings Smyth and Roberts, *J. Amer. Chem. Soc.*, 1920, 42, 2582.

[15] Schröder, *Pogg. Ann. Jubelband*, 1874, 452; compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 55.

[16] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 129.

[17] Thomsen, *Thermochemistry* (Longmans, 1908), 268.

At 1020° C. it is said to lose half its oxygen, forming cuprous oxide.[1] Heating in steam reduces it to cuprous oxide. Under the influence of heat, hydrogen reduces cupric oxide to metallic copper, the reaction being considerably accelerated by the presence of a dehydrating agent, such as barium monoxide.[2] The amorphous form displays a remarkable power of sorption towards gases such as oxygen, nitrogen, and carbon dioxide.[3] For the hydrogenation of unsaturated organic compounds it appears to be a better catalyst than reduced copper.[4] A thin layer precipitated on asbestos and heated ignites an oxy-hydrogen jet.[5] It is reduced by aluminium in accordance with the equation

$$3CuO+2Al=Al_2O_3+3Cu,$$

the heat evolved being 650 cal. per kilogram of mixture.[6] Cupric oxide is completely dissociated at the temperature of the electric furnace.[7] When heated at 1000° C. with fused potassium chloride containing sodium chloride, it yields cuprous oxide, oxygen, and a basic cupric chloride of the formula $3CuO,CuCl_2,4H_2O$.[8] Cupric oxide is somewhat soluble in fused caustic alkalies, and in their concentrated solutions.[9] Several coloured hydrates have been described,[10] including the blue or green CuO,H_2O, the olive-green $CuO,0{\cdot}8H_2O$, and the brown $CuO,0{\cdot}35H_2O$. A magnetic, crystalline *cupric ferrite*, CuO,Fe_2O_3, is formed by precipitating a mixture of cupric and ferric salts with alkali.[11]

The affinity-relations of cupric oxide and of cupric hydroxide have been investigated by Allmand[12] by tensimetric and electrometric methods. His results prove crystalline cupric hydroxide to be stable in ordinary moist air, but to be converted into cupric oxide through elimination of water by agitation with alkaline or ammoniacal solutions at 25° C. To explain the apparent contradiction, Allmand assumes that lapse of time induces an ageing of cupric oxide, due to an irreversible augmentation of molecular complexity. Crystalline cupric hydroxide is stable towards freshly prepared cupric oxide, but unstable towards aged samples of the oxide. The unsaturation with respect to fresh cupric oxide of a saturated solution of cupric hydroxide, and its supersaturation with respect to aged cupric oxide, explain the apparently anomalous stability-relations of cupric hydroxide and of cupric oxide and water. Allmand has deduced the dissociation-pressure of cupric oxide at 1030° C. to be 200 mm., a value in good agreement with the pressure 170–180 mm. experimentally determined at the same temperature by other investigators.[13]

Copper peroxide, CuO_2,H_2O.—At 0° C. neutral hydrogen peroxide converts an aqueous suspension of cupric hydroxide into the brown,

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[1] Wöhler and Frey, *Zeitsch. Elektrochem.*, 1909, 15, 34.

[2] Berger, *Compt. rend.*, 1914, 158, 1798; compare Sabatier and Espil, *ibid.*, 159, 137.

[3] Thudichum and Kingzett, *J. Chem. Soc.*, 1876, 30, 363; Richards, *Amer. Chem. J.*, 1898, 20, 701.

[4] Ipatieff, *Ber.*, 1909, 42, 2089, 2097.

[5] Strachan, *Chem. News*, 1911, 103, 241.

[6] Skinder, *Bull. Acad. St. Pétersbourg*, 1908, 97.

[7] Moissan, *Compt. rend.*, 1892, 115, 1034; *Ann. Chim. Phys.*, 1895, [7], 4, 136.

[8] Hedvall and Booberg, *Zeitsch. anorg. Chem.*, 1921, 119, 213.

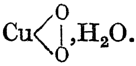
[9] Chodnew, *J. prakt. Chem.*, 1843, 28, 217; Löw, *Zeitsch. anal. Chem.*, 1870, 9, 463.

[10] de Forcrand, *Compt. rend.*, 1913, 157, 441.

[11] Hilpert, *Ber.*, 1909, 42, 2248; *Verh. Deut. physikal. Ges.*, 1909, 11, 293.

[12] Allmand, *Trans. Chem. Soc.*, 1910, 97, 603.

[13] Foote and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1344; Wöhler and Frey, *Zeitsch. Elektrochem.*, 1909, 15, 34.

crystalline peroxide.[1] It is also produced by the interaction of solutions of cupric chloride and hydrogen peroxide with alcoholic potash at −40° or −50° C., and by the action of an ether-solution of hydrogen peroxide on very finely powdered cupric hydroxide at 0° C.[2] The product is always more or less impure. When moist, it decomposes rapidly with evolution of oxygen and formation of cupric oxide, but the decomposition of the dry substance is slow. In its reactions it behaves as a peroxide. Moser assigns to it the formula  $Cu\left\langle\begin{matrix}O\\|\\O\end{matrix}\right.,H_2O$. The name *peroxites* has been suggested for the true salts of hydrogen peroxide.[3]

The compounds obtained by the action of hydrogen peroxide on cupric hydroxide are regarded by Aldridge and Applebey[4] as probably consisting of a mixture in varying proportions of cupric oxide and hydroxide with a yellow, gelatinous peroxide of the formula CuO_2. A solution of sodium copper carbonate,[5] $Na_2Cu(CO_3)_2$, reacts with hydrogen peroxide to precipitate a very unstable, yellowish-brown peroxide, containing more oxygen than would correspond with the formula Cu_2O_3, but less than that required by CuO_2.

In 1844 Krüger[6] obtained pink solutions by the chlorination of alkaline suspensions of cupric hydroxide, and attributed the colour to the presence of salts (" cuprates ") of an acidic peroxide of copper. Aldridge and Applebey[7] regard these so-called cuprates as having no real existence, the pink colour observed by Krüger being considered to be due to the formation of permanganate from traces of manganese dioxide.

This *copper peroxide*, Cu_2O_3, is stated[8] to be formed as an orange-yellow substance by electrolytic oxidation with a high current-density at a copper anode immersed in concentrated caustic alkali, and also by the action of alkaline hypochlorite and hypobromite on cupric hydroxide and copper.[9] Various investigators[10] have described a compound with the same formula. An example is the interaction of potassium persulphate with a mixture of cupric hydroxide and barium hydroxide cooled with ice and salt, colour changes taking place in the solution, and a tenuous, amaranth-red precipitate being deposited.[11] The substance formed yields oxygen with sulphuric acid, liberates chlorine from hydrochloric acid, oxidizes ammonia in the cold to nitrogen and nitrous acid and traces of nitric acid, decolorizes permanganate, and liberates

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[1] Moser, *Zeitsch. anorg. Chem.*, 1907, 54, 121; compare Thénard, *Gmelin-Kraut's Handbuch der anorg. Chem.*, 6th ed., Heidelberg, 1872–1897, 3, 605; Swiontkowsky, *ibid.*, 606; Weltzien, *Annalen*, 1866, 140, 207; Kruss, *Ber.*, 1884, 17, 2593; Osborne, *Amer. J. Sci.*, 1886, [3], 32, 333.

[2] Moser, *Zeitsch. anorg. Chem.*, 1914, 86, 380.

[3] Ebler and Krause, *ibid.*, 1911, 71, 150.

[4] Aldridge and Applebey, *Trans. Chem. Soc.*, 1922, 121, 238; compare Osborne, *Amer. J. Sci.*, 1886, [3], 32, 334; Moser, *Zeitsch. anorg. Chem.*, 1907, 54, 121; Müller, *ibid.*, 418; Scagliarini and Torelli, *Gazzetta*, 1921, 51, ii., 225.

[5] Compare Applebey and Lane, *Trans. Chem. Soc.*, 1918, 113, 609.

[6] Krüger, *Pogg. Annalen*, 1844, 62, 445.

[7] Aldridge and Applebey, *loc. cit.*

[8] Müller and Spitzer, *Zeitsch. Elektrochem.*, 1907, 13, 25; compare Schmiedt, *ibid.*, 1908, 15, 53.

[9] Müller, *Zeitsch. anorg. Chem.*, 1907, 54, 417.

[10] Krüger, *Pogg. Annalen*, 1844, 62, 445; Mawrow, *Zeitsch. anorg. Chem.*, 1900, 23, 233; Moser, *ibid.*, 1907, 54, 121, 417; Crum, *Annalen*, 1845, 55, 213; Osborne, *Amer. J. Sci.*, 1886, [3], 32, 333.

[11] Scagliarini and Torelli, *Gazzetta*, 1921, 51, ii., 225.

iodine from potassium iodide. It is not a peroxide, since with dilute acids it does not yield hydrogen peroxide, and therefore differs from the orange-yellow peroxide obtained by means of hydrogen peroxide. The ratio between the percentages of copper and active oxygen present corresponds with the formula Cu_2O_3.[1]

Cupric hydroxide, $Cu(OH)_2$.—The hydroxide has been prepared in crystalline form by the action of a solution of caustic alkali on a basic cupric nitrate[2] and a basic cupric sulphate,[3] and also by other methods.[4] A hydrogel of varying composition is precipitated by addition of alkali to solutions of cupric salts.[5] Unlike the colloidal form, the blue crystalline variety is stable at 100° C. A solid, colloidal variety has been obtained[6] as blackish-blue, brittle lamellæ which dissolve in water to form the original solution. An amorphous modification is precipitated from ammoniacal copper solutions by the action of alkali-metal hydroxides.[7]

Cupric sulphide, CuS.—By adopting special experimental precautions, it is possible to prepare cupric sulphide free from cuprous sulphide and sulphur by precipitating a solution of cupric sulphate or chloride with hydrogen sulphide,[8] although if no precautions are taken the precipitate is likely to be contaminated with these substances.[9] At 180° C. concentrated sulphuric acid converts copper into a mixture of cupric sulphide and sulphur, from which the sulphur can be removed by heating at 160° C. in a rapid current of hydrogen.[10]

A crystalline variety of cupric sulphide is produced by heating cupric sulphate with ammonium thiocyanate above 180° C.[11] The amorphous form can also be rendered crystalline by heating in a sealed tube with ammonium hydrogen sulphide at 150° to 200° C., the product consisting of lustrous, violet, hexagonal leaflets.[12]

Cupric sulphide occurs in nature as *covellite* or *indigo-copper*, indigo-blue, hexagonal plates, density 4·59 to 4·64, and hardness 1·5 to 2.[13] The dark-green, amorphous variety has the density 4·16,[14] and is a good conductor of electricity.[15] It is decomposed in vacuum at 400° C. into cuprous sulphide and sulphur.[16] Its oxidation by air in ammoniacal, neutral, and acidic suspensions is similar to that of cuprous sulphide

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[1] Compare Moser, *Zeitsch. anorg. Chem.*, 1907, 54, 121.

[2] Becquerel, *Compt. rend.*, 1852, 34, 573.

[3] Böttger, *J. prakt. Chem.*, 1858, 73, 491; *Jahresbericht*, 1858, 198; Habermann, *Zeitsch. anorg. Chem.*, 1906, 50, 318.

[4] Péligot, *Compt. rend.*, 1861, 53, 209; Villiers, *ibid.*, 1895, 120, 322. Kohlschütter and Tüscher (*Zeitsch. anorg. Chem.*, 1920, 111, 193) have summarized the methods employed in the preparation of cupric hydroxide, and described the properties of the various products obtained.

[5] van Bemmelen, *Arch. Néerland*, 1897, 30, 1; compare Dawson, *Trans. Chem. Soc.*, 1909, 95, 370.

[6] Paal and Steyer, *Kolloid Zeitsch.*, 1922, 30, 1.

[7] Dawson, *loc. cit.*

[8] Coppock, *Chem. News*, 1896, 73, 262; 1897, 76, 231; Rössing, *Zeitsch. anorg. Chem.*, 1900, 25, 407; Antony and Lucchesi, *Gazzetta*, 1890, 19, 545; Pickering, *Trans. Chem. Soc.*, 1881, 39, 401.

[9] Brauner, *Chem. News*, 1896, 74, 99.

[10] Pickering, *loc. cit.*

[11] Weinschenk, *Zeitsch. Kryst. Min.*, 1890, 17, 486.

[12] Stanek, *Zeitsch. anorg. Chem.*, 1898, 17, 117.

[13] Ortloff, *Zeitsch. physikal. Chem.*, 1896, 19, 208.

[14] Compare Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 61.

[15] Hittorff, *Pogg. Annalen*, 1851, 84, 1.

[16] Damm and Merz, *Ber.*, 1907, 40, 4775.

(p. 269), but more energetic.[1] Its heat of formation from its elements is 11·6 Cal.[2] It dissolves readily in hot, dilute nitric acid, and in solutions of sodium polysulphides.[3]

Copper polysulphides.—An orange-red substance of the formula CuS_3 is obtained by fusing cupric sulphate with sodium carbonate and sulphur. Heating with carbon disulphide converts it into an amorphous, dark-brown substance, Cu_2S_3.[4] Another polysulphide, Cu_2S_5, is stated to be formed by the interaction at 0° C. of a solution of cupric acetate and calcium polysulphide.[5] It has a reddish-brown colour. It is doubtful whether any of these polysulphides is a true chemical compound.

Cupric sulphite.—The normal sulphite is unstable, and has not been isolated. With solutions of cupric sulphate sodium sulphite gives a green precipitate of varying composition, but containing basic salts.[6]

Cupric sulphate, $CuSO_4$.—The sulphate is prepared by the action of dilute sulphuric acid on cupric oxide or carbonate, the salt crystallizing as *pentahydrate* on evaporation. It can also be obtained by dissolving the metal in nitric acid, and decomposing the nitrate by means of sulphuric acid. With access of air, the metal is also converted into the sulphate by sulphuric acid.

Several methods are applicable to the production of cupric sulphate on the manufacturing scale. Old copper plates are heated with excess of sulphur to bright redness in a reverberatory furnace with closed doors until combination is complete. The doors are then opened, and the mass is oxidized at dull-red heat. When oxidation is complete, the hot product is transferred into dilute sulphuric acid, and the clear solution concentrated after decantation. The crystals formed are of a moderate degree of purity. The process is also applicable to coarse copper, and to copper-glance and other sulphur ores of copper.

When the ores contain iron, it is impossible to separate the ferrous sulphate and cupric sulphate by crystallization. If the mixed sulphides are roasted at a suitable temperature, the ferrous sulphate formed is converted into oxide. Another method of separation depends on heating a solution of the two sulphates under pressure at 180° C., the ferrous salt crystallizing out.[7] For agricultural purposes the removal of the iron is unnecessary.

Crude copper or one of its ores can also be roasted in air, and transformed into the sulphate by the action of sulphur dioxide.[8]

The copper can first be converted into cupric chloride by the action of chlorine and water. With sulphuric acid the salt formed reacts to produce cupric sulphate and hydrochloric acid.[9]

The formation of cupric sulphate can also be effected by dissolving the oxide in sulphuric acid.[10] If the oxide has been produced from an

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[1] Gluud, *Ber.*, 1922, 55, [B], 952.

[2] Wartenberg, *Zeitsch. physikal. Chem.*, 1909, 67, 446.

[3] Rössing, *Zeitsch. anal. Chem.*, 1902, 41, 1.

[4] Rössing, *Zeitsch. anorg. Chem.*, 1900, 25, 407.

[5] Bodroux, *Compt. rend.*, 1900, 130, 1397.

[6] Chevreul, *Ann. Chim. Phys.*, 1812, [1], 83, 181; Rammelsberg, *Pogg. Annalen*, 1846, 67, 397; Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 44; Millon and Commaille, *Compt. rend.*, 1863, 57, 820.

[7] Gin, *French Patent*, 1903, No. 328800.

[8] Gin, *Chem. News*, 1903, 88, 554; *British Patent*, 1903, No. 5230.

[9] Darier, *French Patent*, 1904, No. 350421.

[10] Coste, *ibid.*, 1908, No. 392617.

ore containing silver or gold, addition to the acid of its own volume of water prevents solution of these metals. Another modification of the process involves roasting the argentiferous ore in a reverberatory furnace, digesting the mass with sulphuric acid, decanting the clear solution from the precipitated lead and gold, and running it into lead-lined vats containing copper plates. The silver, and part of the arsenic and antimony, are deposited on these plates, most of the bismuth being simultaneously precipitated as basic sulphate, and the iron reduced to ferrous sulphate. The cupric sulphate is isolated by crystallization.

An electrolytic method for the manufacture of cupric sulphate depends on the electrolysis of a solution of sodium sulphate, using copper electrodes, and passing a current of carbon dioxide through the liquid. The copper dissolves at the anode, and is precipitated as carbonate at the cathode. The carbonate is subsequently dissolved in sulphuric acid.[1]

The pentahydrate forms azure-blue, triclinic crystals, converted by dehydration into the *trihydrate*, the *monohydrate*, and the white *anhydrous salt*.[2] The respective densities[3] of these forms at ordinary temperature are 2·282, 2·663, 3·289, 3·606, and their transition-temperatures on the absolute scale at 0·1 atm. are 325° C., 339° C., and 401° C.[4]

A table giving the solubility of anhydrous cupric sulphate at various temperatures has been compiled by Meyerhoffer[5] from the results obtained by several investigators.[6]

SOLUBILITY OF CUPRIC SULPHATE.

Temperature, °C.	Grams of Anhydrous Salt per 100 grams Water.	Temperature, °C.	Grams of Anhydrous Salt per 100 grams Water.
—1·6	13·5	60	39·0
0	14·9	70	45·7
15	19·3	80	53·5
25	22·3	90	62·7
30	25·5	100	73·5
40	29·5	104	78·0
50	33·6		

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[1] Kroupa and Campagne, *Oesterr. Zeit. Berg.-Hütt.*, 1906, 53, 611; *J. Soc. Chem. Ind.*, 1906, 25, 78; compare Palas and Cotta, *British Patents*, 1899, No. 9806; 1900, No. 17485.

[2] Compare Bell and Taber, *J. Physical Chem.*, 1908, 12, 171; Warijukow, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 688.

[3] Thorpe and Watts, *Trans. Chem. Soc.*, 1880, 37, 106; Retgers, *Zeitsch. physikal. Chem.*, 1889, 3, 311; Clarke, *Constants of Nature*, 2nd ed., Washington, 1888, 1, 86; Andreae, *Zeitsch. physikal. Chem.*, 1911, 76, 421.

[4] Biltz, *Zeitsch. physikal. Chem.*, 1909, 67, 561.

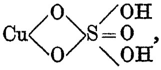
[5] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 537.

[6] Mulder, *Bydragen tot de geschiedenis van het scheikundig gebondenen water*, Rotterdam, 1864, 79; Engel, *Compt. rend.*, 1886, 102, 113; Trevor, *Zeitsch. physikal. Chem.*, 1891, 7, 470; de Coppet, *ibid.*, 1897, 22, 239; Cohen, *Zeitsch. Elektrochem.*, 1903, 9, 433.

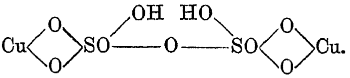
References to other researches on the solubility of cupric sulphate are appended.[1]

The investigations of Lescœur[2] on the vapour-pressure of the hydrates confirm the assumption of the existence of the pentahydrate, trihydrate, and monohydrate. MacLeod-Brown[3] has suggested two formulæ for the pentahydrate to explain the step-by-step removal of water.

A detailed examination of the mechanism of the dehydration of the pentahydrate has been made by Guareschi.[4] Over calcium chloride at 21° to 23° C., or in air at 45° to 50° C., it loses two molecules of water forming the pale sky-blue trihydrate. In a thermostat at 60° C. the trihydrate gives up two more molecules of water, but exposure to air at the ordinary temperature reconverts it into the pentahydrate. The molecule of water present in the monohydrate is expelled at 206° C. and not at 114° C. as stated by Pierre, the elimination of the second hal taking place slowly. Guareschi regards the monohydrate as having the formula



, and the semihydrate as



The heat of formation of the anhydrous salt from its elements i given as 181·7 Cal.[5] and 182·6 Cal.[6]

With excess of cupric sulphate reduction with hypophosphorou acid yields metallic copper, but with excess of the acid cuprous hydrid is precipitated.[7] Cupric sulphate is also reduced by hydroxylamine.[8]

Copper forms a number of basic sulphates, among them the minera *langite*,[9] $CuSO_4,3CuO,4H_2O$, prepared artificially by Sabatier[10] by th interaction of cupric hydroxide and a solution of cupric sulphate. Th mineral *brochantite*, $2CuSO_4,5Cu(OH)_2$, has been prepared in th laboratory from cupric-sulphate solution by the action of limestone.[1 Shenstone[12] has described a crystalline sulphate, $CuSO_4,2Cu(OH)$ On mixing concentrated solutions of cupric sulphate and ammoniur carbonate, and diluting the deep-purple solution, a voluminou blue precipitate of the formula $15CuO,SO_3$ is produced.[13] Othe basic sulphates of this type are $3CuO,SO_3$; $4CuO,SO_3$; $5CuO,SO_3$

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[1] Poggiale, *Ann. Chim. Phys.*, 1843, [3], 8, 463; Tobler, *Annalen*, 1855, 95, 193 Brandes and Firnhaber, *Gmelin-Kraut's Handbuch der anorg. Chem.*, 6th ed., Heidelber 1872–1897, 3, 631; Patrick and Aubert, *Trans. Kansas Acad. Sci.*, 1874, 19; Étar *Compt. rend.*, 1887, 104, 1614; 1892, 114, 112; *Ann. Chim. Phys.*, 1894, [7], 2, 503 Cohen, *Zeitsch. Elektrochem.*, 1903, 9, 433; Cohen, Chattaway, and Tombrock, *Zeitsc physikal. Chem.*, 1907, 60, 706.

[2] Lescœur, *Compt. rend.*, 1886, 102, 1466; *Ann. Chim. Phys.*, 1890, [6], 21, 511 compare Frowein, *Zeitsch. physikal. Chem.*, 1887, 1, 11; Andreae, *ibid.*, 1891, 7, 260 Müller-Erzbach, *ibid.*, 1896, 19, 135.

[3] MacLeod-Brown, *Chem. News*, 1914, 109, 123.

[4] Guareschi, *Atti R. Accad. Sci. Torino*, 1915, 50, 1125; compare Pierre, *Ann. Chi Phys.*, 1846, [3], 16, 241, 250; Merwin, *J. Washington Acad. Sci.*, 1914, 4, 494.

[5] Berthelot, *Thermochimie*, Paris, 1897, 2, 323.

[6] Thomsen, *Thermochemistry* (Longmans, 1908), 324.

[7] Sieverts and Major, *Zeitsch. anorg. Chem.*, 1909, 64, 29.

[8] Adams and Overman, *J. Amer. Chem. Soc.*, 1909, 31, 637.

[9] Graham, *Annalen*, 1839, 29, 29.

[10] Sabatier, *Compt. rend.*, 1897, 125, 10

[11] Becquerel, *Compt. rend.*, 1852, 34, 573.

[12] Shenstone, *Trans. Chem. Soc.*, 1885, 47, 375.

[13] Pickering, *ibid.*, 1909, 95, 1409.

and $10CuO,SO_3$.[1] A basic sulphate of the approximate composition $7CuO,2SO_3,6H_2O$ has been described by Ost.[2] With a saturated solution of cupric sulphate formaldehyde yields a green, crystalline precipitate of the formula $CuSO_4,CuO$.[3] The product is insoluble in water, but is transformed by moist air into a deep-green, crystalline substance of the composition $CuSO_4,Cu(OH)_2$.

Double sulphates of the type $CuSO_4,M_2SO_4,6H_2O$ are produced by the interaction of cupric sulphate and the sulphates of the alkali-metals and ammonium. These double salts are isomorphous.[4] The dissociation-pressures of those with M=K, or Rb, or Cs, or NH_4 have been investigated by Caven and Ferguson.[5] They could not prepare the hexahydrate of sodium cupric sulphate, $CuSO_4,Na_2SO_4,6H_2O$, but only the dihydrate. Potassium cupric sulphate, $CuSO_4,K_2SO_4,6H_2O$, is present in lava from Vesuvius, the mineral being known as *cyanochroite*.[6] A double salt of the formula $CuSO_4,(NH_4)_2SO_4$ has also been prepared.[7] The mineral *kroehnkite*, $CuSO_4,Na_2SO_4,2H_2O$, is found in the Atacama Desert. It was prepared by Graham [8] by the interaction of solutions of cupric sulphate and sodium hydrogen sulphate, although no double salt was obtained by him from the normal sulphate. The solubility-relations of the hydrates $CuSO_4,5H_2O$ and $Na_2SO_4,10H_2O$ have been investigated by Koppel,[9] his results pointing to the possibility of the existence in the solution of a double salt of the formula

$$Na_2[Cu(SO_4)_2],2H_2O.$$

Cupric sulphate forms isomorphous double salts with zinc, ferrous, cobalt, nickel, manganese, cadmium, and magnesium sulphates. With zinc sulphate three crystalline types have been prepared [10]: almost colourless, rhombic prisms with $7H_2O$; pale-blue, monoclinic crystals with $7H_2O$; dark-blue, triclinic crystals with $5H_2O$. With ferrous sulphate monoclinic and triclinic double salts are formed.[11] Cobalt sulphate behaves similarly, the red, monoclinic crystals containing a high percentage of cobalt, and the blue, triclinic crystals a high percentage of copper. Nickel sulphate yields three series of double salts analogous to those obtained from the zinc salt.[12] For manganese sulphate the stable form is the triclinic, with $5H_2O$, but below 18° C. monoclinic crystals with $7H_2O$ also exist.[13] Cadmium sulphate forms two series of double salts: almost colourless, monoclinic crystals with approximately $3H_2O$; and blue, triclinic crystals with $5H_2O$.[14] With

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[1] Pickering, *Trans. Chem. Soc.*, 1907, 91, 1988; 1910, 97, 1851.

[2] Ost, *Zeitsch. angew. Chem.*, 1911, 24, 1892.

[3] Pozzi-Escot, *Bull. Soc. chim.*, 1913, [4], 13, 816.

[4] Fock, *Zeitsch. Kryst. Min.*, 1897, 28, 337.

[5] Caven and Ferguson, *Trans. Chem. Soc.*, 1922, 121, 1406.

[6] Compare Perot, *Archives Genève*, 1893, 29, 28, 121; Tutton, *Trans. Chem. Soc.*, 1896, 59, 344.

[7] Klobb, *Compt. rend.*, 1892, 115, 230.

[8] Graham, *Phil. Mag.*, 1835, [3], 6, 420.

[9] Koppel, *Zeitsch. physikal. Chem.*, 1902, 42, 1.

[10] Retgers, *ibid.*, 1894, 15, 571; Stortenbeker, *ibid.*, 1897, 22, 60; Hollmann, *ibid.*, 1901, 37, 193; 1905, 54, 98; Foote, *Amer. Chem. J.*, 1901, 26, 418.

[11] Retgers, *loc. cit.*

[12] Retgers, *loc. cit.*; Dufet, *Bull. Soc. Min.*, 1888, 11, 217; Fock, *Zeitsch. Kryst. Min.*, 1897, 28, 337.

[13] Retgers, *Zeitsch. physikal. Chem.*, 1895, 16, 583; Stortenbeker, *ibid.*, 1900, 34, 108; Hollmann, *ibid.*, 1901, 37, 193; 1902, 40, 575.

[14] Retgers, *loc. cit.*

magnesium sulphate three types are produced at ordinary temperatures: almost colourless, rhombic prisms with $7H_2O$; light-blue, monoclinic crystals with $7H_2O$; dark-blue, triclinic crystals with $5H_2O$.[1]

Complex salts of cupric sulphate with cupric chloride, potassium sulphate, and potassium chloride have been described.[2]

With ammonia, cupric sulphate combines to form complex derivatives. Thermochemical data[3] indicate the existence of $CuSO_4,NH_3$; $CuSO_4,2NH_3$; $CuSO_4,4NH_3$; and $CuSO_4,5NH_3$. The existence of the complex $CuSO_4,4NH_3$ has also been postulated from physical measurements.[4] The compound $CuSO_4,4NH_3,H_2O$ can be prepared by passing ammonia into a solution of cupric sulphate. It is stable in dry air.[5] The compound $CuSO_4,5NH_3$ has been prepared by Rose[6] and by Mendeléeff.[7]

In alcoholic solution cupric sulphate combines with nitric oxide to form a double compound of the formula $CuSO_4,NO$.[8]

Cupric selenide, $CuSe$.—Hydrogen selenide precipitates cupric selenide from solutions of cupric salts, and it is also produced by the action of selenium-vapour on copper.[9] It is a greenish-black substance, of density 6·66.

Cupric selenite, $CuSeO_3$.—At 360° C. cupric oxide combines with selenium dioxide to form the selenite as green rods insoluble in water.[10]

Double Copper Selenates.—Tutton[11] has investigated the crystallographic properties of double selenates of the series $R_2SeO_4,CuSeO_4,6H_2O$, R representing potassium, rubidium, cæsium, or ammonium. They are isomorphous with the monoclinic double salts formed by cupric sulphate with the sulphates of potassium, rubidium, cæsium, and ammonium.[12]

Cupric telluride, $CuTe$.—The telluride is stated to be formed by the action of tellurium-powder on a solution of cupric acetate in presence of sulphur dioxide.[13] It can also be precipitated from a solution of sodium telluride, Na_2Te; a *sesquitelluride*, Cu_2Te_3, is obtained similarly from the polytelluride Na_4Te_3 (p. 130).[14] A telluride of the formula Cu_4Te_3 occurs as the mineral *rickardite*.

Cupric thiosulphates.—Complex *cupric alkali thiosulphates* have been prepared by Dutoit.[15]

Cupric dithionate, $CuS_2O_6,5H_2O$.—The triclinic pentahydrate is pre-

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[1] Retgers, *Zeitsch. physikal. Chem.*, 1894, 15, 571; Hollmann, *ibid.*, 1901, 37, 193.

[2] Schreinemakers and de Baat, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 533.

[3] Bouzat, *Compt. rend.*, 1902, 135, 292, 534.

[4] Compare Reychler, *Bull. Soc. chim.*, 1895, [3], 13, 387; *Ber.*, 1895, 28, 555; Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 910; Immerwahr, *Zeitsch. anorg. Chem.*, 1900, 24, 269; Dawson and McCrae, *Trans. Chem. Soc.*, 1900, 77, 1239; 1901, 79, 1072; Gaus, *Zeitsch. anorg. Chem.*, 1900, 25, 236; Perman, *Trans. Chem. Soc.*, 1902, 81, 487; Bouzat, *Compt. rend.*, 1902, 134, 1216; *Ann. Chim. Phys.*, 1903, [7], 29, 305; Locke and Forssall, *Amer. Chem. J.*, 1904, 31, 268; Dawson, *Trans. Chem. Soc.*, 1906, 89, 1666; Horn, *Amer. Chem. J.*, 1907, 38, 475.

[5] Horn and Taylor, *Amer. Chem. J.*, 1904, 32, 253; compare Horn, *ibid.*, 1907, 38, 475; Andrée, *Compt. rend.*, 1885, 100, 1138.

[6] Rose, *Pogg. Annalen*, 1830, 20, 150.

[7] Mendeléeff, *Ber.*, 1870, 3, 422.

[8] Manchot, *Ber.*, 1914, 47, 1601.

[9] Little, *Annalen*, 1859, 112, 211.

[10] Espil, *Compt. rend.*, 1911, 152, 378.

[11] Tutton, *Proc. Roy. Soc.*, 1920, [A], 98, 67.

[12] Compare pp. 227–230.

[13] Parkman, *Jahresbericht*, 1861, 126; *Amer. Chem. J.*, 1862, [2], 33, 328.

[14] Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 902.

[15] Dutoit, *J. Chim. phys.*, 1913, 11, 650.

cipitated by the interaction of solutions of cupric sulphate and barium dithionate.[1] It is very soluble in water. The heat of formation of the pentahydrate from the elements and water is 268·4 Cal.[2]

Cupric tetrathionate, CuS_4O_6.—Concentration of a solution of cupric hydroxide in aqueous tetrathionic acid yields the crystalline tetrathionate.[3]

Cupric hydrazoate, $Cu(N_3)_2$.—The only cupric nitride known is the hydrazoate, a highly explosive substance of deep reddish-brown colour. It is formed by dissolving copper in hydrazoic acid, and by the action of sodium hydrazoate on cupric sulphate.[4]

Cupric nitrite.—The nitrite is only known in solution, prepared by addition of lead nitrite to cupric-sulphate solution.[5] Exposure of its dilute solution to air causes slow formation of nitrate. On evaporation of a concentrated solution over sulphuric acid, there is partial decomposition in accordance with the equation [6]

$$3Cu(NO_2)_2=Cu(NO_3)_2+2CuO+4NO.$$

It forms a number of complex nitrites with other metals.[7]

Cupric nitrate.—Crystallization of a solution of cupric oxide or carbonate in dilute nitric acid yields the nitrate in the form of deliquescent hydrates. Below −20·5° C. the *nonahydrate* crystallizes; below 24·5° C. the *hexahydrate* [8] in blue, tabular crystals; and above this temperature the *trihydrate* in prismatic, columnar crystals, m.p.[9] 114·5° C., density [10] 2·047. The *anhydrous salt* is prepared by treating the dried powder with nitric acid containing excess of nitric anhydride, and drying the residue over calcium oxide and phosphoric oxide.[11] It is a white, deliquescent substance, which begins to decompose at 155° to 160° C.[12] At red heat it is converted into cupric oxide. The effect of the radium emanation is mentioned on p. 55. At 8° C. its heat of solution is 10·47 Cal. The heat of formation of the anhydrous salt from its elements is 71·49 Cal.[13]; that in solution is 81·96 Cal.[14] Thomsen's value [15] for the heat of formation of the hexahydrate from the anhydrous salt and liquid water is 21·18 Cal., and from its elements and water 92·94 Cal. It yields a green, *basic salt,* $Cu(NO_3)_2,3Cu(OH)_2$. A complex ammonia derivative, $Cu(NO_3)_2,7NH_3$, is formed in pale-blue crystals by the action of reduced copper on silver nitrate in presence of liquid ammonia. In vacuum over sulphuric acid it changes to pale-violet crystals, $Cu(NO_3)_2,4NH_3$.[16]

Cupric phosphide, Cu_3P_2.—This phosphide is a black substance

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[1] Heeren, *Pogg. Annalen,* 1826, 7, 181.
[2] Compare Thomsen, *Thermochemistry* (Longmans, 1908), 326.
[3] Chancel and Diacon, *Compt. rend.,* 1863, 56, 710.
[4] Curtius and Rissom, *J. prakt. Chem.,* 1898, [2], 58, 261.
[5] Hampe, *Annalen,* 1863, 125, 345.
[6] Râу, *Trans. Chem. Soc.,* 1907, 91, 1405.
[7] Kurtenacker, *Zeitsch. anorg. Chem.,* 1913, 82, 204.
[8] Graham, *Annalen,* 1839, 29, 13.
[9] Funk, *Zeitsch. anorg. Chem.,* 1899, 20, 412.
[10] Playfair and Joule, *Mem. Chem. Soc.,* 1845, 2, 401; 1847, 3, 57.
[11] Guntz and Martin, *Bull. Soc. chim.,* 1909, [4], 5, 1004.
[12] Compare Rolla, *Gazzetta,* 1915, 45, i., 444.
[13] de Forcrand, *Compt. rend.,* 1913, 157, 441.
[14] de Forcrand, *Ann. Chim.,* 1915, [9], 3, 5.
[15] Thomsen, *Thermochemistry* (Longmans), 1908, 324.
[16] Guntz and Martin, *Bull. Soc. chim.,* 1910, [4], 7, 313.

formed by heating cupric chloride in phosphine.[1] Other phosphides of the formulæ Cu_5P_2, CuP_2,[2] and CuP_5[3] have been described, but it is doubtful whether they are true chemical compounds.

Cupric hypophosphite, $Cu(H_2PO_2)_2$.—The solution obtained by addition of slightly less than the equivalent proportion of barium hypophosphite to a solution of cupric sulphate yields, after removal of the barium sulphate and addition of alcohol, the hypophosphite in the form of white crystals.[4] At ordinary temperatures the dry salt does not decompose for several days, but at 90° C. it explodes with evolution of phosphine. On warming in aqueous solution, it decomposes with formation of phosphorous acid, copper, and hydrogen. Its aqueous solution is also decomposed catalytically by palladium :

$$Cu(H_2PO_2)_2+2H_2O=2H_3PO_3+Cu+H_2.$$

Cupric phosphite, $CuHPO_3,2H_2O$.—A phosphite of this formula is obtained by the interaction of solutions of diammonium hydrogen phosphite and cupric chloride, or of phosphorous acid and cupric acetate.[5] It is unstable, but admits of drying at a medium temperature.

Cupric orthophosphate, $Cu_3(PO_4)_2,3H_2O$.—The orthophosphate is prepared by the interaction of disodium hydrogen phosphate and excess of cupric sulphate,[6] or by heating an aqueous solution of orthophosphoric acid with cupric carbonate at 70° C.[7] It is a blue, crystalline powder, almost insoluble in water.

The *basic orthophosphate*, $Cu_3(PO_4)_2,Cu(OH)_2$, occurs as *libethenite* in the form of dark-green crystals, produced artificially by heating the orthophosphate with water.[7] In combination with two molecules of water it also occurs as *tagilite*.

Cupric pyrophosphate, $Cu_2P_2O_7$.—The anhydrous salt is precipitated as a greenish-white powder by addition of sodium pyrophosphate to a solution of a cupric salt.[8] The *pentahydrate* crystallizes from a solution containing cupric sulphate and sodium metaphosphate.[9]

Cupric metaphosphate, $Cu(PO_3)_2$.—The metaphosphate is formed by evaporating to dryness an aqueous solution of cupric nitrate and orthophosphoric acid, and heating the residue at 316° C.[10] The *tetrahydrate* is prepared by precipitating with alcohol a solution of cupric sulphate and sodium metaphosphate.[11]

Cupric arsenites.—A pigment of varying composition is prepared as a canary-green precipitate by mixing solutions of an alkali-metal arsenite and cupric sulphate.[12] It is known as *Scheele's green.* Other cupric derivatives of arsenious acid are also known.[13]

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[1] Rose, *Pogg. Annalen*, 1826, 6, 206 ; 1832, 24, 295 ; compare Böttger, *Jahresbericht*, 1857, 107.

[2] Rubenovitch, *Compt. rend.*, 1898, 127, 270 ; 1899, 129, 336 ; Granger, *ibid.*, 1895, 120, 923 ; 1896, 122, 1484.

[3] Bossuet and Hackspill, *ibid.*, 1913, 157, 720.

[4] Engel, *ibid.*, 1899, 129, 518.

[5] Rose, *Pogg. Annalen*, 1828, 12, 291 ; Wurtz, *Ann. Chim. Phys.*, 1846, [3], 16, 199 ; Rammelsberg, *Pogg. Annalen*, 1867, 132, 491.

[6] Steinschneider, *Dissertation*, Halle, 1890.

[7] Debray, *Ann. Chim. Phys.*, 1861, [3], 61, 439.

[8] Persoz, *ibid.*, 1847, [3], 20, 315 ; Fleitmann and Henneberg, *Annalen*, 1848, 65, 387.

[9] Wiesler, *Zeitsch. anorg. Chem.*, 1901, 28, 201.

[10] Maddrell, *Annalen*, 1847, 61, 60.

[11] Fleitmann, *Pogg. Annalen*, 1849, 78, 242.

[12] Bloxam, *J. Chem. Soc.*, 1862, 15, 281.

[13] Reichard, *Ber.*, 1894, 27, 1019 ; Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 1.

Cupric arsenate, $Cu_3(AsO_4)_2$.—The arsenate occurs as *pentahydrate* under the name *trichalcite.* The *tetrahydrate* is produced by heating cupric nitrate with calcium arsenate, or copper with a solution of arsenic acid,[1] and also by the interaction of cupric chloride and silver arsenate.[2] Concentration at 70° C. of a solution of cupric carbonate in excess of arsenic acid yields pale-blue leaflets of the formula $CuHAsO_4,H_2O$.[3] Other acidic salts,[4] and also basic salts,[5] are known.

Cupric metantimonite, $Cu(SbO_2)_2$.—The metantimonite is obtained in light-green crystals by addition of cupric sulphate to an alkaline solution of antimonious oxide or of potassium antimonyl tartrate.[6]

Cupric pyroantimonate.—The pyroantimonate is known only in the form of a double salt with ammonia, $Cu_2Sb_2O_7,4NH_3,4H_2O$,[7] and as basic and acidic salts.[8]

Cupric metantimonate, $Cu(SbO_3)_2,5H_2O$.—The *pentahydrate* is obtained as a bluish-green precipitate by addition of potassium metantimonate to a solution of cupric sulphate.[9]

Cupric carbide or acetylide.—There is some evidence of the direct combination of copper and carbon at high temperatures to form a carbide. The substance is endothermic, and dissociates rapidly in the neighbourhood of 1600° C., but less rapidly at lower temperatures.[10] With ammoniacal solutions of cupric salts acetylene yields a flocculent, black precipitate of varying composition, but approximating to the formula CCu_2. It explodes at 70° to 80° C.[11]

Cupric carbonates.—The normal salt has not been prepared.[12] *Malachite,* $CuCO_3,Cu(OH)_2$, occurs in monoclinic crystals, density 3·7 to 4. It has been produced artificially.[13] *Azurite,* $2CuCO_3,Cu(OH)_2$, forms monoclinic crystals, density 3·5 to 3·88. It has been obtained by a laboratory method.[14]

The formation of *basic carbonates* of copper by the interaction of solutions of cupric sulphate and of the carbonates of sodium has been investigated by Pickering.[15] Sodium carbonate precipitates a blue, basic carbonate, $5CuO,2CO_2,nH_2O$, which is converted by drying over sulphuric acid at 100° C. into another hydrate of green colour, $5CuO,2CO_2,3H_2O$. In moist air the green hydrate becomes reconverted into the blue form :

$$5CuSO_4+8Na_2CO_3+3H_2O=5CuO,2CO_2+5Na_2SO_4+6NaHCO_3.$$

The blue carbonate is transformed by concentrated aqueous sodium carbonate into cupric hydroxide, and by aqueous sodium hydrogen carbonate into malachite, $2CuO,CO_2,H_2O$. Pickering considered ordinary

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[1] Coloriano, *Bull. Soc. chim.*, 1886, [2], 45, 241, 707, 709.
[2] Hirsch, *Dissertation*, Halle, 1891.
[3] Debray, *Ann. Chim. Phys.*, 1861, [3], 61, 419.
[4] Salkowski, *J. prakt. Chem.*, 1868, 104, 166.
[5] Coloriano, *loc. cit.*, ; Debray, *loc. cit.*
[6] Harding, *Zeitsch. anorg. Chem.*, 1899, 20, 235.
[7] Schiff, *Annalen*, 1862, 123, 39.
[8] Delacroix, *Bull. Soc. chim.*, 1899, [3], 21, 1049; 1901, [3], 25, 289.
[9] Allen, *Chem. News*, 1880, 42, 193; Senderens, *Bull. Soc. chim.*, 1899, [3], 21, 47.
[10] Briner and Senglet, *J. Chim. phys.*, 1915, 13, 351.
[11] Söderbaum, *Ber.*, 1897, 30, 760.
[12] Compare Wagner, *J. prakt. Chem.*, 1867, 102, 235.
[13] Becquerel, *Compt. rend.*, 1852, 34, 573.
[14] Debray, *ibid.*, 1859, 49, 218.
[15] Pickering, *Trans. Chem. Soc.*, 1909, 95, 1409.

commercial copper carbonate to be similar in constitution to malachite, a view questioned by Dunnicliff and Lal.[1]

Sodium hydrogen carbonate and cupric sulphate react to precipitate a blue, basic carbonate, $5CuO,3CO_2,nH_2O$, converted by drying at 100° C. into another blue hydrate, $5CuO,3CO_2,7H_2O$. Another basic carbonate is also produced in the same reaction. It has the formula $8CuO,3CO_2,6H_2O$, is dark blue in colour, and becomes green at 100° C. No other basic carbonate was isolated by Pickering. All the products are insoluble in water and sodium-carbonate solution, but dissolve slightly in solutions of carbon dioxide and of sodium hydrogen carbonate, with production of the normal carbonate or a double carbonate.

Feist[2] has prepared a basic carbonate, $7CuO,4CO_2,H_2O$, by powdering together crystallized cupric sulphate and sodium carbonate, and then adding water. It is difficult to separate the substance from a basic cupric sulphate simultaneously formed. Auger[3] has described an amorphous basic carbonate of the formula $8CuO,5CO_2,7H_2O$. Another basic carbonate, $7CuO,2CO_2,5H_2O$, has been prepared[4] by the interaction of a mixture of sodium carbonate and sodium hydrogen carbonate with cupric sulphate in aqueous solution. Complex carbonates of copper with sodium and potassium have also been obtained.[5] An example of this type of double salt of the formula $Na_2Cu(CO_3)_2,3H_2O$ crystallizes on addition of a solution of cupric acetate to one of sodium carbonate and sodium hydrogen carbonate at 50° C.[6] It forms needles or rosette-like agglomerations, and above 100° C. it is converted into cupric oxide and sodium carbonate with elimination of water and carbon dioxide. It is decomposed by water, but can be recrystallized from a concentrated solution of sodium carbonate containing sodium hydrogen carbonate.

Cupric cyanide, $Cu(CN)_2$.—The cyanide is obtained as a brownish-yellow precipitate by the interaction of solutions of potassium cyanide and cupric sulphate, but it is very unstable, decomposing at ordinary temperatures into *cupric cuprous cyanide,* $Cu[Cu.(CN)_2]_2,5H_2O$, with evolution of cyanogen. On heating, it is converted into cuprous cyanide. With hydrazine cyanide it unites to form a *monohydrazinate,* $Cu(CN)_2,N_2H_4$, yellow needles insoluble in water, m.p. 160° to 162° C.[7]

Cupric thiocyanate, $Cu(CNS)_2$.—The thiocyanate is formed as a velvet-black precipitate by adding basic cupric carbonate or cupric hydroxide to a solution of thiocyanic acid, and by the interaction of potassium thiocyanate and concentrated solutions of cupric salts.[8] It is very unstable, being transformed by contact with water into cuprous thiocyanate.[9] With ammonium hydroxide it yields blue, acicular crystals of *ammonio-cupric thiocyanate,* $Cu(CNS)_2,2NH_3$, also produced by dissolving cupric hydroxide in ammonium thiocyanate.[10]

Cupric silicates.—The emerald-green, hexagonal *dioptase,* $CuSiO_3,H_2O$, has the density 3·28 to 3·35. The turquoise-blue *chrysocolla* has density

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[1] Dunnicliff and Lal, *Trans. Chem. Soc.*, 1918, 113, 718.

[2] Feist, *Arch. Pharm.*, 1909, 247, 439.

[3] Auger, *Compt. rend.*, 1914, 158, 944.

[4] Dunnicliff and Lal, *loc. cit.*

[5] Pickering, *Trans. Chem. Soc.*, 1909, 95, 1409; 1911, 99, 800.

[6] Applebey and Lane, *ibid.*, 1918, 113, 609.

[7] Franzen and Lucking, *Zeitsch. anorg. Chem.*, 1911, 70, 145.

[8] Meitzendorff, *Pogg. Annalen*, 1842, 56, 63. Söderbäck (*Annalen*, 1919, 419, 217) prepared it by the action of thiocyanogen (p. 320) in ether solution on cuprous thiocyanate.

[9] Claus, *J. prakt. Chem.*, 1838, 15, 403.

[10] Grossman, *Zeitsch. anorg. Chem.*, 1908, 58, 265.

2 to 2·34. Colloidal, basic precipitates are obtained by mixing solutions of alkali-metal silicates and cupric salts.

Cupric metaborate, $Cu(BO_2)_2$.—The metaborate is prepared by fusing cupric nitrate with excess of boric acid.[1] It forms blue, doubly refracting crystals, density 3·86, and is also known as a hard, vitreous substance of density 3·6.

DETECTION AND ESTIMATION OF COPPER.

In qualitative analysis copper is detected by precipitation as cupric sulphide from hydrochloric-acid solutions of its salts. To prevent the formation of a colloidal precipitate, the solution should be hot, and should contain excess of the acid. The sulphide is soluble in hot, dilute nitric acid, and in potassium-cyanide solution, but almost insoluble in solutions of alkali-metal sulphides. It dissolves to some extent in ammonium-sulphide solution. Other aids in the detection of copper are the blue colour of solutions of cupric-ammonia salts ; the reddish-brown precipitate of cupric ferrocyanide, produced by addition of potassium ferrocyanide to cupric solutions ; the formation of an intense purple coloration by the interaction of hydrogen bromide and cupric salts, a very delicate reaction [2] ; the formation of a bluish-green borax bead ; and the ready isolation of the metal from its compounds by the action of reducers.

On stirring a mixture of a few cubic centimetres of a solution of titanous sulphate and one litre of a 0·01 per cent. solution of cupric sulphate, metallic copper separates after an interval of a few minutes. Most of the finely divided metal passes through a filter-paper, the colour of the solution being blue by transmitted light, and copper-red by reflected light. The reaction affords a sensitive test for copper, since by its aid one part of the metal can be detected in one million parts of solution.[3]

Another delicate test for copper salts is afforded by the use of the solution obtained by addition of a trace of hydrogen peroxide to the Kastle-Meyer reagent, which consists of a 2 per cent. solution of phenolphthalein in a 20 per cent. solution of potassium hydroxide decolorized by boiling with zinc-powder. The liquid gives a pink coloration with one part of a copper salt dissolved in 100,000,000 parts of water.[4]

Cupric salts in 0·00001 N-concentration can be detected by the formation of a turbidity with a mixture in solution of an alkali-metal thiocyanate and either gallic acid, tannic acid, catechol, or quinol.[5]

Cuprous salts are distinguished from cupric salts by the colourless nature of their solutions, and by the precipitation of yellow to red cuprous oxide on addition of alkali-metal hydroxides.

There is a great variety of quantitative methods available for the estimation of copper. Gravimetrically it is estimated as cupric oxide, obtained by ignition of the precipitated hydroxide ; by precipitation as sulphide, and ignition in an atmosphere of hydrogen to cuprous sulphide ; by precipitation as cuprous thiocyanate, CuCNS, this salt being either weighed directly, or converted into cuprous sulphide ; and by electrolytic

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[1] Guertler, *Zeitsch. anorg. Chem.*, 1904, 38, 456.

[2] Denigès, *Compt. rend.*, 1889, 108, 568 ; *Bull. Soc. chim.*, 1894, [3], 11, 1024 ; Sabatier, *Compt. rend.*, 1894, 118, 980 ; *Revue internat. Falsific.*, 1894, 7, 101.

[3] Knecht, *Ber.*, 1908, 41, 498.

[4] Thomas and Carpentier, *Compt. rend.*, 1921, 173, 1082.

[5] Falciola, *Giorn. Chim. Ind. Applic.*, 1921, 3, 354. The turbidity is due to cuprous thiocyanate.

deposition of the metal from an acidic[1] or alkaline[2] solution. It can also be estimated by precipitation as acetylide from ammoniacal, neutral, or slightly acidic solutions of cupric salts.[3] Another method depends on reduction to copper by hypophosphorous acid or alkali hypophosphite, and ignition to cupric oxide.[4] Hydroxylamine hydrochloride has also been suggested as a reagent for its estimation.[5]

Numerous volumetric methods for the estimation of copper have been described. Volhard's process consists in reducing with sulphurous acid in presence of a slight excess of ammonium thiocyanate, the copper being precipitated as cuprous thiocyanate, and the excess of ammonium thiocyanate estimated by titration with silver nitrate in presence of a ferric salt as indicator.[6] Parkes's method depends on titration of a blue cupric-ammonia solution with standard potassium cyanide, the end-point of the reaction being indicated by the disappearance of the colour. Stannous chloride can also be employed in the volumetric estimation of copper, a boiling solution of cupric chloride in concentrated hydrochloric acid being titrated with this reagent until the yellow colour of the solution is discharged. In Haen's method an acetic-acid solution of the cupric compound is mixed with excess of potassium iodide, and the free iodine estimated with standard thiosulphate. Another process involves conversion of the copper into cuprous thiocyanate, and titration of this salt with potassium iodate.[7] Chloroform is added to dissolve the iodine initially liberated, and the completion of the reaction is marked by the disappearance of the violet colour of the solution:

$$4CuSCN+7KIO_3+14HCl=4CuSO_4+7KCl+7ICl+4HCN+5H_2O.$$

References to other methods are appended.[8]

A gasometric method for the estimation of cupric salts is based on the reduction of cupric-ammonia solutions by a hydrazine salt, a cuprous-ammonia solution being formed, and the hydrazine oxidized to nitrogen and water:

$$4(CuSO_4,5H_2O)+N_2H_4,H_2SO_4+10NaOH$$
$$=5Na_2SO_4+2Cu_2O+28H_2O+N_2.$$

The volume of the evolved nitrogen can be measured,[9] or its weight can be determined by means of an apparatus similar to that employed by von Schrötter in the estimation of carbon dioxide.[10]

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[1] Foerster, *Ber.*, 1906, 39, 3029; *Zeitsch. Elektrochem.*, 1907, 13, 561; Hawley, *Eng. and Min. J.*, 1920, 110, 162.

[2] Spitzer, *Zeitsch. Elektrochem.*, 1905, 11, 345, 391; Flanigen, *J. Amer. Chem. Soc.*, 1907, 29, 455.

[3] Söderbaum, *Ber.*, 1897, 30, 902, 3014.

[4] Dallimore, *Pharm. J.*, 1909, [4], 29, 271; compare Hanuš and Soukup, *Zeitsch. anorg. Chem.*, 1911, 70, 282; Cavazzi, *Boll. chim. Farm.*, 1912, 51, 437; Windisch, *Zeitsch. anal. Chem.*, 1913, 52, 1, 619; Hanuš, *ibid.*, 616.

[5] Bayer, *Zeitsch. anal. Chem.*, 1912, 51, 729.

[6] Compare Theodor, *Chem. Zeit.*, 1908, 32, 889; Kuhn, *ibid.*, 1056.

[7] Jamieson, Levy, and Wells, *J. Amer. Chem. Soc.*, 1908, 30, 760.

[8] Gooch and Ward, *Amer. J. Sci.*, 1909, 62, 348; Bacovescu and Vishuta, *Ber.*, 1909, 42, 2638. A summary of the applications of organic compounds to the estimation of copper and of other metals has been given by Chaston Chapman (*Trans. Chem. Soc.*, 1917, 111, 203).

[9] Ebler, *Zeitsch. anorg. Chem.*, 1905, 47, 371.

[10] de Saporta, *Rev. gén. Chim. pure et appl.*, 1907, 10, 338; Pozzi-Escot, *Bull. Assoc. chim. Sucr. Dist.*, 1908, 26, 267.

CHAPTER X.

SILVER.

Symbol, Ag. Atomic weight, 107·88 (O=16).

Occurrence.—Silver is found in nature both in the free state[1] and in combination. Its principal ores are *argentite*, Ag_2S; *dyscrasite*, Ag_2Sb to Ag_6Sb; *hessite*, Ag_2Te; *horn-silver*, AgCl; *stephanite*, $5Ag_2S,Sb_2S_3$; *pyrargyrite*, $3Ag_2S,Sb_2S_3$; *proustite*, $3Ag_2S,As_2S_3$; *stromeyerite*, Ag_2S,Cu_2S; *polybasite*, $9(Ag_2S,Cu_2S),Sb_2S_3,As_2S_3$; *fahlore*, a complex sulphide of silver, arsenic, and antimony; the bromide and iodide; and amalgams of varying composition. It is also associated with native sulphides, such as galena, chalcopyrite, and zincblende. Sea-water contains about 0·001 mg. per litre.

History.—The metal has been known and prized from prehistoric times, and very early records refer to it as a means of exchange. It has long been employed in the manufacture of articles of jewellery, and for coinage. The alchemical name was *luna*, the sign being that of the crescent moon. The name "lunar caustic," still applied to the nitrate, is obviously a survival of the nomenclature of the alchemists. The name "silver" is probably connected with the bright lustre of the element, the Greek word ἄργυρος being derived from ἀργός, shining. The Latin name, *argentum*, is closely related to the Greek.

Chikashige[2] has observed the presence of silver, in association with other metals, in specimens of Chinese money dating from 722 to 481 B.C.; and also in a Corean mirror of the tenth century A.D.

Preparation.[3]—The methods employed in the manufacture of silver from its ores can be classified in three main divisions: (1) *amalgamation*, employed in countries where fuel is scarce; (2) *lixiviation*; (3) *smelting*, the metal being subsequently separated from metallic lead or copper.

(1) AMALGAMATION.

Various modifications of the amalgamation process have been employed in Mexico and Chile, but in recent years this method has been to a great extent supplanted by the cyanide process, described on p. 291. Extraction by amalgamation is more difficult with silver than with gold. Mercury liberates silver rapidly from the chloride, bromide, and iodide, and very slowly from the sulphide. Other ores have to be converted

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[1] On the origin of the natural "hair-silver," compare Kohlschütter and Eydmann, *Annalen*, 1912, 390, 340; 1913, 398, 1.

[2] Chikashige, *Trans. Chem. Soc.*, 1920, 117, 917.

[3] For full metallurgical details, the reader is referred to *The Metallurgy of Silver*, by H. F. Collins (Griffin).

before amalgamation into the chloride, effected by roasting with common salt, or by the action of common salt and copper compounds at the ordinary summer temperature.

In the *patio process* the finely ground ore is mixed in a *patio* or paved courtyard with mercury, common salt, and a mixture of copper and iron sulphates called *magistral*, prepared by roasting copper pyrites. The ore-heap or *torta* is kept moist. The reactions involved are obscure and complex, but it is supposed[1] that some of them can be represented thus:

$$\begin{gathered}\mathrm{Ag_2S+CuCl_2=2AgCl+CuS}\ ;\\ \mathrm{Ag_2S+2FeCl_3=2AgCl+2FeCl_2+S}\ ;\\ \mathrm{2Ag_3AsS_3+3CuCl_2=6AgCl+3CuS+As_2S_3}\ ;\\ \mathrm{2AgCl+2Hg=2HgCl+2Ag}.\end{gathered}$$

The process of amalgamation requires from a fortnight to a month. The amalgam is decomposed by heating in retorts.

The *pan-amalgamation process* has found more favour than the *patio* process. The ore in the form of fine sludge is stirred in iron pans with a mixture of mercury, common salt, and cupric sulphate. When the action is complete, the excess of mercury is drained off, and the amalgam is allowed to settle, and then decomposed by heat. In the *Boss system* the process is continuous, a series of pans and settlers being employed. Some silver ores, notably those containing sulphides of arsenic, antimony, copper, iron, and zinc, are roasted with common salt before amalgamation.

Among the older methods is the *cauldron* or *cazo process* for ores free from sulphur. The ore was reduced by boiling with a solution of common salt in copper vessels, and then amalgamated. In the *Franketina process* sulphide ores were roasted with common salt, and then boiled with a solution of salt in presence of mercury in copper-bottomed vessels. In the *Krönke process* decomposition of the ore is effected by a hot solution of cuprous chloride and common salt, reduction to metallic silver and amalgamation being effected by addition of mercury and an amalgam of lead or zinc. In the obsolete Freiberg *barrel process* sulphide ores were roasted with salt, and amalgamated in rotating barrels with mercury, iron being added to prevent formation of mercury chlorides.

(2) LIXIVIATION.

The silver is dissolved from the ore by an aqueous solution of a salt, and then precipitated as metal or sulphide. The *cyanide process*[2] is the most important of the lixiviation methods, its application having been considerably extended in recent years, especially in Mexico. The ore is very finely crushed with cyanide solution in a stamp-mill, and the sludge produced submitted to agitation and aëration in contact with cyanide solution. The liquid is separated from the ore by the aid of mechanical filters, and the silver precipitated from the clear solution by addition of zinc in the form of dust or shavings. The product is smelted with nitre, and is sometimes refined by blowing air through the molten mass.

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[1] Vondráček, *Rev. de Métallurgie*, 1908, 5, 678.

[2] Caldecott, *J. Chem. Met. Mining Soc. S. Africa*, 1908, 8, 203, 266.

The bulk of the Mexican ore consists of argentite. The cyanide dissolves the silver sulphide:[1]

$$Ag_2S+4NaCN=2NaAg(CN)_2+Na_2S.$$

The aëration oxidizes sodium sulphide to thiosulphate and hydroxide, and ultimately to sulphate. A side-reaction is the formation of thiocyanate:

$$Na_2S+NaCN+H_2O+O=NaCNS+2NaOH.$$

The elimination of sodium sulphide is facilitated by addition of lead oxide or acetate or mercuric chloride, the corresponding sulphide being precipitated. During aëration, the lead sulphide is assumed to be converted into lead oxide, thus explaining the great effect produced by the presence of a very small percentage of lead salts:

$$PbS+NaCN+O=NaCNS+PbO.$$

A combination of lixiviation and cyaniding has also been applied to certain Mexican ores.[2]

The *Ziervogel process* can be worked with argentiferous copper mattes free from lead, arsenic, antimony, and bismuth. By roasting the matte in an oxidizing atmosphere, the iron is converted into sulphate. About 700° C. this substance is decomposed, the copper being converted into sulphate. At 840° to 850° C. the copper salt is converted into cupric oxide,[3] and silver sulphate simultaneously formed. At this point the roasting is stopped, the silver sulphate is extracted with hot water, and the silver precipitated by means of metallic copper. These mattes are now usually worked for copper, and the silver separated electrolytically.

Other obsolete methods include the *Augustin process*, in which the sulphide ore was roasted with salt, and the silver chloride dissolved in hot brine; the *Patera process*, in which the brine was replaced by a solution of sodium thiosulphate; and the *Kiso process*, in which calcium thiosulphate was employed. In the *Russell process* the ordinary extraction with thiosulphate was followed by treatment with sodium copper thiosulphate, or "extra solution," the object being to extract any metallic silver and undecomposed sulphide present.

(3) SMELTING.

Smelting is applied to argentiferous lead and copper ores, the silver being concentrated in the lead or copper produced. The details of lead smelting are given in Vol. V., p. 366, and those of copper smelting in this volume, p. 244.

The pig lead contains about 2 per cent. of silver, and there are three processes for its *desilverization*, the final stage of each being *cupellation*. In the almost obsolete *Pattinson process* the lead is melted and then allowed to crystallize. The first fractions consist of almost pure lead, and the crystals are removed by means of perforated ladles. The crystallization is continued until the residual lead contains about 1 per cent. of silver. In the *Rozan process* the molten metal is agitated by revolving paddles or jets of steam, and the concentration continued up to 2 per cent. In the *Parke process* the silver is extracted from the

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[1] Compare Göpner, *Metallurgie*, 1909, 6, 134, 137.

[2] Brodie, *Mex. Mining J.*, 1911, 12, 21; *J. Inst. Metals*, 1911, 5, 297.

[3] Friedrich, *Metallurgie*, 1910, 7, 323.

lead by successive additions of zinc, the argentiferous zinc rising in crusts to the surface, and being ladled off. After liquation to remove some of the lead, the zinc is distilled from a retort, the residue consisting of lead and about 5 to 10 per cent. of silver. Where a demand for zinc sulphate exists, the zinc is also converted into this salt by oxidation with steam and solution in sulphuric acid.

Cupellation is effected by oxidizing the argentiferous lead in a reverberatory furnace with a hearth of bone-ash, marl, magnesia, or Portland cement and crushed fire-brick, the litharge formed being kept liquid by maintaining the temperature above 900° C. The litharge and the oxides of other base metals flow to the edge of the bath of molten metal, and are drawn off. By cupellation it is possible to obtain silver containing only 0·2 per cent. of impurities, but it has often to be cupelled again with more lead. Different types of cupellation-furnace are employed in Great Britain, the United States, and Germany.

In the electrolytic refining of copper (p. 249) both silver and gold are deposited in the insoluble sludge at the bottom of the vessel, and are subsequently extracted from this sludge, the silver being dissolved by boiling with sulphuric acid, and subsequently precipitated by copper.

Refining.—Various methods are employed in refining silver. The process of parting it from gold is described on p. 326. In addition to gold, the principal impurities are copper, iron, lead, and zinc.

Physical Properties.—Silver is a white, lustrous metal, and in very thin layers has a violet colour by transmitted light; in thicker layers the colour is purple.[1] Such layers are produced by depositing a silver mirror on glass by the action of sodium potassium tartrate on an ammoniacal solution of silver nitrate.[2] Reduced silver in the form of a fine powder has a grey, earth-like appearance.[3] The metal crystallizes in octahedra belonging to the cubic system. The density of the unrolled metal is 10·4923; that of the metal after rolling, 10·5034.[4] Its melting-point is given as 958·3° C.,[5] 960° C.,[6] 960·5° C.,[7] 960·9° C.,[8] 961° C.,[9] 961·5° C.,[10] and 962° C.;[11] and its boiling-point as 1955° C.,[12] and 2040° C.[13] at 760 mm. With the exception of gold, it is the most malleable and ductile of the metals, and can be hammered into leaves 0·0025 mm. thick. Its conductivity for heat and electricity is higher than that of any other substance. Its specific heat is given as 0·05535,[14] 0·0557,[15] and

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[1] Houllevigue, *Compt. rend.*, 1909, 149, 1368; compare Turner, *Proc. Roy. Soc.*, 1908’ [A], 81, 301.

[2] Compare Kohlschütter, *Annalen*, 1912, 387, 86.

[3] Compare Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 367; *Zeitsch. anorg. Chem.*, 1908, 58, 399.

[4] Kahlbaum, Roth, and Siedler, *ibid.*, 1900, 33, 353.

[5] Day and Clement, *Amer. J. Sci.*, 1908, [4], 26, 405.

[6] Day and Sosman, *ibid.*, 1910, [4], 29, 93.

[7] Heycock and Neville, *Trans. Chem. Soc.*, 1895, 67, 1024; Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186.

[8] Waidner and Burgess, *Bull. Bureau Standards*, 1909, 6, 149.

[9] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1.

[10] Quercigh, *Zeitsch. anorg. Chem.*, 1910, 68, 301.

[11] Berthelot, *Ann. Chim. Phys.*, 1902, [7], 26, 58.

[12] Greenwood, *Zeitsch. Elektrochem.*, 1912, 18, 319; *Proc. Roy. Soc.*, 1909, [A], 82, 396; compare *ibid.*, 1910, [A], 83, 483.

[13] Hansen, *Ber.*, 1909, 42, 210; compare von Wartenberg, *Zeitsch. anorg. Chem.*, 1908, 56, 320.

[14] Brönsted, *Zeitsch. Elektrochem.*, 1912, 18, 714.

[15] Schimpff, *Zeitsch. physikal. Chem.*, 1910, 71, 257; compare Magnus, *Ann. Physik*, 1910, [4], 31, 597; Richards and Jackson, *Zeitsch. physikal. Chem.*, 1910, 70, 414.

0·05608,[1] the corresponding values for the atomic heat being 5·97, 6·00, and 6·04.[2] The mean atomic heat from —75° to —183° C. is 5·31. Its hardness on Mohs's scale is 2·7.[3]

In the state of vapour, silver has a pale-blue colour, and when molten it is luminescent. Liquid silver absorbs oxygen, the gas being evolved as the metal solidifies. The eruption of the gas through the solid exterior crust gives the mass a characteristic appearance, the phenomenon being termed "spitting."[4] At 760 mm. 1 volume of silver dissolves 0·54 vols. of oxygen at 923° C., 20·28 vols. at 973° C., 19·53 vols. at 1024° C., 18·42 vols. at 1075° C., and 17·56 vols. at 1125° C.[5]. Solid silver also dissolves oxygen,[6] but hydrogen [7] and nitrogen [8] are insoluble in either solid or molten silver.

Several investigators [9] have described methods for the preparation of pure silver. In the process adopted by Richards, silver nitrate was purified by repeated crystallization, and converted into silver chloride, which was reduced to metallic silver by the action of invert-sugar in presence of sodium hydroxide. After fusion on a layer of pure charcoal or lime, the silver was purified electrolytically, being dissolved at the anode and deposited in crystalline form at the cathode. The elimination of silver nitrate and gases occluded by the metal was effected by fusion in a boat of pure lime, the last traces of oxygen being removed by the action of hydrogen. After this purification, the metal contained not more than 0·0004 per cent. of occluded hydrogen.[10]

Native silver and the variety obtained by decomposing the sulphide with hydrogen are *amorphous*. Rolled silver and the violet form produced by reduction of the chloride with sugar are also amorphous, but can be rendered *crystalline* by the action of heat. Treatment with hydrochloric acid of a silver-zinc alloy containing 10 per cent. of silver leaves the silver in the form of a greyish-white sponge.[11] The chemical activity of amorphous silver is much greater than that of the crystalline variety, an example being afforded by the spongy deposit of the metal formed during the electrolysis of silver nitrate under certain conditions.[12]

The most unstable form of the amorphous variety is *colloidal silver*, prepared by reduction of an ammoniacal or dilute alcoholic solution of silver nitrate with sodium citrate, sodium potassium tartrate, dextrin, tannin, or formaldehyde, with subsequent addition of ferrous sulphate.[13] If forms a chocolate, pale-lilac, blue, or green mass, and dissolves in water to a deep-red solution. The colour depends partly on the mode of

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[1] Kahlbaum, Roth, and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 177.

[2] Barschall, *Zeitsch. Elektrochem.*, 1911, 17, 341.

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

[4] Chevillot, *Ann. chim.*, 1820, 13, 299.

[5] Sieverts and Hagenacker, *Zeitsch. physikal. Chem.*, 1909, 68, 116; compare Donnan and Shaw, *J. Soc. Chem. Ind.*, 1910, 29, 987.

[6] Dumas, *Ann. Chim. Phys.*, 1878, [5], 15, 289; *Compt. rend.*, 1878, 86, 65.

[7] Sieverts and Krumbhaar, *Ber.*, 1910, 43, 893; *Zeitsch. physikal. Chem.*, 1910, 74, 277; Sieverts, *Zeitsch. Elektrochem.*, 1910, 16, 707.

[8] Sieverts, *loc. cit.*

[9] Compare Stas, *Über die Gesetze der chemischen Proportionen*, Leipsic, 1867, 32.

[10] Richards and Wells, *A Revision of the Atomic Weights of Sodium and Chlorine*, Carnegie Institution, Washington, No. 28, 1905, pp. 1–35 and 57–70; Richards and Forbes, *ibid.*, No. 69, 1907, pp. 47–65.

[11] Palitsch, *Bull. Acad. roy. Belg.*, 1911, 395.

[12] Tananaeff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 197.

[13] Carey Lea, *Amer. J. Sci.*, 1889, 37, 476; 38, 47, 129; 1894, 48, 343; *Phil. Mag.*, 1891, 31, 238, 320, 497; 32, 337.

preparation, and partly on the age of the specimen.[1] Reduction of the monoxide by 60 per cent. formaldehyde at 35° C. yields a very stable solution of colloidal silver, varying in colour from pale-lilac to rich ruby-red.[2] The effect is not produced by employing acetaldehyde. In presence of Irish moss, hydrazine hydrate yields colloidal silver varying in colour from dark-reddish brown to brownish yellow in transmitted light. The more dilute solutions thus prepared are very stable, and can be kept for two months. By this means it has been found practicable to prepare solutions containing 17 per cent. of colloidal silver, but such concentrated forms lack stability.[3] The colloidal solution decomposes hydrogen peroxide slowly.

Colloidal silver can also be prepared by forming an electric arc between silver poles immersed in water, the solutions being brown with a low current, and green with a stronger current.[4] The electric conductivity of the solution produced by the second method is higher than that of the brown solution. Addition of an electrolyte also converts the brown solution into the green form.[5] The conductivity of such solutions has been attributed to the presence of silver oxide.[6]

When silver is boiled with water for a prolonged period, a colloidal solution is formed. It contains 0·0162 gram of silver per 100 c.c.[7] Another procedure involves heating the metal to redness or a higher temperature and plunging it into cold water.[8] Many other methods of preparing colloidal silver have been described.[9]

Plates of copper or zinc precipitate colloidal silver from solution.[10] The solid forms are brittle, and amalgamate with mercury. Acids convert them into grey silver, without evolution of gas.

A therapeutic preparation of colloidal silver is known as "collargol." Credé's ointment also contains this form of silver, and is employed in the treatment of certain types of septic infection. An astringent antiseptic is prepared by the action of an alkaline tannin solution on aqueous solutions of silver salts.[11]

In photography colloidal silver plays an important part, an instance being the image produced in the ordinary printing-out process.

Neither the metal nor any of its salts displays radioactivity.[12]

Chemical Properties.—At the ordinary temperature silver is stable

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[1] Compare Henriot, *Compt. rend.*, 1903, 137, 122; Bancroft, *J. Physical Chem.*, 1919, 23, 554.

[2] Pickles, *Chem. News*, 1918, 117, 358.

[3] Gutbier, Wolf, and Kiess, *Kolloid Zeitsch.*, 1922, 30, 31.

[4] Bredig, *Zeitsch. angew. Chem.*, 1898, 11, 951.

[5] Compare Woudstra, *Zeitsch. physikal. Chem.*, 1908, 61, 607; Lottermoser, *ibid.*, 62, 284; Rebière, *Compt. rend.*, 1912, 154, 1540.

[6] Rebière, *Compt. rend.*, 1909, 148, 354.

[7] Traubi-Mengarini and Scala, *Atti R. Accad. Lincei*, 1909, [5], 18, i., 542.

[8] Kimura, *Mem. Coll. Sci. Eng. Kyōtō*, 1913, 5, 211.

[9] Schneider, *Ber.*, 1891, 24, 3370; 1892, 25, 1164, 1281, 1440; Barus and Schneider, *Zeitsch. physikal. Chem.*, 1891, 8, 278; *Wied. Annalen*, 1893, 48, 357; Oberbeck, *ibid.*, 745; Lottermoser and Meyer, *J. prakt. Chem.*, 1897, 56, 241; 1898, 57, 540; Lottermoser, *ibid.*, 1905, 71, 296; Blake, *Amer. J. Sci.*, 1903, 16, 282; Chassevant, *Bull. Soc. chim.*, 1904, 31, 11; Paal, *Ber.*, 1902, 35, 2206; Küspert, *Ber.*, 1902, 35, 2815, 4066, 4070; Gutbier and Hofmeier, *Zeitsch. anorg. Chem.*, 1905, 45, 77; Castoro, *Gazzetta*, 1907, 37, i., 391; *Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 283; Kohlschütter, *Zeitsch. Elektrochem.*, 1908, 14, 49; *Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 285 (summary); Pieroni, *Gazzetta*, 1913, 43, i., 197.

[10] Philipson, *Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 49.

[11] Sensburg, *German Patent*, 1909, No. 208189.

[12] Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576.

towards moisture and atmospheric oxygen, but at 200° C. an invisible, superficial layer of oxide is produced, detected by its power of reacting with ozone at ordinary temperature.[1] It reacts with sulphur and compounds of sulphur to form silver sulphide.[2] In absence of air, hydrogen sulphide and the sulphides of the alkali-metals do not affect silver, but addition of oxygen or hydrogen peroxide induces instantaneous blackening.[3]

Pure silver is dissolved by pure sulphuric acid at the boiling-point, provided the concentration of the acid is not less than 77·5 per cent., and in presence of impurities the metal is attacked also by the dilute acid:[4]

$$2Ag+2H_2SO_4=Ag_2SO_4+SO_2+2H_2O.$$

Nitric acid reacts energetically at ordinary temperatures, with formation of the nitrate and of the oxides of nitrogen. The behaviour of the metal with hydrochloric acid is similar to that of lead. The action of concentrated sulphuric acid and of nitric acid finds application in the separation of alloys of gold and silver. The corrosive effect of acids is accelerated by the presence of an oxidizer.[5]

The metal is scarcely attacked by fused alkalies,[6] and only slowly by the halogens. In contact with air or hydrogen peroxide it is readily dissolved by potassium cyanide. It is converted by mercury into an amalgam.[7]

At ordinary temperatures and 200 atmospheres hydrogen expels the metal from solutions of its salts.[8] It is precipitated from its salts by the action of phosphorous acid and of sodium hypophosphite.[9]

Argention.—Silver forms a colourless, univalent ion. Its electrochemical equivalent in milligrams per coulomb is given as 1·1172,[10] 1·1180,[11] 1·11827,[12] 1·11829,[13] 1·1183,[14] and 1·1193.[15] In the potential series the metal occupies a position intermediate between mercury and platinum. In correspondence with its low electroaffinity it exhibits a strong tendency to form complex ions. The ionic conductivity of silver at 18° C. is 54·0, and at 25° C. 63·4.

Applications.—The metal alloyed with copper is employed in making coins, plate, and jewellery. It also finds extensive application in electroplating.

Atomic Weight.—The value originally accepted by Berzelius for the atomic weight of silver was about four times the modern number; at a later period he changed it to about twice the modern atomic weight,

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[1] Manchot and Kampschulte, *Ber.*, 1907, 40, 2891; Manchot, *Ber.*, 1909, 42, 3942; compare Schöne, *Ber.*, 1880, 13, 1503.

[2] Compare Cohen and Hefford, *J. Soc. Chem. Ind.*, 1893, 12, 123.

[3] Hahn, *Zeitsch. anorg. Chem.*, 1917, 99, 118.

[4] Pannain, *Gazzetta*, 1909, 39, ii., 234.

[5] Watts and Whipple, *Trans. Amer. Elektrochem. Soc.*, 1917, 32, 257.

[6] Dittmar and Prentier, *J. Soc. Chem. Ind.*, 1893, 12, 248.

[7] This series, Vol. III.

[8] Ipatieff and Werchowsky, *Ber.*, 1909, 42, 2078.

[9] Sieverts and Krumbhaar, *Zeitsch. anorg. Chem.*, 1909, 64, 29.

[10] Richards, Collins, and Heimrod, *Zeitsch. physikal. Chem.*, 1900, 32, 321.

[11] van Dyk, *Arch. Néerland*, 1905, [2], 9, 442; 10, 277; van Dyk and Kunst, *Drude's Annalen*, 1904, 14, 569; Bernoulli, *Zeitsch. physikal. Chem.*, 1909, 65, 391.

[12] Smith, Mather, and Lowry, *Proc. Roy. Soc.*, 1907, [A], 80, 77.

[13] Laporte and Goree, *Compt. rend.*, 1910, 150, 278.

[14] Kohlrausch, *Wied. Annalen*, 1881, 27, 1; *Ann. Physik*, 1908, [4], 26, 580.

[15] Pellat and Leduc, *Compt. rend.*, 1903, 136, 1694.

215·94=2×107·97 (O=16). In 1808 Dalton preferred the value Ag=100 (O=7); in 1817 Meinecke selected Ag=108; and in 1826 Gmelin gave the same value for the equivalent of the metal.

In the section on the atomic weight of sodium (p. 87) mention is made of the close relationship between the atomic weight of this element and the atomic weights of silver, potassium, chlorine, bromine, and iodine. In the sections on the atomic weights of sodium and potassium (*loc. cit.*, and p. 155) an outline of the general principles underlying the methods adopted by the earlier investigators in determining the atomic weights of these elements is given, and the experimental results of a number of researches are summarized. Here it will suffice to describe the determination of ratios not previously mentioned. As with sodium and potassium, the experimental work naturally falls into two main divisions: (1) that of the early investigators, and (2) that carried out under the extremely accurate conditions required of modern atomic-weight research.

In connexion with the early work, only a summary of results need be given. The values for the various ratios $AgXO_3 : AgX$ are stated in the table:

Experimenter.	Year.	Ratio.
$AgClO_3 : 3O = 100 : x$.		
Marignac[1] .	1843	$x = 25·083 \pm 0·0041$
Stas[2] . .	1865	$= 25·0795 \pm 0·0010$
		Mean (Clarke) $= 25·0797 \pm 0·0010$
$AgBrO_3 : 3O = 100 : x$.		
Stas[3] . .	1865	$x = 20·349 \pm 0·0014$
$AgIO_3 : 3O = 100 : x$.		
Millon[4] . .	1843	$x = 17·047 \pm 0·005$
Stas[5] . .	1865	$= 16·9747 \pm 0·0009$
		Mean (Clarke) $= 16·9771 \pm 0·0009$

Determinations of the ratios $Ag : AgX$ are more numerous. The next table summarizes the results:

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[1] Marignac, *Œuvres complètes*, Geneva, 1902, I, 80.
[2] Stas, *Œuvres complètes*, Brussels, 1894, I, 645.
[3] Stas, *ibid.*, 635.
[4] Millon, *Ann. Chim. Phys.*, 1843, [3], 9, 400.
[5] Stas, *Œuvres complètes*, Brussels, 1894, I, 628.

[TABLE.

Experimenter.	Year.	Ratio.
	Ag : AgCl=100 : x.	
Berzelius[1] .	1811–1826	x=132·757 ±0·0019
Turner[2] . .	1829	=132·832 ±0·0038
Penny[3] . .	1839	=132·8363±0·0012
Marignac[4] .	1843	=132·854 ±0·0024
Maumené[5] .	1846	=132·7364±0·0077
Dumas[6] . .	1859	=132·8755±0·0044
Stas[7] . .	1860	=132·8445±0·0008
	Mean (Clarke)	=132·8418±0·0006
	Ag : AgBr=100 : x.	
Marignac[8] .	1843	x=174·077±0·003
Stas[9] . .	1865	=174·081±0·0006
Huntington[10] .	1881	=174·071±0·0072
Richards[11] .	1890–1893	=174·065±0·0035
		=174·067±0·0034
	Mean (Clarke)	=174·080±0·00057
	Ag : AgI=100 : x.	
Marignac[12] .	1843	x=217·5335±0·0036
Stas[13] . .	1865	=217·5325±0·0024
		=217·5373±0·0015
		=217·5334±0·0014
	Mean (Clarke)	=217·5345±0·0009

The early work included analyses and syntheses of silver sulphide, and the analysis of silver sulphate by heating it in a current of hydrogen. The results for silver sulphide are:

Experimenter.	Year.	2Ag : Ag$_2$S=100 : x.
Dumas[14] . .	1859	x=114·8234±0·0029
Stas[15] . .	1865	=114·8522±0·0007
Cooke[16] . .	1877	=114·888 ±0·0012
		=114·8165±0·0044
	Mean (Clarke)	=114·8581±0·0006

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[1] Berzelius, *Afhandlingar i Fysik, Kemi, etc.*, Stockholm, 1806–1818, 3, 194; 5, 108, 389; *Gilbert's Annalen*, 1811, 38, 166, 287; *Schweigger's J.*, 1818, 23, 107; *Trommsdorff's N. J. Pharm.*, 1818, 2, ii., 44; *Thomson's Annals of Philosophy*, 1820, 15, 89; *Pogg. Annalen*, 1826, 8, 17.

[2] Turner, *Phil. Trans.*, 1829, 119, 291.

[3] Penny, *ibid.*, 1839, 129, 28.

[4] Marignac, *Œuvres complètes*, Geneva, 1902, 1, 79.

[5] Maumené, *Ann. Chim. Phys.*, 1846, [3], 18, 41.

[6] Dumas, *ibid.*, 1859, [3], 55, 134.

[7] Stas, *Œuvres complètes*, Brussels, 1894, 1, 341.

[8] Marignac, *Œuvres complètes*, Geneva, 1902, 1, 83.

[9] Stas, *Œuvres complètes*, Brussels, 1894, 1, 587, 603.

[10] Huntington, *Proc. Amer. Acad.*, 1881, 17, 28.

[11] Richards, *ibid.*, 1888, 25, 195; 1891, 29, 55.

[12] Marignac, *Œuvres complètes*, Geneva, 1902, 1, 363.

[13] Stas, *Œuvres complètes*, Brussels, 1894, 1, 562, 581; compare Baxter, *Proc. Amer. Acad.*, 1902, 41, 76.

[14] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 146.

[15] Stas, *Œuvres complètes*, Brussels, 1894, 1, 349.

[16] Cooke, *Proc. Amer. Acad.*, 1877, 13, 47.

For silver sulphate Stas[1] found the precentage of silver to be $69{\cdot}203 \pm 0{\cdot}0012$, and Struve's[2] result was $69{\cdot}230 \pm 0{\cdot}004$. According to Clarke, the weighted mean is

$$Ag_2SO_4 : 2Ag = 100 : 69{\cdot}205 \pm 0{\cdot}0011.$$

Computation of the atomic weight of silver from the data cited involves a knowledge of the mean values for the ratios KCl : 3O, KBr : 3O, KI : 3O, NaCl : 3O, Ag : KCl, Ag : KBr, Ag : KI, and Ag : NaCl, as determined by the early workers. These values are given in the sections on the atomic weights of sodium and potassium (pp. 87 and 155). The two early determinations of the ratios RX : AgX lack accuracy, and are omitted.

Combination of the various ratios gives

$$\frac{KCl}{3O} \times \frac{Ag}{KCl} = \frac{Ag}{3O}. \qquad Ag = 107{\cdot}927 \pm 0{\cdot}0106 \qquad (1)$$

$$\frac{KBr}{3O} \times \frac{Ag}{KBr} = \frac{Ag}{3O}. \qquad Ag = 108{\cdot}196 \pm 0{\cdot}0837 \qquad (2)$$

$$\frac{KI}{3O} \times \frac{Ag}{KI} = \frac{Ag}{3O}. \qquad Ag = 107{\cdot}666 \pm 0{\cdot}0278 \qquad (3)$$

$$\frac{NaCl}{3O} \times \frac{Ag}{NaCl} = \frac{Ag}{3O}. \qquad Ag = 107{\cdot}919 \pm 0{\cdot}0079 \qquad (4)$$

$$\frac{AgCl}{3O} \times \frac{Ag}{AgCl} = \frac{Ag}{3O}. \qquad Ag = 107{\cdot}939 \pm 0{\cdot}0050 \qquad (5)$$

$$\frac{AgBr}{3O} \times \frac{Ag}{AgBr} = \frac{Ag}{3O}. \qquad Ag = 107{\cdot}930 \pm 0{\cdot}0092 \qquad (6)$$

$$\frac{AgI}{3O} \times \frac{Ag}{AgI} = \frac{Ag}{3O}. \qquad Ag = 107{\cdot}906 \pm 0{\cdot}0062 \qquad (7)$$

$$\frac{Ag_2S}{2Ag} \times \left\{\left(\frac{2Ag}{Ag_2S} \times \frac{Ag_2SO_4}{2Ag}\right) - 1\right\} = \frac{4O}{2Ag}. \qquad Ag = 107{\cdot}962 \pm 0{\cdot}0090 \qquad (8)$$

Results (2) and (3) differ sufficiently from the others to compel their rejection. The arithmetic mean of the other six results is Ag = 107·93. With the exception of (4), they depend mainly on the work of Stas, and when his results only are employed in the calculations the same mean value is obtained, but the individual results are more concordant.

Despite the agreement of these results, they are now known to be very erroneous,[3] although the value Ag = 107·93 was given in the International Atomic Weight Committee's table down to 1908. The probability of the correct result being nearer to 107·89 or 107·88 was inferred by Guye[4] in 1905 as a necessary consequence of changing the

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[1] Stas, *Œuvres complètes*, Brussels, 1894, 1, 410.

[2] Struve, *Annalen*, 1851, 80, 203.

[3] For criticisms of the work of Stas, reference should be made to the papers by Richards and others cited later, particularly the paper by Richards and Wells. Compare also Dumas, *Ann. Chim. Phys.*, 1878, [5], 14, 289; Stas, *Œuvres complètes*, Brussels, 1894, 3, 106; Dubreuil, *Compt. rend.*, 1908, 147, 856, 1300; *Bull. Soc. chim.*, 1909, [4], 5, 260, 313, 341, 1049; Leduc, *Compt. rend.*, 1908, 147, 972; 1909, 148, 42; Hinrichs, *ibid.*, 1908, 147, 1302.

[4] Guye, *Arch. Sci. phys. nat.*, 1905, [4], 20, 351; *Bull. Soc. chim.*, 1905, [3], 33, 1; *J. Chim. phys.*, 1906, 4, 174; *Chem. News*, 1906, 93, 35; Guye and Ter-Gazanair, *Compt. rend.*, 1906, 143, 411; Guye and Germann, *J. Chim. phys.*, 1916, 14, 204.

number representing the atomic weight of nitrogen from 14·04 to the modern value 14·01. Recent research has verified the accuracy of this assumption.

In 1907 Richards and Forbes[1] effected the synthesis of silver nitrate from silver and nitric acid. Minute precautions to ensure the purity of the silver nitrate were taken, and the mean of six experimental results differing only by one unit in the third decimal place gave

$$Ag : NO_3 = 100 : 57{\cdot}479,$$

allowance being made for traces of water, ammonium nitrate, and occluded air in the silver nitrate. Taking 14·008 as the atomic weight of nitrogen, determined directly with respect to oxygen,[2] the ratio gives *Ag=107·879.*

This value was confirmed in 1909, the work of Richards, Köthner, and Tiede[3] establishing the ratio

$$AgCl : NH_4Cl = 100 : 37{\cdot}3217.$$

This result is best utilized in conjunction with the ratio last cited and that of Richards and Wells:[4]

$$Ag : AgCl = 100 : 132{\cdot}867.$$

Taking oxygen as the standard, and assuming with Morley that H=1·00762, there are three equations for deducing by simple algebra the atomic weights of silver, chlorine, and nitrogen, the result being *Ag=107·880.* Accepting Noyes's value H=1·0078, then *Ag=107·878.* The modern value for the atomic weight of silver is based mainly on these results.

The old value for silver was derived from numerous ratios. Some of them have been redetermined in the light of modern knowledge, examples being $KClO_3 : KCl$, $KCl : Ag$, and $KCl : AgCl$. The first of these values was measured by Stähler and Meyer[5] in 1911, and the others by Richards and Stähler[6] in 1907:

$$\begin{aligned} &(1)\quad KCl : KClO_3 = 100 : 164{\cdot}382\,; \\ &(2)\quad AgCl : KCl = 100 : 52{\cdot}0118\,; \\ &(3)\quad Ag : KCl = 100 : 69{\cdot}1073. \end{aligned}$$

Hence,

$$\frac{Ag}{AgCl} \times \frac{AgCl}{KCl} = \frac{Ag}{KCl} = \frac{100}{69{\cdot}1064}.$$

In conjunction with that numbered (3), this ratio gives the mean value $Ag : KCl = 100 : 69{\cdot}1069$. Then

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[1] Richards and Forbes, *Carnegie Institution of Washington*, 1907, Publication No. 69; *J. Amer. Chem. Soc.*, 1907, 29, 808; *Chem. News*, 1907, 96, 180, 190.

[2] This series, Vol. VI.

[3] Richards, Köthner, and Tiede, *J. Amer. Chem. Soc.*, 1909, 31, 6; *Chem. News*, 1909, 99, 54, 64, 76; compare Hinrichs, *Mon. Scient.*, 1909, [4], 23, 1, 383.

[4] Richards and Wells, *Carnegie Institution of Washington*, 1905, Publication No. 28; *J. Amer. Chem. Soc.*, 1905, 27, 459; *Chem. News*, 1906, 93, 175 *et seq.*

[5] Stähler and Meyer, *Zeitsch. anorg. Chem.*, 1911, 71, 378; compare Guye, *J. Chim. phys.*, 1912, 10, 145.

[6] Richards and Stähler, *Carnegie Institution of Washington*, 1907, Publication No. 69; *J. Amer. Chem. Soc.*, 1907, 29, 623; *Chem. News*, 1907, 96, 133, 145.

$$\frac{3O}{KCl}\times\frac{KCl}{Ag}=\frac{3O}{Ag}=0{\cdot}64382\times0{\cdot}691069;$$

$$=0{\cdot}444924;$$

$$=48:107{\cdot}884;$$

or

$$Ag=107{\cdot}884.$$

A similar method of calculation can be applied to the results of Richards and Willards's analyses of lithium chloride and lithium perchlorate, as indicated in connexion with the atomic weight of lithium (p. 57); it gives *Ag=107·871.*

Another calculation of the atomic weight of silver can be made from modern determinations of the ratios $2Ag : I_2O_5$ and $Ag : I$:

$$\frac{I}{Ag}\times\left\{\left(\frac{I_2O_5}{2Ag}\times\frac{Ag}{I}\right)-1\right\}=\frac{5O}{2Ag}.$$

The iodine-pentoxide ratio was very carefully determined by Baxter and Tilley[1] in 1909 to be

$$I_2O_5 : 2Ag=100 : 64{\cdot}6230,$$

and the composition of silver iodide was found by Baxter[2] in 1910 to be

$$Ag : I=100 : 117{\cdot}6601.$$

Combination of the two ratios gives the value *Ag=107·864.*

In 1913 Scheuer[3] dissolved silver in sulphuric acid, collected and weighed the sulphur dioxide evolved, and dried, fused, and weighed the silver sulphate:

$$2Ag+2H_2SO_4=Ag_2SO_4+SO_2+2H_2O.$$

The weights are in the ratios $2Ag : Ag_2SO_4 : SO_2$, and the atomic weight of silver is readily calculated, since

$$\frac{2Ag}{Ag_2SO_4-2Ag-SO_2}=\frac{2Ag}{2O}.$$

The mean of five experimental results gave *Ag=107·884.*

The modern values for the atomic weight of silver vary between 107·864 and 107·884. The current table of the International Committee on Atomic Weights gives **Ag=107·88**, but possibly **107·87** is a better approximation to the true value, as has been pointed out by Guye.[4] As an essential factor in the calculation of many other atomic weights, the atomic weight of silver is of fundamental importance.

ALLOYS AND COMPOUNDS OF SILVER.

Alloys.[5]—A description of various alloys of silver with copper and with gold[6] has been given by several authors.[7] British silver coin and stan-

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[1] Baxter and Tilley, *J. Amer. Chem. Soc.*, 1909, 31, 201.

[2] Baxter, *ibid.*, 1910, 32, 1591; compare Baxter, *ibid.*, 1904, 26, 1577; 1905, 27, 876.

[3] Scheuer, *Arch. Sci. phys. nat.*, 1913, [4], 36, 381.

[4] Guye, *J. Chim. phys.*, 1917, 15, 549; 1919, 17, 171.

[5] For silver-amalgam see this series, Vol. III.

[6] Compare pp. 297, 301, 333, and 336.

[7] Kurnakoff and Schemtschushny, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1067; Lepkowski, *Zeitsch. anorg. Chem.*, 1908, 59, 285; Kurnakoff, Puschin, and Senkowski, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 733; *Zeitsch. anorg. Chem.*, 1910, 68, 123; Waidner and Burgess, *Bull. Bureau of Standards*, 1909, 6, 149; Jänecke, *Zeitsch. angew. Chem.*, 1912, 25, 935 (summary of previous work); Raydt, *Zeitsch. anorg. Chem.*, 1912, 75, 58.

dard plate contain 7·5 per cent. of copper, the product being termed "925 fine." This alloy resembles pure silver in malleability and colour, but is harder and melts at a lower temperature. It solidifies without "spitting," an important point in the production of good castings. In view of the remarkable appreciation in the value of silver, the standard for coinage has been lowered to "500 fine," with addition of nickel.

Alloys with the alkali-metals have also been described.[1]

Silver fluoride, AgF.—Evaporation in vacuum of a solution of silver oxide in hydrofluoric acid yields the fluoride in the form of an amorphous, yellow mass, of density[2] 5·852 at 15·5° C. At red heat it melts to a black liquid, which on cooling solidifies to a crystalline mass.[3] It is very soluble in water, its solubility at 15·5° C. being 181·8 grams per 100 grams of water. The solution has a neutral reaction. In its solubility the fluoride presents a marked contrast to the other silver halides. The anhydrous salt can absorb 844 times its volume of ammonia.

Two hydrates have been described. The *monohydrate*, AgF,H_2O, forms yellowish cubes,[4] or large, deliquescent, tetragonal crystals,[5] decomposed by heat with formation of a basic salt, $Ag_2F(OH)$, and evolution of hydrogen fluoride. The *dihydrate*, $AgF,2H_2O$, crystallizes from concentrated solution in hard, transparent prisms.[6]

From a solution of the fluoride in dilute hydrofluoric acid there crystallizes an *acid salt*, AgF,HF, in brown, deliquescent crystals.[7] On cooling, a solution of the fluoride in pure hydrogen fluoride deposits white crystals of the formula $AgF,3HF$.[8]

An aqueous solution containing 0·0002 per cent. of silver fluoride has been employed as a sterilizer to render water potable.[9] The salt is sensitive to light.[10]

Silver subfluoride, Ag_2F.—When a saturated solution of silver fluoride is heated with finely divided silver, a golden-yellow, crystalline precipitate of the composition Ag_2F is produced.[11] The reaction is attended by the evolution of 0·7 Cal.,[12] and the heat of formation of the subfluoride from its elements is 26·3 Cal. At 180° C. water-vapour converts the fluoride into the suboxide, Ag_4O.[13]

The *dihydrate*, $Ag_2F,2H_2O$, is obtained in colourless octahedra by evaporating a solution of silver fluoride in absence of light, and removing excess of silver fluoride by extracting with alcohol.[14]

Silver chloride, $AgCl$.—Addition of a solution of hydrogen chloride or a metallic chloride to one of a silver salt gives a heavy, white, amor-

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[1] Bornemann, *Metallurgie*, 1909, 6, 236, 296, 326.

[2] Gore, *Proc. Roy. Soc.*, 1870, 18, 157.

[3] Compare Vanino and Sachs, *Zeitsch. anal. Chem.*, 1911, 50, 623; Wöhler, *Zeitsch. anorg. Chem.*, 1912, 78, 239.

[4] Frémy, *Ann. Chim. Phys.*, 1856, [3], 47, 39.

[5] Marignac, *Ann. Mines*, 1857, [5], 12, 21.

[6] Compare Guntz, *Compt. rend.*, 1884, 98, 819; 1913, 157, 977; Vanino and Sachs, *Zeitsch. anal. Chem.*, 1914, 53, 154.

[7] Gore, *loc. cit.*

[8] Guntz, *Bull. Soc. chim.*, 1895, [3], 13, 114.

[9] Paternò and Cingolani, *Gazzetta*, 1907, 37, i., 313.

[10] Wöhler, *Zeitsch. anorg. Chem.*, 1912, 78, 239.

[11] Guntz, *Compt. rend.*, 1890, 110, 1337; Wöhler and Rodewald, *Zeitsch. anorg. Chem.*, 1909, 61, 54; Wöhler, *ibid.*, 1912, 78, 239; compare Guntz, *Bull. Soc. chim.*, 1912, [4], 11, 845; Vanino and Sachs, *Zeitsch. anal. Chem.*, 1911, 50, 623.

[12] Wöhler and Rodewald, *loc. cit.*

[13] Guntz, *Compt. rend.*, 1891, 112, 861.

[14] Wöhler, *loc. cit.*; *Zeitsch. anal. Chem.*, 1914, 53, 375; Vanino and Sachs, *ibid.*, 154.

phous precipitate of silver chloride, which can be converted into a crystalline form by evaporating its solution in concentrated hydrochloric acid or ammonium hydroxide. The native variety is known as *horn-silver*, and crystallizes in the cubic system. Its density is 5·31 to 5·55. The crystalline form is also produced by slow diffusion of a solution of hydrogen chloride into one of silver nitrate. Its cubic crystals are isomorphous with those of silver bromide.[1]

The *melting-point* of amorphous silver chloride is given as 451° C.,[2] 452° C.,[3] and 455° C.,[4] the substance fusing to a yellow liquid. After solidification its density is 5·45 to 5·59. The specific heat is 0·08775.[5] At 18° C. its solubility[6] is $1{\cdot}17\times10^{-5}$ gram-molecules per litre of water, and at 25° C., $1{\cdot}6\times10^{-5}$. Silver chloride also dissolves in solutions of ammonia,[7] sodium thiosulphate, potassium cyanide, mercuric nitrate, and in concentrated hydrochloric acid and saturated chloride solutions. For the heat of formation from the elements Berthelot gives 29·2 Cal., and Thomsen[8] 29·38 Cal. Wolff[9] considers their results too low, and gives the value 30·612 Cal., that stated by Braune and Koref[10] being 30·41 Cal. The intermediate value 29·940 Cal. is given by Fischer.[11]

Chlorine reacts with an aqueous solution of silver nitrate to form chloride and chlorate of silver, the hypochlorite being an intermediate product:

$$6AgNO_3+3Cl_2+3H_2O=5AgCl+AgClO_3+6HNO_3.$$

Silver chloride absorbs gaseous ammonia, forming double compounds of the composition $2AgCl,3NH_3$ and $AgCl,3NH_3$. The first crystallizes in rhombic plates from ammoniacal solutions of silver chloride[12]; the second is formed in long prisms by heating the chloride with a saturated aqueous solution of ammonia under pressure.[13] The dissociation-pressures of these compounds have measurable values.[14] Other compounds of similar type with the formulæ $AgCl,3NH_3$ (9·16), $AgCl,1\frac{1}{2}NH_3$ (10·52), and $AgCl,NH_3$ (11·11) have also been prepared,[15] the figures in parentheses giving the calculated heats of formation in large calories. The interaction at 200° C. of iodic acid and ammoniacal solutions of the chloride to form silver iodide has been the subject of investigation.[16] A cold ammoniacal solution of sodium peroxide reduces silver chloride,[17] and it is also reduced to the metal by the action of zinc in the course of a

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[1] Kurnakoff and Schemtschushny, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1067.

[2] Schemtschushny, *ibid.*, 1916, 48, 203.

[3] Monkemeyer, *Jahr. Min. Beil.-Bd.*, 1909, 22, 1.

[4] Truthe, *Zeitsch. anorg. Chem.*, 1912, 76, 161.

[5] Brönsted, *Zeitsch. Elektrochem.*, 1912, 18, 714; compare Magnus, *Ann. Physik*, 1910, [4], 31, 597.

[6] Holleman, *Zeitsch. physikal. Chem.*, 1893, 12, 125; Kohlrausch and Rose, *ibid.*, 234; compare Hill, *J. Amer. Chem. Soc.*, 1908, 30, 68; Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, 64, 129; van Rossem, *Chem. Weekblad*, 1912, 9, 396.

[7] Compare Peters, *Ber.*, 1908, 41, 3175.

[8] Thomsen, *Thermochemistry* (Longmans, 1908), 284.

[9] Wolff, *Zeitsch. Elektrochem.*, 1914, 20, 19.

[10] Braune and Koref, *Zeitsch. anorg. Chem.*, 1914, 87, 175.

[11] Fischer, *Zeitsch. Elektrochem.*, 1912, 18, 283.

[12] Kane, *Ann. Chim. Phys.*, 1840, 72, 290.

[13] Terreil, *Compt. rend.*, 1884, 98, 1279.

[14] Isambert, *ibid.*, 1868, 66, 1529; Horstmann, *Ber.*, 1876, 9, 749; Biltz, *Zeitsch. physikal. Chem.*, 1909, 67, 561.

[15] Biltz and Stollenwerk, *Zeitsch. anorg. Chem.*, 1920, 114, 174.

[16] Baubigny, *Compt. rend.*, 1908, 146, 1097.

[17] Booth, *Chem. News*, 1911, 103, 288.

few days.[1] With sodium thiosulphate it probably combines to form a soluble double salt, $2Na_2S_2O_3,Ag_2S_2O_3,2H_2O$, but the compound has not been isolated.[2]

Potassium ferrocyanide and silver chloride react to form insoluble silver potassium ferrocyanide in accordance with the equation

$$3AgCl+K_4Fe(CN)_6=Ag_3KFe(CN)_6+3KCl.$$

Neither silver bromide nor iodide react thus, and it is possible to estimate silver chloride in presence of iodides by means of this reaction, the excess of potassium ferrocyanide remaining after filtration being determined by titration with standard permanganate.[3]

Silver chloride is sensitive to light, though not in so great a degree as the bromide or iodide. On exposure to light it develops a violet colour, with evolution of 4·1 per cent. of chlorine in air, and of 81·0 per cent. of chlorine in vacuum,[4] and formation of the so-called "photochloride." On removing the liberated chlorine a loss in weight of 8·57 per cent. is stated to have been observed,[5] although Koch and Schrader[6] consider it not to exceed between 1 and 2 per cent. If diffusion of the chlorine is prevented, the reaction is found to be reversible:[7]

$$2AgCl \rightleftharpoons Ag_2Cl+Cl.$$

Ordinary photographic printing-out paper contains silver chloride with a basis of albumin, collodion, or gelatin. On exposure to light, the organic material reduces the salt to metallic silver, with intermediate production of the subchloride. The metal is liberated in the colloidal form, and the image is rendered more stable by "toning," gold or platinum being deposited on it from solution.

Silver subchloride, Ag_2Cl.—When silver subfluoride is heated with phosphorus trichloride at 140° C., silver subchloride is formed.[8] It is also a product of the interaction of silver nitrate and cuprous chloride, of a colloidal solution of silver and chlorine-water,[9] and of silver-foil and weak oxidizers such as cupric chloride.

The product of these reactions is a brown powder, but it is doubtful whether that prepared by the interaction of colloidal silver and chlorine-water is a definite chemical compound, since successive chlorinations of colloidal silver produce a series of homogeneous mixtures of silver and silver chloride.[9]

Photohalides.—The rose-red to purple-brown mixtures of silver subchloride and silver chloride are called by Carey Lea "photochlorides." They are formed by the interaction of colloidal silver and a suspension of silver chloride; by the action of organic reducers and of light on silver chloride[10]; and by the electrolytic chlorination of sheet silver.[11] The

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[1] Gawalowski, *Oesterr. Chem. Zeit.*, 1916, 19, 150.

[2] Lumière and Seyewetz, *Rev. gén. Chim.*, 1907, 10, 291.

[3] Bonino, *Gazzetta*, 1921, 51, ii., 261.

[4] Hartung, *Trans. Chem. Soc.*, 1922, 121, 682.

[5] Hitchcock, *Amer. J. Sci.*, 1876, [3], 11, 474; compare Guntz, *Compt. rend.*, 1891, 113, 72.

[6] Koch and Schrader, *Zeitsch. Physik*, 1921, 6, 127.

[7] Morren, *Chem. News*, 1868, 18, 112.

[8] Guntz, *Compt. rend.*, 1891, 112, 861.

[9] Baur, *Zeitsch. physikal. Chem.*, 1903, 45, 613.

[10] Carey Lea, *Amer. J. Sci.*, 1887, [3], 33, 349.

[11] Compare Zenker, *Lehrbuch der Photochromie*, Brunswick, 1900.

photochlorides are characterized by their great sensitiveness to light, blue light producing a blue coloration, and red light a red coloration. This action is reversible, the blue coloration being transformed into red by the action of red light, and so on. This phenomenon is inapplicable to the production of colour-photographs, for white light causes a darkening in colour.

There are several theories as to the constitution of the silver subhalides in the latent image. The *molecular theory* regards the subhalides as definite chemical compounds. The *adsorption theory* regards them as adsorption-compounds of colloidal silver and subhalides. The molecular theory is advocated by Trivelli,[1] who considers the colour-changes to indicate the existence of several silver subhalides, which yield solid solutions with each other and with the silver halides. He also regards the mechanism of "reduction" with ammonium persulphate as favouring the molecular theory.

Light reacts with silver halides, producing a series of subhalides containing a diminishing proportion of halogen, the colour-changes taking place for all the halides in the sequence green, bluish-green, blue, violet, red, orange, yellow.[2] Guareschi[3] has noted that the darkening of silver salts by light was observed before the time of Boyle (1663), and that investigations made by Schulze (1727), Beccari (1757), and Scheele (1777) were very important for the development of photography. In a more recent paper, Boruttau[4] states that the colour-changes undergone by silver salts under the influence of light were first mentioned by Konrad Gessner in 1565 in his work *De omni verum fossilium genere libri aliquot*, where the darkening of native horn-silver is cited. Hydrogen peroxide has no action on silver bromide, but with the green, blue, or red photohalide oxygen is immediately evolved, with formation of silver bromide and silver monoxide.[5]

Lüppo-Cramer prefers the adsorption-theory because the red, blue, or violet photohalides are formed from the hydrosols of the silver halides in presence of colloidal silver by precipitation with any electrolyte, and treatment of the resulting gel with nitric acid. He attributes the action to adsorption of colloidal silver by the gel of the normal silver halide. He states that identical silver halides are produced by the action of light on silver chloride and bromide, and regards the assumption of the existence of subhalides as unjustifiable.[6] An investigation of the action of light on silver halides has been made by Hartung[7] with the aid of the microbalance, and has furnished evidence in support of Lüppo-Cramer's view. On exposure to light and air, silver bromide loses 2·4 per cent. of its total bromine, its colour changing from pale yellow to pale purple; but exposure to the action of bromine in absence of light restores the original colour, the initial weight being regained almost completely. In air, silver chloride loses 4·1 per cent. of its chlorine, and in vacuum 81·0 per cent., the original weight being restored by the action of

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[1] Trivelli, *Zeitsch. wiss. Photographie*, 1908, *6*, 358, 438.

[2] Trivelli, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 11, 730.

[3] Guareschi, *Atti R. Accad. Sci. Torino*, 1914, 49, 1083.

[4] Boruttau, *Zeitsch. angew. Chem.*, 1918, 31, 139.

[5] Trivelli, *Chem. Weekblad*, 1909, 6, 525; compare Trivelli, *ibid.*, 1910, 7, 321, 404; *Zeitsch. wiss. Photographie*, 1911, 9, 185.

[6] Lüppo-Cramer, *Zeitsch. angew. Chem.*, 1909, 22, 2330; compare Lüppo-Cramer, *Zeitsch. Ind. Kolloide*, 1910, 6, 7, 168; 7, 42, 99, 304; 1911, 8, 42.

[7] Hartung, *Trans. Chem. Soc.*, 1922, 121, 682.

chlorine in absence of light. In air, silver iodide loses 1·1 per cent. of iodine, and in vacuum the action is much more rapid, though relatively slower than with the chloride or bromide. The fact that Lüppo-Cramer's photobromide plates, containing colloidal silver and silver bromide, are unaffected by hydrogen peroxide is advanced by Trivelli[1] as an objection to the adsorption-theory.

Reinders[2] has suggested that the photohalides are normal silver halides coloured by admixture of a small proportion of colloidal silver. The divergence in properties between the photohalides and the latent image is attributed by him to differences in the number, form, and distribution of these colloidal silver particles throughout the silver halide. He regards this theory as explaining, *inter alia*, the production of different colours by the action of light.

Lorenz and Hiege[3] state that exposure of silver chloride or bromide to light causes the separation of colloidal, metallic silver, the particles increasing in size as the action continues. They regard this phenomenon as constituting important evidence in support of the view that the latent photographic image consists of colloidal silver in an ultra-microscopic form.

According to Sichling,[4] the photohalides may consist of—

1. Amorphous silver and silver halide, either mixed together, or with the silver adsorbed by the halide.
2. A mixture of silver subhalide, Ag_2X, and silver halide.
3. A solid solution of silver subhalide, Ag_2X, and silver halide.
4. A solid solution of silver and silver halide. He considers the most probable theory is one assuming a condition of solid solution.

Silver bromide, AgBr.—Precipitation of a solution of a silver salt with a bromide solution yields a flocculent to pulverulent, amorphous precipitate of silver bromide, its colour being white, yellowish-white, or lemon-yellow according to the conditions of precipitation. Its melting-point is given as 422° C.[5] and 427° C.,[6] and the density of the precipitated salt as 6·39 to 6·52, and after fusion as 6·32 to 6·49.

Addition of water to a 0·1 per cent. solution of the amorphous form in concentrated ammonium hydroxide yields hexagonal plates; slow evaporation of a similar solution produces green, lustrous octahedra.

At 18° C. the solubility of the bromide is 0·109 mg. per litre of water.[7] Besides ammonium hydroxide, it dissolves in sodium-thiosulphate solution, forming the double salt $2Na_2S_2O_3,Ag_2S_2O_3,2H_2O$,[8] and in solutions of bromides and potassium cyanide. Its heat of formation from its elements is given as 22·7 Cal.,[9] and 20·7 to 23·7 Cal. according to the condition of the bromide produced.[10]

In ammoniacal solution at 200° C., silver bromide is converted by

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[1] Trivelli, *Chem. Weekblad*, 1910, 7, 351.

[2] Reinders, *ibid.*, 1910, 7, 961, 993; 1911, 8, 299, 316; *Zeitsch. physikal. Chem.*, 1911, 77, 213, 356; *Zeitsch. Ind. Kolloide*, 1911, 9, 10.

[3] Lorenz and Hiege, *Zeitsch. anorg. Chem.*, 1915, 92, 27.

[4] Sichling, *Zeitsch. physikal. Chem.*, 1911, 77, 1; compare Baur, *ibid.*, 58; Weisz, *ibid.*, 1906, 54, 305.

[5] Monkemeyer, *Jahr. Min. Beil.-Bd.*, 1909, 22, 1.

[6] Compare Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 735.

[7] Prud'homme, *J. Chim. phys.*, 1911, 9, 519; compare Hill, *J. Amer. Chem. Soc.*, 1908, 30, 68.

[8] Lumière and Seyewetz, *Rev. gén. Chim.*, 1907, 10, 291.

[9] Thomsen, *Thermochemistry* (Longmans, 1908), 284.

[10] Berthelot, *Ann. Chim. Phys.*, 1883, [5], 29, 241.

iodic acid into the iodide.[1] Double compounds with ammonia of the formulæ $AgBr,3NH_3$ (8·64); $AgBr,1\frac{1}{2}NH_3$ (9·95); and $AgBr,NH_3$ (10·65) have been prepared,[2] the figures in parentheses indicating the calculated heats of formation in large calories.

The action of light is similar to that on silver chloride, *silver photobromide* being produced with liberation of bromine.[3] The change in weight under the influence of light does not exceed 2·4 per cent.[4] Silver bromide is more sensitive to light than any other substance, and is extensively employed in the manufacture of dry photographic plates. The glass is coated with an emulsion produced by addition of ammoniacal silver nitrate to a solution of potassium bromide containing gelatin, the mixture being digested at 40° to 45° C. for about an hour to increase the size of the bromide granules.[5] The emulsion is solidified by cooling with ice, washed with water, liquefied, and poured over the glass. It is usual to add a small proportion of silver iodide as a decelerator, and a slight excess of potassium bromide to eliminate silver nitrate.

A short exposure in the camera to light produces the "latent image," the process being attended by slight reduction, and the formation of photobromide, probably a solid solution of silver and silver subbromide in silver bromide.[6] The latent image is developed by immersing the plate in an alkaline reducer, such as pyrogallol or quinol, in presence of alkali. The reduction takes place first at those points where it has been initiated by the action of light. Development must not be continued so long as to cause general blackening of the plate or "chemical fog." When it is complete, the image is "fixed" by dissolving the unaltered silver salt in a solution of sodium thiosulphate. The velocity of reduction is lowered by the presence of bromine ions, so that the operator can control the rate of reduction by addition of a solution of potassium bromide to the developer.

Collodion can be substituted for gelatin in the preparation of the emulsion, but the plates are less sensitive than the gelatin plates. Gelatin exerts a reducing action on silver bromide, but collodion does not; the collodion plates are consequently free from the trace of fog characteristic of gelatin plates, and therefore give a very sharp, well-defined image suitable for technical reproduction. Collodion plates are rendered more sensitive by the presence of silver nitrate in the emulsion, but such plates have to be exposed in the wet condition, and are not well adapted for field work. The increase in sensitiveness depends on the reaction

$$6AgNO_3+3H_2O+3Br_2=5AgBr+AgBrO_3+6HNO_3.$$

Silver bromide is most sensitive to blue light, but can be rendered sensitive to the green, red, and ultra-red portions of the spectrum by dyeing the emulsion with members of the eosin group or the cyanine

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[1] Baubigny, *Compt. rend.*, 1908, 146, 1097.

[2] Biltz and Stollenwerk, *Zeitsch. anorg. Chem.*, 1920, 114, 174.

[3] On the liberation of bromine by sunlight, compare Schwarz and Stock, *Ber.*, 1921, 54, [B], 2111.

[4] Hartung, *Trans. Chem. Soc.*, 1922, 121, 682; compare Koch and Schrader, *Zeitsch. Physik*, 1921, 6, 127.

[5] Cohen, *Eder's Jahrbuch*, 1895, 103; Eder, *Handbuch der Photographie*, Halle, 1893, Part III.; Abegg and Herzog, *Arch. wiss. Phot.*, 1900, 1, 115; Baur and Postius, *Physikal. Zeitsch.*, 1902, 3, 491.

[6] Compare Weisz, *Zeitsch. physikal. Chem.*, 1906, 54, 305.

group, the resulting plates being orthochromatic or panchromatic. The sensitiveness of gelatino-bromide plates is much diminished by immersion in water or developer, especially for yellow and green rays.[1]

An *oxybromide*, Ag_5Br_7,Ag_2O, is formed by the oxidation of finely divided silver by *p*-benzoquinone.[2] It consists of colourless, glistening lamellæ, and is converted by potassium iodide into the corresponding *oxyiodide*.

Silver subbromide, Ag_2Br.—Bromine-water reacts with a solution of colloidal silver to form the subbromide as a brownish-violet powder. Homogeneous mixtures of this substance and silver bromide probably constitute Carey Lea's coloured photobromides.

Silver iodide, AgI.—The iodide can be synthesized by heating silver with iodine, and is precipitated by mixing solutions of iodides and silver salts. It is also formed by the decomposition of hydrogen iodide by silver,[3] and by the action of iodine on silver chloride or bromide.

Silver iodide is known in an amorphous form, and also in hexagonal and cubic crystals. Its melting-point is 352° C.[4]; after fusion and resolidification it expands with fall in temperature, a phenomenon explained [5] by assuming that the affinity of silver for iodine diminishes with the temperature. Its density is given as 5·609; 5·71 (native cubic crystals); 5·687 (fused); 5·669 (crystalline at 14° C.); 5·596 (compressed amorphous). The transition-point of the hexagonal to the cubic form is 146° to 147° C., the colour changing from pale yellow to golden yellow.[6] The transition-curve is given in fig. 13.[7]

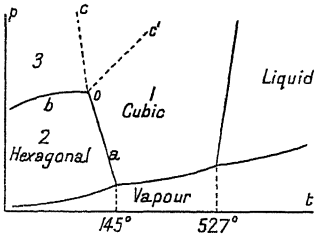

FIG. 13.—Transition-curve of silver iodide.

The specific heat of the hexagonal form is 0·0544, and that of the cubic form 0·0577.[8] The solubility at 20·8° C. is given as $1{\cdot}5\times10^{-8}$ gram-molecule per litre of water,[9] another value being $1{\cdot}23\times10^{-8}$ gram-molecule.[10] The heat of formation from the elements is given

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[1] Lumière and Seyewetz, *Rev. gén. Chim.*, 1907, 10, 291.
[2] Seyewetz, *Compt. rend.*, 1912, 154, 355.
[3] Compare Danneel, *Zeitsch. physikal. Chem.*, 1900, 33, 415.
[4] Monkemeyer, *Jahr. Min. Beil.-Bd.*, 1909, 22, 1.
[5] Jones, *J. Amer. Chem. Soc.*, 1909, 31, 191; compare Fizeau, *Annalen*, 1867, 132, 292.
[6] Steger, *Zeitsch. physikal. Chem.*, 1903, 43, 595; compare Kohlrausch, *Wied. Annalen*, 1882, 17, 642; Tammann, *ibid.*, 1899, 68, 646; Roozeboom, *Heterogene Gleichgew.*, 1901, 1, 128; van 't Hoff, *Boltzmann Festschrift*, Leipsic, 1904, 239.
[7] Compare Baur, *Abegg and Auerbach's Handbuch der anorg. Chem.*, Leipsic, 1908, 2, i., 692.
[8] Bellati and Romanese, *Atti R. Inst. Ven.*, 1883, 6, 1; compare Magnus, *Ann. Physik*, 1910, [4], 31, 597.
[9] Kohlrausch, *Zeitsch. physikal. Chem.*, 1905, 50, 356.
[10] Hill, *J. Amer. Chem. Soc.*, 1908, 30, 68.

as 13·8 Cal.,[1] 14·3 Cal.,[2] 14·57 Cal.,[3] 15·1 Cal.,[4] 15·158 Cal.,[5] and 15·17 Cal.[6]

Silver iodide is only slightly soluble in ammonia, but dissolves in sodium thiosulphate, concentrated hydriodic acid, and saturated solutions of potassium iodide.[7] It forms a series of double salts with silver bromide,[8] with mercuric iodide,[9] and with the iodides of the alkali-metals.[10] Double compounds of silver iodide and ammonia of the formulæ $AgI,3NH_3$ (6·92); $AgI,1\frac{1}{2}NH_3$ (7·25); AgI,NH_3 (8·56); $AgI,2NH_3$ (7·05); and $AgI,\frac{1}{2}NH_3$ (11·59) have also been prepared,[11] the figures in parentheses indicating the calculated heats of formation in large calories.

Like the other silver halides, silver iodide is sensitive to light, the loss in weight not exceeding 1·1 per cent.[12] The sensitiveness to light is diminished by the presence of potassium iodide, and increased by that of silver nitrate. In the second instance the liberated iodine reacts with the silver nitrate :

$$6AgNO_3+3H_2O+3I_2=5AgI+AgIO_3+6HNO_3.$$

The possibility of developing the latent image was discovered by Daguerre, who at first employed a silver plate coated with the iodide, development being effected by exposing the plate to the action of mercury-vapour. Later, he substituted glass for silver, and developed with a mixture of silver nitrate and ferrous sulphate. His discovery led to the introduction of the wet collodion-process with silver iodide as the sensitive material.

Silver hypochlorite, $AgOCl$.—A very unstable solution of the hypochlorite is formed by the action of chlorine-water on excess of silver monoxide. It soon decomposes into silver chloride and chlorate.

Silver chlorite, $AgClO_2$.—Silver nitrate and potassium chlorite react to form yellow crystals of the chlorite, an unstable substance decomposing energetically at 105° C.

Silver chlorate, $AgClO_3$.—The chlorate can be prepared by dissolving the monoxide in chloric acid, or by passing chlorine through a suspension of the monoxide in water, the hypochlorite being an intermediate product. It forms tetragonal crystals, melting at 230° C., and decomposing at 270° C. into silver chloride and oxygen. At ordinary temperatures its solubility is 20 grams per 100 grams of water.[13] Its solution in ammonium hydroxide yields prismatic crystals, $Ag(NH_3)_2ClO_3$, melting at 100° C.

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[1] Thomsen, *Thermochemistry* (Longmans, 1908), 284.

[2] Berthelot, *Ann. Chim. Phys.*, 1883, [5], 29, 241.

[3] Jones and Hartmann, *J. Amer. Chem. Soc.*, 1915, 37, 752.

[4] Braune and Koref, *Zeitsch. anorg. Chem.*, 1914, 87, 175; compare Taylor and Anderson, *J. Amer. Chem. Soc.*, 1921, 43, 2014.

[5] Gerth, *Zeitsch. Elektrochem.*, 1921, 27, 287.

[6] Fischer, *ibid.*, 1912, 18, 283; *Zeitsch. anorg. Chem.*, 1912, 78, 41.

[7] Hellwig, *Zeitsch. anorg. Chem.*, 1900, 25, 183; Berthelot, *Compt. rend.*, 1880, 91, 1024; compare Krym, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 382.

[8] Thiel, *Zeitsch. anorg. Chem.*, 1900, 24, 32.

[9] Steger, *Zeitsch. physikal. Chem.*, 1903, 43, 595.

[10] Marsh and Rhymes, *Trans. Chem. Soc.*, 1913, 103, 781.

[11] Biltz and Stollenwerk, *Zeitsch. anorg. Chem.*, 1920, 114, 174.

[12] Hartung, *Trans. Chem. Soc.*, 1922, 121, 682; compare Koch and Schrader, *Zeitsch. Physik*, 1921, 6, 127.

[13] Wächter, *J. prakt. Chem.*, 1843, 30, 330.

Silver perchlorate, $AgClO_4$.—The monoxide dissolves in perchloric acid, forming the perchlorate. It is also produced by double decomposition from barium perchlorate and silver sulphate. The unstable, deliquescent salt melts at 486° C., and decomposes at higher temperatures.

Silver bromate, $AgBrO_3$.—Potassium bromate precipitates silver bromate from silver nitrate. The bromate is dimorphous, forming tetragonal bi-pyramids stable below 98·5° C., and hair-like crystals stable above that temperature.[1] Its melting-point is 308° to 310° C.[1]

Solubility of Silver Bromate.[2]

Temperature, °C.	25	35	45	55	65	75	85	90
Grams of silver bromate in 100 grams of water	0·196	0·269	0·371	0·497	0·648	0·832	1·055	1·325

In absence of moisture and organic matter it is stable towards heat and light; but in presence of water it darkens slowly at ordinary temperatures, and rapidly at high temperatures, while the presence of such an impurity as dust induces explosive decomposition of the heated bromate. It can be employed as a standard in iodometry. Its solution in ammonium hydroxide yields crystals of the formula $Ag(NH_3)_2BrO_3$.

Silver perbromate, $AgBrO_4$.—The perbromate is prepared by double decomposition from potassium perbromate and silver nitrate, and is but slightly soluble in cold water.

Silver iodate, $AgIO_3$.—Potassium iodate reacts with silver sulphate to form a white precipitate of the iodate. It crystallizes from ammoniacal solution in rectangular columns. At 18° C. its solubility is $1·89 \times 10^{-4}$ gram-molecule per litre of water.[3]

Silver periodates.—A solution of sodium periodate, $Na_4I_2O_9$, gives with silver nitrate a precipitate of a silver periodate. It crystallizes from dilute nitric acid in straw-coloured, hexagonal crystals of the formula $2Ag_2O,I_2O_7,3H_2O$, transformed at 100° C. into the corresponding monohydrate, a dark-red, crystalline powder. Prolonged boiling of the trihydrate with water yields $3Ag_2O,I_2O_7$ or $5Ag_2O,I_2O_7$. The substance with the second formula is also produced as a black, crystalline powder by the action of silver nitrate on the trihydrate. Evaporation with nitric acid converts the trihydrate into the yellow, crystalline anhydrous salt, Ag_2O,I_2O_7. Ammonia transforms the trihydrate into a black powder, $4Ag_2O,I_2O_7$.[4] The trihydrate, $2Ag_2O,I_2O_7,3H_2O$, is also formed by the interaction at ordinary temperatures of silver nitrate and a nitric-acid solution of the periodate $Na_2H_3IO_6$. At 100° C. the action produces a black precipitate, $3Ag_2O,I_2O_7$.[5]

Silver suboxide, Ag_4O.—Several experimenters have described the formation of a suboxide by reduction of silver compounds, but the subject seems to merit further investigation. Silver subfluoride is said to react with water-vapour at 180° C., yielding a black powder of the

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[1] Reedy, *J. Amer. Chem. Soc.*, 1921, 43, 1440.

[2] Reedy, *loc. cit.*; compare Böttger, *Zeitsch. physikal. Chem.*, 1903, 46, 602.

[3] Noyes and Kohr, *Zeitsch. physikal. Chem.*, 1903, 42, 336; compare Kohlrausch, *ibid.*, 1908, 64, 129; Böttger, *ibid.*, 1903, 46, 602.

[4] Rammelsberg, *Pogg. Annalen*, 1865, 124, 386.

[5] Rosenheim and Liebknecht, *Annalen*, 1899, 308, 40.

formula Ag_4O.[1] It is also said to be produced by reduction of silver monoxide by hydrogen at 38° C.,[2] and by other methods.[3]

Silver monoxide, Ag_2O.—Addition of the hydroxide of barium or of an alkali-metal to silver-nitrate solution precipitates the monoxide as a blackish, amorphous powder, which crystallizes from ammoniacal solution in violet crystals. Its density is given as 7·143 and 7·250. Ammoniacal silver oxide has been known to explode, the phenomenon being probably due to the formation of "fulminating silver" (compare p. 315).[4]

The monoxide is decomposed by heat into silver and oxygen, the liberated metal playing the part of an autocatalyst in accelerating the reaction.[5] Finely divided platinum and manganese dioxide also cause acceleration of the transformation. It is decomposed by the action of light, with evolution of oxygen, and possibly formation of silver suboxide.

Silver monoxide dissolves in water, forming an alkaline solution which turns red litmus blue. At 25° C. its solubility corresponds with $2{\cdot}16\times10^{-4}$ gram-molecule per litre of water,[6] and at 15° C. Rebière[7] found the same value. It is a strong base, its salts having a neutral reaction. The solution is coloured reddish and decomposed by the action of light, the change being possibly attended by deposition of the suboxide or of colloidal silver.

Its heat of formation is about 6·4 Cal.[8] It decomposes hydrogen peroxide, with liberation of metallic silver.[9] With carbon tetrachloride it reacts at 250° C. in accordance with the equation[10]

$$Ag_2O+CCl_4=2AgCl+COCl_2.$$

In the moist condition it finds extensive application in organic chemistry to the replacement of halogen by hydroxyl.[11] It can act as a reducer.[12]

Argentic oxide, AgO.—A hot alkaline solution of potassium permanganate partially oxidizes silver monoxide to argentic oxide:[13]

$$Ag_2O+2KMnO_4+2NaOH=2AgO+K_2MnO_4+Na_2MnO_4+H_2O.$$

The reaction is reversible. This oxide is said to be formed by anodic oxidation of silver in alkaline solution.[14] It is a weaker base than the monoxide, but its solution in concentrated nitric acid contains $Ag(NO_3)_2$. Barbieri regards it as belonging to the class of ozonides, and differing

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[1] Guntz, *Compt. rend.*, 1891, 112, 861.

[2] Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 9.

[3] Wöhler, *Annalen*, 1857, 101, 363; 1860, 114, 119; Rose, *Pogg. Annalen*, 1852, 85, 304; Muthmann, *Ber.*, 1887, 20, 983; von der Pfordten, *ibid.*, 1407; Leduc and Labrouste, *Compt. rend.*, 1907, 145, 55.

[4] Matignon, *Bull. Soc. chim.*, 1908, [4], 3, 618.

[5] Lewis, *Zeitsch. physikal. Chem.*, 1905, 52, 310.

[6] Noyes and Kohr, *ibid.*, 1903, 42, 336.

[7] Rebière, *Bull. Soc. chim.*, 1915, [4], 17, 309.

[8] Lewis, *Zeitsch. physikal. Chem.*, 1906, 55, 449; compare Thomsen, *Thermochemistry*, (Longmans, 1908), 284; Berthelot, *Compt. rend.*, 1878, 87, 575, 667; *Ann. Chim. Phys.*, 1878, [5], 15, 186.

[9] Compare von Baeyer and Villiger, *Ber.*, 1901, 34, 749, 2769.

[10] Michael and Murphy, *Amer. Chem. J.*, 1910, 44, 365.

[11] Compare Madsen, *Zeitsch. anorg. Chem.*, 1912, 79, 195.

[12] Chandrasena and Ingold, *Trans. Chem. Soc.*, 1922, 121, 1552.

[13] Barbieri, *Atti R. Accad. Lincei*, 1907, [5], 16, ii., 72.

[14] Luther and Pokorný, *Zeitsch. anorg. Chem.*, 1908, 57, 290; compare Baborovsky and Kuzma, *Zeitsch. Elektrochem.*, 1908, 14, 196.

from the type of oxide exemplified by hydrogen peroxide, because its solution in concentrated nitric acid does not react with lead peroxide, manganese dioxide, or potassium permanganate.

Higher oxides.—Electrolysis of silver-nitrate solution at 0° C. yields at the anode a black, crystalline substance of metallic lustre. It readily loses oxygen, silver nitrate entering into solution, and the residual crystals of *silver peroxynitrate* have the formula $2Ag_3O_4,AgNO_3$. It changes slowly, with evolution of oxygen, into $3Ag_2O,AgNO_3$.[1] According to Weber,[2] the presence of between 15 and 25 per cent. of nitric acid inhibits the deposition of the peroxynitrate at the anode, but produces a brown solution. Weber regards the oxide portion of the salt as having the formula $Ag(AgO_2)_2$, analogous to that of magnetic iron oxide, and considers it to be the silver salt of an unstable *argentic acid*, $HAgO_2$. It is a compound of silver in which the metal has a valency greater than unity.

An analogous derivative of the oxide Ag_3O_4 has been prepared by the electrolysis of silver fluoride. It has the formula $2Ag_3O_4,AgF$.[3]

A *peroxide*, probably Ag_2O_3, is stated to be produced by anodic oxidation of silver in acid solution.[4] When solutions of sodium or potassium persulphate react with silver or silver nitrate, a peroxide with a higher percentage of oxygen than Ag_2O_2 is produced, the process being attended by catalytic decomposition of the persulphate with formation of the acid sulphate. Ammonium persulphate does not yield a peroxide, but the ammonium radical becomes oxidized to nitric acid.[5]

Silver subsulphide, Ag_4S.—Hydrogen sulphide precipitates from silver subfluoride a black, amorphous substance, possibly Ag_4S, but probably only a mixture of silver and its sulphide.[6]

Silver sulphide, Ag_2S.—The sulphide occurs in nature as argentite, and also in combination with many other sulphides. It is formed by direct synthesis from its elements at ordinary temperatures,[7] and also by immersion of the metal in solutions of alkali-metal polysulphides. It can be prepared in cubic crystals by passing sulphur-vapour over heated silver, or by the action of hydrogen trisulphide, H_2S_3, on silver oxide.[8] It is the only definite compound produced by fusion of mixtures of silver and sulphur in different proportions.[9] The black, amorphous form is precipitated by the action of hydrogen sulphide or a soluble sulphide on a solution of a silver salt. It is also produced by the action of hydrogen sulphide on metallic silver, a reversible reaction.[10]

The melting-point of the sulphide is given as 812° C.,[11] 815° C.,[12] and 834° C.[13] It is the most insoluble of the silver salts, its solubility corre-

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[1] Mulda and Heringa, *Rendiconti*, 1882, 15, 1; 1883, 16, 57; 1884, 17, 129; Sulc, *Zeitsch. anorg. Chem.*, 1896, 12, 89.

[2] Weber, *Trans. Amer. Electrochem. Soc.*, 1917, 32, 391.

[3] Tanatar, *Zeitsch. anorg. Chem.*, 1901, 28, 331.

[4] Luther and Pokorný, *loc. cit.*

[5] Higson, *Trans. Chem. Soc.*, 1921, 119, 2048; compare Marshall and Inglis, *Proc. Roy. Soc. Edin.*, 1902, 24, 88.

[6] Compare Bissett, *Trans. Chem. Soc.*, 1914, 105, 1223.

[7] Compare Spring, *Bull. Soc. chim.*, 1884, [2], 41, 492.

[8] Bloch and Höhn, *Ber.*, 1908, 41, 1971.

[9] Bissett, *Trans. Chem. Soc.*, 1914, 105, 1223.

[10] Pélabon, *Compt. rend.*, 1898, 126, 1864.

[11] Friedrich, *Metallurgie*, 1908, 5, 23.

[12] Bissett, *loc. cit.*

[13] Truthe, *Zeitsch. anorg. Chem.*, 1912, 76, 161.

sponding with $1{\cdot}2\times10^{-16}$ gram-atom of silver per litre.[1] When heated with silver sulphate at 300° C., both salts are reduced to metallic silver.[2] In the fused state it is miscible with molten silver in all proportions. When heated in vacuum, it decomposes into its elements rapidly at 810° C.[3]

The interaction of silver sulphide and mercury is considered on p. 290, and that with cyanides on p. 292.

Silver sulphite, Ag_2SO_3.—The sulphite is prepared by precipitating silver nitrate with the theoretical proportion of sulphurous acid or sodium sulphite, the salt being decomposed by excess of the acid, and dissolved by excess of the sulphite. It is a white substance, its colour changing under the influence of light to purple and then to black. Its solubility [4] in water is less than 1 : 20000. When boiled with water, it decomposes in accordance with the equation

$$2Ag_2SO_3 = Ag_2SO_4 + 2Ag + SO_2.$$

When heated alone, 10 per cent. decomposes as indicated, and the remainder is converted into silver dithionate and metallic silver : [5]

$$2Ag_2SO_3 = Ag_2S_2O_6 + 2Ag.$$

Several complex sulphites of silver with sodium and ammonium have been described.[6]

Silver sulphate, Ag_2SO_4.—The sulphate is produced by dissolving the metal in sulphuric acid, and by the action of this acid on the nitrate.[7] It forms white, rhombic crystals, isomorphous with those of the corresponding sodium salt, and melting at low red heat. Its density is 5·45.[8] The solubility of silver sulphate in water at various temperatures has been only partially investigated. At 14·5° C., 100 grams of saturated solution contain 0·730 gram of silver sulphate[9]; at 25° C. the solubility is 0·0267 gram-molecule per litre of water.[10] Its heat of formation from the metal, oxygen, and sulphur dioxide is 96·20 Cal.[11]

When the sulphate is heated to fusion in a current of hydrogen chloride, it is converted completely into chloride : [12]

$$Ag_2SO_4 + 2HCl = 2AgCl + H_2SO_4.$$

Heating with silver sulphide causes partial reduction to metallic silver : [13]

$$Ag_2SO_4 + Ag_2S = 4Ag + 2SO_2.$$

From the solution in dilute sulphuric acid three *acid salts* have been obtained: $AgHSO_4$, pale yellow prisms ; $2Ag_2O,5SO_3,5H_2O$, lustrous

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[1] Bodländer and Lucas, *Zeitsch. anorg. Chem.*, 1904, 41, 192.
[2] Sackur, *Ber.*, 1908, 41, 3356.
[3] Damm and Merz, *Ber.*, 1907, 40, 4775.
[4] Baubigny, *Compt. rend.*, 1909, 149, 858.
[5] Baubigny, *ibid.*, 735, 858.
[6] Svensson, *Ber.*, 1871, 4, 713 ; Rosenheim and Steinhäuser, *Zeitsch. anorg. Chem.*, 1900, 25, 72.
[7] Compare Stas, *Bull. Acad. roy. Belg.*, 1860, [2], 9, 322.
[8] Richards and Jones, *Zeitsch. anorg. Chem.*, 1907, 55, 72.
[9] Barre, *Ann. Chim. Phys.*, 1911, [8], 24, 145.
[10] Rothmund, *Zeitsch. physikal. Chem.*, 1909, 69, 523.
[11] Thomsen, *Thermochemistry* (Longmans, 1908), 323.
[12] Richards and Jones, *loc. cit.*
[13] Sackur, *Abegg and Auerbach's Handbuch der anorg. Chem.*, Leipsic, 1908, 2, i., 714.

laminæ; and $Ag_2O,4SO_3,5H_2O$, colourless prisms.[1] The saturated solution in ammonium hydroxide yields tetragonal crystals of the formula $Ag_2SO_4,4NH_3$.[2] The dry sulphate absorbs ammonia, forming a compound $Ag_2SO_4,2NH_3$.[3]

Silver selenide, Ag_2Se.—Measurements of E.M.F. in selenide cells indicate the existence of the monoselenide only.[4] It is formed by the action of selenium on the nitrate (p. 316).

Silver telluride, Ag_2Te.—Silver and tellurium unite directly to form silver telluride.[5] It can also be produced by the reduction of tellurites[6]; by the interaction of tellurium and silver salts[7]; and by the action of a solution of sodium telluride, Na_2Te, on silver acetate dissolved in dilute acetic acid.[8] When prepared by the method last mentioned, it forms a grey, brittle, crystalline substance, melting at 959° C.[9] It is also formed by heating silver and tellurium, another substance, possibly AgTe, being produced simultaneously.

Silver thiosulphate, $Ag_2S_2O_3$.—Precipitation of a solution of sodium thiosulphate with silver nitrate yields the thiosulphate as a white precipitate of sweetish taste. It dissolves in solutions of other thiosulphates, forming double salts. As examples of such salts isolated from solutions of silver chloride in thiosulphates may be cited $Ag_2S_2O_3,2Na_2S_2O_3,2H_2O$, leaflets of silk-like lustre, readily soluble in water[10]; $Ag_2S_2O_3,Na_2S_2O_3,H_2O$, small, hard, columnar crystals of slight solubility and sweet taste; $Ag_2S_2O_3,3K_2S_2O_3,2H_2O$; $Ag_2S_2O_3,(NH_4)_2S_2O_3$, columnar crystals of intensely sweet taste. A double salt of the formula $3Ag_2S_2O_3,5K_2S_2O_3$ crystallizes in prismatic needles from a solution of silver nitrate and sodium thiosulphate on addition of potassium carbonate.[11] Additive compounds of this type, and others with ammonia, have been exhaustively studied by Jonsson.[12]

Silver dithionate, $Ag_2S_2O_6$.—The dithionate is formed by heating the sulphite (p. 313), and also by dissolving silver carbonate in dithionic acid. The rhombic crystals darken under the influence of light, and dissolve in twice their weight of water at 16° C.

Silver azide, AgN_3.—Hydrazoic acid reacts with silver nitrate, forming the azide.[13] It is also produced by the interaction of silver nitrite and hydrazine sulphate in aqueous solution:

$$AgNO_2+H_2N{\cdot}NH_2=H_2N{\cdot}N:NOAg+H_2O=AgN_3+2H_2O.$$

A solution of sodium azide gives with silver nitrate a greyish precipitate of silver azide.[14] The salt crystallizes in white needles, melting at 250° C.,

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[1] Schulz, *Pogg. Annalen*, 1868, 133, 137.
[2] Mitscherlich, *ibid.*, 1828, 12, 141.
[3] Rose, *ibid.*, 1830, 20, 153.
[4] Pélabon, *Compt. rend.*, 1912, 154, 1414.
[5] Rose, *Pogg. Annalen*, 1830, 18, 64.
[6] Brauner, *Trans. Chem. Soc.*, 1889, 55, 389.
[7] Hall and Lenher, *J. Amer. Chem. Soc.*, 1902, 24, 918.
[8] Tibbals, *ibid.*, 1909, 31, 902.
[9] Pellicini and Quercigh, *Atti R. Accad. Lincei*, 1910, [5], 19, ii., 415.
[10] Lenz, *Annalen*, 1841, 40, 94; compare Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 176.
[11] Rosenheim and Steinhäuser, *Zeitsch. anorg. Chem.*, 1900, 25, 72.
[12] Jonsson, *Ber.*, 1921, 54, [B], 2556; compare Schwicker, *Ber.*, 1889, 22, 1730; Julius Meyer and Eggeling, *Ber.*, 1907, 40, 1351.
[13] Curtius and Rissom, *J. prakt. Chem.*, 1886, [2], 58, 261.
[14] Raschig, *Ber.*, 1908, 41, 4194.

and is exploded energetically by percussion or by exposure to green light. It is suitable for use as a general primer.[1]

Berthollet's "fulminating silver" is produced by addition of alcohol to a concentrated solution of silver monoxide in ammonium hydroxide. It forms small, black crystals, exploded by friction, and soluble in potassium-cyanide solution. It probably has the formula NAg_3 or $NAgH_2$;[2] and it has no connexion with silver fulminate, C:N.O.Ag.

Silver hyponitrite, $Ag_2N_2O_2$.—Addition of silver nitrate to solutions of alkali-metal hyponitrites produces the hyponitrite as a yellowish precipitate. It is very slightly soluble in water, is sensitive to light, and is decomposed by heat into silver, nitrogen oxides, and nitrogen.[3]

Silver nitrite, $AgNO_2$.—Sodium nitrite[4] and the corresponding salts of potassium and barium react with silver nitrate to form silver nitrite. It crystallizes in long, greenish-yellow, rhombic needles, the density at 0° C. being 4·542, and between 21° and 31° C. 4·453.[5] At 15° C. its percentage-solubility is 0·2752,[6] and at 18° C. 0·0216 gram-molecules dissolve in 1 litre of water.[7]

In the moist condition the salt is readily reduced by organic matter.[8] When heated rapidly *in vacuo*, it is completely decomposed into silver and nitrogen peroxide. Slower heating in air causes side-reactions in accordance with the equations[9]

$$Ag+2NO_2=AgNO_3+NO;$$
$$AgNO_2+NO_2=AgNO_3+NO.$$

Several double salts with alkali-metal nitrites have been described.[10] Double compounds with ammonia of the formulæ $AgNO_2,NH_3$; $AgNO_2,2NH_3$; and $AgNO_2,3NH_3$ have also been prepared.[11] A double salt with cæsium, $AgCs(NO_2)_2$, is formed by the interaction of cæsium nitrite and silver nitrite. It crystallizes in lemon-yellow needles.[12]

Silver nitrate, $AgNO_3$.—Silver, silver monoxide, silver sulphide, and silver carbonate dissolve in nitric acid. Concentration of the solutions yields colourless, rhombic crystals of silver nitrate, of melting-point 208·6° C., and density 4·3554. It is characterized by its caustic action on the skin, its power of blackening it, its antiseptic properties, and its metallic taste.

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[1] Wöhler and Matter, *Zeitsch. ges. Schiess- und Spreng-stoffwesen*, 1907, 2, 181, 203, 244, 265.

[2] Raschig, *Annalen*, 1886, 233, 93; compare Sieverts, *Zeitsch. angew. Chem.*, 1909, 22, 6.

[3] Kirschner, *Zeitsch. anorg. Chem.*, 1898, 16, 424; Hantzsch and Kaufmann, *Annalen*, 1896, 292, 317; Divers, *Trans. Chem. Soc.*, 1899, 75, 108; *Proc. Chem. Soc.*, 1907, 23, 266; Angeli and Marchetti, *Atti R. Accad. Lincei*, 1908, [5], 17, i., 695; Rây and Gañguli, *Trans. Chem. Soc.*, 1907, 99, 1402.

[4] Oswald, *Ann. Chim. Phys.*, 1914, [9], 1, 32.

[5] Rây, *Trans. Chem. Soc.*, 1908, 93, 997.

[6] Creighton and Ward, *J. Amer. Chem. Soc.*, 1915, 37, 2333.

[7] Abegg and Pick, *Ber.*, 1905, 38, 2571; *Zeitsch. Elektrochem.*, 1906, 12, 592; *Zeitsch. anorg. Chem.*, 1905, 51, 1.

[8] Oswald, *loc. cit.*

[9] Oswald, *Compt. rend.*, 1911, 152, 381; compare Abegg and Pick, *Ber.*, 1905, 38, 2571; *Zeitsch. Elektrochem.*, 1906, 12, 592; *Zeitsch. anorg. Chem.*, 1906, 51, 1.

[10] Fischer, *Pogg. Annalen*, 1878, 74, 120.

[11] Reychler, *Ber.*, 1883, 16, 2425.

[12] Jamieson, *Amer. Chem. J.*, 1907, 38, 614.

The solubility of silver nitrate in water has been the subject of more complete investigation than that of any other salt of silver.

Solubility of Silver Nitrate.[1]

Temperature, °C.	0	10	20	30	40	50	60	80	100	120
Grams of silver nitrate in 100 g. of water	122	170	222	300	376	455	525	669	952	1900

To render the aqueous solution of silver nitrate stable, Liebert[2] recommends exposing it to the action of light until the organic matter is exhausted. Light has no further action on a solution thus prepared.

The latent heat of fusion of silver nitrate is 17·6 Cal.,[3] and its heat of formation from its elements is 28·74 Cal.[4]

Above 160° C. the stable form of silver nitrate belongs to the rhombohedral system. At lower temperatures the crystals are rhombic, the transition-temperature between the two varieties being between 159·2° and 159·7° C.[5]

When heated, silver nitrate begins to decompose at 320° C. in accordance with the equation

$$2AgNO_3 = 2AgNO_2 + O_2.$$

At a higher temperature the decomposition becomes more complex, being attended by evolution of oxygen and nitrogen, and reduction to metallic silver.[6]

Silver nitrate is readily reduced by red-hot charcoal, but only slowly by hydrogen. Ozone converts it into a bluish-black peroxide.[7] A solution of silver nitrate reacts with hydrogen peroxide containing a small proportion of potassium or sodium hydroxide, with formation of a black to greyish precipitate of silver and silver oxide, there being no silver peroxide formed.[8] Brown[9] has observed during the electrolytic oxidation of silver nitrate with non-corrodible electrodes the deposition of a black substance on the anode, and regards it as being probably *silver peroxynitrate*, $2Ag_3O_4,AgNO_3$. Silver nitrate is transformed by chlorine into the chloride and chlorate. Boiling sulphur gives the sulphide; and selenium the selenide, Ag_2Se, and selenite, Ag_2SeO_3.[10] Phosphorus, hypophosphorous acid,[11] and phosphorous acid reduce it to metallic silver, with formation of phosphoric acid. Phosphine produces an unstable, intermediate, yellow substance, $PAg_3,3AgNO_3$, which rapidly darkens in colour, with separation of silver.

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[1] Compare Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, Table 176.

[2] Liebert, *Chem. Weekblad*, 1919, 16, 74.

[3] Guinchant, *Compt. rend.*, 1907, 145, 320.

[4] Thomsen, *Thermochemistry* (Longmans, 1908), 324; compare Colson, *Compt. rend.*, 1909, 148, 837.

[5] Schwarz, *Beiträge zur Kenntniss der umkehrbaren Umwandlungen polymorphen Körper*, Göttingen, 1894; Hissink, *Zeitsch. physikal. Chem.*, 1900, 32, 537; compare Jänecke, *ibid.*, 1915, 90, 296.

[6] Oswald, *Ann. Chim. Phys.*, 1914, [9], 1, 32.

[7] Mailfert, *Compt. rend.*, 1882, 94, 860.

[8] Salkowski, *J. prakt. Chem.*, 1921, 102, 194.

[9] Brown, *J. Physical Chem.*, 1916, 20, 680.

[10] Senderens, *Compt. rend.*, 1887, 104, 175.

[11] Sieverts and Loessner, *Zeitsch. anorg. Chem.*, 1912, 76, 1.

Arsine[1] reacts with a concentrated solution of silver nitrate, precipitating yellow $Ag_3As,3AgNO_3$, decomposed by water with liberation of metallic silver. With dilute silver nitrate the reaction occurs in two stages:

$$AsH_3+3AgNO_3=Ag_3As+3HNO_3;$$
$$Ag_3As+3AgNO_3+3H_2O=H_3AsO_3+6Ag+3HNO_3.$$

In presence of dilute ammonium hydroxide reduction to metallic silver takes place in three stages, ammonium arsenate and nitrate being simultaneously formed:

$$AsH_3+3(AgNH_3)NO_3=Ag_3As+3NH_4NO_3;$$
$$Ag_3As+3(AgNH_3)NO_3+NH_4OH+H_2O=NH_4AsO_2+6Ag+3NH_4NO_3;$$
$$NH_4AsO_2+2(AgNH_3)NO_3+2NH_4OH=(NH_4)_3AsO_4+2Ag+2NH_4NO_3.$$

The action of stibine[2] is similar to that of arsine, but only about 2 per cent. of the antimonious acid formed dissolves, the rest remaining in the precipitate:

$$SbH_3+3AgNO_3=Ag_3Sb+3HNO_3;$$
$$Ag_3Sb+3AgNO_3+3H_2O=H_3SbO_3+6Ag+3HNO_3.$$

Excess of silver nitrate reacts with iodine in accordance with the equation

$$6AgNO_3+6I+3H_2O=AgIO_3+5AgI+6HNO_3.$$

When the iodine is in excess, the reaction is represented by the equation

$$5AgNO_3+6I+3H_2O=HIO_3+5AgI+5HNO_3.$$

The second reaction is applicable to iodometry, the titration of alkali-metal hydroxides, and the titration of silver nitrate.[3]

With mercury a solution of silver nitrate yields various amalgams and crystalline double compounds of silver and mercury.[4]

Silver nitrate forms double salts with the halides, cyanide, and thiocyanate of silver.[5] It also yields with silver sulphide a compound containing equimolecular proportions of the two salts, prepared as a yellowish-green precipitate by the action of hydrogen sulphide on a concentrated solution of silver nitrate. It forms other double salts with the nitrates of lithium and sodium,[6] potassium,[7] ammonium,[8] and thallium.[9] The solution of silver nitrate in ammonium hydroxide yields rhombic prisms, $AgNO_3,2NH_3$, isomorphous with silver nitrate.[10]

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[1] Reckleben, Lockemann, and Eckardt, *Zeitsch. anal. Chem.*, 1907, 46, 671; Reckleben and Lockemann, *ibid.*, 1908, 47, 126.

[2] Reckleben, *Ber.*, 1909, 42, 1458.

[3] Pawloff and Schein, *J. Russ. Phys. Chem. Soc.*, 1907, 39, 943.

[4] Compare Reinders, *Zeitsch. physikal. Chem.*, 1902, 42, 225; 1906, 54, 607; Ogg, *ibid.*, 1898, 27, 285.

[5] Hellwig, *Zeitsch. anorg. Chem.*, 1900, 25, 183; Jaeger, *Zeitsch. Kryst. Min.*, 1907, 44, 169; Scarpa, *Atti R. Accad. Lincei*, 1913, [5], 22, ii., 452.

[6] Hissink, *Zeitsch. physikal. Chem.*, 1900, 32, 543.

[7] Retgers, *ibid.*, 1889, 4, 608; Schreinemakers, *ibid.*, 1909, 65, 553; Schreinemakers and de Baat, *Chem. Weekblad*, 1910, 7, 259.

[8] Schreinemakers, *loc. cit.*; Schreinemakers and de Baat, *loc. cit.*

[9] van Eyck, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, 2, 543.

[10] Reychler, *J. Chim. phys.*, 1903, 1, 345; compare Castoro, *Gazzetta*, 1907, 37, i., 310; Hantzsch, *Zeitsch. anorg. Chem.*, 1899, 19, 104.

Silver phosphides.—At 400° C. silver and phosphorus-vapour combine to form the *diphosphide*, AgP_2, a grey, crystalline mass.[1] White phosphorus dissolves in molten silver, yielding white, crystalline products containing up to 20 per cent. of phosphorus. They are probably solid solutions of silver and phosphorus. *Silver phosphide*, Ag_2P_5, is precipitated as a brown, amorphous substance by the interaction of silver nitrate and a solution in liquid ammonia of rubidium phosphide, Rb_2P_5.[2]

Silver hypophosphate, $Ag_4P_2O_6$.—Silver nitrate gives with sodium hypophosphate, $Na_4P_2O_6$, a white precipitate of silver hypophosphate. It is also produced in crystalline form by boiling a solution of silver nitrate in nitric acid with phosphorus. Heat decomposes it into silver metaphosphate and metallic silver :[3]

$$Ag_4P_2O_6=2AgPO_3+2Ag.$$

Silver orthophosphate, Ag_3PO_4.—With solutions of normal or secondary sodium orthophosphate silver nitrate gives a yellow precipitate of silver orthophosphate, containing silver nitrate which cannot be removed by washing. *Secondary silver orthophosphate*, Ag_2HPO_4, is obtained in white crystals from the solution of the normal orthophosphate in aqueous phosphoric acid. At 170° C. it changes to the pyrophosphate.

Silver pyrophosphate, $Ag_4P_2O_7$.—Precipitation of sodium pyrophosphate with silver nitrate yields the pyrophosphate in the form of a white powder, fusible at red heat. Secondary sodium orthophosphate converts it into silver orthophosphate. A double salt of the formula $NaAg_3P_2O_7$ is also known. On heating, its colour changes from white to yellow, a phenomenon which has been attributed to decomposition into sodium metaphosphate and silver orthophosphate, but which is considered by Balareff [4] to have probably a physical origin.

Silver metaphosphate, $AgPO_3$.—With a concentrated solution of sodium metaphosphate silver nitrate gives a white precipitate of the *semihydrate*, $AgPO_3,\frac{1}{2}H_2O$.[5] Other metaphosphates have been described.[6]

Silver arsenite, Ag_3AsO_3.—Addition of potassium hydroxide to a concentrated solution of silver nitrate and arsenious acid precipitates yellow silver arsenite, Ag_3AsO_3. It is also produced, along with another yellow salt, $2Ag_2O,As_2O_3$, by the action of potassium or ammonium arsenite on silver nitrate. Silver arsenite melts above 150° C., decomposing into silver and silver arsenate. It is soluble in potassium-arsenite solution; and also dissolves in potassium-hydroxide solution and in ammonium hydroxide, yielding solutions from which metallic silver is gradually deposited.[7]

Silver arsenate, Ag_3AsO_4.—Silver nitrate reacts with solutions of arsenic acid and arsenates, giving a chocolate-coloured precipitate of silver arsenate containing a small proportion of silver nitrate, possibly

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[1] Granger, *Ann. Chim. Phys.*, 1898, [7], 14, 5; *Compt. rend.*, 1897, 124, 896.
[2] Bossuet and Hackspill, *Compt. rend.*, 1913, 157, 720.
[3] Philipp, *Ber.*, 1883, 16, 749.
[4] Balareff, *Zeitsch. anorg. Chem.*, 1921, 118, 123.
[5] Langheld, Oppmann, and Meyer, *Ber.*, 1912, 45, 3753.
[6] Fleitmann, *Pogg. Annalen*, 1849, 78, 253.
[7] Santos, *Chem. News*, 1878, 38, 94.

in solid solution. Addition of silver arsenate to an aqueous solution of arsenic acid precipitates a white, crystalline compound, $Ag_2O,2As_2O_5$, decomposed by water into silver arsenate and arsenic acid.[1]

Silver carbide, Ag_2C_2.—Excess of an aqueous solution of acetylene precipitates from ammoniacal silver nitrate the greyish-yellow carbide. On exposure to light it darkens rapidly. When heated, the dry salt explodes. With hydrochloric acid it evolves acetylene, and with nitric acid it undergoes complete decomposition. Water causes hydrolysis to some extent, with production of silver monoxide. Agitation with sodium-chloride solution causes similar hydrolysis, the solution becoming strongly alkaline.[2] The heat of formation from the elements is given by Berthelot as —87·15 Cal. It forms a series of double salts with the halides, sulphate, and nitrate of silver.[3]

Silver carbonate, Ag_2CO_3.—When the equivalent proportion of potassium carbonate or potassium hydrogen carbonate is added to a solution of silver nitrate, silver carbonate is precipitated as a yellow powder. Addition of excess of potassium carbonate causes simultaneous precipitation of a proportion of silver monoxide. Pure silver carbonate is white, but is sensitive to light. At 200° C. it decomposes with evolution of carbon dioxide.[4] Its heat of formation is 120·8 Cal.[5] Silver nitrate precipitates from a hot, concentrated solution of potassium carbonate a double salt of the formula Ag_2CO_3,K_2CO_3. A crystalline double compound with ammonia of the formula $Ag_2CO_3,4NH_3,H_2O$ is produced by the spontaneous evaporation in air of an ammoniacal solution of silver oxide. Under the influence of sunlight the crystals become black; and on exposure to air they lose water and ammonia, yielding silver carbonate.[6]

Silver cyanide, AgCN.—A white, amorphous precipitate of the cyanide is obtained by interaction of a silver salt and a cyanide in aqueous solution. It crystallizes from a hot concentrated solution of potassium carbonate in fine needles. It is unaffected by light, but heat eliminates one-half of the cyanogen, with production of silver "paracyanide."[7] Both hydrochloric acid and mercuric chloride convert it into silver chloride. With hydrogen sulphide it yields silver sulphide, and heating with sulphur transforms it into silver thiocyanate. Its heat of formation from silver and cyanogen is 3·6 Cal.[8] There is some evidence of the existence of silver cyanide in two polymeric forms, AgCN and $Ag_2(CN)_2$.[9] With hydrazine cyanide it forms colourless crystals, $AgCN,N_2H_4$, which blacken in contact with air.[10]

Solution of silver or its cyanide in potassium cyanide forms *potassium silver cyanide,* $KAg(CN)_2$, octahedral crystals stable in air, but blackened by light. As 20° C. its solubility is 25 grams per 100 grams of water.[11]

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[1] Hurtzig and Geuther, *Annalen,* 1859, 111, 168.

[2] Bredig and Usoff, *Zeitsch. Elektrochem.,* 1896, 3, 116.

[3] Compare Berthelot, *Compt. rend.,* 1899, 129, 361; Lossen, *Annalen,* 1893, 272, 139; Keiser, *Amer. J. Sci.,* 1902, [4], 14, 285; Plimpton, *Chem. News,* 1892, 65, 295.

[4] Joulin, *Ann. Chim. Phys.,* 1873, [4], 30, 260.

[5] Colson, *Compt. rend.,* 1909, 148, 837.

[6] Dervin and Olmer, *ibid.,* 1921, 172, 1662.

[7] Rammelsberg, *Pogg. Annalen,* 1848, 73, 80.

[8] Berthelot, *Ann. Chim. Phys.,* 1883, [5], 29, 241.

[9] Wagner, *Verh. Ges. deut. Naturforsch. Aerzte,* 1902, i., 69.

[10] Franzen and Lucking, *Zeitsch. anorg. Chem.,* 1911, 70, 145.

[11] Baup, *Ann. Chim. Phys.,* 1858, [3], 53, 464.

Its heat of formation from the two cyanides is 5·6 Cal.[1] Addition of silver chloride to its solution precipitates silver cyanide : [2]

$$KAg(CN)_2+AgCl \rightleftharpoons 2AgCN+KCl.$$

A solution of the double cyanide is extensively employed as a bath for silver-plating.

Silver thiocyanate, $AgCNS$.—Solutions of thiocyanates precipitate the thiocyanate from silver solutions. It is a white, cheese-like precipitate, soluble in excess of thiocyanate solution. At 25° C. its solubility is $1{\cdot}08\times10^{-6}$ gram-molecule per litre of water.[3] It forms a number of double salts with potassium thiocyanate; [4] and with bromine in organic solvents it yields a solution of thiocyanogen, $(CNS)_2$.[5]

Silver borate, $AgBO_2$.—A solution of borax reacts with one of silver nitrate to precipitate the white *metaborate*, $AgBO_2$. It is also produced by dissolving silver monoxide in boric acid, an equilibrium being attained. Conversely, water causes partial hydrolysis of silver borate to silver monoxide and boric acid.[6]

DETECTION AND ESTIMATION OF SILVER.

Silver salts are reduced to the metal by heating on charcoal, a bead of silver being formed. The presence of silver in solutions can be detected by addition of hydrochloric acid. The white, curd-like precipitate of silver chloride is insoluble in nitric acid, but readily soluble in ammonium hydroxide. On exposure to light, the chloride acquires a violet tint. Traces of silver salts can be detected by adding ammonium salicylate and ammonium persulphate to the solution, the presence of silver being indicated by the development of a brown coloration. The reaction will indicate the presence of 0·01 mg. of silver. It is probably catalytic, since the brown substance does not contain any silver.[7] An alkaline solution of formaldehyde gives a violet coloration with 1 part of silver in 200,000 parts of solution.[8] Very small quantities can also be detected by conversion into chloride, solution of this salt in ammonium hydroxide, and heating the liquid with potassium hydroxide and glycerol, the metal being precipitated in the form of a greyish-black powder.[9] Silver salts in nitric-acid solution give with alkali-metal chromates a turbidity or black precipitate of silver suboxide, the reaction detecting 0·005 mg. of silver.[10]

Bayer's microchemical method, mentioned in connexion with rubidium (p. 199) and cæsium (p. 210), serves to detect one-hundredth of a microgram of silver.

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[1] Berthelot, *Compt. rend.*, 1873, 77, 388.

[2] Cohen, *Zeitsch. physikal. Chem.*, 1895, 18, 61.

[3] Küster and Thiel, *Zeitsch. anorg. Chem.*, 1903, 33, 139; compare Böttger, *Zeitsch. physikal. Chem.*, 1903, 46, 602; 1906, 56, 93; Hill, *J. Amer. Chem. Soc.*, 1908, 30, 68.

[4] Wells and Merriam, *Amer. Chem. J.*, 1902, 28, 265; Foote, *Zeitsch. physikal. Chem.*, 1903, 46, 79.

[5] Söderbäck, *Annalen*, 1919, 419,, 217.

[6] Abegg and Cox, *Zeitsch. physikal. Chem.*, 1903, 46, 1; *Zeitsch. Elektrochem.*, 1903, 9, 892.

[7] Gregory, *Proc. Chem. Soc.*, 1908, 24, 125.

[8] Armani and Barboni, *Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 290.

[9] Donath, *Chem. Zeit.*, 1908, 32, 629; compare Whitby, *Zeitsch. anorg. Chem.*, 1910, 67, 62.

[10] Malatesta and Nola, *Boll. Chim. Farm.*, 1913, 52, 533.

The relative insolubility of some of the salts of silver is in the order *chloride*, *cyanide*, *thiocyanate*, *bromide*, *iodide*, and *sulphide*. The metal is usually estimated gravimetrically as chloride, or by electrolytic deposition. It can also be weighed as chromate.[1] Other gravimetric methods are reduction to metal by hypophosphorous acid,[2] and by alkaline glycerol and other reagents.[3]

Volumetric estimation[4] in neutral solution can be effected by titration with standard sodium chloride, potassium chromate being employed as indicator; and in nitric-acid solution with thiocyanate, using ferric alum as indicator, or with sodium chloride without any external indicator.

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[1] Gooch and Bosworth, *Zeitsch. anorg. Chem.*, 1909, 62, 69, 74.

[2] Mawrow and Mollow, *ibid.*, 1909, 61, 96.

[3] Whitby, *ibid.*, 1910, 67, 62.

[4] Compare also Gooch and Bosworth, *loc. cit.*

CHAPTER XI.

GOLD.

Symbol, Au. Atomic weight, 197·2 (O=16).

Occurrence.—The greater part of the world's gold is found in the metallic state either in primary deposits in veins in association with quartz, or as *alluvial* gold in secondary deposits in the form of dust, grains, fine leaves, or in larger pieces.

In the quartz-veins the metal is found in varying degrees of fine division, and is usually associated with arsenic or sulphur compounds such as iron pyrites, arsenical pyrites, copper pyrites, zinc-blende, galena, antimony-glance, and various silver ores.[1] The metal is frequently present in crystalline form, examples being cubes and octahedra belonging to the cubic system, and also hexagonal forms. The amount of gold in the ore ranges from a few grams per ton up to several hundred grams per ton in different localities, and also varies at different levels in the same locality, diminishing with increase of depth. Such is the value of the metal that 3 ounces of gold per 50 tons of gangue can be profitably worked.

Alluvial gold is a product of the disintegration of gold-bearing rocks, due to weathering by the atmosphere and water. It is present in river-sand and in sand-deposits in all auriferous regions, as well as in districts where quartz-gold formerly occurred. It is usually associated with such materials as quartz-sand, clay, mica, titaniferous iron ore, chrome iron ore, magnetic iron ore, tinstone, granite, spinell, zirconium, platinum, and diamonds. Large pieces, or nuggets, weighing several kilograms are sometimes found.

Combined gold is always found in union with tellurium.[2] *Muthmannite* contains a considerable proportion of gold, and is represented by the formula (Ag, Au)Te. The molecular proportion of the gold is always less than that of the silver. Other examples of such minerals are *sylvanite*, with 24–30 per cent. of gold, 3–15 per cent. of silver, and 58–62 per cent. of tellurium, found in Transylvania, California, and Colorado; *hessite*, or silver telluride, with part of the silver replaced by gold; *calaverite*, $AuTe_2$, containing a small proportion of silver; *petzite*, with a large proportion of silver; *nagyagite*, containing lead, copper, sulphur, tellurium, and antimony; and *white tellurium*, containing silver, lead, tellurium, and antimony; these ores are found in Transylvania.

Gold is almost always associated with silver and copper. It is found in South Africa, America, Russia, Australia, Hungary, Sweden, and

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[1] Compare Eissler, *Metallurgy of Gold*, London, 1900, 4.

[2] Compare Muspratt, *Handbuch der technischen Chemie*, Brunswick, 1891, 3, 1687.

Norway. The cyanide-process has been highly developed in South Africa, and the electrolytic separation from copper in America.

History.—Gold has been esteemed a precious metal from prehistoric times. The high value placed on it is indicated by the writings of Homer and of Biblical authors. The locality of the ancient sources of supply is now a matter of doubt, but there appear to have been extensive deposits, now probably worked out.

In the code of Menes, who was King of Egypt about 3600 B.C., the ratio in value between gold and silver is given as 1 part of gold to 2·5 parts of silver. Corresponding with the period about 2500 B.C. there are extant Egyptian rock-carvings illustrating the washing of auriferous sands and the subsequent smelting. The sands were washed over smooth, sloping rocks by running water, and the gold was caught in the hair of raw hides spread on rocks. The "Legend of the Golden Fleece" probably originated in the use of sheepskins for this purpose. It narrates the story of a piratical expedition made about 1200 B.C. with the object of stealing gold obtained from rivers by the aid of sheep or goat skins in the region now termed Armenia.

Chikashige[1] found gold associated with other metals in a Buddhist statue of the third century A.D., and also in a Corean bronze mirror of the tenth century A.D.

The word "gold" is probably derived from the Sanskrit *Jvalita*, from *Jval*, meaning to shine.[2]

Gold coins were first made in the Western world about 700 B.C. The parting of gold and silver was then practised, ancient Greek coins containing 99·7 to 99·8 per cent. of gold. The process was one of cementation. At a later period, parting was accomplished by means of nitric acid. At the present time the parting of gold from silver is effected by chlorine in Australia, by electrolysis in America, and by sulphuric acid in Europe.[3]

Extraction.[4]—There are four main processes of gold extraction :

1. Mechanical processes for preparing and washing the ore.
2. Preparation of the ores, with simultaneous or subsequent amalgamation.
3. Chemical extraction-processes.
4. Smelting of certain ores.

(1) WASHING PROCESSES.

Gold can be extracted by washing only when it is present as metal in the form of particles which are not too minute. The washing removes the specifically lighter parts of the material, the heavier gold particles sinking to the bottom. The process is applicable directly to gold-bearing sand, and to gold-bearing rocks after crushing. The crushing is effected by stone-crushers, rolling-mills, and stamp-mills. The washing is carried out either by subjecting the material to the prolonged

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[1] Chikashige, *Trans. Chem. Soc.*, 1920, 117, 917.

[2] Compare Rose, *Metallurgy of Gold*, 6th ed. (Griffin, 1915), 2.

[3] Compare Sir T. Kirke Rose's Presidential Address to the Institute of Mining and Metallurgy, March 18, 1915; *Nature*, 1915, 95, 100.

[4] For full metallurgical details reference should be made to *The Metallurgy of Gold*, by Sir T. Kirke Rose (Griffin), and *The Sampling and Assay of Precious Metals*, by E. A. Smith (Griffin).

action of flowing water, or by mechanical agitation with water in deep iron pans or "cradles." In California hydraulic jets are employed to disintegrate the material, the water being allowed to flow into long channels, and the gold extracted by amalgamation with mercury.[1]

(2) AMALGAMATION-PROCESS.

With pyritic ores a preliminary roasting to eliminate sulphur is necessary. The ore is reduced to a fine state of division and amalgamated simultaneously in a stamp-mill, the solid gold-amalgam separated from the liquid mercury by filtration through leather under pressure, and the mercury distilled. Complete extraction of the gold by amalgamation is impossible, a part remaining in the mud of the stamp-mills. Concentration is effected by washing, and the "concentrates" are chlorinated by the Plattner process. A further operation divides the waste products into 60 per cent. of "tailings" and 40 per cent. of "slimes," and these materials are further extracted by the cyanide-process.

(3) CHEMICAL EXTRACTION-PROCESSES.

Plattner's Chlorination-process.—As a preliminary step the material is submitted to an oxidizing and chlorinating roasting, to convert metals other than gold into chlorides. After chlorination of the gold, preferably with chlorine under pressure,[2] the metal is precipitated by hydrogen sulphide or ferrous sulphate, or the gold is precipitated by filtration through charcoal, and recovered by combustion of the charcoal. Direct generation of the chlorine in the liquid has also been suggested. It can be effected by addition of bleaching-powder and sulphuric acid [3]; or by means of manganese dioxide, sodium chloride, and sulphuric acid; or electrolytically. Bromine acts more energetically than chlorine, and has also been employed in the extraction. The recovery of the gold is effected similarly, and the bromine is then liberated by the action of chlorine, but it is impossible to prevent loss of bromine.[4]

Cyanide-process.[5]—The extraction of gold by the cyanide-method is of great technical importance. It is effected by lixiviation with a solution of potassium cyanide, the gold being precipitated either by addition of zinc or electrolytically. The process was suggested by MacArthur and Forrest in 1885, and is based on the well-known solubility of gold in potassium-cyanide solution, a phenomenon said [6] to have been discovered by Prince Bagration in 1843. It was first employed on the large scale in the Australian goldfields in 1888.

The removal of metallic salts, such as ferrous sulphate, and acids from the material being handled is effected by lixiviation with dilute

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[1] Compare Muspratt, *Handbuch der technischen Chemie*, Brunswick, 1891, 3, 1687.

[2] Munktell, *Dingler's Polytech. J.*, 1888, 269, 578.

[3] Newberry-Vautin, *Ber.*, 1888, 21, 279; Rothwell, *Berg- und Hütten-männische Zeit.*, 1898, 57, 116.

[4] Lossen, *Ber.*, 1894, 27, 2726; McIlhinney, *J. Amer. Chem. Soc.*, 1896, 18, 451; Lodge, *Trans. Amer. Inst. Mining Eng.*, 1895, March.

[5] Compare Uslar and Erlwein, *Cyanidprozesse zur Goldgewinnung*, Halle, 1903; MacArthur, *J. Soc. Chem. Ind.*, 1890, 9, 267; de Mosenthal, *ibid.*, 1894, 13, 326; Butters and Clennell, *Mon. Scient.*, 1893, [4], 7, 47; Abraham, *Berg- und Hütten-männische Zeit.*, 1894, 53, 261; Kroupa, *Öst. Zeitsch. Berg- und Hütten-wesen*, 1895, 43, 583.

[6] Brand, *Berg- und Hütten-männische Zeit.*, 1894, 53, 73, 381, 389.

alkali. The residue is extracted with 0·35 per cent. solution of potassium cyanide, then with 0·08 per cent. solution, and ultimately with water. The extract is transferred to tanks, and the gold precipitated as a powder by addition of zinc. It is then washed out from the bottom of the tanks, dried, and freed from zinc by roasting and fusing.

In the electrolytic precipitation of the gold an iron anode and a sheet-lead cathode are employed, the current-density being very low, about 0·5 amp. per sq. mètre.[1] The gold is deposited on the lead, and after removal of this metal still contains a considerable proportion of both lead and silver. It is freed from them by the operation called "parting."

Access of air is essential to solution of gold in potassium cyanide,[2] the process being attended by evolution of hydrogen. Lead, bismuth, antimony, cadmium, silver, and mercury also dissolve in presence of air; but copper, iron, aluminium, nickel, cobalt, and zinc dissolve in absence of air. Gold and silver are distinguished by the fact that their maximum solubility corresponds with a very low concentration of the potassium-cyanide solution, a phenomenon probably due to the slight solubility of air in concentrated solutions of this salt.[3] The solution of gold in the cyanide solution is accompanied by the intermediate formation of hydrogen peroxide, and the process is accelerated by addition of this substance: [4]

$$2Au+4KCN+2H_2O+O_2=2KAu(CN)_2+2KOH+H_2O_2;$$
$$2Au+4KCN+H_2O_2=2KAu(CN)_2+2KOH.$$

A similar accelerating effect is exerted by other substances, such as potassium ferricyanide, potassium permanganate, potassium chromate,[5] sodium peroxide,[6] barium peroxide,[7] cyanogen bromide,[8] cyanogen chloride,[9] persulphates, and certain organic compounds.[10] The best method of reducing the proportion of the other metals is to maintain the cyanide solution dilute.

In precipitating the gold by zinc, the proportion required is about seven times that indicated by the equation

$$Zn+2Au^{\cdot}=2Au+Zn^{\cdot\cdot},$$

the discrepancy being due to solution of part of the zinc in the cyanide solution, with evolution of hydrogen.[11] Purity of the zinc is an important factor in counteracting this loss.

In the electrolytic deposition of gold from cyanide solutions hydrogen is liberated at the cathode, and an equivalent number of hydroxyl ions give up their charges at the anode, the solution developing an alkaline reaction. Cyanogen ions also give up their charges at the anode, being

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[1] Siemens, *Zeitsch. Elektrochem.*, 1895, **2**, 532.

[2] Watts and Whipple, *Trans. Amer. Electrochem. Soc.*, 1917, **32**, 257.

[3] Maclaurin, *Chem. News*, 1893, **67**, 191; 1895, **71**, 73.

[4] Bodländer, *Zeitsch. angew. Chem.*, 1896, **19**, 583.

[5] Moldenhauer, *Ber.*, 1893, **26**, 340.

[6] Montgomerie, *J. Soc. Chem. Ind.*, 1893, **12**, 767.

[7] Schilz, *Mining J.*, 1902, March 1.

[8] Sulman and Teed, *German Patent*, No. 83292; Mulholland, *Berg- und Hüttenmännische Zeit.*, 1896, **55**, 66; Louis, *J. Soc. Chem. Ind.*, 1899, **18**, 229.

[9] Morgans, *British Patent*, No. 18279.

[10] Schering, *Zeitsch. Elektrochem.*, 1896, **2**, 507.

[11] Uslar and Erlwein, *Cyanidprozesse zur Goldgewinnung*, Halle, 1903.

probably converted partly into cyanate, and partly into complex derivatives of iron and cyanogen, such as Prussian blue. The formation of this product is prevented by replacement of the iron anode by one made of lead peroxide.[1]

In the Pelatan-Clerici process the gold is dissolved electrolytically and precipitated in a single operation.[2] Cathodes of mercury or amalgamated copper are employed, so that large particles of gold which fail to dissolve are directly amalgamated.

(4) SMELTING PROCESS.

The smelting process consists in the formation of an alloy of gold with silver and lead, and is similar to that employed in extracting silver. It is applicable to ores rich in silver, and also to refractory ores containing arsenic and antimony, for which the other processes are unsuitable.

PARTING OF GOLD FROM SILVER.

The parting of gold from silver is effected by melting the raw product with sufficient silver to make the ratio of the gold to silver 1 : 3, or "quartering," the alloy being then treated with concentrated sulphuric acid or nitric acid. Another method of parting consists in transforming the silver present in the alloy into chloride, as in the *aqua-regia* and electrolytic processes.

Quartering.—This designation is applied to the parting with nitric acid mentioned above, although it is also employed to describe the sulphuric-acid process. Usually, the gold-silver alloy is made to contain 2 parts of gold to 5 parts of silver. It is granulated, and boiled with nitric acid. The silver solution produced is either worked up into "lunar caustic," or precipitated as chloride by addition of sodium chloride, and then reduced to metal.

Refining.—The gold is alloyed with silver and granulated, as in quartering. It is then boiled with concentrated sulphuric acid in cast-iron boilers, silver, copper, lead, and other metals being converted into sulphates. The silver and lead salts are partly dissolved in the strong acid, but copper sulphate remains chiefly undissolved, and by coating the granules exercises a retarding influence on the solution of the silver, thus necessitating a repetition of the boiling with acid. All the gold is in the undissolved residue, and after washing thoroughly it is dried and fused. It still contains traces of silver, but is suitable for most purposes without further purification. The silver solution is diluted with water, the metal precipitated by the action of copper, and the solution formed worked up for cupric sulphate. Other processes are reduction of the silver sulphate by ferrous sulphate;[3] and by iron, which precipitates silver only, but no copper.[4]

When the gold contains platinum and related metals, it is submitted to further refining. Part of the platinum is dissolved out by the treatment with nitric acid. Iridium was formerly slagged off by fusion with potassium nitrate, but all the platinum is simultaneously slagged, and

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[1] Andreoli, *J. Soc. Chem. Ind.*, 1897, 16, 96.

[2] Compare Uslar and Erlwein, *Cyanidprozesse zur Goldgewinnung*, Halle, 1903.

[3] Gutzkow, *Ber.*, 1871, 4, 114.

[4] Rössler, *Annalen*, 1876, 180, 240.

can be recovered only by a cumbrous process.[1] To obviate this difficulty the metal, either after parting from silver or in its original state, is dissolved, and the gold and platinum precipitated separately.

Parting by aqua regia is effected by dissolving the alloyed gold in the acid, silver being converted into its chloride, which is then precipitated by dilution with water. The platinum dissolves completely, and the iridium partially, the gold being precipitated by addition of ferrous sulphate or chloride. With a large proportion of silver some of the gold is occluded, and escapes solution in the acid, thus necessitating a repetition of the treatment with acid. The process lacks many of the advantages characteristic of the electrolytic method.

The *electrolytic process*[2] was introduced in 1863 by Charles Watt at Sydney, started in 1878 by Wohlwill at Hamburg, and in 1902 by Tuttle at the Philadelphia Mint. In the gold-chloride method the electrolyte is a solution of auric chloride containing free hydrochloric acid, the crude metal forming the anode, and pure sheet gold the cathode. The gold dissolved at the anode is deposited in a pure condition at the cathode. Other metals are converted into chlorides at the anode, and either remain dissolved or pass into the anodic slime. Silver is converted into its chloride, this substance partly dissolving, partly depositing in the slime, and partly adhering to the anode. With solutions containing more than 3 to 10 per cent. of hydrochloric acid, and with bullion having more than 6 per cent. of silver, the coating of the anode raises the density of the current and causes evolution of chlorine.

Rose has found that with an electrolyte containing 29 per cent. of free hydrochloric acid, and with a current-density of 5000 ampères per square mètre of anode surface, no chlorine is evolved, even with an anode containing 20 per cent. of silver. The heavy current causes the silver chloride to separate from the anode, and as aurous chloride is not allowed to form, deposition of gold in the anode-slime is prevented.

A solution of auric chloride containing 3 to 5 per cent. of gold and a current-density of 1000 ampères per square mètre are usually employed, but Rose has found that with a current-density of 5000 ampères per square mètre an electrolyte with 20 per cent. of gold yields a coherent deposit capable of being readily washed, and malleable after melting. By this modification the time required for solution of the anode is reduced from one week to one day.

In addition to the malleable nature of the product obtained by electrolytic refining, the process also extracts platinum, a constituent of nearly all samples of Transvaal gold. The United States of America Mint has found the electrolytic method more economical than that with sulphuric acid.

Miller's *dry parting process*[3] involves the action of chlorine on molten gold covered with a layer of borax to prevent spurting. The gold is not attacked, but the silver is converted into chloride. When the gold has solidified, the molten silver chloride collected on the surface is run off, carrying with it a small proportion of gold. When silver is the chief

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[1] Pettenkofer, *Dingler's Polytech. J.*, 1847, 104, 118, 198.

[2] Compare Wohlwill, *Zeitsch. Elektrochem.*, 1898, 4, 379, 421; Sir T. Kirke Rose, Presidential Address to the Institute of Mining and Metallurgy, March 18, 1915; *Nature*, 1915, 95, 100.

[3] Miller, *J. prakt. Chem.*, 1869, 106, 503; *Dingler's Polytech. J.*, 1868, 188, 251; 1870, 197, 43; 1872, 205, 535; 1873, 208, 342.

impurity in the gold, as in that found in Australia, the process is specially applicable. The gold has a degree of purity of 99·1 to 99·7 per cent.

Preparation of chemically Pure Gold.—The "pure" gold of commerce is dissolved in dilute *aqua regia*, most of the silver precipitated as chloride by dilution, and the gold reduced by sulphur dioxide, oxalic acid, or ferrous chloride. After boiling with concentrated sulphuric acid, the reduced gold is fused with potassium hydrogen sulphate, and then with potassium nitrate. The product is dissolved in *aqua regia*, and again precipitated with one of the reducers cited.[1]

Modifications of Gold.—The metal is known in several modifications. In the crystallized state it belongs to the cubic system, a great variety of forms having been observed.[2] Hexagonal forms have also been described.[3] Artificial crystals can be prepared by heating 5 per cent. gold-amalgam at 80° C., and acting on the product with nitric acid of density 1·35.[4] References are appended to other modes of producing crystals.[5] Rolled, non-crystalline gold becomes crystalline by exposure to red heat.[6] This process is reversed by polishing or hammering, with formation of a superficial layer of amorphous gold.[7]

Reducers precipitate gold from different solutions in divergent forms. Ferrous chloride and sulphate, arsenious acid, antimonious acid, and stannous chloride throw it down as a brown powder of varying degrees of subdivision, the precipitate with ferrous chloride being more finely divided when the gold solution is poured into the iron solution than that produced by the reverse method.[8] The more dilute the gold solution, the finer is the subdivision of the precipitate. From concentrated solutions the metal often separates in lustrous laminæ. A soft, yellow gold sponge is produced by addition of a small proportion of oxalic acid and a large proportion of potassium carbonate to a concentrated solution, the resulting mixture being then boiled with more oxalic acid.[9]

The so-called "brown gold" is formed by the action of nitric acid on an alloy of gold and silver containing 20 per cent. of gold. The silver dissolves, leaving the gold as a brown, spongy sheet, reconverted at 1040° C. into ordinary gold. The brown form (β) differs from ordinary (α) gold in density and magnetic properties. Above 700° C. it undergoes slow transformation into the ordinary variety. It is uncertain whether the difference is caused by dimorphism or by allotropy.[10]

Thomsen believed that he had demonstrated the existence of three allotropic modifications of gold, relying on thermochemical measurements,[11]

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[1] Krüss, *Annalen*, 1887, 238, 43.

[2] Compare Dammer, *Handbuch der anorganischen Chemie*, Stuttgart, 1893, 3, 756; Rose, *Pogg. Annalen*, 1831, 23, 196; Naumann, *ibid.*, 1831, 24, 384; Chester, *Amer. J. Sci.*, 1878, [3], 16, 29.

[3] Blake, *Amer. J. Sci.*, 1884, [3], 28, 57; *Zeitsch. Kryst. Min.*, 1885, 10, 313.

[4] Knaffl, *Dingler's Polytech. J.*, 1863, 168, 282; von Lang, *Phil. Mag.*, 1863, [4], 25, 435.

[5] Rose, *Pogg. Annalen*, 1848, 73, 8; Averkieff, *Zeitsch. anorg. Chem.*, 1903, 35, 329; Dykes, *Chem. News*, 1904, 91, 180.

[6] Kalischer, *Ber.*, 1882, 15, 702; compare Beilby, *Phil. Mag.*, 1904, [6], 8, 273; *Chem. News*, 1905, 92, 85.

[7] Fawsitt, *Proc. Roy. Soc. Edin.*, 1906, 26, 1.

[8] Compare Gmelin-Kraut, *Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1004.

[9] Jackson, *Amer. J. Sci.*, 1848, [2], 6, 182.

[10] Henriot, *Compt. rend.*, 1910, 151, 1355; 1911, 152, 138, 369, 704; *Bull. Soc. chim.* 1911, [4], 9, 139.

[11] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 400.

but in opposition to his conclusions is the fact that there is no potential difference between his supposed modifications.[1]

With very dilute solutions most precipitants yield a turbidity or coloration, gold being only slowly deposited as a brown powder. Various organic reducers give intensely coloured red or blue solutions of *colloidal gold*, also prepared by Faraday[2] by the action of white phosphorus on auric-chloride solution, his product being a red liquid from which metallic gold gradually deposited. Other reducers available for the preparation of colloidal gold solutions are oxalic acid, sulphurous acid, glycerol,[3] sodium hypophosphite,[4] formaldehyde,[5] hydrazine hydrate,[6] acetylene,[7] phenylhydrazine hydrochloride,[8] sodium hyposulphite,[9] a mixture of carbon monoxide and dioxide,[10] an alcoholic solution of phosphorus,[11] alcohol,[12] oil of turpentine,[13] acraldehyde,[14] allyl alcohol,[15] polyhydric phenols,[16] aluminium,[17] humic acid,[18] starch,[19] and hydrogen peroxide.[20] Adrenaline, alloxan, tannic acid, and *p*-phenylenedimethyldiamine have also been employed.[21]

In using sodium hypophosphite, Carey Lea mixed a 10 per cent. solution of the reagent with 1 c.c. of auric-chloride solution containing 0·1 gram of gold and a drop of sulphuric acid, and added 30 c.c. of water as soon as darkening of the solution had begun. A gradual precipitation of bluish-black metallic gold supervened, and the precipitate was removed by filtration, but the green filtrate gradually became turbid, and deposited gold on the walls of the container. By reflected light the precipitated metal was yellowish brown in colour; by transmitted light it was bright blue.

Henriot[22] employed catechol in presence of sodium carbonate as a reducer.[23]

Sunlight greatly facilitates the formation of colloidal gold, but the light of a mercury lamp is less energetic.[24] Certain soaps are said to

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[1] van Heteren, *Chem. Weekblad,* 1904, 2, 47; Cohen and van Heteren, *Zeitsch. Elektrochem.*, 1906, 12, 589.

[2] Faraday, *Ann. Physik,* 1857, 101, 383; *Phil. Trans.*, 1857, 147, 154.

[3] Knaffl, *Dingler's Polytech. J.*, 1863, 168, 191; Winkler, *Ber.*, 1889, 22, 893.

[4] Carey Lea, *Amer. J. Sci.*, 1897, [4], 3, 64; *Zeitsch. anorg. Chem.*, 1897, 13, 446.

[5] Zsigmondy, *Annalen,* 1898, 301, 29; *Zeitsch. anal. Chem.*, 1902, 40, 710; Küspert, *Ber.*, 1902, 35, 4071; compare Mukherjee and Papaconstantinou, *Trans. Chem. Soc.*, 1920, 117, 1563.

[6] Gutbier, *Zeitsch. anorg. Chem.*, 1902, 31, 448.

[7] Blake, *Amer. J. Sci.*, 1903, [4], 16, 381, 433.

[8] Gutbier and Resenschenk, *Zeitsch. anorg. Chem.*, 1904, 39, 112.

[9] Brunck, *Annalen,* 1905, 327, 240.

[10] Donau, *Monatsh.*, 1905, 26, 525.

[11] Vanino and Hartl, *Ber.*, 1904, 37, 3620.

[12] Vanino, *Ber.*, 1905, 38, 463; compare Vanino, *Zeitsch. Chem. Ind. Kolloide,* 1907, 2, 51.

[13] Vanino and Hartl, *Ber.*, 1906, 39, 1696.

[14] Castoro, *Zeitsch. anorg. Chem.*, 1904, 41, 126; *Zeitsch. Chem. Ind. Kolloide,* 1910, 6, 283.

[15] Castoro, *Zeitsch. anorg. Chem.*, 1904, 41, 126.

[16] Henrich, *Ber.*, 1903, 36, 609.

[17] Dauvé, *J. Pharm. Chim.*, 1909, [6], 29, 241.

[18] Ehrenberg and Pick, *Zeitsch. Chem. Ind. Kolloide,* 1909, 5, 30.

[19] de Coninck, *Bull. Acad. roy. Belg.*, 1910, 664.

[20] Doerinckel, *Zeitsch. anorg. Chem.*, 1909, 63, 344; compare Svedberg, *Zeitsch. physikal. Chem.*, 1909, 66, 752; 67, 249.

[21] Richter, *Kolloid. Zeitsch.*, 1919, 25, 208.

[22] Henriot, *Compt. rend.*, 1904, 138, 1044.

[23] Compare Naumov, *Zeitsch. anorg. Chem.*, 1914, 88, 38.

[24] Hartwagner, *Kolloid. Zeitsch.*, 1915, 16, 79.

exert a very pronounced protective action in the formation of gold hydrosols.[1]

A summary of investigations on colloidal gold has been given by Ostwald,[2] and also by Cornejo.[3] Its optical properties have been examined by Steubing,[4] and the various colours of the product have been studied by Bancroft.[5]

Purple of Cassius,[6] first prepared by Andreas Cassius at Leyden in 1683, is produced as a dark-brown precipitate, purple-red by transmitted light, by the action of stannous salts on dilute gold solutions. Its preparation is effected by boiling an aqueous solution of stannous chloride with freshly precipitated ferric hydroxide, dissolving the precipitated stannous hydroxide in hydrochloric acid, and adding the solution drop by drop to a very dilute gold solution. Metallic tin or stannous sulphate or nitrate can be substituted for stannous chloride.[7] Another technical method for its preparation is to heat "pink salt," $SnCl_4,2NH_4Cl$, with tin-foil and water until solution of the tin is complete, dilute with water, and pour the solution into a dilute aqueous gold solution.[8] It is also produced by dissolving gold-tin alloys in nitric acid.[9]

The percentage of gold in purple of Cassius varies between 24 and 43 per cent. with the experimental conditions of its preparation. The substance contains 7 to 14 per cent. of water, a part of this water being expelled at 100° C., and the remainder at red heat.[10] As "gold lake" it finds technical application in colouring glass ruby-red, and also in colouring enamels and glazes.

There has been much diversity of opinion as to the constitution of purple of Cassius. Macquer[11] regarded it as a mixture of gold and hydrated oxide of tin, since increase in the amount of gold changes the colour of the solution to a darker purple. This view is apparently in opposition to Proust's observation that moist purple of Cassius is soluble in ammonium hydroxide, but trituration with mercury fails to effect separation of the gold. Proust regarded it as a mixture of auro-stannous stannate and stannic hydroxide. Debray[12] compared it to the *lakes*, suggesting it to be stannic and metastannic acids coloured by finely divided gold, the metal being rendered insoluble in mercury by a process analogous to that undergone by dyes during deposition on the fibre. This view is supported by the possibility of depositing gold from ammoniacal solutions of purple of Cassius under the influence of light, since there is no method known for precipitating gold from its oxides by means of ammonia. Zsigmondy[13] regarded purple of

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[1] Iredale, *Trans. Chem. Soc.*, 1921, 119, 625; compare Zsigmondy, *Zeitsch. anal. Chem.*, 1901, 40, 709; Hiege, *Zeitsch. anorg. Chem.*, 1915, 91, 145.

[2] Ostwald, *Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 5.

[3] Cornejo, *ibid.*, 1913, 12, 1.

[4] Steubing, *Ann. Physik*, 1908, [4], 26, 329.

[5] Bancroft, *J. Physical Chem.*, 1919, 23, 554.

[6] An account of purple of Cassius is given by Grünwald, *Sprechsaal*, 1910, No. 29, July 21; compare Hodgson, *The Technology of Iron Enamelling and Tinning*, chap. v. (Griffin, 1912).

[7] Fuchs, *Berzelius's Lehrbuch der Chemie*, 4th ed., Dresden, 1835–1841, 3, 182.

[8] Bolley, *Annalen*, 1841, 39, 244.

[9] Mercadieu, *Ann. Chim. Phys.*, 1827, [2], 34, 147.

[10] Fischer, *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1041.

[11] Macquer, *Compt. rend.*, 1872, 75, 1025.

[12] Debray, *Dingler's polytech. J.*, 1870, 83, 292; *Compt. rend.*, 1872, 75, 1025.

[13] Zsigmondy, *Zur Kenntniss der Kolloide*, Jena, 1905.

Cassius as a mixture of colloidal gold and colloidal stannic acid, a view practically identical with that of Debray expressed in modern phraseology.[1]

Physical Properties.—Gold is a metal of characteristic yellow colour. Its melting-point is given as 1035° C.,[2] 1037° C.,[3] 1059·3° C.,[4] 1061·7° C.,[5] 1062·4° C.,[6] 1063° C.,[7] 1063·9° C.,[8] 1064° C.,[9] 1071° C.,[10] and 1072° C.[11] The most probable value is about 1063° C. Capua[12] found that the presence of between 6 and 7 per cent. of silicon lowers the melting-point about 800° C. Its boiling-point was determined by Moissan[13] with the aid of the electric furnace to be about 2530° C., being higher than that of copper and lime. Its density is given as 19·21,[14] 19·2685,[15] 19·28,[16] 19·43,[17] that for unpressed gold being 18·884.[18] The approximate value may be taken as 19·3. The specific heat at low temperatures is given as 0·0297,[19] as 0·0302 at 0° C.,[20] as 0·0380 at 18° C.,[21] and as 0·0324[22] and 0·0316[23] at 0° to 100° C. The latent heat of fusion per gram is 0·0163 Cal.[24] The hardness on Auerbach's scale is 2·5 to 3.[25] Gold is the most malleable of the metals, and can be beaten out to leaves 0·0001 mm. thick.[26] One gram of the metal can be drawn out to a wire 166 mètres in length. Thin layers deposited on glass by heating *in vacuo* are almost colourless in reflected light, but appear of a rose to violet colour by transmitted light.[27] Neither hydrogen nor nitrogen is absorbed by gold, either in the solid or fused state.[28] It is a good conductor of both heat and electricity.

Chemical Properties.—The chemical character of the metal accords with its low electroaffinity, an example being its stability towards the action of strong acids; although boiling, concentrated nitric acid dissolves

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[1] Compare Schneider, *Zeitsch. anorg. Chem.*, 1893, 5, 80; Grünwald, *Sprechsaal*, 1910, 43, 419.

[2] Violle, *Compt. rend.*, 1879, 89, 702.

[3] Becquerel, *ibid.*, 1863, 57, 855.

[4] Day and Clement, *Amer. J. Sci.*, 1908, [4], 26, 405.

[5] Heycock and Neville, *Trans. Chem. Soc.*, 1895, 67, 1024.

[6] Day and Sosman, *Amer. J. Sci.*, 1910, [4], 29, 93.

[7] Guertler and Pirani, *Zeitsch. Metallkunde*, 1919, 11, 1; Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186.

[8] Holborn and Day, *Drude's Annalen*, 1901, 4, 99.

[9] Berthelot, *Compt. rend.*, 1898, 126, 473.

[10] Ruff and Goecke, *Zeitsch. angew. Chem.*, 1911, 24, 1459.

[11] Holborn and Wien, *Wied. Annalen*, 1892, 47, 107.

[12] Capua, *Atti R. Accad. Lincei*, 1920, [5], 29, i., 111.

[13] Moissan, *Compt. rend.*, 1905, 141, 977; compare von Wartenberg, *Zeitsch. anorg. Chem.*, 1908, 56, 320.

[14] *Wiss. Abhandl. Phys.-Tech. Reichsanstalt*, 1900, 3, 269.

[15] Kahlbaum and Roth, *Zeitsch. anorg. Chem.*, 1901, 29, 177.

[16] Voigt, *Wied. Annalen*, 1893, 49, 709.

[17] Averkieff, *Zeitsch. anorg. Chem.*, 1903, 35, 335.

[18] Kahlbaum and Roth, *ibid.*, 1901, 29, 177.

[19] Richards and Jackson, *Zeitsch. physikal. Chem.*, 1910, 70, 414; compare Nordmeyer, *Ber. Deut. physikal. Ges.*, 1908, 6, 202.

[20] Schimpff, *Zeitsch. physikal. Chem.*, 1910, 71, 257.

[21] *Wiss. Abhandl. Phys.-Tech. Reichsanstalt*, 1900, 3, 269.

[22] Regnault, *Ann. Chim. Phys.*, 1840, [2], 73, 1.

[23] Violle, *Compt. rend.*, 1879, 89, 702.

[24] Compare Rudorf, *Das Periodische System*, Hamburg and Leipsic, 1904, 145.

[25] Landolt, Börnstein, and Meyerhoffer, *Tabellen*, 3rd ed., Berlin, 1905, 57.

[26] Compare Muspratt, *Handbuch der Technischen Chemie*, Brunswick, 1891, 3, 1829.

[27] Houllevigue, *Compt. rend.*, 1909, 149, 1368.

[28] Sieverts, *Zeitsch. Elektrochem.*, 1910, 16, 707.

it to a slight extent.[1] It is also dissolved by selenic acid.[2] The metal is readily brought into solution by the action of powerful oxidizers such as chlorine, and by mixtures in which chlorine is generated. Such mixtures are formed by hydrochloric acid with peroxides, chromic acid, permanganate, or nitric acid, and by hypochlorites with sulphuric acid. Other oxidizing mixtures have a similar effect, examples being solid potassium permanganate and sulphuric acid[3]; the higher oxides and peroxides of manganese with concentrated sulphuric acid, arsenic acid, or phosphoric acid; those of lead, nickel, and chromium with concentrated sulphuric acid or phosphoric acid; and concentrated nitric acid with sulphuric acid.[4] At 160° C. gold is attacked by sulphuryl chloride, SO_2Cl_2, with formation of auric chloride and evolution of sulphur dioxide.[5] It is also attacked by pyrosulphuryl chloride, $S_2O_5Cl_2$.[6] *Aqua regia* converts it into aurichloric acid, with evolution of nitric oxide:[7]

$$Au+HNO_3+4HCl=HAuCl_4+NO+2H_2O.$$

The metal does not combine directly with oxygen.[8]

Normally, gold does not display radioactivity, neither the metal nor its salts affecting the photographic plate.[9] Cobb[10] states that after exposure to a high-tension discharge between platinum electrodes amorphous gold does not affect a photographic plate, and further alleges that traces of copper are produced in the metal.

Gold Ions.—The metal forms univalent and tervalent ions characterized by their low electroaffinity. This property finds expression in the formation of complex derivatives with most anions, in the comparatively low solubility of the halides and oxides, and in the hydrolytic decomposition of its salts.

Aurous Ion.—This ion is known almost exclusively in the form of complex anions of the type $Au(CN)_2'$. Aurous compounds are converted by water into auric compounds, with separation of metallic gold, a reaction facilitated by the presence of halogen ions, complex derivatives of auric ion being formed:

$$3Au^{\cdot} \rightleftharpoons Au^{\cdot\cdot\cdot}+2Au.$$

Auric Ion.—This ion is characterized by its strong tendency to form complex derivatives, and also by its low electroaffinity. This second property accords with the ease of liberation of the metal by the action of numerous reducers, examples of this phenomenon being cited in the section on the modifications of gold (p. 328). The reddish-violet stain produced on the skin by gold solutions is due to deposition of the metal. Many reductions are accelerated by the action of light,[11] and many of them take place more rapidly in alkaline solution than in acidic solution.

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[1] Dewey, *J. Amer. Chem. Soc.*, 1910, 32, 318; compare Watts and Whipple, *Trans. Amer. Electrochem. Soc.*, 1917, 32, 257.
[2] Mitscherlich, *Pogg. Annalen*, 1826, 9, 623.
[3] Allen, *Chem. News*, 1872, 25, 85.
[4] von Lenher, *Electrochem. Ind.*, 1904, 2, 316.
[5] North, *Bull. Soc. chim.*, 1911, [4], 9, 646.
[6] Ditte, *Compt. rend.*, 1900, 131, 143.
[7] Přiwosnik, *Oesterr. Zeitsch. Berg- und Hütten-wesen*, 1910, 58, 549.
[8] Compare Dudley, *Amer. Chem. J.*, 1902, 28, 59.
[9] Levin and Ruer, *Physikal. Zeitsch.*, 1909, 10, 576.
[10] Cobb, *Chem. News*, 1909, 99, 209.
[11] Compare Kohlrausch, *Zeitsch. physikal. Chem.*, 1900, 33, 287.

Although derivatives of bivalent gold are known, there is no certainty as to the existence of an $Au^{\cdot\cdot}$ ion.

Applications.—Alloys of gold with copper, silver, and other metals are employed in the manufacture of plate, jewellery, and coins. In the British coinage the metal is alloyed with copper, the coins containing $916{\cdot}\dot{6}$ parts of gold per 1000. This alloy has a lower melting-point than gold, and is harder. In the United Kingdom there are five legal standards for gold wares ; 22-carat (containing 22 parts of gold in 24), 18-carat, 15-carat, 12-carat, and 9-carat.

Gold leaf contains 90 to 98 per cent. of gold alloyed with copper and silver. It is employed in gilding. Gold-plating is carried out in a bath of potassium auricyanide with a gold anode, the strength being maintained at about 6·85 grams of gold per litre by addition of auric chloride.

The metal finds application in photographic toning as sodium aurichloride. The chloride is employed in medicine, and in alloys in dentistry. " Purple of Cassius " is useful for colouring glass. *Gold lace* consists of a silk body with very fine strips of gold twined round the silk.[1]

Atomic Weight.—In the early years of the nineteenth century the subject of the ratio of gold to oxygen in gold oxide was investigated with divergent results by several chemists, including Richter, Prout, Oberkampf, Dalton, and Thomsen. Dalton regarded the value of the atomic weight as being between 140 and 200 ($O=7$). In 1813 Berzelius[2] formulated aurous oxide as AuO, and auric oxide as AuO_3, the corresponding atomic weight being $Au=2486$ ($O=100$) or $2\times 198{\cdot}8$ ($O=16$). This figure is about twice the modern value $Au=197{\cdot}2$. In 1826 Berzelius was induced by a knowledge of the existence of oxides of the type R_2O_3 to assign to gold the atomic weight $Au=1243$ ($O=100$), corresponding with $Au=198{\cdot}8$ ($O=16$), and to formulate the oxides of gold as Au_2O and Au_2O_3. Later he substituted for these formulæ the so-called " equivalent formulæ " written with letters having a central, horizontal stroke, Au^{I} and Au^{III}, corresponding with AuO and AuO_3. He took 2458·3 as the equivalent, and 1229·165 ($O=100$) as the atomic weight of gold.[3] In 1817 Meinecke gave the value $Au=200$, and in 1826 Gmelin gave as the equivalent $Au=66$. Later, the equivalent was assumed to be identical with the atomic weight $Au=196$ to 199, the corresponding formulæ for the oxides being written as AuO and AuO_3, and for the chlorides as $AuCl$ and $AuCl_3$.

The principal types of gold compounds are AuX and AuX_3, those of the formula AuX_2 being not improbably formed by combination of the other two forms. The atomic weight $Au=197{\cdot}2$ is supported by cryoscopic and ebullioscopic observations of solutions of gold in other metals, indicating the monatomicity of the element. The vapour-density of gold has not been determined, nor that of any of its compounds. The atomic heat calculated from the specific heat and the atomic weight 197·2 has the normal value 6·4. The element is isomorphous with copper and silver. Its properties and those of its compounds are functions of the atomic weight 197, belonging to an element of the eleventh row of Group I. or of the tenth row of Group VIII. of the periodic system of Mendeléeff.

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[1] For a bibliography of gold, see Rose, *Metallurgy of Gold*, 5th ed. (Griffin, 1906).

[2] Berzelius, *K. Svenska Vet.-Akad. Handl.*, 1813, 185 ; *Schweigger's J.*, 1813, 7, 47.

[3] Berzelius, *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 3, 1212.

In the subjoined numerical account the results have been recalculated, employing the antecedent data

$O = 16{\cdot}000$	$Br = 79{\cdot}916$	$Ba = 137{\cdot}37$
$Ag = 107{\cdot}880$	$K = 39{\cdot}100$	$Hg = 200{\cdot}6$
$Cl = 35{\cdot}457$	$S = 32{\cdot}065$	

In 1813 Berzelius[1] precipitated metallic gold from auric-chloride solution by the action of mercury, and as the mean of two experiments found that

$$3Hg : 2Au = 100 : 65{\cdot}68,$$

whence

$$Au = 197{\cdot}64.$$

In 1819 Pelletier[2] found Au=238 by analysing aurous iodide. Two years later, Javal[3] found Au=201 by analysing auric oxide, and Au=104 by analysing potassium aurichloride. In 1823 Figuier[4] found Au=179 from the analysis of sodium aurichloride. These very inaccurate results are in striking contrast to Berzelius's value.

Five analyses of potassium aurichloride by reduction with hydrogen were made in 1844 by Berzelius,[5] the loss in weight and the quantities of potassium chloride and gold produced being determined. His mean value for the ratio Au : KCl leads to Au=196·63, a less accurate value than that obtained by him in 1813.

In 1850 Levol[6] converted a weighed quantity of gold into the trichloride, reduced this derivative with sulphurous acid, precipitated as barium sulphate the sulphuric acid formed, and weighed the precipitate. The mean of two values for the ratio $2Au : 3BaSO_4$ leads to Au=196·49.

Thomsen[7] determined in 1876 the proportion of gold and bromine in the compound $HAuBr_4,5H_2O$, the result being

$$Au : 4Br = 32{\cdot}11 : 52,$$

whence

$$Au = 197{\cdot}39.$$

Krüss[8] published in 1887 the first modern determinations of any value. The gold employed was carefully purified, special attention being devoted to the elimination of silver and the metals of the platinum group. In his analyses of auric chloride, an aqueous solution of that salt was first prepared. With one weighed portion of the solution the gold was estimated by reduction with sulphurous acid; with another the chlorine was determined by conversion into silver chloride. Eight experiments gave the mean result

$$3AgCl : Au = 100 : 45{\cdot}824,$$

whence

$$Au = 197{\cdot}048.$$

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[1] Berzelius, *K. Svenska Vet.-Akad. Handl.*, 1813, 185; *Schweigger's J.*, 1813, 7, 47.

[2] Pelletier, *Ann. Chim. Phys.*, 1819, 15, 5.

[3] Javal, *ibid.*, 1821, 17, 337; compare Krüss, *Annalen*, 1887, 238, 30, 241; *Ber.*, 1887, 20, 2365; 1888, 21, 126.

[4] Figuier, *Ann. Chim. Phys.*, 1823, 19, 177.

[5] Berzelius, *K. Svenska Vet.-Akad. Handl.*, 1813, 185; *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 3, 1212.

[6] Levol, *Ann. Chim. Phys.*, 1850, [3], 30, 59.

[7] Thomsen, *J. prakt. Chem.*, 1876, [2], 13, 345.

[8] Krüss, *Annalen*, 1887, 238, 30, 241; *Ber.*, 1887, 20, 2365; 1888, 21, 126.

Krüss's analyses of carefully purified and dried potassium auribromide, $KAuBr_4$, were more elaborate. In some experiments the percentage of gold in the salt was determined by reduction with sulphurous acid, in others by heating the auribromide in hydrogen. With sulphurous acid the bromine in the filtrates from the precipitated gold was estimated as silver bromide; with hydrogen the loss in weight on heating in this gas, proportional to 3Br, was ascertained, and the potassium bromide dissolved from the residue by water was recovered and weighed, in addition to the gold. The results were

$KAuBr_4$: Au=100 : 35·461, whence *Au=197·123**;
Au : 4AgBr=100 : 381·021, ,, ,, *=197·150**;
Au : 3Br=100 : 121·678, ,, ,, *=197·035**;
Au : KBr=100 : 60·390, ,, ,, =197·374*.[1]

The work of Thorpe and Laurie [2] was published in 1887. Like Krüss, they employed potassium auribromide as the basis of their research. By heating, the salt was decomposed into gold and potassium bromide, the mixture weighed and extracted with water, and the residual gold weighed. The amount of potassium bromide was ascertained by difference, and the filtrate containing this salt was analysed for bromine by titrating it against silver according to the procedure of Stas. The silver bromide produced was also collected and weighed. The results were

Au : KBr=100 : 60·331, whence *Au=197·272**;
Ag : Au=100 : 182·827, ,, ,, *=197·234**;
Au : AgBr=100 : 95·208, ,, ,, *=197·248**.

The elaborate research of Mallet [3] appeared in 1889. Extreme care was exercised in this investigation, an example of the refinement of the methods employed being the substitution of quartz-sand for filter-paper, to avoid reduction of the gold salts to the metal during filtration.

All Mallet's analyses of auric chloride, auric bromide, and potassium auribromide were made by the same method. The gold in one sample of the compound was determined by reducing with sulphurous acid, collecting the precipitate, heating it in the vacuum of a Sprengel pump, cooling, and weighing. From another sample the halogen was precipitated by a slight excess of silver nitrate prepared from a known weight of silver, and the excess of silver was determined by titration with a standard solution of hydrobromic acid. To avoid weighing the gold salts, they were dissolved in water, and weighed portions of the solutions were employed for the analyses. The results were

($AuCl_3$) 3Ag : Au=100 : 60·910, whence *Au=197·129**;
($AuBr_3$) 3Ag : Au=100 : 60·927, ,, ,, *=197·184**;
($KAuBr_4$) 4Ag : Au=100 : 45·689, ,, ,, *=197·157**.

A further series of five experiments was made to determine the ratio of the electrochemical equivalents of gold and silver, by passing the same quantity of electricity through solutions of potassium aurocyanide,

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[1] The value calculated from the ratio Au : KBr has been increased by 0·295, to correct it to vacuum standard. Compare Brauner, *Abegg und Auerbach's Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i. 758.

[2] Thorpe and Laurie, *Trans. Chem. Soc.*, 1887, 51, 565, 866.

[3] Mallet, *Phil. Trans.*, 1889, 180, 395.

$KAu(CN)_2$, and potassium silver cyanide, $KAg(CN)_2$, and comparing the amounts of gold and silver deposited :

Ag : Au=100 : 182·808, whence *Au=197·213**.

Mallet also determined the ratio $N(CH_3)_3HAuCl_4$: Au by estimating the gold left on ignition of trimethylammonium aurichloride, but the values obtained were too high. The same is true of two series of determinations of the ratio H : Au. One of them was carried out by determining the electrochemical equivalent of the metal with respect to hydrogen, both elements being liberated by the same electric current. The other experimental method consisted in the determination of the equivalent of hydrogen with respect to zinc, and also that of gold with respect to this metal by precipitation from auric chloride.

According to Brauner,[1] the results marked with an asterisk (*) and obtained by Krüss, Thorpe and Laurie, and Mallet, are the most reliable. Their arithmetic mean is *Au=197·208.* Employing the value 107·883 for the atomic weight of silver, Brauner has calculated from them a mean value for the atomic weight of gold, **Au=197·20.**

The International Atomic Weight Committee's current table gives

Au=197·2.

ALLOYS AND COMPOUNDS OF GOLD.

Alloys of Gold.[2]—Alloying the metal with copper[3] increases the hardness, elasticity, and tensile strength, but lowers the malleability, ductility, density, and melting-point. The alloys have a reddish tint. The minimum melting-point is 905° C., corresponding with 82 per cent. of gold and 18 per cent. of copper, the alloy of this composition being brittle. The British standard for coinage corresponds with eleven parts of gold in twelve of alloy, or 91·6̇ per cent. The alloys with silver are soft, malleable, and ductile, their properties being intermediate between those of the two metals. Below 37·5 per cent. of gold their colour is similar to that of pure silver. The solution of alloys of gold and silver in *aqua regia* is much facilitated by the presence of a mixture of ammonium nitrate and ammonium chloride.[4] For additional alloys of gold reference should be made to the other volumes of this series.

AUROUS COMPOUNDS.

Aurous fluoride, AuF.—At red heat, gold combines with fluorine, forming a dark-coloured fluoride. At higher temperatures this salt decomposes into gold and fluorine.[5]

Aurous chloride, AuCl.—Partial elimination of chlorine from auric chloride by means of heat yields aurous chloride, but it is difficult to

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[1] Brauner, *Abegg und Auerbach's Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i. 762.

[2] For *gold-amalgam* see this series, Vol. III.

[3] Compare Kurnakov, Schemtschushny, and Zasedatelev, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 871.

[4] Pollard, *Trans. Chem. Soc.*, 1920, 117, 79.

[5] Moissan, *Compt. rend.*, 1889, 109, 807; *Ann. Chim. Phys.*, 1891, [6], 24, 224, 282.

prepare it free from gold and auric chloride, and there is much divergence in the temperatures cited by various experimenters, the values ranging between 120° and 300° C.[1] The auric chloride can be washed out of it by means of ether, but it is difficult to prevent decomposition of the aurous chloride into auric chloride and gold under the influence of traces of water:

$$3AuCl=AuCl_3+2Au.$$

The decomposition by water is accelerated by rise of temperature.

The chloride[2] is a yellowish-white substance, soluble in aqueous alkali-metal chlorides[3] with formation of complex anions, the solutions soon decomposing with precipitation of metallic gold and the formation of complex auric derivatives. The transformation is more rapid in bromide solutions. At 110° to 120° C. aurous chloride and excess of phosphorus trichloride combine to form a double compound of the formula $AuCl,PCl_3$, colourless prisms insoluble in water.[4]

Aurous bromide, AuBr.—When auric bromide is heated, bromine is evolved, and aurous bromide left as a green mass.[5] It is also formed by heating auribromic acid, $HAuBr_4$, the auric bromide formed decomposing at 115° C. Above this temperature it is decomposed into gold and bromine, and reacts with water like aurous chloride. Aqueous hydrobromic acid converts it into gold and auribromic acid, $HAuBr_4$:

$$3AuBr=AuBr_3+2Au;$$
$$AuBr_3+HBr=HAuBr_4.$$

It dissolves in solutions of alkali-metal bromides.[6]

Aurous iodide, AuI.—The iodide is produced by decomposition of auric iodide at ordinary temperature; by the interaction of auric oxide and hydriodic acid[7]; by precipitation of auric chloride with potassium iodide,[8] hydrogen iodide, or ferrous iodide; by the interaction of gold and iodine in ether solution or in a sealed tube at 50° C., or ferric iodide, or manganese tetraiodide[9]; by boiling powdered gold with hydriodic acid and nitric acid, filtering, and pouring the hot filtrate into aqueous hydriodic acid[10]; and by the interaction of aurous chloride and potassium iodide.[11]

Aurous iodide is a lemon-yellow powder, and is very difficult to prepare in the pure state, as it is decomposed by moist air at ordinary temperatures. The excess of iodine is best eliminated by sublimation at 30° C. It is decomposed by heating with water, dilute sulphuric acid,

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[1] Dammer, *Handbuch der anorganischen Chemie*, Stuttgart, 1893, 3, 761; Berzelius, *Lehrbuch der Chemie*, 4th ed., Dresden, 1835–1841, 4, 691; Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 386; Leuchs, *J. prakt. Chem.*, 1872, [2], 6, 156; Krüss, *Annalen*, 1887, 237, 276.

[2] Compare Diemer, *J. Amer. Chem. Soc.*, 1913, 35, 552.

[3] Lengfeld, *Amer. Chem. J.*, 1901, 26, 324.

[4] Lindet, *Compt. rend.*, 1884, 98, 1382; compare Abegg, *Zeitsch. anorg. Chem.*, 1904, 39, 333.

[5] Fernand Meyer, *Compt. rend.*, 1909, 148, 346.

[6] Lengfeld, *loc. cit.*

[7] Compare Pelletier, *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1015.

[8] Fordos, *J. Pharm.*, 1841, 27, 653.

[9] Compare Nicklès, *Ann. Chim. Phys.*, 1867, [4], 10, 318; *Compt. rend.*, 1866, 62, 755; 63, 21.

[10] Compare Gmelin-Kraut, *Handbuch der anorganischen Chemie*, 7th ed., Heidelberg, 1914, 5, ii., 282.

[11] Compare Fernand Meyer, *Compt. rend.*, 1904, 139, 733.

and nitric acid, although not so readily as the corresponding chloride and bromide. Chlorine and bromine exert an oxidizing action, liberating iodine and forming auric compounds. Potassium hydroxide precipitates metallic gold, producing potassium iodide and iodate.[1] Alcohol, ether, and other organic compounds cause precipitation of metallic gold. The iodide dissolves readily in potassium-iodide solution, probably with formation of complex anions.[2]

Complex Derivatives of Ammonia and Aurous Halides.—Liquid ammonia reacts with aurous chloride to form compounds $AuCl,3NH_3$ and $AuCl,12NH_3$; at 18° C. gaseous ammonia and aurous bromide give a white powder, $AuBr,2NH_3$. Liquid ammonia converts aurous iodide into a compound $AuI,6NH_3$, from which ammonia is eliminated by rise of temperature, the substance being completely transformed at 20° C. into AuI,NH_3, a compound also formed by the action of ammonia-gas on aurous iodide.[3]

Aurous oxide, Au_2O.—This oxide is produced by the action of potassium hydroxide on soluble auric salts or on the comparatively slightly soluble aurohalides, but the product is contaminated with metallic gold.[4] It can be prepared in the pure state by reducing potassium auribromide, $KAuBr_4$, to potassium aurobromide, $KAuBr_2$, by the action of sulphurous acid, and adding dilute potassium hydroxide to the solution.[5] Aurous hydroxide is precipitated as a dark-violet substance, converted into a greyish-violet product by drying over phosphoric oxide. On heating, it loses water up to 200° C. At 205° to 210° C. oxygen is also evolved, and at 250° C. there is rapid decomposition into gold and oxygen. When freshly precipitated, aurous hydroxide dissolves in water, yielding a colloidal solution of indigo-blue colour, and characterized by a brownish fluorescence in reflected light. It also dissolves in alkali-metal hydroxides with formation of complex anions.[6] It has the character of a very weak base.

Aurous sulphide, Au_2S.—The pure sulphide can be prepared[7] by saturation of a solution of potassium aurocyanide with hydrogen sulphide, and precipitation of the salt by acidifying the solution with hydrochloric acid. It is not produced by the action of hydrogen sulphide on a hot solution of auric chloride, as supposed by Berzelius.[8] The moist substance has a steel-grey colour; when dried, it becomes brownish black. When freshly prepared, the sulphide dissolves in water to a colloidal solution, from which it is reprecipitated by addition of hydrochloric acid. The sulphide is unaffected by dilute acids, but is decomposed by powerful oxidizers such as *aqua regia* and chlorine. It is readily dissolved by solutions of polysulphides,[9] and less readily by those of monosulphides. It also dissolves in a solution of potassium

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[1] Compare Gmelin-Kraut, *Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1914, 5, ii., 282.

[2] Campbell, *Trans. Faraday Soc.*, 1907, 3, 24; *Chem. News*, 1907, 96, 15.

[3] Fernand Meyer, *Compt. rend.*, 1906, 143, 280; compare Herrmann, *Ber.*, 1905, 38, 2813.

[4] Berzelius, *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 4, 176; compare Figuier, *Ann. Chim. Phys.*, 1844, [3], 11, 340.

[5] Krüss, *Annalen*, 1887, 237, 276.

[6] Berzelius, *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 3, 176.

[7] Gutbier and Dürrwächter (*Zeitsch. anorg. Chem.*, 1922, 121, 266) were unable to prepare this substance in accordance with the literature.

[8] Berzelius, *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 3, 188; compare Levol, *Ann. Chim. Phys.*, 1850, [3], 30, 356; Krüss, *Ber.*, 1887, 20, 2372.

[9] Krüss, *Annalen*, 1887, 237, 276.

cyanide. With sodium sulphide [1] and with potassium sulphide,[2] aurous sulphide forms double sulphides of the type $NaAuS$.

Complex Derivatives of Aurous sulphite.—Although aurous sulphite itself has not been isolated, double sulphites of aurous gold with sodium, potassium, ammonium, and barium have been obtained.[3] The sodium salt is formed by the interaction of auric chloride and sodium sulphite in alkaline solution, or by the action of sodium hydrogen sulphite on a boiling solution of a gold salt, or by that of sulphurous acid on a similar solution at 30° to 50° C. It has the formula $Au_2SO_3,3Na_2SO_3,3H_2O$ or $Na_3Au(SO_3)_2,1\frac{1}{2}H_2O$, containing the complex anion $Au(SO_3)_2'''$, since it does not display the reactions characteristic of sulphites. It is readily soluble in water.

The corresponding potassium salt forms white needles, and the barium salt is a purple-red, amorphous substance. The constitution of the ammonium salt produced by the interaction of auric chloride and an ammoniacal solution of ammonium sulphite is uncertain, but is given as

$$2Au_2SO_3,(NH_4)_2SO_3,6NH_3,4H_2O,$$

or

$$5Au_2SO_3,2(NH_4)_2SO_3,10NH_3,4H_2O.$$

Aurous thiosulphate, $Au_2S_2O_3,3H_2S_2O_3,H_2O$.—This substance is to be regarded as a complex aurothiosulphuric acid. It is prepared by the action of dilute sulphuric acid on the barium salt.[4]

Sodium thiosulphate reacts with a solution of auric chloride to form *sodium aurothiosulphate*,

$$Au_2S_2O_3,3Na_2S_2O_3,H_2O, \text{ or } Na_3Au(S_2O_3)_2,\tfrac{1}{2}H_2O,$$

colourless, acicular crystals. At 150° to 160° C. it loses water, and at higher temperatures it is decomposed. Hydrogen sulphide and ammonium sulphide precipitate aurous sulphide from its solution, and iodine transforms it into sodium tetrathionate and aurous iodide. In accordance with the presence of a complex anion, hydrochloric acid and sulphuric acid do not precipitate sulphur, a contrast to their action on ordinary thiosulphates. The complexity of the anion is further manifested in the inability of the usual gold reducers to precipitate the metal.

Aurous Derivatives of Nitrogen.—Aurous oxide and ammonia combine to form an explosive product,[5] $Au_3N,NH_3,4H_2O$.[6] When boiled with water, half of the nitrogen is eliminated, with formation of another nitride, $Au_3N,5H_2O$. A highly explosive *aurous hydrazoate* has also been prepared.[7]

Aurous cyanide, $AuCN$.—The cyanide is produced by the interaction of hydrogen cyanide and auric hydroxide[8]; by double decomposition

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[1] Antony and Lucchesi, *Gazzetta*, 1896, 26, ii., 350; Dammer, *Handbuch der anorganischen Chemie*, Stuttgart, 1893, 3, 769; Yorke, *Liebig and Kopp's Jahresbericht für* 1847–1848, Giessen, 1849, 451.

[2] Yorke, *loc. cit.*; Oberkampf, *Ann. Chim.*, 1811, 80, 140; compare Hofmann and Höchtlen, *Ber.*, 1903, 36, 3090.

[3] Haase, *Einwirkung von schwefliger Säure auf Goldchlorid*, Rostock, 1869; *Krit. Zeit. Chem.*, 1869, 12, 535; compare Rosenheim, Hertzmann, and Pritze, *Zeitsch. anorg. Chem.*, 1908, 59, 198.

[4] Fordos and Gélis, *Ann. Chim. Phys.*, 1845, [3], 13, 394.

[5] Figuier, *ibid.*, 1844, [3], 11, 336.

[6] Raschig, *Annalen*, 1886, 235, 349.

[7] Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 261.

[8] Dammer, *Handbuch der anorganischen Chemie*, Stuttgart, 1893, 3, 774.

from auric chloride and mercuric cyanide, with simultaneous production of complex derivatives[1]; and by the decomposition of auric cyanide, as well as by the action of hydrochloric acid on its complex salts at 50° C.:[2]

$$NaAu(CN)_2+HCl=AuCN+NaCl+HCN.$$

Aurous cyanide forms yellow, microscopic laminæ, very slightly soluble in water. It is more stable than aurous iodide, but at red heat is decomposed into gold and cyanogen. Its insolubility renders it immune to the action of dilute acids and hydrogen sulphide, but solutions of ammonia, potassium hydroxide, ammonium sulphide, and sodium thiosulphate dissolve it, probably forming complex derivatives. In aurous cyanide the tendency to form complex compounds is much more marked than in the corresponding chloride, bromide, and iodide.[3] Its interaction with potassium ferrocyanide has been studied by Beutel.[4]

A solution of potassium cyanide dissolves aurous cyanide, and also finely divided gold in presence of air, forming *potassium aurocyanide*, $KAu(CN)_2$, a substance also produced by anodic solution of gold in a solution of potassium cyanide. The anhydrous salt crystallizes from water in colourless, rhombic octahedra.[5] At ordinary temperatures its solubility is 11·66 grams in 100 grams of water. Its solution absorbs chlorine, bromine, and iodine, forming complex halogen derivatives,[6] containing ions of the type  $\mathrm{Au}^{\mathrm{CN}}_{\mathrm{Cl}_2}\mathrm{CN}'$.

Double decomposition of ammonium sulphate and potassium aurocyanide yields *ammonium aurocyanide*, $NH_4Au(CN)_2$. This substance begins to decompose at 100° C. into aurous cyanide, hydrogen cyanide, and ammonia.[7] *Sodium aurocyanide*, $NaAu(CN)_2$, resembles the corresponding potassium salt in both preparation and properties. Salts of the aurocyanic radical, $Au(CN)_2'$, with other metals are also known.[8] The compound $HAu(CN)_2$ has not been isolated, since it decomposes readily with production of hydrogen cyanide.

Potassium aurothiocyanate, $KAu(CNS)_2$, is formed by warming auric chloride with a solution of potassium thiocyanate at 80° C.[9] It forms yellow prisms, melting above 100° C., and decomposing into gold, potassium thiocyanate, carbon disulphide, and sulphur. It contains the complex aurothiocyanic radical, $Au(CNS)_2'$, and with silver nitrate yields the corresponding *silver aurothiocyanate*, $AgAu(CNS)_2$.

COMPOUNDS OF BIVALENT GOLD.

Gold dichloride, $AuCl_2$.—At 170° C. dry chlorine unites with dried gold-powder to form the dichloride, a very hygroscopic, dark-red substance, decomposed by the action of moist air.[10] The individuality

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[1] Desfosses, *Neues J. Pharm.*, 1820, 4, 385; compare Schmidt, *Chem. Zeit.*, 1896, 20, 633.

[2] Himly, *Annalen*, 1842, 42, 157.

[3] Compare Bodländer, *Ber.*, 1903, 36, 3933.

[4] Beutel, *Monatsh.*, 1910, 31, 883.

[5] Lindbom, *Ber.*, 1877, 10, 1725.

[6] Compare Lindbom, *loc. cit.*; Himly, *Annalen*, 1842, 42, 157; Blomstrand, *J. prakt. Chem.*, 1871, [2], 3, 213; Lindbom, *Bull. Soc. chim.*, 1878, [2], 29, 416.

[7] Lindbom, *Bull. Soc. chim.*, 1878, [2], 29, 416.

[8] Compare Christy, *Berg- und Hütten-männische Zeit.*, 1898, 57, 228, 238.

[9] Dammer, *Handbuch der anorganischen Chemie*, Stuttgart, 1893, 3, 775; Cleve, *J. prakt. Chem.*, 1865, 94, 14.

[10] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 383.

of this compound has been a matter of dispute,[1] and it has been assumed to be a molecular compound of the formula $AuCl,AuCl_3$, containing equimolecular proportions of aurous chloride and auric chloride. Thermochemical data indicate that this assumption is incorrect.[2]

Gold dibromide, $AuBr_2$.—Bromine converts powdered gold at 170° C. into the dibromide, a black substance slowly soluble in water with decomposition.[3] It is also decomposed by heat, and by the action of acids. The individuality of the dibromide has also been disputed,[4] but it is supported by thermochemical evidence.[5]

Gold monoxide, AuO.—An oxide of this formula is said to be formed by the action on gold of a small proportion of *aqua regia* containing excess of hydrochloric acid, addition of sufficient primary carbonate to the solution to redissolve the precipitate first formed, and heating the solution.[6] The product separates as an olive-green hydrate, which dries in the air to a hard mass. It is doubtful whether the oxide is a true chemical compound or not.

A hydrated gold oxide of the formula $Au_3O_2(OH)_2$ is prepared by the action of boiling water on the monosulphate, $AuSO_4$.[7] It is a deep-black powder, decomposed at 160° to 205° C.

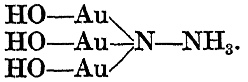
Gold monosulphide, AuS.—Hydrogen sulphide or an alkali-metal sulphide precipitates the monosulphide from solutions of auric chloride,[8] and it is also produced by the action of hydrogen sulphide on sodium aurothiosulphate. It is a black substance, insoluble in acids except *aqua regia,* but soluble in alkali-metal sulphides.[9]

Gold monosulphate, $AuSO_4$.—Evaporation of a solution in concentrated sulphuric acid at 250° C. of the so-called *acid auryl sulphate,* $AuOHSO_4$ (p. 347), yields large crystals of the monosulphate.[10] It is characterized by its scarlet-red colour. Exposure to moist air changes it into the black hydrated monoxide.

Nitride of Bivalent Gold.—Ammonia converts gold monoxide into a nitride containing gold and nitrogen in the atomic proportions 3 : 2, but different from the product formed by the interaction of ammonia and aurous oxide.[11] The reaction is possibly expressed by the equation

$$3AuO+2NH_3=Au_3N_2+3H_2O.$$

The substance is explosive, and is regarded by Raschig as probably having the constitution



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[1] Compare Krüss and Schmidt, *Ber.*, 1887, 20, 2634; *J. prakt. Chem.*, 1888, [2], 38, 77; Thomsen, *ibid.*, 1888, [2], 37, 105; Petersen, *ibid.*, 1892, [2], 46, 328.

[2] Petersen, *J. prakt. Chem.*, 1892, [2], 46, 328.

[3] Thomsen, *ibid.*, 1888, [2], 37, 386.

[4] Krüss and Schmidt, *ibid.*, 1888, [2], 38, 77.

[5] Petersen, *ibid.*, 1892, [2], 46, 328.

[6] Prat, *Compt. rend.*, 1870, 70, 840.

[7] Schottländer, *Annalen*, 1883, 217, 337.

[8] Oberkampf, *Ann. Chim.*, 1811, 80, 140; compare Levol, *ibid.*, 1850, [3], 30, 356; Fellenberg, *Pogg. Annalen*, 1840, 50, 71; Hoffmann and Krüss, *Ber.*, 1887, 20, 2705.

[9] Gutbier and Dürrwächter (*Zeitsch. anorg. Chem.*, 1922, 121, 266) failed to prepare this substance in accordance with the literature.

[10] Schottländer, *Annalen*, 1883, 217, 337.

[11] Raschig, *ibid.*, 1886, 235, 351.

AURIC COMPOUNDS.

Auric chloride, $AuCl_3$.—Under certain conditions gold is converted by chlorine into auric chloride. At ordinary temperatures such reagents as chlorine-water, *aqua regia*, and the higher chlorides of manganese, nickel, and cobalt effect this change.[1] At 300° C. the dry gas transforms the metal into the chloride, the product subliming in reddish, bulky crystals.[2] An aqueous solution can be prepared by the action of water on the dichloride, or on aurous chloride :

$$3AuCl_2 = 2AuCl_3 + Au.$$
$$3AuCl = AuCl_3 + 2Au.$$

Spontaneous evaporation of the solution of the chloride yields dark, orange-yellow crystals of the dihydrate, $AuCl_3,2H_2O$, which changes to the anhydrous salt on exposure to the air. The monohydrate, $AuCl_3,H_2O$, is supposed to exist in solution in the form of an acid, H_2AuCl_3O.[3] With silver carbonate this acid yields a yellowish silver salt, Ag_2AuCl_3O. The constitution of the acid and of its salts is a matter of uncertainty.

On rapid evaporation of a solution of auric chloride in an acidic solution capable of generating chlorine, and subsequently drying the product at 150° C., the salt is obtained in anhydrous form as a dark-brown crystalline mass, reducible to a reddish-brown powder.[4] Its melting-point in an atmosphere of chlorine or in a sealed tube is 287° to 288° C., and its density is 3·9.[5] On heating in a closed space it dissociates,[6] the reaction beginning at 190° to 200° C.:[7]

$$AuCl_3 \rightleftharpoons AuCl + Cl_2.$$

Under a pressure of two atmospheres in contact with chlorine there is no separation of metallic gold, even at the melting-point.

Auric chloride is reduced by carbon in accordance with the equation [8]

$$4AuCl_3 + 6H_2O + 3C = 4Au + 12HCl + 3CO_2.$$

It is also reduced to metallic gold by phosphorous acid and sodium hypophosphite,[9] and by cupric sulphide in accordance with the equation [10]

$$CuS + 2AuCl_3 + 3H_2O + O = 2Au + CuSO_4 + 6HCl.$$

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[1] Nicklès, *Ann. Chim. Phys.*, 1867, [4], 10, 318.

[2] Debray, *Compt. rend.*, 1869, 69, 985; Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 382; Krüss, *Annalen*, 1887, 238, 249; Prat, *Dingler's Polytech. J.*, 1860, 158, 59.

[3] Hittorf and Salkowski, *Zeitsch. physikal. Chem.*, 1898, 28, 546.

[4] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 382.

[5] Rose, *Trans. Chem. Soc.*, 1895, 67, 905.

[6] Rose, *ibid.*, 881; compare Robert Boyle, *Philosophical Works* (abridged by P. Shaw), 2nd ed. (London, Innys and Manby, and T. Longman, 1738), 1, 263; Prat, *Dingler's Polytech. J.*, 1860, 158, 59; Thompson, *J. Soc. Arts*, 1840, 53; Debray, *Compt. rend.*, 1869, 69, 985; Krüss, *Annalen*, 1887, 238, 249; Krüss and Schmidt, *Ber.*, 1887, 20, 2641.

[7] Diemer, *J. Amer. Chem. Soc.*, 1913, 35, 552.

[8] Avery, *J. Soc. Chem. Ind.*, 1908, 27, 255.

[9] Sieverts and Major, *Zeitsch. anorg. Chem.*, 1909, 64, 29.

[10] Freise, *Zeitsch. Berg- und Hütten-wesen*, 1912, 60, 227, 241, 260, 270; compare Lenher, *J. Amer. Chem. Soc.*, 1913, 35, 546.

A test of the purity of the salt is its complete solubility in ether.[1] It is unaffected by the prolonged action of radium bromide.[2]

In dissolving alloys of gold and silver in *aqua regia* in presence of ammonium chloride and nitrate, purplish-brown crystals of the formula

$$3AgCl,4AuCl_3,8NH_4Cl$$

are sometimes obtained as a by-product.[3]

Aurichloric Acid, $HAuCl_4$.—A solution of this substance is produced by the action of hydrochloric acid on auric chloride, or by addition of excess of this acid to a solution of gold in *aqua regia* to decompose the nitric acid present. It crystallizes in yellow needles, which deliquesce in moist air to a yellow solution.[4] The acid exists in the form of two distinct hydrates, one with three[5] and the other with four[6] molecules of water, the individuality of the two being indicated by the heats of solution.[7] In the solution of this acid the gold is present in the anion $AuCl_4'$.[8] Its action on potassium ferrocyanide has been investigated.[9]

A great number of *aurichlorides* is known. *Potassium aurichloride*, $KAuCl_4$, is prepared in the anhydrous form by evaporating a solution of auric chloride in concentrated hydrochloric acid in presence of potassium chloride.[10] It melts at the temperature of boiling mercury.[11] It is also known as *semihydrate* and *dihydrate*.[12] It dissolves readily in water. Heating converts it into potassium aurochloride, $KAuCl_2$.

Sodium aurichloride, $NaAuCl_4,2H_2O$, forms rhombic columnar crystals or laminæ.[13] Its water of crystallization cannot be expelled without decomposing the salt, a distinction from the potassium derivative. Its solubility in ether is another characteristic point of difference.[14] It can be employed as a test for iodides in presence of bromides, the liberated iodine imparting a violet colour to chloroform.[15]

Two *ammonium aurichlorides* are known:

$$4NH_4AuCl_4,5H_2O\ ^{16} \text{ and } 2NH_4AuCl_4,5H_2O.^{17}$$

The first is prepared in yellow, monoclinic plates from a solution of auric chloride in concentrated hydrochloric acid in presence of ammonium chloride; the second in yellow laminæ from a neutral or slightly acidic solution of auric chloride. At 100° C. they give up their water of crystallization, and at higher temperatures decompose.

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[1] Frank, *Schweiz. Wochensch. Chem. Pharm.*, 1913, 51, 386.

[2] Perman, *Trans. Chem. Soc.*, 1908, 93, 1775.

[3] Pollard, *ibid.*, 1920, 117, 99.

[4] Berzelius, *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 4, 692.

[5] Weber, *Pogg. Annalen*, 1867, 131, 445; Schottländer, *Annalen*, 1883, 217, 312.

[6] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 382.

[7] Compare Lengfeld, *Amer. Chem. J.*, 1901, 26, 324; Schmidt, *Apotheker-Zeit.*, 1906, 21, 661.

[8] Hittorf, *Pogg. Annalen*, 1859, 106, 523.

[9] Beutel, *Monatsh.*, 1910, 31, 871.

[10] Lainer, *ibid.*, 1890, 11, 220.

[11] Ephraim, *Ber.*, 1919, 52, [B], 241.

[12] Topsöe, *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1030.

[13] Compare Topsöe, *loc. cit.*

[14] Fasbender, *Nederl. Tijdsch. Pharm.*, 1894, 6, 1, 227.

[15] Reichardt, *Pharm. Zeit.*, 1909, 54, 58.

[16] Topsöe, *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1026.

[17] Topsöe, *ibid.* (with Darmstädter and Forchhammer).

Salts of lithium,[1] rubidium,[2] cæsium [2] (which melts at a somewhat higher temperature than the potassium salt[3]), calcium, strontium, barium, magnesium, zinc, manganese,[4] and complex salts of the last three metals and nickel and cobalt[5] have been prepared. Other complex derivatives are also known.[6] An example is the cæsium compound [7] of the formula $Cs_5Au_3Cl_{14}$, minute, deep-red crystals formed by the action of excess of a concentrated solution of cæsium chloride on auric chloride in presence of strong hydrochloric acid. The triple chloride formulated by Pollard [8] as $(NH_4)_8Ag_3Au_4Cl_{23}$ is represented by Wells [9] as $(NH_4)_6Ag_2Au_3Cl_{17}$. An amorphous series of triple salts of the general formula $Cs_4MAu'''_2Cl_{12}$ has been prepared by Wells,[9] M representing Ag_2, Zn, Hg″, Cu″, or Au'_2. It exemplifies the isomorphous replacement of two univalent atoms by one bivalent atom. Triple chlorides of gold, silver, and rubidium (or cæsium) are also known.[10]

Auric chloride also forms a number of addition-products. A substance of the formula $AuCl_3,PCl_5$ is obtained in lemon-yellow needles by chlorination of the phosphorus-trichloride addition-product of aurous chloride, and also by heating a solution of aurous chloride in phosphorus trichloride with the pentachloride under pressure.[11] Sulphur tetrachloride yields a compound of the formula $AuCl_3,SCl_4$, unstable, yellow needles decomposed by moist air.[12] Prolonged heating of nitrosyl chloride at 100° C. under pressure with finely divided gold gives a derivative $AuCl_3,NOCl$.[13] Addition-products with selenium chloride, antimony pentachloride, stannic chloride, silicon tetrachloride, and titanic chloride have also been prepared.

Auric bromide, $AuBr_3$.—The bromide is formed in aqueous solution by the action of water on gold dibromide.[14] It can be obtained in the solid state from the same source by the action of moist ether, the aurous bromide formed remaining undissolved, and auric bromide being left on evaporation of the dried ether solution. It is also produced by the interaction of aqueous bromine and gold,[15] as well as by the action of solutions of such perbromides as cobalt tribromide, manganese tetrabromide, and ferric bromide on the metal.[16] The aqueous solution and the crystals deposited from it have a scarlet-red colour, but the pure salt contained from solution in ether is a dark-brown

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[1] Fasbender, *Nederl. Tijdsch. Pharm.*, 1894, 6, 1, 227.

[2] Wells, Wheeler, and Penfield, *Zeitsch. anorg. Chem.*, 1893, 2, 304.

[3] Ephraim, *Ber.*, 1919, 52, [B], 241.

[4] Bonsdorff, *Pogg. Annalen*, 1829, 17, 261; 1834, 33, 64.

[5] Topsöe, *Sitzungsber. K. Akad. Wiss. Wien.*, 1874, 69, 261.

[6] Compare Gibbs and Genth, *Amer. J. Sci.*, 1857, [2], 23, 330; 1857, [2], 24, 90; Wohlwill, *Zeitsch. Elektrochem.*, 1898, 4, 379; Herrmann, *Ber.*, 1894, 27, 596; Schottländer, *Annalen*, 1883, 217, 312; Schmidt, *Chem. Zeit.*, 1896, 20, 483; Lengfeld, *Amer. Chem. J.*, 1901, 26, 324.

[7] Wells, *Amer. J. Sci.*, 1922, [5], 3, 414.

[8] Pollard, *Trans. Chem. Soc.*, 1920, 117, 99.

[9] Wells, *Amer. J. Sci.*, 1922, [5], 3, 257, 315.

[10] Bayer, *Monatsh.*, 1920, 41, 223; Emich, *ibid.*, 243.

[11] Lindet, *Compt. rend.*, 1884, 98, 1382; compare Pickard and Kenyon, *Trans. Chem. Soc.*, 1906, 89, 262.

[12] Lindet, *Compt. rend.*, 1885, 101, 1492.

[13] Sudborough, *Trans. Chem. Soc.*, 1891, 59, 73, 270.

[14] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 388.

[15] Balard, *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1016.

[16] Nicklès, *Ann. Chim. Phys.*, 1867, [4], 10, 318.

powder. At 160° C. it is completely transformed into aurous bromide[1] in the form of a green mass,[2] and bromine. When prepared by the action of bromine on precipitated gold, it forms black crystals, volatile in bromine at 300° C.[2]

Auribromic Acid, $HAuBr_4$.—Solutions of auric bromide and of gold in bromine-generating liquids are converted by hydrogen bromide into a solution of auribromic acid. The substance is also formed in solution by the action of the same reagent on a solution of auric chloride, and can be extracted by ether from the dark-red liquid.[3] Evaporation of the concentrated aqueous solution yields the acid in dark-red crystals of the formula $HAuBr_4,5H_2O$ [4] or $HAuBr_4,6H_2O$,[5] melting at 27° C. in its own water of crystallization, and decomposed by concentrated sulphuric acid at 155° C. into aurous bromide and bromine.[6]

Potassium auribromide, $KAuBr_4$, is produced by the action of bromine on gold and the equivalent proportion of potassium bromide.[7] On evaporation of the solution, potassium auribromide crystallizes in dark-red prisms containing two molecules of water of crystallization[8]; and by drying the crystals over phosphoric oxide it is obtained in the form of purple-red, monoclinic crystals[9] free from water. On exposure to air, it takes up two molecules of water.[10] Its solubility at 15° C. is 19·53 grams in 100 grams of water.

Ammonium auribromide, NH_4AuBr_4, is produced by the action of ammonia on the acid, and forms bluish-black crystals of fat-like lustre. The anhydrous *rubidium* and *cæsium salts* give prisms of metallic lustre, the colour of the first being cinnabar-red, and of the second deep black.[11]

Auribromides of sodium, barium, zinc, manganese,[12] and magnesium[13] have been prepared. Triple bromides of gold, silver, and rubidium (or cæsium) have also been described.[14] Double compounds of auric bromide and phosphorus derivatives can be obtained by methods analogous to those employed for the corresponding chlorine addition-products.[15]

Auric iodide, AuI_3.—Gradual addition of a solution of auric chloride to one of potassium iodide yields complex AuI_4-ions, converted by further addition of auric chloride into auric iodide:[16]

$$3AuI_4{}' + Au^{\cdot\cdot\cdot} = 4AuI_3.$$

On drying, the dark-green product decomposes into aurous iodide and iodine. It is soluble with difficulty in water to an unstable solution.

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[1] Schmidt, *Chem. Zeit.*, 1896, 20, 483.

[2] Fernand Meyer, *Compt. rend.*, 1909, 148, 346.

[3] Gutbier and Huber, *Zeitsch. anorg. Chem.*, 1914, 85, 353; compare *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1016.

[4] Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 3, 390.

[5] Lengfeld, *Amer. Chem. J.*, 1901, 26, 324.

[6] Schmidt, *Chem. Zeit.*, 1896, 20, 483.

[7] Schottländer, *Annalen*, 1883, 217, 315.

[8] Gutbier and Huber, *loc. cit.*

[9] Compare Muthmann, *Annalen*, 1887, 237, 259; Bonsdorff, *Pogg. Annalen*, 1830, 19, 346; 1834, 33, 64.

[10] Compare Muthmann, *loc. cit.*

[11] Gutbier and Huber, *loc. cit.*

[12] Bonsdorff, *Pogg. Annalen*, 1829, 17, 261; 1834, 33, 64.

[13] Leuchs, *J. prakt. Chem.*, 1872, [2], 6, 156.

[14] Suschnig, *Monatsh.*, 1921, 42, 399.

[15] Lindet, *Compt. rend.*, 1885, 101, 164.

[16] Johnston, *Phil. Mag.*, 1836, 9, 266.

A complex iodide having the formula CsI,AuI_3 is produced in glistening, black crystals by the interaction of gold dichloride and cæsium iodide.[1]

Auri-iodic Acid, $HAuI_4$.—Hydrogen iodide converts aurous iodide, auric iodide, and gold in presence of free iodine into auri-iodic acid. It forms small, black crystals.

Crystallization of a solution containing auric chloride and potassium iodide in the molecular proportions 1 : 4 yields *potassium auri-iodide*, $KAuI_4$. It forms black crystals which begin to decompose at 66° C., and on strong heating leave a residue of crystalline gold.[2] Water decomposes it, forming auric iodide. Johnston has also prepared an auri-iodide of sodium, ammonium, barium, and ferrous iron respectively ; and a strontium auri-iodide in solution.

Auric iodate.—Iodic acid or potassium iodate precipitates the iodate from auric-chloride solution as a yellow substance soluble in a large proportion of water.[3] It is the only auric salt of a halogen oxy-acid.

Auric hydroxide, $AuO{\cdot}OH$.—A 5 per cent. yield of the pure hydroxide is obtained by precipitating auric chloride with basic magnesium carbonate, and treating the precipitate with 30 per cent. nitric acid, most of the auric hydroxide dissolving in this solvent.[4] The poor yield is probably explicable on the assumption of the formation of insoluble complex salts which are precipitated with the hydroxide, and render necessary the drastic process of treatment with nitric acid, thus dissolving a large proportion of the hydroxide itself. The hydroxide has also been prepared in an impure state by several other methods.[5]

In the pure condition auric hydroxide resembles ferric hydroxide in appearance, and has the colour of brown ochre, but impurities impart to it a yellowish or greenish tint. It is soluble in nitric acid and hydrochloric acid, and in hot potassium-hydroxide solution, but insoluble in solutions of the carbonates of the alkali-metals and ammonium.[6] It dissolves in solutions of the chlorides of sodium, potassium, and barium with production of complex salts.[7] Prolonged heating at 140° to 150° C. eliminates all its water, with formation of *auric oxide*, Au_2O_3. At 155° to 165° C. auric oxide is converted into gold monoxide, AuO.[8]

Auric hydroxide behaves as a very weak acid having the anion $AuO_2{}'$. Evaporation of its solution in aqueous potassium hydroxide yields yellow needles of *potassium aurate*, $KAuO_2,3H_2O$.[9] In accordance with the weak nature of the acid, the solution of this salt in water is strongly alkaline.

For the preparation of *aurates*, Meyer[10] recommends fusing precipitated gold with sodium or barium peroxide, the corresponding aurate being formed. On extraction with water a greenish-yellow solution is

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[1] Gupta, *J. Amer. Chem. Soc.*, 1914, 36, 747.

[2] Johnston, *Phil. Mag.*, 1836, 9, 266.

[3] Ditte, *Dammer's Handbuch der anorganischen Chemie*, Stuttgart, 1893, 3, 769.

[4] Krüss, *Annalen*, 1887, 237, 290.

[5] Figuier, *J. Pharm.*, 1847, [3], 12, 401 ; Dumas, *Ann. Chim. Phys.*, 1830, 44, 179 ; Pelletier, *Schweigger's J.*, 1821, 31, 327 ; Wittstein, *Vierteljahresschrift prakt. Pharm.*, 1866, 15, 51 ; Frémy, *Ann. Chim. Phys.*, 1851, [3], 31, 480 ; Schottländer, *Annalen*, 1883, 217, 340 ; Thomsen, *Thermochemische Untersuchungen*, Leipsic, 1882–1883, 4, 391.

[6] Rose, *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1011.

[7] Pelletier, *Schweigger's J.*, 1821, 31, 327.

[8] Krüss, *Annalen*, 1887, 237, 290.

[9] Frémy, *Ann. Chim. Phys.*, 1851, [3], 31, 483.

[10] Fernand Meyer, *Compt. rend.*, 1907, 145, 805.

produced, and addition of sulphuric acid liberates auric hydroxide, $AuO{\cdot}OH,H_2O$, which is converted by alkalies into the corresponding aurate, $M'AuO_2$ or $M''(AuO_2)_2$, containing water of crystallization. The products are pale-green, acicular crystals, the dry salts being stable to heat. They are reduced by sulphurous acid and by alcohol to metallic gold. Dilute sulphuric acid and nitric acid yield the corresponding metallic nitrate and auric hydroxide; hydrochloric acid produces the metallic chloride and auric chloride. The calcium, barium, and magnesium salts are not readily soluble in water.[1]

A complex derivative of auric oxide and higher oxides of manganese has been described.[2]

Auric sulphide, Au_2S_3.—Gold does not combine directly with sulphur,[3] but at −2° C. a rapid current of hydrogen sulphide transforms aurichloric acid, $HAuCl_4$, in dilute solution in normal hydrochloric acid, into pure auric sulphide.[4] Lithium aurichloride, $LiAuCl_4,2H_2O$, at −10° C. is converted by hydrogen sulphide into a mixture of lithium chloride and impure auric sulphide, with evolution of hydrogen chloride. After extraction of the lithium chloride with alcohol, the sulphide is dried in a current of nitrogen at 70° C.[5] It is an amorphous, black powder, at once decomposed by the action of water. At 200° to 205° C. it is converted into a mixture of gold and sulphur. It forms double sulphides with the alkali-metals [6]; and also unites with the sulphides of elements of weak positive, or even of negative, character, such as arsenic, tellurium, molybdenum, and carbon.[7] The last class of compound is probably to be regarded as an auric salt of a complex acid containing sulphur and one of the elements mentioned.

Auric sulphate, $Au_2(SO_4)_3$.—The sulphate has not been isolated. Gold dissolves in concentrated sulphuric acid in presence of a small proportion of nitric acid, forming a yellow liquid, but dilution reprecipitates the gold, either as the hydroxide, or in presence of reducers as the metal.[8] The nitric acid can be replaced by other oxidizers, such as iodic acid [9] and manganese dioxide [10]; and a solution of the sulphate is also formed by the action of concentrated sulphuric acid on auric oxide.[11]

Acid auryl sulphate, $AuOHSO_4$.—This sulphate is produced by the action of concentrated sulphuric acid on auric hydroxide at 180° C., the brown, basic salt formed being converted by heating at 200° C. into the yellow acid auryl sulphate.[12] It is decomposed by water with formation of auric hydroxide, but dissolves in concentrated sulphuric acid to a yellowish-red solution, from which it separates unchanged. When this acid solution is heated with potassium hydrogen sulphate, a yellow, crystalline salt of the formula $KAu(SO_4)_2$ separates. It is more stable than acid auryl sulphate, but is slowly decomposed by water, with

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[1] Weigand, *Zeitsch. angew. Chem.*, 1906, 19, 139.

[2] Schottländer, *Annalen*, 1883, 217, 340.

[3] Pélabon, *Compt. rend.*, 1909, 148, 1176; *Ann. Chim. Phys.*, 1909, [8], 17, 526.

[4] Gutbier and Dürrwächter, *Zeitsch. anorg. Chem.*, 1922, 121, 266.

[5] Antony and Lucchesi, *Gazzetta*, 1889, 19, 545; 1890, 20, 601.

[6] Ditte, *Ann. Chim. Phys.*, 1907, [8], 12, 229.

[7] Berzelius, *Lehrbuch der Chemie*, 5th ed., Dresden, 1843–1848, 3, 698.

[8] Reynolds, *Chem. News*, 1864, 10, 167; Spiller, *ibid.*, 173; Allen, *ibid.*, 1872, 25, 85.

[9] Prat, *Dingler's Polytech. J.*, 1870, 198, 59.

[10] Lenher, *Electrochem. Ind.*, 1904, 2, 316.

[11] Compare Gmelin-Kraut, *Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1014.

[12] Schottländer, *Wied. Annalen*, 1883, 217, 368.

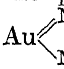
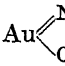
formation of auric hydroxide, potassium sulphate, and sulphuric acid. A silver salt of similar type has also been prepared.

Auric selenide.—Although gold and selenium do not combine directly,[1] hydrogen selenide precipitates auric selenide from solutions of auric chloride in absence of light.[2] It is an amorphous, black substance, of density 4·65 at 22° C., and is decomposed by heat with separation of selenium. It dissolves in *aqua regia* and in solutions of alkali-metal sulphides.

Auric selenate, $Au_2(SeO_4)_3$.—At 230° to 300° C. gold dissolves in concentrated selenic acid, with formation of auric selenate and selenious acid. The salt forms yellow crystals, insoluble in water, but soluble in concentrated acids.[3]

Auric telluride, Au_2Te_4.—When heated *in vacuo* with tellurium, gold dissolves, forming the telluride.[4] It was originally prepared by Berzelius, and subsequently by Brauner,[5] by direct union of the elements. It is found as the minerals *sylvanite, calaverite, krennerite,* and *petzite.*

Auric Chromate.—For an account of the preparation and properties of auric chromate reference should be made to this series, Vol. VII.

Derivatives of Gold and Nitrogen.—The so-called "fulminating gold" has long been known, and derives its name from its explosive character. Its composition varies with the mode of preparation. Explosive products classed as fulminating gold are obtained by the interaction of ammonia or ammonium salts and auric oxide[6]; by that of ammonia or ammonium carbonate and auric-chloride solution[7]; and by that of ammonia and the sulphuric-acid and nitric-acid derivatives of gold.[8] The colour of the product varies between green and brownish yellow; and on heating, percussion, or rubbing it decomposes explosively into gold, nitrogen, and ammonia. The explosive power is augmented by boiling with water or potassium-hydroxide solution, and by careful heating at 100° C. It is reduced by mixing the powder with salts of the alkali-metals or alkaline-earth metals, and with metallic oxides. Raschig[9] assigns to the product obtained from auric oxide the constitutional formula  $Au{<}^{NH}_{NH_2}$, the union of both nitrogen atoms with gold being indicated by the small proportion of nitrogen eliminated by boiling with water, alkalies, or acids. He has shown the product obtained from auric chloride to consist of this substance with an admixture of a chloro-derivative,  $Au{<}^{NH}_{Cl}$.

Another method of preparation has been described by Jacobsen.[10]

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[1] Pélabon, *Compt. rend.*, 1909, 148, 1176; 1922, 174, 391; *Ann. Chim. Phys.*, 1909, [8], 17, 526.

[2] Uelsmann, *Selenverbindungen*, Göttingen, 1860.

[3] Mitscherlich, *Pogg. Annalen*, 1827, 12, 639; compare Lenher, *J. Amer. Chem. Soc.*, 1902, 24, 354.

[4] Pélabon, *Compt. rend.*, 1909, 148, 1176; *Ann. Chim. Phys.*, 1909, [8], 17, 526.

[5] Brauner, *Trans. Chem. Soc.*, 1889, 55, 389.

[6] Scheele and Bergmann, *Gmelin-Kraut's Handbuch der anorganischen Chemie*, 6th ed., Heidelberg, 1872–1897, 3, 1023.

[7] Dumas, *Ann. Chim. Phys.*, 1830, 44, 167.

[8] Compare Abegg and Auerbach, *Handbuch der anorganischen Chemie*, Leipsic, 1908, 2, i. 822.

[9] Raschig, *Annalen*, 1886, 235, 355.

[10] Jacobsen, *Compt. rend.*, 1908, 146, 1213.

Silver nitrate reacts with aurichloric acid in accordance with the equation

$$4AgNO_3+HAuCl_4+3H_2O=Au(OH)_3,4AgCl+4HNO_3.$$

The brown precipitate formed is converted by ammonia into fulminating gold, which after drying explodes violently downwards when touched with a knife. Jacobsen regards it as having the constitution $Au(OH)_2{\cdot}NH_2$ or $(AuN,2H_2O),H_2O$. When boiled with potassium-hydroxide solution, it is converted into a blackish-brown substance of even more explosive character, probably having the constitution $Au(OH)_2{\cdot}NH{\cdot}Au(OH)_2$.

Auric nitrates.—Complex derivatives with the anion $Au(NO_3)_4'$ are known. Auric hydroxide and nitric acid yield a substance of the formula $HAu(NO_3)_4,3H_2O$, crystallizing in octahedra, and soluble in concentrated nitric acid.[1] Aurinitric acid melts at 72° to 73° C., and its density is 2·84. When heated above its melting-point, it is converted into a black substance, possibly auric nitrate, $Au(NO_3)_4$. Aurinitrates of rubidium, potassium, thallium, and ammonium have been prepared. From the ammonium salts a yellowish-brown, explosive substance, similar in properties to fulminating gold, has been obtained. Several basic nitrates of gold are also known.

Compounds of Gold and Phosphorus.—Phosphine reacts with a solution of auric chloride in anhydrous ether, forming *auric phosphide*, AuP, a substance decomposed by water or potassium-hydroxide solution, with formation of phosphine and phosphoric acid.[2] At 100° to 110° C. it undergoes oxidation in the air. Heating in a current of carbon dioxide causes volatilization of phosphorus. Nitric acid oxidizes the phosphorus, leaving a residue of metallic gold. These reactions indicate the substance to be an alloy of gold and phosphorus.

Gold phosphides.—*Gold sesquiphosphide*, Au_2P_3, is said to be formed by heating phosphorus with gold.[3]

Another phosphide, Au_3P_4, is produced by the interaction of phosphorus vapour and gold.[3] It is a grey, brittle substance, of density 6·67, and is formed only in the neighbourhood of 400° C.[4] Acids react with it as with an alloy.

Gold arsenides.—Arsenic precipitates from auric-chloride solution an arsenide, Au_2As.[5] Fusion of this substance with potassium cyanide converts it into a yellow arsenide, Au_4As_3, of density 16·2. Both substances have the character of alloys.

Auric antimonide, AuSb.—This substance is a white, brittle product, of density 11·13.[6] It behaves as an alloy. Other alloys of gold and antimony are known.[7]

Auric cyanide, $Au(CN)_3$.—Potassium auricyanide is transformed by strong acids such as hydrofluosilicic acid into auric cyanide. The reaction is more complex than is indicated by the equation

$$2KAu(CN)_4+H_2SiF_6=2Au(CN)_3+K_2SiF_6+2HCN.$$

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[1] Schottländer, *Wied. Annalen*, 1883, 217, 356.
[2] Cavazzi, *Gazzetta*, 1885, 15, 40.
[3] Schrötter, *Sitzungsber. K. Akad. Wiss. Wien*, 1849, 2, 308.
[4] Granger, *Compt. rend.*, 1897, 124, 498.
[5] Descamps, *ibid.*, 1878, 86, 1022; Lindbom, *Bull. Soc. chim.*, 1878, [2], 29, 416.
[6] Christofle, *Combinaisons de l'Antimoine*, Göttingen, 1863.
[7] Compare Dammer, *Handbuch der anorganischen Chemie*, Stuttgart, 1893, 3, 773.

Evaporation of the solution over sulphuric acid yields the salt in large colourless leaflets of the formula $Au(CN)_3,3H_2O$ or $2Au(CN)_3,3H_2O$, which melt at 50° C., and decompose at higher temperatures. On evaporation, its solution in water decomposes.[1]

Salts of Auricyanic Acid.—The free acid has not been prepared, as it decomposes as indicated under auric cyanide. *Potassium auricyanide*, $2KAu(CN)_4,3H_2O$, is obtained in colourless crystals by the action of auric chloride on potassium cyanide in aqueous solution. It is readily soluble in water. At 200° C. all the water of crystallization is eliminated, the salt being converted into potassium aurocyanide, $KAu(CN)_2$.[2] *Ammonium auricyanide*, $NH_4Au(CN)_4,H_2O$, is produced by evaporating a solution of auric hydroxide in ammonium cyanide. It forms large plates, readily soluble in water. At 100° C. the water of crystallization is expelled, and at higher temperatures the salt decomposes. The *silver salt* is produced as a yellowish precipitate, sensitive to light, by the action of silver nitrate on potassium auricyanide. It is readily soluble in ammonia, and much less readily in nitric acid. A *cobaltous auricyanide*, $Co(Au(CN)_4)_2,9H_2O$, and a number of complex salts have been prepared.[3]

Double Salts of Auric thiocyanate.—Only complex derivatives of the thiocyanate are known, such as *potassium aurithiocyanate*, $KAu(CNS)_4$, formed by the interaction of potassium thiocyanate and auric chloride in presence of potassium carbonate. It is decomposed by water.[4] The corresponding *sodium aurithiocyanate* forms a pale orange-red powder.[5]

Gold carbide, Au_2C_2.—A solution of aurous thiosulphate reacts with acetylene, precipitating a very unstable, highly explosive carbide.[6]

Gold and Silicon.—Gold does not take up silicon directly,[7] but can be made to absorb up to 10 per cent. by heating with sodium under a layer of potassium silicofluoride. Alloys with 10 per cent. of silicon are grey in colour and very brittle.[8]

Detection and Estimation of Gold.

When heated in the reducing flame,[9] or with fusion-mixture on charcoal, gold compounds are reduced to metallic gold. The metal is precipitated as sulphide by the action of hydrogen sulphide in presence of hydrochloric acid. The precipitated sulphide dissolves along with the sulphides of arsenic, antimony, and tin in ammonium sulphide, and is reprecipitated from this solution by addition of acids. The mixed sulphides are separated by removing arsenic sulphide with ammonium carbonate, and the other sulphides by hydrochloric acid, the residue consisting of gold sulphide[10]; or by heating the mixed sulphides in a current of hydrogen chloride[11]; or by volatilizing the other elements as

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[1] Rammelsberg, *Pogg. Annalen*, 1837, 42, 133.
[2] Himly, *Wied. Annalen*, 1842, 42, 337; Lindbom, *Ber.*, 1877, 10, 1725.
[3] Schmidt, *Chem. Zeit.*, 1896, 20, 633; Lindbom, *loc. cit.*
[4] Cleve, *J. prakt. Chem.*, 1865, 94, 14.
[5] Kern, *Chem. News*, 1876, 33, 243.
[6] Mathews and Watters, *J. Amer. Chem. Soc.*, 1900, 22, 108.
[7] Warren, *Chem. News*, 1889, 60, 5; 1893, 67, 303.
[8] Winkler, *J. prakt. Chem.*, 1864, 91, 193.
[9] Bunsen, *Annalen*, 1866, 138, 257.
[10] Compare Classen, *Methoden der analytischen Chemie*, Brunswick, 1901, 1, 239.
[11] de Koninck and Lecrenier, *Zeitsch. anal. Chem.*, 1888, 27, 462.

chlorides by heating the sulphides with a mixture of potassium nitrate and ammonium chloride.[1]

The metal can also be precipitated with hydrazine chloride in alkaline solution.[2] The precipitate is freed from mercury, copper, cadmium, and bismuth by extraction with nitric acid, and the residual gold and platinum dissolved in *aqua regia*. The gold is precipitated from this solution by the action of sodium hydroxide and hydroxylamine, the platinum remaining dissolved. Another method is to precipitate tin, lead, and bismuth with ammoniacal hydrogen peroxide, eliminate the hydrogen peroxide, and precipitate the gold with the mercury and part of the platinum by heating with hydroxylamine.

The presence of gold in any of the precipitates described can be detected by solution in *aqua regia*, and reduction to metallic gold by various reagents, including ferrous chloride, ferrous sulphate, mercurous nitrate, stannous chloride, hypophosphorous acid, oxalic acid,[3] sulphurous acid, hydrogen peroxide and potassium hydroxide, formaldehyde, and hydroxylamine hydrochloride.[4]

Among the reagents applicable to the detection of small quantities of gold[5] are alkaline hydrogen peroxide; ferrous salts; stannous chloride, which gives the characteristic purple coloration with one part in 100,000,000 parts of solution; alkaline formaldehyde, which gives a violet coloration with one part in 100,000 parts of solution[6]; and titanium trichloride, $TiCl_3$, which gives a deep-violet coloration with one part in 20,000,000 parts of solution, the action resembling that of stannous chloride.[7]

A colorimetric test described by Pollard[8] depends on the production of a bright yellow coloration when a 0·1 per cent. solution of *o*-tolidine in hydrochloric acid of 10 per cent. strength is added to a solution of auric chloride containing one part of gold in 1,000,000 parts of water. Osmic acid, vanadates, and salts of ruthenium and of iron also give a yellow coloration, and in presence of copper a green coloration may be obtained instead of a pure yellow colour. Other metals do not interfere with the test, but traces of hypochlorites give a grass-green coloration.

A method of detection by means of the metaphosphate-bead has also been described.[9]

One-tenth of a microgram of gold can be detected by Bayer's microchemical method, mentioned in connexion with rubidium (p. 199) and cæsium (p. 210).

Gold is estimated quantitatively by methods similar to those employed in its qualitative detection. It can be precipitated with a standard solution of ferrous sulphate or potassium oxalate,[10] and the excess estimated by titration with permanganate; or precipitated with stannous chloride in alkaline solution, the excess of tin being ascertained by titration with iodine.[11] Other methods are direct titration with stannous

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[1] Fresenius, *Zeitsch. anal. Chem.*, 1886, 25, 200.

[2] Knoevenagel and Ebler, *Ber.*, 1902, 35, 3055.

[3] Compare Purgotti, *Zeitsch. anal. Chem.*, 1870, 9, 127.

[4] Lainer, *Dingler's Polytech. J.*, 1892, 284, 17.

[5] Compare Classen, *Methoden der analytischen Chemie*, Brunswick, 1901, 1, 239.

[6] Armani and Barboni, *Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 290.

[7] Stähler and Bachran, *Ber.*, 1911, 44, 2906.

[8] Pollard, *Analyst*, 1919, 44, 94.

[9] Donau, *Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 9, 273.

[10] Franceschi, *Apothek.-Zeit.*, 1894, 9, 121.

[11] Franceschi, *Zeitsch. anorg. Chem.*, 1892, 1, 238.

chloride using a mixture of potassium ferricyanide and ferric chloride as indicator, the end-point being marked by the development of a blue coloration[1]; liberation of iodine from potassium iodide by an auric-chloride solution, and estimation of the liberated iodine by standard thiosulphate[2] or sulphurous acid[3]; reduction of auric chloride by heating with sucrose or dextrose on the water-bath[4]; and electrolytic deposition from potassium-cyanide solution.

The *assay of gold ores* can be effected by heating with litharge on a cupel, which absorbs the molten lead oxide and dissolves impurities. The residual metallic button is then alloyed with silver, and parted by means of nitric acid. Zinc[5] and cadmium[6] can be substituted for the silver in this process. Any platinum present is dissolved by repeated alloying and treatment with nitric acid.[7]

In gold assay the nature of the ore is of much importance, and many modifications have been devised to suit special grades of ore.[8]

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[1] Franceschi, *L'Orosi*, 1892, 15, 112.

[2] Petersen, *Zeitsch. anorg. Chem.*, 1898, 19, 59.

[3] Lenher, *J. Amer. Chem. Soc.*, 1913, 35, 733.

[4] Leidler, *Zeitsch. Chem. Ind. Kolloide*, 1907, 2, 103.

[5] Jüptner, *Zeitsch. anal. Chem.*, 1879, 18, 104.

[6] Balling, *ibid.*, 1880, 19, 200.

[7] Compare Přiwoznik, *Zeitsch. Berg- und Hütten-wesen*, 1895, 43, 272.

[8] Compare Přiwoznik, *ibid.*, 1899, 47, 356; Martin, *Amer. Chem. J.*, 1896, 18, 309; Allen, *Analyst*, 1876, 1, 178; Opificius, *Chem. Zeit.*, 1888, 12, 525; Cotton, *J. Pharm. Chim.*, 1890, [5], 21, 85; Skey, *Chem. News*, 1870, 22, 245; Whitehead, *ibid.*, 1892, 66, 19.

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