A TEXT-BOOK OF

INORGANIC CHEMISTRY.

VOLUME VIII.

THE PERIODIC TABLE.*

(table reproduced from the original landscape frontispiece)

Periods.	Group 0.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
First short period	He 3·99	H 1·008 / Li 6·94	Gl 9·1	B 11·0	C 12·00	N 14·01	O 16·00	F 19·0	
Second short period	Ne 20·2	Na 23·00	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·07	Cl 35·46	
First long period — Even series	A 39·88	K 39·10	Ca 40·07	Sc 44·1	Ti 48·1	V 51·06	Cr 52·0	Mn 54·93	Fe 55·84 Co 58·97 Ni 58·68
First long period — Odd ,,	...	Cu 63·57	Zn 65·3	Ga 69·9	Ge 72·5	As 74·96	Se 79·2	Br 79·92	
Second long period — Even series	Kr 82·9	Rb 85·45	Sr 87·63	Y 89·0	Zr 90·6	Cb 93·5	Mo 96·0	...	Ru 101·7 Rh 102·9 Pd 106·7
Second long period — Odd ,,	...	Ag 107·88	Cd 112·4	In 114·8	Sn 119·0	Sb 120·2	Te 127·5	I 126·92	
Third long period — Even series	X 130·2	Cs 132·81	Ba 137·37	THE RARE EARTH METALS	...	...	...	...	...
Third long period — Odd ,,	...	...	...		...	...	...	...	...
Fourth long period — Even series	...	...	...		...	Ta 181·5	W 184·0	...	Os 190·9 Ir 193·1 Pt 195·2
Fourth long period — Odd ,,	...	Au 197·2	Hg 200·6		Pb 207·1	Bi 208·0	...	...	...
Fifth long period	Nt 222·4	...	Ra 226·4		Th 232·4	...	U 238·5	...	...
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 1915 are adopted in this Table.

A TEXT-BOOK OF
INORGANIC CHEMISTRY.

EDITED BY

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

VOLUME VIII.

THE HALOGENS AND THEIR ALLIES.

BY

GEOFFREY MARTIN,   AND   **E. A. DANCASTER,**
D.Sc. (LOND. & BRISTOL), PH.D. (ROSTOCK)   B.Sc. (LOND.)

With Frontispiece and 30 Illustrations.

THE EDITOR'S PREFACE TO VOLUME VIII.

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

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

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

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

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

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded

as forming part of Physical Chemistry. Yet these are subjects of supreme importance to the student of Inorganic Chemistry, and are accordingly included in the Introduction.

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

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

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

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

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

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

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

Our aim has not been to make the volumes absolutely exhaustive, as this would render them unnecessarily bulky and expensive ; rather has it been to contribute concise and suggestive accounts of the various topics,

and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined list.

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

<div style="text-align: right">J. NEWTON FRIEND.</div>

July 1915.

PREFACE.

THE present volume aims at giving a tolerably complete, but not exhaustive, account of the chief chemical and physical properties of the Elements of the seventh group of the Periodic Table, comprising the halogens and manganese, together with those of their compounds. The most important manufacturing operations are briefly described, but not minutely, since technical details are best reserved for treatises specially devoted to that branch of chemistry.

The halogens are of peculiar interest to the modern chemist, inasmuch as they enter prominently into the spheres of Organic, Inorganic, Physical, and Analytical Chemistry. Not only have some of the most important researches in pure chemistry centred about the halogens, but great industries involving millions of pounds sterling, and giving employment to tens of thousands of men, have been developed in connection with their manufacture and that of their compounds. During the last decade the value of manganese has been increasingly realised, particularly in regard to the manufacture of special alloys and steels. Reference will be made to these in Volume IX. of this series. The more important salts of manganese, together with the manganates and permanganates, are described in the present work. As might be expected, the literature relating to these elements ramifies into that of so many different sciences that it is difficult to follow it completely, even when the resources of a large library are placed at one's disposal. It is hoped, therefore, that the present volume will prove of use to the reader, not only by presenting to him in a clear and concise manner a general account of the elements concerned, but by virtue of the numerous references cited to the standard literature bearing on different phases of the subjects dealt with in the text. Every effort has been made to render these references accurate and reliable; nearly all of them have been checked against the original memoirs. Most of the figures in this work have been drawn by Mr J. S. Scholer, B.Sc., to whom the Authors have pleasure in expressing their indebtedness; and some of the drawings illustrating the manufacturing processes, and certain descriptive matter relating to the manufacture of chlorine, hydrochloric acid, etc., are included by kind permission of Messrs Crosby Lockwood & Son. The Authors are indebted to Mr F. W. Clifford, Librarian of the Chemical Society, for kindly checking the list of Journals given on pages xvii and xviii, and for making some useful suggestions in connection therewith.

In conclusion, the Authors wish to thank the Editor, Dr J. Newton Friend, and Mr H. F. V. Little, B.Sc., for the great trouble they have taken in checking the mass of physical data and in recalculating some of them to modern units. The Authors' labour has been materially lightened by this assistance.

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GEOFFREY MARTIN.
ERNEST DANCASTER.

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CONTENTS OF VOLUME VIII.

LIST OF CHIEF ABBREVIATIONS EMPLOYED
IN THE REFERENCES.

Abbreviated Title.	Journal.
Amer. Chem. J.	American Chemical Journal (Baltimore).
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science and Arts (New Haven).
Analyst	The Analyst (London).
Annalen	Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914 +).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. applicata	Annali de Chimica applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Report	Annual Reports of the Chemical Society.
Arch. Pharm.	Archiv der Pharmazie (Halle).
Arch. Farm. Sperim.	Archivio di Farmacologia Sperimentali e Scienze affini.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Archiv för Kemi, Mineralogi och Geologi.
Atti Acc. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb (Leipzig).
Biochem. Bull.	Biochemical Bulletin.
Biochem. J.	The Biochemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bolletino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci., Petrograd	Bulletin de l'Académie Impériale des Sciences de Petrograd.
Bull. Soc. chim.	Bulletin de la Société chimique de France (Paris).
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. d'Enc. p. l'Ind. nationale	Bulletin de la Société d'Encouragement pour l'Industrie nationale.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Chem. and Drug.	Chemist and Druggist.
Chem. News	Chemical News (London).
Chem. Rev. Fett Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Deutsch. med. Wochensch.	Deutsche medizinische Wochenschrift.
Dingl. Poly. J.	Dingler's Polytechnisches Journal (Stuttgart).
Gazzetta	Gazzetta chimica italiana (Palermo).
Jahresber.	Jahresbericht über die Fortschritte der Chemie (Giessen).
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society (Easton).
J. Anal. Chem.	Journal of Analytical and Applied Chemistry (Easton).
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Sci. Tokyo	Journal of the College of Science, Tokyo.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Hygiene	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.

ABBREVIATED TITLE.	JOURNAL.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie (Paris).
J. Physique	Journal de Physique.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. prakt. Chem.	Journal für praktische Chemie (Leipzig).
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Micros. Soc.	Journal of the Royal Microscopical Society.
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.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid. Zeitsch.	Kolloid-Zeitschrift.
Kolloid. Chem. Beihefte	Kolloidchemische Beihefte.
Landw. Jahrb.	Landwirtschaftliche Jahrbucher.
Mém. Acad. Roy. Belg.	Mémoires de l'Académie Royale de Belgique.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere
Pharm. Zentr.-h.	Pharmaceutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. Amer. Acad.	Proceedings of the American Academy of Arts and Sciences (Boston).
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Manchester Lit. Phil. Soc.	Proceedings of the Manchester Literary and Philosophical Society.
Proc. London Phys. Soc.	Proceedings of the London Physical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Tokyo Math. Phys. Soc.	Proceedings of the Tokyo Mathematical and Physical Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sitzungsber. K. Akad. Wiss. Berlin	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
South African J. Sci.	South African Journal of Science.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie (Wiesbaden).
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie (Berlin).
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie (Hamburg and Leipzig).
Zeitsch Biol.	Zeitschrift für Biologie.
Zeitsch. Chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie (Halle).
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie (Leipzig).
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre (Leipzig).
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

A TEXT-BOOK OF
INORGANIC CHEMISTRY.

VOL. VIII.
THE HALOGENS AND THEIR ALLIES.

CHAPTER I.

INTRODUCTORY.

THE ELEMENTS OF THE SEVENTH GROUP CONSIDERED AS A WHOLE.

THE elements fluorine, chlorine, bromine, and iodine form a natural group of closely allied bodies known as "The Halogens." Manganese, on the other hand, constituting the electropositive branch of the seventh group, is quite dissimilar in its properties.

Occurrence and Relative Abundance of the Halogens and Manganese.—All the four elements, fluorine, chlorine, bromine, and iodine are very widely distributed, occurring principally in the form of minerals, as enumerated under the respective elements. All also occur in organic matter, both vegetable and animal, and also in minute traces in certain waters.

When we compare the relative abundance of these elements, however, we must at once be struck with the fact that they occur to very unequal extents. Chlorine and fluorine are far more abundant, both absolutely and relatively, than any of the other two halogens. Many thousands of millions of tons of chlorine are stored up combined with sodium and other metals in sea-water, and in the great solid salt deposits which occur in various parts of the world and in the seas. The quantities of bromine and iodine found are, compared with the amount of chlorine, relatively insignificant. For example, according to Vogt,[1] the earth's crust, taken as a whole, contains 0·175 per cent. of chlorine, 0·025 to 0·040 per cent. of fluorine, but only about 0·001 per cent. bromine and 0·0001 per cent. of iodine ; or, roughly, to every 1000 parts by weight of chlorine present in the earth's crust, there occur 140 to 230 parts of fluorine but only about 6 parts of bromine and 0·6 part of iodine.

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[1] As regards data on the relative abundance of the elements, including the halogens, the reader should see J. H. L. Vogt, *Zeitsch. prakt. Geologie*, 1898, pp. 225, 314, 377, 413 ; 1899, p. 10. Also F. W. Clarke, *Bull. Phil. Soc. Washington*, B. II., 1889 ; *Bull. U.S. Geol. Survey*, 1891, No. 78 ; 1897, No. 148 ; 1900, No. 168.

Analyses of sea-water show that there are about 10 to 12 parts of bromine present to every 1 part of iodine, and 150 parts of chlorine to 1 part of bromine, while the amount of fluorine in sea-water is very small indeed. The quantity of manganese present in the earth's crust amounts to between 0·07 and 0·08 per cent.

The causes why one element occurs in such relatively large quantities, while others occur only in minute traces, have never been satisfactorily explained, but they are evidently connected with the wider cosmical questions of the formation and decay of elements, such as have come greatly to the fore since the discovery of radioactive elements.[1]

Comparative Methods of Preparing the Halogens.—Three main methods are employed for isolating the halogens :—

    (1) Oxidation of the aqueous solution of the hydracid.
    (2) Electrolysis of halides.
    (3) Decomposition of a perhalide by heat.

    (1) The oxidation of the hydracid proceeds according to the general equation :—

$$2HX + O_2 = H_2O + X_2.$$
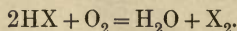
Obviously the possibility of this action depends upon the magnitude of the affinity of the halogen for hydrogen. Fluorine, for example, has such a great affinity for hydrogen that it combines with it in the dark, and decomposes water, instantly liberating oxygen.

Consequently fluorine cannot be obtained by the above reaction. The other halogens, however, have a decreasing affinity for hydrogen as we go from chlorine towards iodine, and so are obtainable with increasing ease by the action of oxidising agents on the hydracids. To give examples, if a mixture of oxygen with the moist hydracid is passed through a heated tube, no change takes place in the case of HF, partial oxidation with liberation of chlorine in the case of HCl,[2] while complete oxidation and resulting liberation of halogen takes place in the case of HBr and HI. Similarly when the moist hydracids are mixed with oxygen gas and exposed to sunlight at ordinary temperatures, the reaction extends from zero with HF to a maximum with HI, the same being true also with aqueous solutions of the acid. The usual method of liberating chlorine by acting on HCl with MnO_2, is essentially a process of oxidation, which does not work in the case of HF. This gradation of oxidisability is further apparent in the fact that sulphuric acid does not oxidise either HF or HCl, whereas it liberates bromine and iodine from HBr and HI, by the following reaction : $2HX + H_2SO_4 = SO_2 + 2H_2O + X_2.$

    (2) Chlorine, bromine, and iodine are all easily obtainable by electrolysis of aqueous solutions of corresponding alkali halides.

Fluorine, however, on account of its decomposing water, liberating oxygen and forming HF, cannot be obtained by this method. It was isolated by Moissan[3] in 1886 by electrolysing a solution of KF in HF, such a solution being quite free from moisture. All the halides can be obtained by electrolysing molten halides, e.g. molten NaCl or AgCl yields very pure chlorine at the positive pole, while the metal is deposited at the negative pole.

    (3) The liberation of halogen by the decomposition of a perhalide by heat

[1] See Geoffrey Martin, *Chemical News*, 1903, **88**, 280 ; 1904, **89**, 47, 58, 118.
[2] This is, in fact, Deacon's Process for the Manufacture of Chlorine, see p. 60.
[3] Moissan, *Ann. Chim. Phys.*, 1887, [vi.], **12**, 473 ; 1891, [vi.], **24**, 226.

depends upon the existence of polyhalides of certain elements which decompose into lower halides on heating with liberation of free halogen. Thus cerium tetrafluoride, CeF_4, breaks up on heating into free fluorine and a lower fluoride.[1]

A similar liberation of fluorine occurs when potassium hydrogen fluorplumbate[1] is heated :—

3KF HF PbF₄

$$K_3HPbF_8 = K_3PbF_7 + HF$$

3KF PbF₄

$$K_3PbF_7 = 3KF + PbF_2 + F_2.$$
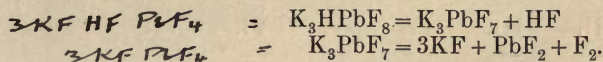
In an analogous manner the unstable lead tetra-chloride $PbCl_4$ breaks up on warming into the di-chloride $PbCl_2$ and free chlorine. The liberation of chlorine from manganese di-oxide and hydrochloric acid on warming is supposed to be due to the formation of an unstable chloride, $MnCl_3$ or $MnCl_4$, which then splits up into the stable lower chloride, $MnCl_2$ and free chlorine.[2]

Relationship of the Halogens to the other Elements of the Periodic System.—Before considering the halogen group as a whole, a few

words must be said as regards their relationship to the other elements of the periodic system.

In the first place, when we contrast the properties of the elements at the extremities of each cycle of the periodic system, a very remarkable fact appears. The elements fluorine, chlorine, bromine, and iodine are the opposite in chemical properties to the elements hydrogen, lithium, sodium, potassium, rubidium, and cæsium. The one series, indeed, may be considered to be the chemical antipodes of the other series of elements.

This fact is best illustrated
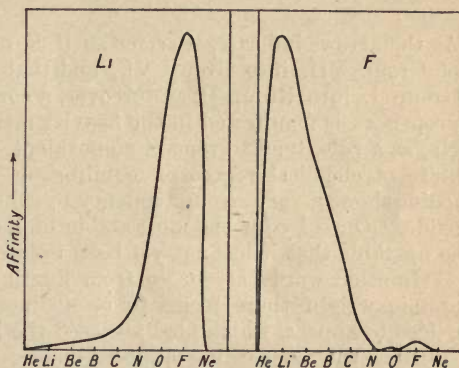
FIG. 1.—Affinities of lithium and fluorine compared.

by a contrast of the chemical attractions that the two series of elements exhibit. For example, fig. 1 shows the "affinity curve" exhibited by the two elements lithium and fluorine for the elements Li, Be, B, C, N, O, F, considered in succession; while corresponding curves may be shown for the elements sodium and chlorine. It will be noticed that the two curves are diametrically opposite in character, and that the curves for the alkali metals are almost "mirror images" of those for the halogen elements.[3]

Moreover, a close study of the chemical properties of the individual members of the alkali metals and halogen series of elements and those of neighbouring elements brings to light the fact that F, Cl, Br bear almost exactly the same relationship to the elements of Groups VII. and VI. as do Li, Na, and K to the elements of Groups I. and II. The resemblance goes into detail. For example, Li differs appreciably in properties from Na and

[1] Brauner, *Trans. Chem. Soc.*, 1882, **41**, 68 ; 1894, **65**, 399.
[2] Discussed on p. 53.
[3] Geoffrey Martin, *Researches on the Affinities of the Elements* (Churchill, 1905), p. 183 ; *Inaug. Dissert.*, Rostock, 1905.

K, and tends to resemble somewhat the elements of the next group, namely Be and Mg. So also the corresponding element at the other extreme of the cycle of elements Li, Be, B, C, N, O, F, namely F, differs appreciably in properties from Cl and Br, and tends to resemble the element of the next group, namely O. We give part of the periodic system to illustrate this remark :—

Groups	I.	II.	III.	IV.	V.	VI.	VII.
	H	—	—	—	—	—	•
	Li→	Be	B	C	N	O	←F
	↑						↑
	Na	Mg	Al	Sc	P	S	Cl
	↑						↑
	K						Br
	↑						↑
	Rb						I
	↑						
	Cs						

As the arrows indicate, it seems as if F, on the one hand, tends to pass out of Group VII. into Group VI., and that Li, similarly, tends to pass out of Group I. into Group II. Moreover, a corresponding similarity in change of properties is manifested in the heavier members of each series. Thus F and Na, as a rule, tend to remain monovalent,—or at least attain their greatest state of chemical repose or equilibrium in a monovalent state. However, iodine shows a very strong tendency to exhibit a multiple valency : its highest oxide, I_2O_5, is by far the most stable of its oxides; the lowest oxide, I_2O, is so unstable that it has not yet been isolated.

In other words, as we go from fluorine towards iodine, with increase of atomic weight there seems to be an increasing tendency for stable higher oxides to appear, which finally exceed the lower oxides in stability.

Now the same thing appears among the elements of Group I., as we proceed downwards from Li towards Cs, e.g. the higher oxides of potassium, cæsium, and rubidium are much more stable than the lower oxides of the type M_2O. In fact, the analogy of F, Cl, Br, and I, when compared with Li, Na, K, and Cs may be followed into detail by the curious reader :—e.g. both series of elements are usually monovalent when they combine with elements of the opposite polarity ; there is also a curious parallelism in the successive increase in the atomic weights as we go from member to member (only in the halogen series of elements the member strictly corresponding with Li is missing) : for example, the difference in atomic weight between F and Cl is 16·5, and between Na and K it is 16 ; between Cl and Br it is 44·5, and between K and Rb it is 46 ; between Br and I the difference is 44, between Rb and Cs it is 48.

So striking in many respects is the analogy between the halogens on the one hand and the alkali metals on the other, that Orme Masson [the writers believe erroneously][1] actually proposed to classify hydrogen—the first element of the alkali group—with the halogens instead of with the alkalies.

The causes of this analogy between the halogens and the alkali elements are quite unknown. No doubt when the causes which brought the periodic system of elements into existence are known, this and similar problems will

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[1] See Orme Masson, *Chem. News*, 1896, **73**, 283 ; Geoffrey Martin, *Chem. News*, 1901, **84**, 154. See also W. Crookes, *Proc. Roy. Soc.*, 1898, **63**, 408.

receive their explanation, as the resemblances here discussed are far too numerous and detailed to be the result of chance. The relationship between the *halogens* and *manganese* is considered on p. 20.

Relationship of the Halogens to each other.—We now proceed to discuss the relationships which the successive elements of the halogen group, viz. F, Cl, Br, I, bear to each other.

In the first place, chlorine, bromine, and iodine form a closely connected triad of elements, the atomic weight of bromine, and also many of its properties, being intermediate between those of chlorine and iodine. Fluorine stands outside this triad, and, like the first members of most groups, has properties which diverge considerably from those of chlorine, bromine, and iodine. This appears, for example, in the following table of atomic weights and differences :—

					At. Wt.	Differences.
F	.	.	.	.	19	
						16·46
Cl	.	.	.	.	35·46	
						44·46
Br	.	.	.	.	79·92	
						47·00
I	.	.	.	.	126·92	

An examination of the physical properties of the halogen elements, which are set forth in the accompanying table, p. 6, shows that there exists a regular gradation in property as we pass from fluorine to iodine. For example, there is a continuous deepening in colour, a steady rise in the melting- and boiling-points, a gradual increase in the density of the halogens when in a liquid state, and a steady diminution of solubility in water as we pass from fluorine to iodine. The atomic volume (*i.e.* the volume occupied by the atomic weight of the solidified halogen) also steadily increases from fluorine to iodine ; likewise the power of dissociating into atoms with rise of temperature. For example, no dissociation has been detected with fluorine [1] (although the experimental data do not seem very reliable in this case), whereas chlorine diminishes very sensibly in density at temperatures upwards of 1400° ; [2] bromine vapour at 1570° C. has diminished by one-third of its normal value, showing that the dissociation of the bromine, Br_2, molecules into single atoms is well developed at this temperature.[3] In the case of iodine we get a perceptible diminution of the vapour density at as low a temperature as 700°, and the dissociation is complete at 1700° C. when iodine gas exists entirely in the form of single atoms.[4]

This general behaviour is only to be expected in view of the increase in electropositive (*i.e.* metallic) character with increase of atomic weight, since metallic vapours usually exist in a monatomic state and iodine approaches in character to a metal far more closely than either chlorine or bromine.

In the accompanying table of properties manganese is also included.

Fluorine is the most electronegative, not only of this series of elements, but of all the known elements as well.

There is an increase of electropositiveness from fluorine through chlorine and bromine to iodine, and consequently a corresponding decrease in chemical

[1] Moissan, *Compt. rend.*, 1904, **138**, 728.
[2] Langer and Meyer, *Pyrochemische Untersuchungen*, p. 46 (Vieweg, 1885).
[3] V. Meyer and Züblin, *Ber.*, 1880, **13**, 405 ; Crafts, *Compt. rend.*, 1880, **90**, 183 ; Perman and Atkinson, *Zeitsch. physikal. Chem.*, 1900, **33**, 215.
[4] V. Meyer, *Ber.*, 1880, **13**, 394, 1010, 1103 ; V. Meyer and Biltz, *Ber.*, 1889, **22**, 725 ; Meier and Crafts, *Compt. rend.*, 1880, **90**, 690 : 1881, **92**, 39.

SUMMARY OF PROPERTIES OF GROUP VII.[1]

Properties of Element.	Fluorine.	Chlorine.	Bromine.	Iodine.	Manganese.
Atomic weight	19·0	35·46	79·92	126·92	54·93
Appearance	Pale greenish-yellow gas	Greenish-yellow gas	Reddish-brown liquid	Violet-black solid with metallic lustre	Shining metal
M.P.	−233°	−102°	−7·3°	114°	1245
B.P. at 760 mm.	−187°	−33·6°	58–59°	184°	...
Density of liquid	1·14 (at B.P.)	1·507 (at B.P.)	2·982 (at B.P.)	...	...
„ solid		>1·66 (at M.P.)	...	4·95	8·0
Hydrides, HX	HF, (H₂F₂, HₙFₙ) Liquid, B.P. 19·4°	HCl Gas, B.P. −83·7°	HBr Gas, B.P −64·9°	HI Gas, B.P. −34·1°	...
Oxides:					
R₂O	...	Cl₂O	...	...	MnO (basic)
RO	...	...	...	...	Mn₃O₄ (neutral)
R₃O₄	...	...	...	...	Mn₂O₃ (basic)
R₂O₃	...	...	...	...	MnO₂ (peroxide)
RO₂	...	ClO₂	...	I₂O₄	...
R₂O₅	...	...	...	I₂O₅	MnO₃ (acidic)
RO₃	...	...	...	...	Mn₂O₇
R₂O₇	...	Cl₂O₇	...	I₂O₇	
Hydroxides and Oxy-acids:					
R.OH	...	Cl.OH ⎫	BrOH ⎫	I.OH ⎫	...
RO.OH	...	ClO.OH ⎬ Acids	... ⎬ Acids	... ⎬ Acids	MnO.OH (basic)
RO₂.OH	...	ClO₂.OH ⎭	Br.O₂.OH ⎭	IO₂.OH ⎭	...
RO₂(OH)₂	...	...	...	...	MnO₂(OK)₂ (acidic)
RO₃.OH	...	ClO₃.OH	...	IO₃.OH	MnO₃.OH
Y₃R.OH	...	...	...	Y₃IOH (iodonium)	...

activity towards the positive element hydrogen. This is only a particular instance of the general law observable among the elements of any one group of the periodic system, that increase of atomic weight tends to bring out metallic properties (*cf.* C, Si, Ge, Sn, Pb or N, P, As, Sb, Bi) ; and so as we go from fluorine towards iodine, metallic properties (*i.e.* electropositiveness) tend to appear, as will be seen when we come to deal with iodine.

The extraordinary chemical attraction fluorine has for hydrogen shows itself in its power of combining with this element in the dark with the evolution of heat and light, and by its power of displacing chlorine from hydrogen chloride and also from its combination with such metals as sodium and potassium. This extraordinary affinity of fluorine for hydrogen, however, is simultaneously accompanied by a complete inability to combine with oxygen under any known conditions.

It thus seems that the atoms of the extremely electronegative element fluorine, although capable of combining stably with each other to form the molecule F_2, are yet incapable of combining with the atoms of the somewhat less negative element oxygen : so feeble, indeed, is the affinity of fluorine for oxygen that it actually does not unite with oxygen and hydrogen together so as to produce oxyacids analogous to chloric or bromic acids, $HClO_3$, $HBrO_3$, or hypochlorous or hypobromous acids, $HClO$, $HBrO$. Even bromine, which is incapable of producing oxides, produces oxy-acids of this sort, and so the affinity of fluorine for oxygen is considerably less than that of bromine for the same element, and much less than that of chlorine for oxygen.

It is also incapable of combining chemically with the strongly electronegative element chlorine, although it forms well-defined compounds with the more electropositive elements Br and I ; for example, BrF_3 and IF_5 are well known. It is thus obvious that the two most electronegative elements contiguous to fluorine in the periodic system, viz. O and Cl, possess such a feeble affinity for fluorine that they produce no compounds with it. This is a general law. Elements which approach each other nearest in either their positive or negative character possess the least affinity for each other.

Fluorine also does not unite with nitrogen directly, although nitroxyfluorides are known.

The fluoride NF_3 is unknown, and is certainly less stable than NCl_3, since it cannot be produced by methods analogous to those which produce NCl_3. The affinity of nitrogen for fluorine, therefore, appears to be very small. Thus, by inspecting the periodic table, we see that there exists a restricted area around fluorine which contains those elements which do not form compounds with fluorine, thus :—

—	—	—	—	—	—	—	He *
Li	Be	B	C	N *	O *	F	He *
Na	Mg	Al	Sc	P	S	Cl *	Ar *
				As	Se	Br	Kr *
				Te	I		Xe *

Those elements marked with * do not unite with fluorine.

Fluorine, however, is so intensely electronegative that it is capable of combining with most electronegative elements (which in respect to it are electropositive) to form stable compounds.

Thus, although producing no compound with oxygen or chlorine, fluorine

forms stable fluorides with bromine, iodine, sulphur, selenium, and tellurium —all negative elements.

The analogy of fluorine to oxygen is very marked. This analogy was first pointed out by Moissan [1] in 1891, but Geoffrey Martin [2] appears to have been the first who undertook a detailed study of the causes which make fluorine the element which most strongly resembles oxygen in its general properties and in those of its compounds. He showed, for example, from a detailed study of the oxides, fluorides, chlorides, and bromides of the elements, that fluorine resembles oxygen more closely than does chlorine, etc., because fluorine approaches oxygen more closely than chlorine as regards the intensity of the force with which it attracts a given radicle. In other words, the chemical similarity of these two elements arises from the fact that they both attract the same radicles with nearly the same intensity of force. Again, the heats of formation of the fluorides stand closer to the heats of formation of the corresponding oxides than to those of the corresponding chlorides, thus proving that the intensity of the force which holds the atoms together in the fluorides stands nearer to that which holds the atoms together in the corresponding oxides than in the corresponding chlorides. Thus we have :—

$$(H, Cl) = 22 \quad Cals. \quad (H, F) = 37 \cdot 6 \ Cals. \quad (H, O_{\frac{1}{2}}) = 34 \cdot 2 \ Cals.$$
$$(Si_{\frac{1}{4}}, Cl) = 39 \cdot 4 \quad ,, \quad (Si_{\frac{1}{4}}, F) = 67 \cdot 3 \quad ,, \quad (Si_{\frac{1}{4}}, O_{\frac{1}{4}}) = 54 \cdot 8 \quad ,,$$

Moreover, the fluorides and oxides approach each other more closely as regards solubility, volatility, and fusibility than do chlorides and oxides ; the resemblance in this respect is much closer between fluorides and oxides than between chlorides and oxides : for example, the non-metallic fluorides and also oxides are more volatile than the corresponding non-metallic chlorides. Conversely the metallic fluorides and also metallic oxides are less volatile than the corresponding metallic chlorides.

These facts are strikingly illustrated by a comparison of hydrogen fluoride with water (oxygen hydride) and the other halogen acids.

The following table [3] shows that hydrogen fluoride approaches more closely to oxygen hydride (water), both in chemical and physical properties, than any of the other halogen compounds : —

Substance.	B. P.	M. P.	Range of Fluidity. B.P.–M.P.	Equivalent Heat of Formation.
	° C.	° C.	° C.	Cals.
H_2O . . .	+ 100	0	100	+ 34·2
HF	+ 19·4	− 92·3	111·74	+ 37·6
HCl	− 83·7	−111·1	27·4	+ 22·0
HBr	− 64·9	− 87·9	23	+ 8·4
HI	− 34·1	− 50·8	16·7	− 6·0

Notice that of all these hydrides HF is the one whose heat of formation approaches nearest to that of water ; that its boiling-point lies nearest to

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[1] Moissan, *Compt. rend.*, 1891, **24**, 226.
[2] Martin, *Researches on the Affinities of the Elements* (Churchill, 1905), p. 69 ; also see *J. Physical Chemistry*, 1905, **9**, 562 ; *Chem. News*, 1904, **89**, 49.
[3] Taken, modified, from Martin's *Affinities of the Elements*, p. 85.

that of water; that its range of fluidity (*i.e.* the difference between the B.P. and M.P. approaches nearest to that of water ($H_2O = 100°$, $HF = 111°\cdot7$); that while all the other hydrides are so volatile as to be gaseous at ordinary temperatures, water and HF alone are colourless mobile liquids at ordinary temperatures; that while HCl, HBr, and HI are all exceedingly powerful acids at ordinary temperatures, HF is an extremely weak acid, being nearly twenty times weaker than hydrochloric acid, and over thirteen times weaker than even hydriodic acid, as shown in the following numbers :—

						"Avidity."
HF .	.	.	.	.	.	$0\cdot05$ (Thomsen)
HCl	.	.	.	.	.	$1\cdot00$
HBr	.	.	.	.	.	$0\cdot89$
HI .	.	.	.	.	.	$0\cdot70$

Now, water also is a very weak acid, and in this respect also hydrogen fluoride approaches water more closely than any of the other halogen acids; also in its possessing, like water, a polymerised molecule $(HF)_n$ when in a liquid state.

Oxygen and fluorine both tend to make an element with which they combine exhibit a higher grade of valency than does chlorine.[1] For example, the stablest oxide of manganese at ordinary temperatures is Mn_2O_3. Also the stablest fluoride is MnF_3, whereas the stablest chloride is $MnCl_2$, $MnCl_3$ being an excessively unstable body, spontaneously decomposing at ordinary temperatures into $MnCl_2$ and free chlorine. Again, SO_3 is, at ordinary temperatures, a quite stable body, not parting with O below a red heat. Similarly SF_6 is very stable. But SCl_6 is too unstable to exist at ordinary temperatures, and SCl_4 is only capable of existing below $-20°$ C. The same relation exists between the oxide, fluoride, and chloride of P and I. The fluorides, in fact, almost invariably follow the oxides and not the chlorides as regards stability.

Comparison of the Compounds of the Halogens with Positive Elements, such as Hydrogen and the Metals.—These are by far the most stable and characteristic compounds of the halogens, as indeed is only to be expected from the pronounced negative character of all the elements of the halogen group. Compared with these compounds, the substances produced by the union of halogens among themselves, or with other non-metals such as oxygen or nitrogen, are at best excessively unstable. We will first deal with the compounds the halogens produce with hydrogen.

The stability of the compounds which the halogens form with hydrogen decreases as we proceed from fluorine towards iodine; so that hydrofluoric acid is the most and hydriodic acid is the least stable of these compounds. This is shown by their heats of formation :—[2]

|						
HF .	.	.	.	.	.	38,600 calories.
HCl	.	.	.	.	.	22,000 ,,
HBr	.	.	.	.	.	8400 ,,
HI .	.	.	.	.	.	-6000 ,,

Fluorine, therefore, displaces chlorine, bromine, or iodine from their compounds with hydrogen, or, in general, electropositive elements such as

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[1] Martin, *opus cit.*
[2] Berthelot and Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **23**, 570; Thomsen, *Thermo-chemische Untersuchungen* (Leipzig, 1882-6), ii. pp. 20, 28, and 36.

metals ; chlorine will similarly displace bromine and iodine, and bromine will displace iodine only.

The relative instability of hydrobromic and hydriodic acid, as compared with hydrofluoric and hydrochloric acid, explains why the two former acids cannot be obtained pure by the action of concentrated sulphuric acid on the corresponding alkali salts. Bromine and iodine are liberated owing to the oxidation of the hydracids by sulphuric acid, thus :—

$$2HX + H_2SO_4 = SO_2 + 2H_2O + X_2,$$
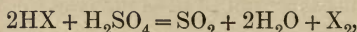
whereas, owing to their great stability, HF and HCl are not thus decomposed, and so can be liberated, thus :—

$$MX + H_2SO_4 = HX + MHSO_4.$$
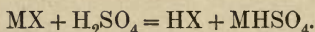
Here M stands for a metal and X for a halogen.

Consequently HBr, and still more markedly HI, are reducing agents on account of the ease with which decomposition occurs, hydrogen separating at moderate temperatures :—

$$2HX = H_2 + X_2.$$
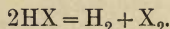
This reducing action is not exhibited by HCl or HF on account of their superior stability.

By substituting phosphoric acid for sulphuric acid, however, in their preparation we can get HBr and HI liberated in an undecomposed state, as phosphoric acid is more difficult to reduce than sulphuric :—

$$H_3PO_4 + 3MX = 3HX + M_3PO_4.$$
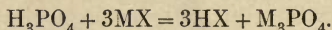
This explains why HBr and HI are usually prepared by the action of bromine or iodine on phosphorus and water—

$$2P + 5X_2 = 2PX_5, \qquad 2PX_5 + 8H_2O = 2H_3PO_4 + 10HX.$$
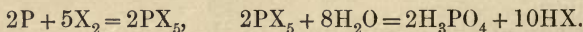
The points of difference between HF and the other halogen hydrides have already been commented on on p. 9. In addition to the remarks made there, the following remarks should be added. In the first place, the solubility in water of the acids increases from HCl to HI, but HF forms an exception to this series, being *more* not less soluble in water than HCl.[1] This is illustrated by the following table,[2] the figures representing the weight of acid which dissolves in 1 gram of water at 10° C. :—

HF	.	.	.	.	.	(miscible in all proportions).
HCl	.	.	.	.	.	2·10
HI	.	.	.	.	.	2·48

The greater solubility in water of HF is due to its greater chemical similarity to water, a fact first pointed out by Geoffrey Martin.[3] Chemically similar substances are usually miscible in all proportions owing to the fact that their molecules exert forces of the same relative intensity, and so can replace each other in solution.

[1] Deussen, *Zeitsch. anorg. Chem.*, 1906, **49**, 297.
[2] Caven and Lander, *Systematic Inorganic Chemistry*.
[3] Geoffrey Martin, *J. Physical Chemistry*, 1905, **9**, 154 ; *Researches on the Affinity of the Elements*, pp. 85, 124.

Thomsen [1] gives the heat of neutralisation and the avidities of the acids as follows :—

	Heat of Neutralisation.	"Avidity."
HF . . .	16,300 calories	0·05
HCl . . .	13,700 ,,	1·00
HBr . . .	13,800 ,,	0·89
HI . . .	13,700 ,,	0·70

Ostwald [2] gives the degree of electrolytic dissociation of the acids at 25° C. and at different dilutions as follows :—

Dilution per gram-molecule.	Degree of Electrolytic Dissociation.			
	HF.	HCl.	HBr.	HI.
10 litres . . .	0·10	0·95	0·95	0·95
100 ,, . . .	0·29	0·98	0·98	0·98
1000 ,, . . .	0·59	0·99	0·99	0·99

Since the "strength" of an acid is measured by its degree of electrolytic dissociation at a given dilution, it is clear that whilst HCl, HBr, and HI are all strong acids of nearly equal strength, HF is a very much weaker acid— as is also confirmed by Thomsen's values for the "avidity" of HF.

It might at first be thought that such an active and extremely negative element as fluorine would produce an extremely powerful hydracid, exceeding even the strength of HCl—which, as we have seen, is far from the case. There is no doubt that where an atom of fluorine is a constituent of an *oxy-acid*, it does by its presence tend to promote the separation of hydrogen ions, and so increase the strength of the acid. For example, when chlorine is substituted for hydrogen in acetic acid, CH_3COOH, the resulting chloracetic acids are stronger than the original acetic acid, the strength increasing as we increase the number of Cl atoms in the molecule. In the same way Swarts [3] proved that the acid nature of acetic acid is increased by the substitution of fluorine, and to a greater extent than through the substitution of chlorine.

The case, however, is not quite the same when we deal with hydracids, for here we have the halogen *directly* united to the hydrogen, and no doubt the mechanical cause of the weakness of HF is that suggested by Caven and Lander [4]—namely, the extraordinary strength with which H is united to F in HF renders the dissociation into ions difficult. The excess heat of neutralisation over 13,700 cals. (viz. 2,600 cals.) being, according to the same authority, the heat evolved by the same acid in reaching a state of complete ionisation in solution during the process of neutralisation.

The causes of the weakness of hydrofluoric acid have already been considered on p. 9 as being due to the greater chemical similarity of F towards oxygen because water, oxygen hydride, is also only a very weak acid.

It is certain that the relative strengths of these hydracids of the halogens are not in the order of the electronegativeness of the halogen elements which they contain, and the absolute stability of these compounds appears to bear no connection to their strengths as acids.

Lastly, it should be observed that the salts of these acids, especially those

[1] Thomsen, *Thermochemische Untersuchungen.*
[2] Ostwald, *J. prakt. Chem.*, 1878, **18**, 362 ; 1885, **31**, 313, 433, **32**, 303.
[3] Swarts, *Bull. Soc. chim. Belg.*, 1907, **21**, 278.
[4] Caven and Lander, *opus cit.*, 1911, p. 290.

of HCl, HBr, and HI, resemble each other in most of their properties, the chlorides being the most stable and the iodides the least stable—as corresponds to the stability of the acids from which they are derived. The fluorides, however, stand somewhat apart. The fluorides of certain metals differ markedly from the corresponding chlorides, bromides, and iodides. For example, calcium fluoride is insoluble in water, whereas the chloride, bromide, and iodide of this metal are all soluble.

Silver fluoride is a deliquescent soluble salt, whereas the other silver halides are insoluble in water. Mercuric fluoride is, unlike the chloride, bromide, and iodide, completely hydrolysed by water, thus resembling the oxysalts of this metal. In fact, the fluorides approach to the corresponding oxides as regards many of their chemical and physical properties.[1]

The great tendency the fluorides have to unite among themselves and form double fluorides also differentiates them from many chlorides and accentuates the analogy of the fluorides to oxides, e.g. KF.HF is a very stable body, whereas KCl.HCl is unknown.

An elaborate investigation into the molecular association of the halides, both organic and inorganic, was made by W. E. S. Turner in 1911,[2] and his results are of considerable importance. He showed, for example, in the case of the halogen salts of organic bases, that molecular association always occurs, the degree of association depending upon two factors, one for the acid and the other for the base. He also showed that, on comparing similar salts, the degree of association increases in the order : chloride—→bromide—→iodide.

Turner also investigated the molecular condition of metallic halogen salts, and came to the conclusion that metallic halogen salts are associated substances, that the degree of association depends both upon the acid and bases and rises in the order : chloride—→bromide—→iodide, and lastly, in a series of similar salts the degree of association *decreases* with increase in the atomic weight of the metal.

Comparison of the Compounds the Halogens form with Negative Elements.

—As regards the capacity of the halogens to combine with each other, it may be remarked that fluorine appears incapable of uniting with chlorine ;[3] it unites, however, with bromine to form BrF_3, and also with iodine to form the compound IF_5. Chlorine, apparently, does not unite with bromine directly, but with iodine it forms the two compounds ICl and ICl_3. Bromine unites with iodine to form IBr and a somewhat doubtful substance, IBr_5.

The following table gives a synopsis of these compounds :—

COMPOUNDS OF THE HALOGENS WITH EACH OTHER.

Compounds with :—	F.	Cl.	Br.	I.
F	F_2	...	F_3Br	F_5I
Cl	...	Cl_2	...	ClI, Cl_3I
Br	BrF_3	...	Br_2	BrI, Br_2I (?)
I	IF_5	ICl, ICl_3	IBr, IBr_3 (?)	I_2

[1] Geoffrey Martin, *opus cit.*
[2] W. E. S. Turner, *Trans. Chem. Soc.*, 1911, **99**, 880 ; 1912, **101**, 1923.
[3] Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **24**, 224.

It will be observed that the power possessed by the halogens of forming compounds with each other increases as the electrochemical difference between the various atoms accentuates. For example, the fluorides of iodine are relatively much more stable than the chlorides, and still more so than the bromides. At best, however, the halogens have only a feeble affinity for each other, even the most stable of the above-mentioned compounds being unstable when compared with the halogen compounds of hydrogen and the metals generally.

The halogens have a feeble but perceptible affinity for oxygen, the affinity increasing markedly as we go from fluorine towards iodine.

The following table gives a synopsis of the oxides formed by the halogens :—

Type of Oxide.	F.	Cl.	Br.	I.
X_2O	...	Cl_2O	...	...
XO	...	...	...	...
X_2O_3	...	...	...	...
XO_2	...	ClO_2	...	$(IO_2 ?)$
X_2O_5	...	...	...	I_2O_5
XO_3	...	...	...	...
X_2O_7	...	Cl_2O_7	...	I_2O_7

All the oxides of chlorine are excessively unstable, dangerously explosive bodies. The oxides of iodine are far more stable, but all are decomposed much below a red heat. Chlorine monoxide, Cl_2O, and chlorine di-oxide, ClO_2, are both very unstable, dangerously explosive gases, while chlorine heptoxide, Cl_2O_7, is a slightly more stable (since it will bear distillation without decomposition) but very explosive oil. Iodine di-oxide, IO_2, is far more stable, being a lemon-yellow solid which decomposes into its elements at 130° C. Iodine pentoxide, I_2O_5, is a white solid sufficiently stable to bear heating up to 300° C., at which temperature it decomposes into its elements.

The following table gives a list of the oxy-acids formed by those elements :—

| Type of Oxy-acid.	F.	Cl.	Br.	I.
HOX	..	HOCl *	HOBr *	HOI *
HOXO	...	HOClO *	...	...
$HOXO_2$	...	$HOClO_2$ *	$HOBrO_2$ *	$HOIO_2$
$HOXO_3$	...	$HOClO_4$	...	$HOIO_3$
				$I_2O_5(OH)_4$
				$I_2O_4(OH)_6$
				$I_2O_3(OH)_8$
				$I_2O_2(OH)_{10}$
				$I_2O(OH)_{12}$
				$I_4O_9(OH)_{10}$†
				$I_6O_{16}(OH)_{10}$†

* Known only in solutions.   † Known only in form of salts.

The feeble affinity of fluorine towards oxygen is shown by the two preceding tables. No oxides or oxy-acids of fluorine have been obtained,

these compounds being apparently too unstable to exist at ordinary temperatures.

The stability of the compounds which the halogens form with oxygen *increases* as we proceed from fluorine towards iodine, although bromine in many respects appears to have a somewhat more feeble *absolute* (but not *relative* to its other affinities) affinity for oxygen than chlorine ; *e.g.* bromine oxides are unknown, although bromine oxy-acids are well known. The superior affinity of iodine for oxygen is clearly indicated not only by the comparatively stable higher oxides and oxy-acids it forms, but also by the fact that iodine actually displaces chlorine from potassium chlorate (see p. 243) according to the equation :— [1]

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$
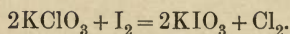
Moreover, iodine can be directly oxidised to iodic acid merely by warming with concentrated nitric acid.

The reason why oxides of bromine are unknown, although undoubtedly the *relative* affinity for oxygen increases as we go from fluorine to oxygen, is the result of another general rule, which is this :—

In any one series of elements, as the atomic weights increase, in general, the intensity of the chemical affinities diminish, so that very heavy atoms, in general, exert much weaker chemical forces than the lighter elements of the same series. Now, although the *relative* affinity of bromine for oxygen (*i.e.* its affinity compared with the affinities it exerts on the other elements of the periodic system) may be more developed than that of chlorine towards oxygen, yet this is more than counterbalanced by the *absolutely* weaker chemical forces which bromine exerts—the forces which chlorine exerts being, as we shall see later, 1·1 to 1·3 times more intense than the corresponding forces exerted by bromine ; so that in practice this greater absolute affinity of chlorine causes the oxides of chlorine to be just capable of existence at ordinary temperatures, whereas the forces exerted by bromine on oxygen just sink below the critical value necessary to bring bromine oxides into existence at ordinary temperatures. The general affinities of iodine are, as we shall see, much weaker than the affinities of either bromine or chlorine, yet the greater *relative* affinity of iodine for oxygen causes iodine to produce a series of relatively stable oxides.

The oxy-acids of the type HOX are weak and unstable, and, owing to their instability, none of them have been obtained pure. Their salts, especially those of hypochlorous acid, HClO, are, technically, very important, being used for bleaching and disinfecting. The stability of acids of the type HOX diminishes from chlorine to iodine, just as the stability of the hydracids themselves diminishes. However, hypo-iodous acid, HIO, is much less stable than hypobromous acid, HBrO, or hypochlorous acid, HClO, and cannot be distilled like the two latter. The instability of these acids depends upon a tendency to yield oxygen, thus :—

$$HOX = HX + O.$$
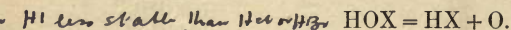
They also decompose when hydracids are added, thus :—

$$HOX + HX = H_2O + X_2.$$
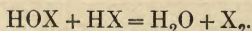
[1] See Potilitzin, *Ber.*, 1887, **20**, [iii.], 772 ; Thorpe and Perry, *Trans. Chem. Soc.*, 1892, **61**, 925.

The acids themselves can yield halogen and also oxygen by spontaneous decomposition, but when excess of halogen acid is added only halogen is liberated.

The acids and their salts are very prone to oxidise into higher oxyacids of the type HXO_3. Thus, when alkali hypochlorites are heated, we get a change of this type, chlorates being formed :—

$$3NaOX = NaXO_3 + 2NaX.$$
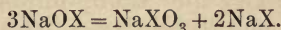
The tendency of hypo-iodides, MOI, to pass into iodides, MI, and iodates, MIO_3, is much greater than the tendency of hypochlorous and hypobromous acids to pass into chlorides and chlorates, bromides and bromates, respectively. Not only are the hypo-iodites, MOI, much less stable than the corresponding chlorine and bromine compounds, but the iodates, MIO_3, are much more stable than the chlorates or bromates, as shown by the heats of formation :— [1]

	Cl.	Br.	I.
H, X, O_3, Aq. . .	23,900 cals.	12,200 cals.	55,900 cals.

Chlorine has no power of decomposing bromic acid or potassium bromate. However, iodine displaces both chlorine and bromine from chloric and bromic acid, forming iodic acid, HIO_3—a fact which indicates the superior stability of iodic acid, and the greater affinity of iodine for oxygen. The reaction, however, which accentuates most strikingly the superior stability of iodic acid over bromic and chloric acids is the direct oxidation of iodine to iodic acid by nitric acid.

Perchloric acid, $HClO_4$, is one of the most stable oxy-acids of chlorine, and, curiously enough, it is more stable than chloric or the lower acids of chlorine. In fact the stability increases as we go from $HClO$ to $HClO_4$, $HClO$ being the least stable, and $HClO_4$ the most stable, of the oxy-acids of chlorine. In $HClO_4$ chlorine is probably heptavalent.

Perbromic acid, $HBrO_4$, is unknown, and appears too unstable to exist. *Per-iodic acid,* HIO_4, is a well-defined stable substance in which iodine is heptavalent. It is formed by the action of iodine on a solution of perchloric acid, $HClO_4$—a fact which indicates its superior stability over that acid. As a matter of fact, however, a very large number of per-iodates, or their salts, are known. Per-iodic acid is the acid corresponding to the oxide I_2O_7. The following stages of hydroxylation of I_2O_7 are theoretically possible, and salts corresponding to most of them have actually been isolated :—

Anhydride.	Acid.			
I_2O_7	$I(OH)_7$	.	.	. (unknown) ortho-per-iodic acid.
	$IO(OH)_5$	.	.	. para-per-iodic acid.
	$IO_2(OH)_3$	.	.	. meso-per-iodic acid.
	$IO_3(OH)$	.	.	. meta-per-iodic acid.

Derivatives of even more complicated types have been isolated : for example, salts corresponding to the acids $I_4O_9(OH)_{10}$ and $I_6O_{16}(OH)_{10}$ are known.

It will thus be seen that a wide and sharply defined family of substances occur as derivatives of the acids corresponding to the anhydride I_2O_7, in which iodine is heptavalent, and that per-iodic acid and its salts are consider-

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[1] Thomsen, *Thermochemische Untersuchungen.*

ably more stable than their chlorine analogues—all of which accentuates the greater affinity for oxygen which iodine possesses over chlorine and bromine.

As regards the *relative strengths of the halogen oxy-acids*, the acids of the type HOX are very weak, the strength of the acids increasing with the addition of oxygen—chloric acid, $HClO_3$, for example, being nearly as strong an acid as hydrochloric.

Comparison of the Organic Compounds of the Halogens.—A comparison of these bodies properly belongs to "Organic Chemistry," and therefore will not be treated of here. We may mention, however, that the compounds formed by the union of carbon with fluorine are remarkably stable, and that the stability of the organic compounds decreases as we proceed from the organic fluorides to the iodides.[1] On the other hand, the acidity of organic acids is increased to a greater extent by the substitution of F for H, than of Cl or Br for H (Swarts). As regards the molecular association of the compounds of organic bases with the halogen acids, see W. E. S. Turner;[2] see also p. 12.

Comparison of the Affinities of the Halogens.—The relative differences of the affinities of these elements as we pass from fluorine to iodine, especially the increase in the chemical attraction for non-metallic negative elements like oxygen, and the accompanying decrease in their affinities for positive elements like H and the metals, have already been referred to in the preceding pages.

We now proceed to compare the affinities exhibited by the halogens for other elements.

This is best done graphically in the following simple manner :—First the periodic system of the elements is constructed in the usual manner. Thus :—[3]

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Sc	P	S	Cl	Ar
Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ag	Cd	In	Sn	Sb	Te	I	Xe
Au	Hg	Tl	Pb	Bi	—	—	—

Next, we erect a perpendicular from every element shown in this table of a length proportional to the attractive forces or affinities which it exerts towards, say, the element fluorine. A surface is then described through the summits of these perpendiculars, and we thus get a surface corresponding to fluorine such as is shown in fig. 2.[4] We repeat the process for the elements chlorine, bromine, and iodine, and we get the similar surfaces (fig. 2) for these elements.

The shapes of these surfaces, then, show at a glance the relative magnitude of the affinities exerted by chlorine and the other halogens, respectively, on the different elements of the periodic system.

The numerical measurements of the affinities which the halogens exert on the various members of the periodic system are founded on their heats of

[1] See Swarts, *Bull. Soc. chim. Belg.*, 1907, **21**, 278 ; *Bull. Acad. roy. Belg.*, 1912, 481–523.

[2] W. E. S. Turner, *Trans. Chem. Soc.*, 1911, **99**, 880 ; 1912, **101**, 1923.

[3] We confine ourselves solely to the elements of the uneven series, as there are not sufficient data for the elements of the even series.

[4] From Martin's *Researches on the Affinities of the Elements.*
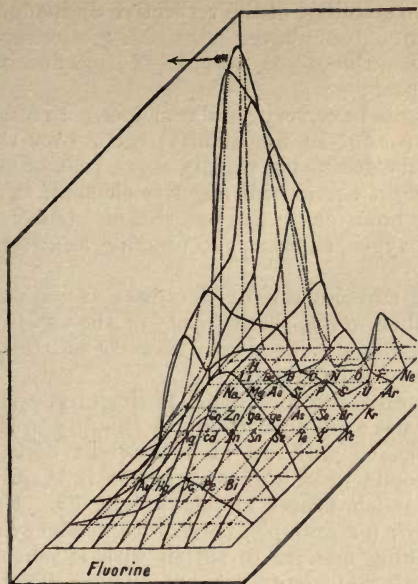
F = 19·0.

Cl = 35·46.

Br = 79·92.

I = 126·92.

FIG. 2.—Affinity surfaces of the halogens.

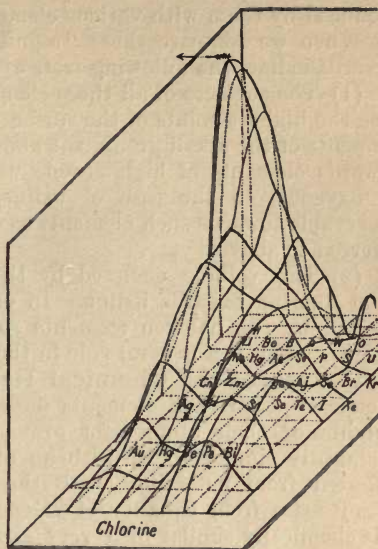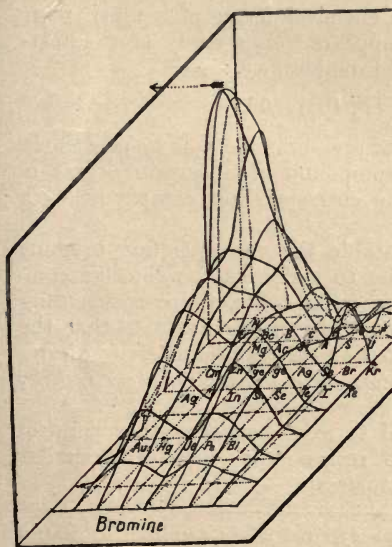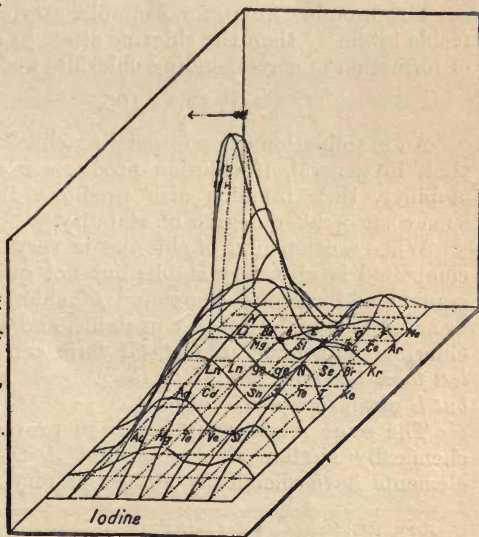formation, coupled with a study of the stability, of the respective compounds produced by them with various elements given above.[1]

When we compare these "affinity surfaces" as we proceed from fluorine towards iodine, the following facts appear :—

(1) The surfaces of all these elements have very similar shapes. In each case the highest points of the surface (*i.e.* maximum affinity) occur over the elements of the alkali group, the affinity decreasing rapidly as we pass either towards elements of high atomic weight or towards negative elements such as oxygen. In the case of iodine, however, a marked rise of affinity is observable towards such elements as oxygen, chlorine, and bromine, as already referred to above.

(2) The volume enclosed by the surfaces rapidly decreases as we pass from fluorine towards iodine. In other words, the intensity of the affinities exerted by the halogen elements *rapidly decreases* with increase of atomic weight. This is a general rule in the periodic system.

Causes of the Chemical Resemblance of the Halogens.

—The chemical similarity of elements does not arise on account of equality in the weights of their atoms—for example, Cl with an atomic weight $35\cdot5$ is chemically similar to Br with an atomic weight of 80, whereas it is quite different from potassium, with the much nearer atomic weight 39. Nor does it arise from equality of valency ; for example, boron with a valency of 3 is chemically similar in a very striking manner to silicon with a valency of 4. Sodium and chlorine are both univalent, yet are chemically and physically very unlike.

There is, however, a simple condition which determines the similarity of different atoms.[2] It is this : *Chemically similar elements must attract the same radicles with proportional intensities of force, whereas chemically unlike elements attract them with unlike intensities.*

The bromine atom, for example, exerts chemical forces of a much more feeble intensity than the chlorine atom, as appears from a study of the heats of formation of corresponding chlorides and bromides, *e.g.* :—

$$(P, Cl_5) = 105, \qquad (P, Br_5) = 63.$$

An examination of corresponding chlorine and bromine compounds shows that, in general, if chlorine produces a compound of a certain degree of stability, then bromine also produces the corresponding compound of a somewhat weaker degree of stability.

When a compound of chlorine is very stable, the corresponding bromine compound is also very stable, but not quite so stable as the chlorine compound ; and when a compound of chlorine is unstable, the corresponding bromine compound is also unstable, and somewhat more unstable than the chlorine compound ; *in fact, the force exerted by the bromine atom is always less than the force exerted by the chlorine atom on a given element or radicle, but is always proportional to it.*

The same relationship has been proved to exist between other pairs of chemically similar elements,[2] and is the reason why chemically similar elements have chemically similar affinity surfaces.

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[1] The details are set forth in *Researches on the Affinities of the Elements*, by Martin (J. & A. Churchill, 1905), to which the reader is referred for further particulars, as a full description of the data on which numerical estimates of these affinities are founded will occupy more space than is possible in a text-book such as the present one.

[2] See Martin, *opus cit.*

Mathematically this may be expressed thus : If we denote the attractions which an element A exerts on the various radicles A, B, C, D . . . by $f_1, f_2, f_3, \ldots f_n$; and the corresponding attractions which an element B exerts by $f_1', f_2', f_3', \ldots f_n'$. Then, if the elements A and B are chemically similar, the following relation holds :—

$$\frac{f_1}{f_1'} = \frac{f_2}{f_2'} = \frac{f_3}{f_3'} = \ldots = \frac{f_n}{f_n'} = K \quad . \quad . \quad . \quad . \quad (1)$$

Further we will show that the closer K approaches unity, the closer the elements approach each other in their chemical properties. When $K = 1$ the forces the two elements exert are equal, and this is obviously the condition that the elements A and B may be perfectly chemically similar, for in this case one may replace the other in any chemical reaction without altering the nature and direction of the reaction which is determined by these forces.

When $K = n$ the one element possesses the same chemical properties as the other, but intensified n-fold. For example, for the system fluorine and chlorine, K has the value 1·7, as the following thermal data show (see later) :—

$$\left(F, Si\frac{1}{4}\right) = 67\cdot3 = f_1, \qquad \left(Cl, Si\frac{1}{4}\right) = 39\cdot4 = f_1',$$

$$(F, H) = 37\cdot6 = f_2, \qquad (Cl, H) = 22\cdot0 = f_2',$$

where

$$\frac{f_1}{f_1'} = \frac{67\cdot3}{39\cdot4} = 1\cdot71,$$

$$\frac{f_2}{f_2'} = \frac{39\cdot4}{22\cdot0} = 1\cdot79.$$

This means that fluorine possesses the same chemical properties as chlorine, but intensified 1·7-fold.

In the case of the system Cl and Br, K has the average value 1·22, showing that chlorine possesses the same chemical properties as bromine, but intensified 1·2-fold. Thus we have, on comparing the heats of formation in large calories of corresponding chlorides and bromides, the following figures :—

CHLORINE AND BROMINE.

$(Cl, Cu) = 32\cdot9 = f_1$	$(Br, Cu) = 25 = f_1'$	
$(Cl, Ag) = 29\cdot2 = f_2$	$(Br, Ag) = 22\cdot7 = f_2'$	
$(Cl, Li) = 93\cdot8 = f_3$	$(Br, Li) = 80 = f_3'$	
$(Cl, Na) = 97\cdot7 = f_4$	$(Br, Na) = 85\cdot8 = f_4'$	
$(Cl, K) = 105\cdot6 = f_5$	$(Br, K) = 95\cdot3 = f_5'$	
$(Cl, Ca\frac{1}{2}) = 84\cdot6 = f_6$	$(Br, Ca\frac{1}{2}) = 70\cdot4 = f_6'$	
$(Cl, Sr\frac{1}{2}) = 92\cdot3 = f_7$	$(Br, Sr\frac{1}{2}) = 78\cdot8 = f_7'$	
$(Cl, Ba\frac{1}{2}) = 97\cdot3 = f_8$	$(Br, Ba\frac{1}{2}) = 85\cdot0 = f_8'$	
$(Cl, Zn\frac{1}{2}) = 48\cdot6 = f_9$	$(Br, Zn\frac{1}{2}) = 40\cdot0 = f_9'$	
$(Cl, Hg\frac{1}{2}) = 27\cdot2 = f_{10}$	$(Br, Hg\frac{1}{2}) = 20\cdot3 = f_{10}'$	
$(Cl, Hg) = 32\cdot6 = f_{11}$	$(Br, Hg) = 24\cdot5 = f_{11}'$	
$(Cl, Al\frac{1}{3}) = 53\cdot66 = f_{12}$	$(Br, Al\frac{1}{3}) = 41\cdot0 = f_{12}'$	
$(Cl, As\frac{1}{3}) = 23\cdot8 = f_{13}$	$(Br, As\frac{1}{3}) = 19\cdot7 = f_{13}'$	
$(Cl, Sb\frac{1}{3}) = 30\cdot46 = f_{14}$	$(Br, Sb\frac{1}{3}) = 25\cdot63 = f_{14}'$	
$(Cl, Pb\frac{1}{2}) = 41\cdot0 = f_{15}$	$(Br, Pb\frac{1}{2}) = 36\cdot0 = f_{15}'$	

Whence

$$\frac{f_1}{f_1{}'} = \frac{32 \cdot 9}{25} = 1 \cdot 32 \qquad \frac{f_8}{f_8{}'} = \frac{97 \cdot 3}{85 \cdot 0} = 1 \cdot 15$$

$$\frac{f_2}{f_2{}'} = \frac{29 \cdot 2}{22 \cdot 7} = 1 \cdot 29 \qquad \frac{f_9}{f_9{}'} = \frac{48 \cdot 6}{40 \cdot 0} = 1 \cdot 21$$

$$\frac{f_3}{f_3{}'} = \frac{93 \cdot 8}{80} = 1 \cdot 17 \qquad \frac{f_{10}}{f_{10}{}'} = \frac{27 \cdot 2}{20 \cdot 3} = 1 \cdot 34$$

$$\frac{f_4}{f_4{}'} = \frac{97 \cdot 7}{85 \cdot 8} = 1 \cdot 14 \qquad \frac{f_{11}}{f_{11}{}'} = \frac{32 \cdot 6}{24 \cdot 5} = 1 \cdot 33$$

$$\frac{f_5}{f_5{}'} = \frac{105 \cdot 6}{95 \cdot 3} = 1 \cdot 11 \qquad \frac{f_{12}}{f_{12}{}'} = \frac{53 \cdot 66}{71 \cdot 0} = 1 \cdot 30$$

$$\frac{f_6}{f_6{}'} = \frac{84 \cdot 6}{70 \cdot 4} = 1 \cdot 20 \qquad \frac{f_{13}}{f_{13}{}'} = \frac{23 \cdot 8}{19 \cdot 7} = 1 \cdot 21$$

$$\frac{f_7}{f_7{}'} = \frac{92 \cdot 3}{78 \cdot 8} = 1 \cdot 18 \qquad \frac{f_{14}}{f_{14}{}'} = \frac{30 \cdot 46}{25 \cdot 63} = 1 \cdot 19$$

$$\frac{f_{15}}{f_{15}{}'} = \frac{41}{36} = 1 \cdot 14.$$

Position of Manganese in the Periodic System.—Each group of the periodic system is divided into an odd and even series of elements, and Group VII. is no exception to this rule—the halogens, F, Cl, Br, and I forming the components of the uneven series, and manganese being the only known representative of the even series of this group.

When we contrast manganese with the halogens, however, there appears superficially to be practically no resemblance between them, either physically or chemically—manganese being a pronounced metal while, F, Cl, Br, and I are typical non-metals.

This, however, is only in conformity with the general rule that the odd and even series of extreme groups of the periodic system exhibit little resemblance ; for example, in Group I. of the periodic system there is little resemblance between Li, Na, K, Rb, and Cs, on the one hand, and Cu, Ag, Au, on the other, these being the elements of the even and odd series of this group. Again in Group VI., the group immediately preceding that in which manganese occurs, there is considerable dissimilarity between the odd series O, S, Se, Te, on the one hand, and the even series Cr, Mo, W, Ur, on the other. Consequently in Group VII. we should expect this dissimilarity between the elements of the even and odd series to be even more pronounced, as is indeed the case.

The resemblance between manganese and the halogens, indeed, is confined to the highest oxide, Mn_2O_7 and its derivatives ; for only when thus combined with the maximum proportion of oxygen does manganese exhibit oxygenic properties at all resembling those possessed by the halogens. Permanganic acid, $HMnO_4$, is, for example, analogous to perchloric acid, $HClO_4$, and potassium permanganate, $KMnO_4$, is isomorphous with potassium perchlorate, $KClO_4$. When, however, these compounds are reduced, so that the type R_2O_7, from which they are derived, is departed from, the similarity at once disappears ; for whilst chlorine maintains its electronegative character in compounds devoid of oxygen, manganese in its lower oxidised state yields

compounds in which the element is entirely basigenic, and exhibits relationships with its neighbours in the periodic system, chromium and iron.[1]

Thus the resemblance between metallic manganese, chromium and iron is very close, all being hard brilliant metals of high melting-points : like chromium, manganese forms a basic oxide, R_2O_3 ; a di-oxide, RO_2 ; and an acidic tri-oxide, RO_3, which is analogous to CrO_5, since the manganates, M_2MnO_4, are isomorphous with chromates, M_2CrO_4. However, both MnO_3 and the corresponding manganates are much less stable than CrO_3 and the corresponding chromates.

On the other hand, manganese resembles iron in forming three oxides of the types $RO.R_2O_3$ and R_3O_4. The analogy between Mn_2O_3 and Fe_2O_3 reveals itself in a capacity for producing isomorphous salts —manganic alum, $(NH_4)_2SO_4.Mn_2(SO_4)_3.24H_2O$, being isomorphous with iron alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$,—although the iron compounds greatly exceed the manganese in stability.

The analogy between the oxides MnO and FeO shows itself in the fact that these oxides dissolve in acids to produce manganous and ferrous salts which unite with certain salts of the alkali metals to produce isomorphous double salts. However, manganous salts are much more stable than ferrous salts, the latter tending to oxidise to ferric salts, whereas manganic salts, as a rule, tend to break down into manganous salts.

The explanation of the resemblance between manganese on the one hand and chromium and iron on the other (although all are in entirely different groups of the periodic system) is due to the fact that manganese occurs intermediate between them, as shown in the scheme :—

$$\text{Cr} (52 \cdot 0), \qquad \text{Mn} (54 \cdot 9), \qquad \text{Fe} (55 \cdot 8).$$

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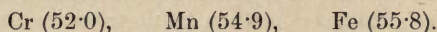
[1] Caven and Lander, *Systematic Inorganic Chemistry* (1911). p. 303.

CHAPTER II.

FLUORINE AND ITS COMPOUNDS.

FLUORINE.

Symbol, F. Atomic weight, 19·0 (O = 16).

Occurrence.—It is a matter of dispute whether or not free fluorine occurs in nature. It has long been known that when certain fluorine-rich minerals, such as certain specimens of calcium fluoride, are ground up an intense ozone-like smell becomes perceptible, which Kenngott[1] in 1853 and Wöhler[2] in 1861 stated was due to the presence of free fluorine. Loew[3] attributes the smell to free fluorine resulting from the dissociation of an unstable fluoride such as cerium fluoride present in traces. H. Becquerel and H. Moissan[4] proved that certain specimens of fluorspar contained an enclosed gas which could be seen to develop when small particles were crushed under the microscope, and that the evolved gas contained traces of fluorine, although they could not decide whether the fluorine resulted from the dissociation of a perfluoride or not.

Some specimens of the mineral smaragdart contain, according to Lebeau,[5] either free fluorine or an easily dissociable fluoride.

Combined fluorine, however, is a widely distributed substance, and, indeed, in the rocks, is as abundant as chlorine.

Thus Clarke[6] estimates the proportion of fluorine and chlorine in the older crust of the earth to amount each to about 0·01 per cent.

Vogt[7] thinks that this is too low; he estimates the amount of fluorine in the rocks as 0·024 to 0·04 per cent., and the amount of chlorine is 0·025 to 0·04 per cent.

Vogt pointed out that fluorine occurs more abundantly than chlorine in "acid" rocks, whereas chlorine is more abundant than fluorine in "basic" rocks.

In the outer crust of the earth and in sea-water, however, chlorine is much more abundant than fluorine, amounting, according to Vogt, to about 0·175 per cent. of chlorine and 0·025 to 0·004 per cent. of fluorine.

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[1] Kenngott, *Ber. Wien. Akad.*, 1853, **10**, 296 ; 1853, **11**.
[2] Wöhler, *Liebig's u. Wöhler's Briefwechsel*, 1888, vol. ii. p. 107.
[3] Loew, *Ber.*, 1881, **14**, 1144, 2441. See also B. Brauner, *Ber.*, 1881, **14**, 1944.
[4] H. Becquerel and H. Moissan, *Compt. rend.*, 1890, **111**, 669.
[5] Lebeau, *Compt. rend.*, 1895, **121**, 601. See also J. Garnier, *Chem. Zeit.*, 1901, **25**, p. 89 ; Loew, *loc. cit.*, p. 355 ; Th. Zettel, *loc. cit.*, p. 385 ; and Moissan, *loc. cit.*, p. 480.
[6] F. W. Clarke, *Bull. U.S. Geol. Survey*, No. 168 (1900), p. 5.
[7] J. H. L. Vogt, *Zeitsch. prakt. Geol.*, 1898, pp. 225, 314, 377, 413 ; 1899, p. 10.

Sea-water only contains about 0·001 per cent. of fluorine.

A. Gautier[1] found 0·110 mg. of fluorine per litre in gas evolved from Vesuvius.

The most common compound of fluorine is the mineral "fluorspar," CaF_2, which is found in Derbyshire, the Harz, Bohemia, in large quantities in Mexican ores, and in large masses in the volcanoes of the Campagna—to mention only a few localities.

Large quantities of fluorine also occur in *cryolite* ($3NaF + AlF_3$), a mineral containing more than 50 per cent. of fluorine, which is found in large masses in Greenland; it occurs close to the coast, embedded in granite in layers which extend right under the sea, and it is here extensively mined, no less than 10,000 tons being annually exported, principally to North America. Fluorine also occurs in a large number of other minerals, such as fluor-apatite, lepidolite, topaz, yttrocerite, nocerin, fluellite, hieratite, etc., etc. Fluorine also occurs in minute quantities in sea-water and in the waters of many mineral springs. P. Carles,[2] for example, found that of 93 mineral springs investigated no fewer than 87 contained fluorine compounds to the extent of 0·018 gram per litre, while there is some evidence that free hydro-fluoric acid occurs in the emanations from volcanoes.[3]

Fluorine also occurs in the teeth and bones of animals; for example, the enamel of the teeth contains, according to Hoppe,[4] CaF_2, up to 2 per cent. According to Hempel and Scheffler,[5] human teeth contain 0·33 to 0·52 per cent. F, and the teeth of horses 0·2 to 0·39 per cent. F. A decaying human tooth only contained 0·19 per cent. F. The bones of mammals contain only 0·005 per cent. of the dried bone substance, but bone ash contains 0·41 to 0·61 CaF_2.[6] The rather remarkable fact was pointed out by J. Stocklasa[7] in 1889 that while new bones contain only very little fluorine, nearly all very old fossil bones, especially those out of Tertiary times and before, are much richer in this substance, and A. Carnot (1892)[8] holds it as possible that the antiquity of bones could actually be determined by determining the percentage of fluorine they contain.

The shells of oysters contain 0·012 per cent. fluorine, about ten times as much as is contained in sea-water,[9] while the shells of fossil oysters contained 0·15 per cent.

Fluorine also had been detected in traces in the blood, brains, and milk of animals, also in vegetables.[10] G. Tammann[11] in 1888 investigated the distribution of fluorine in eggs. He found that only a very small amount occurred in the shell, somewhat more in the albuminous "white," but most in the yellow yolk. According to Ost[12] the ash of healthy plants contains 0·1 per cent.

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[1] A Gautier, *Compt. rend.*, 1913, **157**, 820–25.
[2] P. Carles, *Compt. rend.*, 1907, **144**, 37, 201.
[3] See A. Brun, *Quelques recherches sur le Volcanisme* (Gèneve, 1905); *l'Éruption du Vésuve de septembre* 1904 (Gèneve, 1904); Matteucci, *Compt rend.*, 1899, **129**, 65; Stocklasa, *Chem. Zeit.*, 1906, **30**, 740.
[4] Hoppe, *Arch. pathol. Anat.*, 1862, **24**, 13.
[5] Hempel and Scheffler, *Zeitsch. anorg. Chem.*, 1899, **20**, 1.
[6] Zalesky, *Jahresber.*, **1866**, p. 757.
[7] J. Stocklasa, *Jahresber.*, **1889**, 2360.
[8] A. Carnot, *Compt. rend.*, 1892, **114**, 1189; **115**, 243.
[9] P. Carles, *Compt. rend.*, 1907, **144**, 437.
[10] See Wilson, *Chem. Gaz.*, **1850**, 366; Horsford, *Annalen*, 1866, **139**, 202.
[11] Tammann, *Zeitsch. physiol. Chem.*, 1888, **12**, 322.
[12] Ost, *Ber.*, 1893, **26**, 151.

fluorine, while Phipson [1] found no less than 3·9 per cent. in fossil wood from the Isle of Wight.

History.[2]—Fluorspar, CaF_2, was first mentioned by Basilius Valentine and Agricola as a flux suitable for use in the smelting of ores.[3] The etching of glass when exposed to the vapours was known towards the end of the seventeenth century, Schwankhard of Nürnberg being aware of it in 1670; this action was further studied by Marggraf,[4] who, in 1764, commented on the eating away of glass retorts in which fluorspar was heated with sulphuric acid, and on the simultaneous production of a white earthy sublimate.

Scheele,[5] in 1771, first stated that fluorspar was the calcium salt of a peculiar acid, which he obtained by distilling fluorspar with sulphuric acid in a tin retort, and he also obtained silicon tetrafluoride, SiF_4, by allowing the hydrofluoric acid thus obtained to act upon silica. Priestley was the first to collect the gas SiF_4 over quicksilver. Gay-Lussac and Thénard [6] advanced our knowledge of hydrofluoric acid very considerably. In 1808 they prepared the anhydrous acid, HF, and discovered gaseous BF_3. Up to this time hydrofluoric acid was considered to contain oxygen and was called "fluoric acid." Ampère,[7] however, in 1810, and afterwards H. Davy,[8] demonstrated that the acid is analogous to hydrochloric acid and that fluorspar is analogous to calcium chloride, since it contained the metal calcium combined with an element analogous to chlorine, which was termed "fluorine," because of the use of fluorspar as a flux (*Fluo*, I flow). In 1812 J. Davy [9] investigated BF_3 and SiF_4, while Berzelius [10] in 1824 investigated the metallic fluorides. The isolation of the element fluorine for a long time defied the efforts of chemists on account of its enormous chemical activity, but this difficult task was achieved by Moissan [11] in 1886.

In 1897 Moissan and Dewar [12] liquefied the substance, and in 1903 obtained it in a solid condition.

Preparation.—Fluorine was first isolated in quantity by Moissan [13] by the electrolysis of anhydrous hydrofluoric acid, to which potassium hydrogen fluoride had been added in order to make the liquid conduct, as perfectly pure anhydrous hydrofluoric acid will not allow a current to pass through it. Moissan used a U-tube of platinum (better an alloy of iridium and platinum, containing 10 per cent. of the former metal) of 160 c.c. capacity; to this U-tube were attached two small platinum side tubes, as seen in fig. 3. The open ends of the U-tube were closed by fluorspar stoppers (F) ground so as to nearly fit the platinum tube and wrapped round with thick platinum foil so as to fit tightly into the tube. Through the stoppers passed the two

[1] F. L. Phipson, *Chem. News*, 1892, **66**, 181.
[2] A complete account of this element, including literature up to 1900, will be found in H. Moissan's book *Le fluor et ses composés* (Paris, 1900). An interesting account is given by F. D. Chattaway, *Chem. News*, 1913, **107**, 37–39.
[3] Agricola, *De ortu et causis subterraneorum, etc.* (1588), p. 458.
[4] Marggraf, *Mémoires de Berlin* (1768), 3; *J. Phys.*, **2**, 247 (1773).
[5] Scheele, *K. Svenska Vet.-Akad. Handl.*, 1771, p. 120; *J. Phys.*, 1773, p. 473; *Crell's Annalen*, 1782, **8**, 117, Opusc. **21**, 1242.
[6] Gay-Lussac and Thénard, *Recherch.*, **2**, 1; *Ann. Chim. Phys.*, 1809, [i.], **69**, 204.
[7] See Ampère, *Ann. Chim. Phys.*, 1885, [vi.], **4**, 5 (Posthumous).
[8] H. Davy, *Phil. Trans.*, 1808, **98**, 43; 1813, **103**, 263.
[9] J. Davy, *Phil. Trans.*, 1812, **103**, 352.
[10] Berzelius, *Pogg. Annalen*, 1824, **1**, 1 and 161; **2**, 111; 1825, **4**, 1 and 117; 1862, **8**, 18.
[11] Moissan, *Ann. Chim. Phys.*, 1887, [vi.], **12**, 473.
[12] Moissan and Dewar, *Proc. Chem. Soc.*, 1897, p. 175; *Compt. rend.*, 1903, **136**, 641.
[13] Moissan, *Ann. Chim. Phys.*, 1887, [vi.], **12**, 473; 1891, [vi.], **24**, 224.

electrodes (*e, e*) of iridium-platinum alloy (containing 10 per cent. iridium). The stoppers were held in position by brass caps and screws (E), the joints being rendered air-tight by leaden washers at *p* and shellac-varnishing all the surfaces. In the U-tube was placed 100 c.c. of anhydrous hydrofluoric acid and 20 grams of potassium hydrogen fluoride, KF.HF; when a current of 4 ampères and 38 volts was passed through the liquid, 2 to 4 litres [1] of fluorine per hour were liberated according to the following equations :—

$$(1) \quad 2KF = 2K + F_2,$$
$$(2) \quad 2K + 2HF = 2KF + H.$$
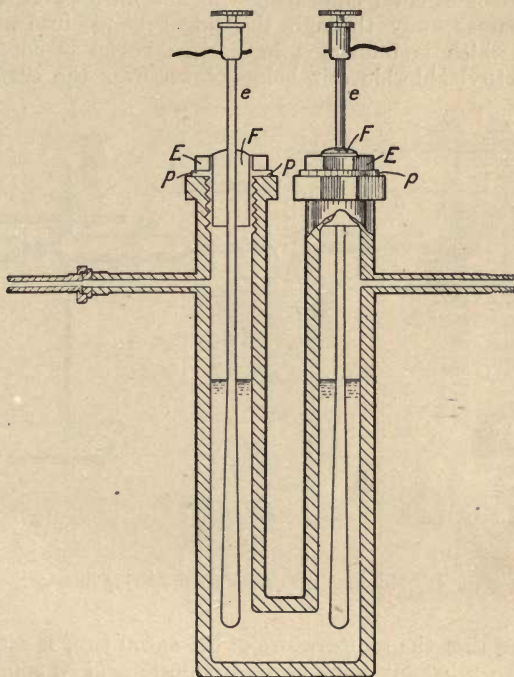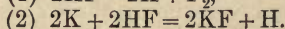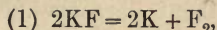
FIG. 3.—Preparation of fluorine.

As a matter of fact, however, the action appears to be considerably more complex than this. It appears that the fluorine first liberated at the anode attacks the platinum, forming platinum fluoride, PtF_4.

The PtF_4 then appears to unite with the KF to form a double compound which is electrolysible, and hydrogen is liberated at the negative pole together with a complicated compound containing an atom of K to every atom of Pt, and which contains a considerable amount of F or HF. This compound is deposited as a black mud. These facts explain why the electrolysis takes place in its initial stages not uniformly, but in a series of jerks as it were, and that only after the lapse of over an hour is the fluorine regularly liberated because the substances have already gone into solution in sufficient amount to make the passage of the current regular.

The passage of the current through the liquid produces a considerable heating effect, and as hydrofluoric acid is a very volatile liquid somewhat

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[1] Fifty volts and 15 ampères yielded 5 litres of fluorine per hour; 50 volts and 20 ampères gave 8 litres per hour (Moissan).

elaborate cooling arrangements had to be adopted for condensing and arresting the hydrofluoric acid coming over with the fluorine. For this purpose Moissan immersed the U-tube in a glass cylinder (fig. 4) A, into which liquid methyl chloride is passed from a steel cylinder B. This liquid, boiling, reduces the temperature of the U-tube to about $-23°$, at which temperature the electrolysis takes place.

To prevent the formation of hoar-frost on the interior of the cold surface of the glass vessel containing the boiling methyl chloride, a second glass cylinder is made to surround it as shown, the air inside being maintained dry by a few pieces of calcium chloride. The fluorine gas, escaping from the positive pole, passes away through the side tube (a) into a spiral tube of platinum (bb), which is immersed in a glass vessel D containing rapidly evaporating methyl chloride (air being blown over the surface to aid the
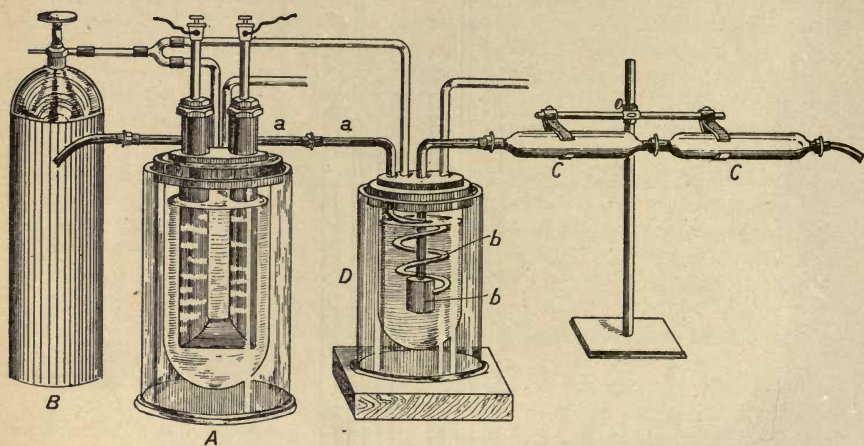

FIG. 4.—Moissan's apparatus for preparing fluorine.

evaporation)—so that the temperature of the spiral tube is maintained as low as $-50°$ C.; whereby any gaseous hydrofluoric acid vapours coming over with the fluorine are retained, whereas the gaseous fluorine passes on, through two tubes (C, C) made of platinum and filled with fused lumps of sodium fluoride, NaF, which retains the last traces of any hydrofluoric acid vapours, by uniting with them, thus : $NaF + HF = NaF.HF$.

Many modifications of this method have been proposed. Thus Moissan,[1] on account of the expensive platinum being rapidly attacked by fluorine, constructed an apparatus of copper, which metal, he found, is not sensibly attacked by hydrofluoric acid, provided the latter be perfectly anhydrous, because the copper becomes covered with a protecting coating of cupric fluoride, CuF_2, which is insoluble in anhydrous hydrofluoric acid.

However, platinum electrodes had to be retained, as copper electrodes very soon dissolved.

Instead of methyl chloride as the cooling agent, a mixture of solid CO_2 and acetone has been proposed, which allows of a temperature of $-80°$ C.

[1] Moissan, *Compt. rend.*, 1899, **128**, 1543.

being reached. Ruff and Ipsen [1] use a mixture of calcium chloride and snow in place of methyl chloride, for cooling the fluorine-generating U-tube, and the evolved gas is led into a copper vessel cooled in liquid air, which condenses all the hydrofluoric acid coming over with the fluorine.

As regards a copper apparatus for producing fluorine in large quantities see the *Deut. Reich. Patent*, 129,825 (1900).

Other Methods of Preparation.—Loew [2] in 1881 showed that when cerium tetrafluoride, $CeF_4.H_2O$, is heated fluorine in small quantity is evolved. Brauner [3] in the same year, and later in 1894, showed that lead tetrafluoride, PbF_4, and, still better, its double salt, $3KF.HF.PbF_4$, when heated in a platinum tube splits off fluorine below a red heat, after first losing hydrofluoric acid at 230°–250° C. According to Ruff,[4] only small amounts of fluorine are thus evolved.

As regards the history of the older non-successful attempts to isolate fluorine the very extensive literature in Moissan's book [5] may be consulted. The experiments of Gore [6] should be particularly mentioned in this connection, as it appears probable that he actually liberated the gas in small quantities.

Properties.—Fluorine, when viewed through a layer 50 cm. long, appears as a greenish-yellow gas, paler and more yellow in tint than chlorine. The gas has a very intense penetrating smell, somewhat recalling that of hypochlorous acid ; it exerts an intensely irritating action on the mucous membrane—even when present in the atmosphere in minute traces. The gas, when brought into contact with the skin, causes a bad burn and rapidly destroys the tissues.

Pure fluorine possesses [7] a density of 1·31 (air = 1), which is in good agreement with that required for F_2.

The absorption spectra of the gas show thirteen lines in the red portion of the spectrum,[8] of wave-lengths 7440, 7400, 7340 (very weak), 7140, 7040, 6910, 6875, 6855, 6835 (weak), 6770, 6405, 6340, 6230 (strong). The element has a negative atomic dispersion (Gladstone [9]) and a very small atomic refraction, which varies according as the element is combined in a saturated or unsaturated hydrocarbon.

Swarts [10] gives the values 0·941 for Hα, 1·015 for D, and 0·963 for Hγ— all for fluorine in saturated compounds. Gladstone [11] calculates the refraction equivalent as intermediate between 0·015 and 0·044. According to Abegg and Immerwahr [12] the voltage required to separate fluorine from its compounds is 1·75 volts.

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[1] Ruff and Ipsen, *Ber.*, 1904, 36, 1177 ; Ruff, *Zeitsch. angew. Chem.*, 1907, 20, 1217.

[2] Loew, *Ber.*, 1881, 14, 1144, 2441.

[3] Brauner, *Ber.*, 1881, 14, 1944 ; *Zeitsch. anorg. Chem.*, 1894, 7, 1 ; *Journ. Chem. Soc.*, 1882, 68 ; 1894, 399. [4] Ruff, *Zeitsch. angew. Chem.*, 1907, 20, 1217.

[5] H. Moissan, *Le Fluor et ses composés* (Paris, 1900).

[6] See G. Gore, *Trans. Chem. Soc.*, 1869, 7, 368 ; also *Chem. News*, 1869, 19, 74 ; 21, 28 ; 23, 13.

[7] Moissan, *Compt. rend.*, 1904, 138, 728.

[8] See Moissan, *Compt. rend.*, 1889, 109, 937 ; C. de Watteville, *Compt. rend.*, 1906, 142, 1078 ; G. Urbain and C. Scal, *Chem. Zeit.*, 1907, 31, 100 ; C. Porlezza, *Gazzetta*, 1912, 42, ii. 42.

[9] J. H. Gladstone and G. Gladstone, *Phil. Mag.*, 1891, [v.], 31, 1.

[10] Fréd. Swarts, *Central Blatt.*, 1903, 1, 14 ; *Mem. Acad. roy. Belg.*, 61, 1901.

[11] G. Gladstone, *Phil. Mag.*, 1885, [v.], 20, 481.

[12] R. Abegg and C. E. Immerwahr, *Zeitsch. physikal. Chem.*, 1900, 32, 142 ; see also W. Roy Mott, *Central Blatt.*, 1904, ii, 936.

Fluorine gas, when cooled by rapidly boiling liquid air,[1] condenses to a clear yellow liquid boiling at $-187°$ C. at 760 mm.; and its specific gravity at $-200°$ C. is given[1] as $1·14$, and at its boiling-point ($-187°$ C.) it is given[2] as $1·108$. Its specific volume is $0·9025$; its molecular volume is $34·30$.

When cooled by liquid hydrogen it condenses to a pale yellow solid, M.P. $-233°$, which becomes quite white[3] at $-252°$ C.

Fluorine is diamagnetic and has a specific magnetic susceptibility of $-3·447 \times 10^{-7}$. As regards its magnetic properties in combination, it behaves like oxygen and unlike chlorine.[4]

Fluorine is one of the most chemically active elements known so far as its attraction for *positive elements* goes. Thus it combines explosively with cold hydrogen *in the dark*, with the production of a red-bordered flame :—

$$H_2 + F_2 = 2HF.$$
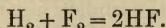
The production of this flame may be observed by inverting a jar filled with hydrogen over the fluorine exit-tube of Moissan's electrolytic apparatus, when a blue, red-bordered flame instantly makes its appearance at the end of the platinum tube. The hydrofluoric acid gas formed slowly attacks the glass jar, dry fluorine itself having no marked action on dry glass.

In consequence of this great attraction of fluorine for hydrogen, the gas instantly decomposes water, liberating oxygen in the form of ozone :—

$$3H_2O + 3F_2 = 6HF + O_3.$$
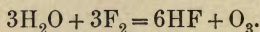
Moissan[5] showed that if a very small quantity of water is poured into a platinum tube filled with fluorine, the ozone is produced in such quantity that the contents of the tube become a deep indigo-blue colour. However, the ozone thus produced rapidly decomposes, and in the course of a few minutes the blue colour fades and finally disappears. This decomposition of moisture by fluorine and the resulting production of hydrofluoric acid explains why it is that while fluorine does not fume in *dry* air, it does so in *moist* air.

The strong attraction of fluorine for hydrogen also explains why fluorine so violently attacks organic compounds,[6] withdrawing their hydrogen with inflammation, with the production of hydrofluoric acid, while the carbon burns (see below) to form CF_4. (Compare the action of chlorine on turpentine.)

It will thus be seen that fluorine performs the same actions as chlorine, but with considerably more vigour, and just as chlorine is capable of displacing bromine and iodine from their compounds, so also fluorine in turn displaces chlorine. Thus when fluorine is brought into contact with potassium chloride or with carbon tetrachloride at ordinary temperatures chlorine is at once evolved :—

$$2KCl + F_2 = 2KF + Cl_2, \qquad CCl_4 + 2F_2 = CF_4 + 2Cl_2.$$
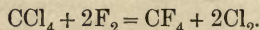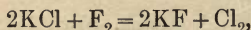
[1] See Moissan and Dewar, *Compt. rend.*, 1897, **124**, 1202 ; **125**, 505 ; 1903, **136**, 785.
[2] Drugmann and Ramsay, *Trans. Chem. Soc.*, 1900, **77**, 1228.
[3] Moissan and Dewar, *Compt. rend.*, 1903, **136**, 641 ; *Proc. Chem. Soc.*, 1897, 175.
[4] Paul Pascal, *Bull. Soc. chim.*, 1911, [iv.], **9**, 336.
[5] Moissan, *Compt. rend.*, 1889, **109**, 937.
[6] Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **24**, 224 ; Swarts, *Bull. Soc. chim. Belg.*, 1907, **21**, 278. The heat of formation of organic fluorine compounds is discussed by Swarts, *Bull. Acad. Roy. Belg.*, 1912, 481–523.

Chlorine does not combine[1] with fluorine, even at $-182.5°$ C., yet bromine and iodine unite with fluorine at ordinary temperatures with the production of luminous flames. According to Moissan,[2] not much heat is evolved when bromine unites with fluorine, the product being BrF_3 (which see). In the case of iodine, however, the combination takes place with the evolution of much heat, a colourless, strongly fuming liquid, IF_5, being produced, which strongly attacks glass, and which, when poured into water, is decomposed with a hissing sound (see iodine pentafluoride).

When fluorine is passed into a 50 per cent. solution of hydrofluoric acid a very energetic action takes place, and a flame is produced in the midst of the liquid. HCl, HBr, and HI also inflame when brought into contact with fluorine, no matter whether they are in the gaseous state or in aqueous solution.

Sulphur takes fire when brought into contact with the gas, burning to a remarkable gaseous fluoride, SF_6 (see under Sulphur, Vol. VII.).

Selenium and tellurium likewise catch fire when brought into contact with fluorine, producing solid crystalline fluorides. Other sulphur compounds, such as SO_2 or H_2S, are instantly decomposed by fluorine, with inflammation. Sulphuric acid, H_2SO_4, however, is only slightly attacked.

Phosphorus, arsenic, and antimony all take fire in fluorine gas at ordinary temperatures, burning to fluorides.[2]   Boron, silicon, and, what is more remarkable, carbon, all inflame in fluorine gas to produce fluorides.[2] As regards carbon, however, while finely divided varieties such as lamp-black or charcoal spontaneously inflame at ordinary temperatures, the diamond is not attacked by the gas, even at a red heat (Moissan).

The action of fluorine on organic compounds of carbon has been referred to above. They are usually completely destroyed[3] with inflammation or even explosion, even at so low a temperature as $-190°$ C. HF, CF_4, and C are usually produced.

Carbon monoxide and di-oxide are not attacked in the cold, but carbon disulphide inflames and burns brilliantly to CF_4 and SF_6, whereas CCl_4 at $30°$ gives free chlorine and CF_4. CN takes fire and burns at ordinary temperatures.

Anhydrous boric acid reacts very energetically with fluorine at ordinary temperatures, BCl_3 is decomposed with production of chlorine and BF_3; $SiCl_4$ is similarly decomposed at $30°$ with inflammation, while SiO_2 is destroyed with incandescence in the cold.

It is a remarkable fact, however, in view of the above-mentioned proofs of fluorine's chemical activity, that perfectly dry fluorine will not attack perfectly dry *glass*, and indeed Moissan[4] showed that glass vessels filled with pure dry fluorine could be heated for two hours at $100°$ without being sensibly attacked. Hydrofluoric acid behaves similarly in this respect; when perfectly dry it is without action on glass, but the presence of the slightest trace of moisture causes it to becomes active, the silica being attacked with the formation of silicon tetrafluoride and water. This water then increases the activity of the hydrofluoric acid. Fluorine atoms, as will be seen presently, have no chemical attraction for oxygen, and so do not tend to remove oxygen from silica contained in glass.

[1] Lebeau, *Compt. rend.*, 1906, **143**, 425 ; Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **24**, 224 ; Karsten, *Zeitsch. anorg. Chem.*, 1907, **53**, 365.
[2] Moissan, *Compt. rend.*, 1890, **110**, 276 ; Ruff, *Zeitsch. angew. Chem.*, 1907, **20**, 1217.
[3] Swarts, *Bull. Soc. chim. Belg.*, 1907, **21**, 278 ; Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **24**, 224.   [4] Moissan, *Compt. rend.*, 1899, **129**, 799.

As regards the action of fluorine towards oxygen, or even ozone, apparently no action whatever takes place between them, either at high or at low temperatures.[1] Nitrogen gas, also, is not attacked by fluorine, nor is nitrous oxide, N_2O, even at a red heat. However, by sparking together a mixture of fluorine and oxides of nitrogen it is possible to produce some oxyfluorides.

Nitric oxide, NO, inflames when brought into contact with fluorine at ordinary temperatures : when nitric oxide, NO, is allowed to act on excess of fluorine at the temperature of liquid oxygen,[2] a white solid substance is first produced, which, as the temperature rises, changes into a colourless fluid ; simultaneously there condenses at $-80°$ C. another colourless liquid, which proved to be nitryl fluoride, NO_2F, which is produced thus :—

$$2NO + F = NO_2F + N.$$
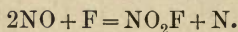
Nitrogen peroxide, NO_2, does not react with fluorine at ordinary temperatures.[2]

Ammonia gas is decomposed with inflammation,[3] and a mixture of the vapours of fluorine and ammonia spontaneously explode. Argon could not be brought to unite with fluorine, either at ordinary temperatures or under the influence of an electrical discharge.[4]

Metals, in general, are attacked by fluorine,[5] but many of them when brought into contact with the gas become coated with a layer of fluoride which protects them from further action. At ordinary temperatures, for example, Moissan was able to generate fluorine in copper vessels (see p. 26) and also in platinum. When, however, metals are heated in the gas they are nearly all attacked, usually burning with vivid incandescence. Thus the alkali metals and those of the alkaline earths take fire and burn in the gas at ordinary temperatures.

Aluminium, iron, manganese, chromium, zinc, tin, bismuth, copper, silver, gold, palladium, iridium, ruthenium, platinum, are all scarcely attacked by fluorine in the cold—or, if so, only very slowly,—owing to the formation of a protecting film of fluoride. However, when these metals are actually heated in the gas to a red heat, the great majority catch fire and burn vividly to fluorides. Thus silver at a red heat burns vividly to AgF, gold is only slowly attacked at a red heat, and platinum at $500°-600°$ C., forming PtF_4. Lead, even at ordinary temperatures, is very slowly converted into a white fluoride. Antimony catches fire at ordinary temperatures, but not bismuth, which is only superficially attacked, even at a red heat. Zinc and tin, although scarcely affected by fluorine at ordinary temperatures, burst into a brilliant flame when heated to $100°$ C. in the gas.

It is rather curious that fluorine gas can be collected and kept over mercury (so long as the vessel is kept still), as a protecting layer of mercury fluoride is formed. When, however, the mercury is shaken with the gas it is rapidly and completely absorbed.[5]

Fluorine, when gently warmed, readily acts on columbium, tantalum, and uranium, producing the fluorides CbF_5, TaF_5, and UF_6 respectively.[6] The action of fluorine on uranium is very vigorous.

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[1] Moissan, *Compt. rend.*, 1889, **109**, 937 ; Ruff and Zedner, *Ber.*, 1909, **42**, 1037–46 ; Gino Gallo, *Atti R. Accad. Lincei*, 1910, [v.] **19**, i. 295, 753.

[2] Moissan and Lebeau, *Compt. rend.*, 1905, **140**, 1573.

[3] Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **24**, 224.

[4] Moissan, *Bull. Soc. chim.*, 1895, [iii.], **13**, 973.

[5] Moissan, *Compt. rend.*, 1899, **129**, 799.

[6] Ruff, Zedner, Schiller, and Heinzelmann, *Ber.*, 1909, **42**, 492–97.

Most substances when cooled to very low temperature become chemically inert. Fluorine, however, possesses very great chemical activity even at the lowest temperatures attainable.[1] For example, Moissan and Dewar [1] brought a glass tube containing solid fluorine at $-252 \cdot 5°$ in contact with liquid hydrogen at the same temperature—which is a temperature only $20 \cdot 5°$ removed from the absolute zero of temperature itself; and yet, on smashing the tube containing the frozen fluorine and thus allowing the liquid hydrogen to come into contact with it, a violent explosion took place which completely shattered to dust the glass apparatus in which the experiment was performed. Even at $-210°$ fluorine still retains its power of withdrawing hydrogen from some organic substances. Thus when turpentine, $C_{10}H_{16}$, at this temperature is brought into contact with fluorine at $-210°$ the turpentine inflames; while anthracene similarly treated causes explosion with separation of carbon. Sulphur burns in fluorine at $-187°$ C., forming SF_6; selenium causes an explosion at the same temperature; lime also becomes incandescent in liquid fluorine; red phosphorus and arsenic also inflame.

However, there are distinct indications that at its boiling-point fluorine is much less chemically active than at ordinary temperatures. For example, liquid fluorine does not liberate iodine from potassium iodide; neither does it unite with iodine at $-187°$; also substances such as Fe, B, Si, C, when previously cooled in liquid oxygen, do not react with liquid fluorine; Moissan showed that if a piece of charcoal or soot is allowed to drop into a vessel containing liquid fluorine, it becomes incandescent when it passes through the gaseous vapours, but the incandescence is quenched when the charcoal reaches and is immersed in the liquid fluorine.

Atomic Weight Determinations.[2]—The International Atomic Weight Commission in 1907 gave fluorine the atomic weight $19 \cdot 00$. O.T. Christensen [2] in 1887, by analysing the compound $4NH_4F.Mn_2F_6$, obtained $F = 19 \cdot 00$.

Moissan, in 1890, determined the atomic weight by converting the fluoride NaF into the sulphate Na_2SO_4, and in five experiments obtained numbers varying from $19 \cdot 04$ to $19 \cdot 08$ (O $= 16$). He next carried out a similar series of determinations by converting calcium fluoride, CaF_2, into calcium sulphate, $CaSO_4$, and as the result of four different determinations obtained numbers ranging from $19 \cdot 02$ to $19 \cdot 08$. Five similar experiments with BaF_2 gave $19 \cdot 05$ to $19 \cdot 09$ for the atomic weight of fluorine. The mean of all the determinations gave $F = 19 \cdot 05$.

J. Meyer, in 1903, transformed calcium oxide, CaO, into calcium fluoride, CaF_2, and thus obtained the number $19 \cdot 036$ for the atomic weight.

M'Adam and E. F. Smith,[3] in 1912, determined the atomic weight of fluorine by converting NaF into NaCl by passing dry HCl gas over the salt at $450°$ C. They obtained the values $F = 19 \cdot 0176$, $F = 19 \cdot 0133$ (Na $= 23 \cdot 000$).

The following table shows some older determinations (O $= 16$, Na $= 23$, S $= 32$, Ca $= 40$) :—

[1] Moissan and Dewar, *Compt. rend.*, 1897, **124**, 1202 ; 1903, **136**, 641, 785.

[2] The chief literature relating to the atomic weight of fluorine is as follows :—Davy, *Trans. Roy. Soc.*, **1814**, 64 ; Berzelius, *Ann. Chim. Phys.*, 1824, [ii.], **27**, 53, 167, 287 ; Louyet, *Ann. Chim. Phys.*, 1849, [iii.], **25**, 291 ; Fremy, *Ann. Chim. Phys.*, 1856, [iii.], **47**, 1 ; Dumas, *Ann. Chim. Phys.*, 1859, [iii.], **55**, 169 ; De Luca, *Compt. rend.*, 1860, **51**, 299 ; O. T. Christensen, *J. prakt. Chem.*, 1886, [ii.], **34**, 41 ; 1887, **35**, 541 ; H. Moissan, *Compt. rend.*, 1890, **111**, 570, 571 ; J. Meyer, *Zeitsch. anorg. Chem.*, 1903, **36**, 313.

[3] D. J. M'Adam and Edgar F. Smith, *J. Amer. Chem. Soc.*, 1912, **34**, 592.

Observer.	Atomic Weight.	Method.
Davy (1814) .	19·03	CaF_2 into $CaSO_4$.
Berzelius (1824) .	19·16, 18·85	CaF_2 into $CaSO_4$.
Louyet (1849) .	19·19, 18·99	Alkali- and alkaline-earth fluorides into sulphates.
Fremy (1856) .	18·85	Analysis of metallic fluorides.
Dumas (1859) .	18·96	Alkali- and alkaline-earth fluorides into sulphates.
De Luca (1860) .	18·96	Analysis of alkali- and alkaline-earth fluorides.

Detection of Fluorine.—A small piece of glass is covered with a thin film of melted beeswax, cooled, and some lines are made by a sharp but not hard point (otherwise the glass itself will be scratched, and the scratch may be mistaken for an etching), whereby the protective coat of wax is removed along the lines. The substance to be tested is placed in a dry condition in a small leaden cup or in a platinum crucible ; next it is covered with some concentrated sulphuric acid, and the crucible is gently warmed. If fluorides are present, hydrofluoric acid vapours are now evolved. The source of heat is now removed and the slip of waxed glass laid over the mouth of the vessel, waxed side downwards so as to be exposed to the action of the hydrofluoric acid vapours, and it is allowed to remain in this position for about ten minutes. The vapours etch the naked glass along the lines, but the wax protects the rest of the glass from its action ; consequently, on melting off the wax and rubbing with blotting-paper, the etched lines can be seen. If only a very small amount of fluorine is present, the etching may be hard to see, but is usually rendered visible by breathing on the surface of the glass.

Another very delicate test indeed for the presence of a fluoride consists in heating the substance with sand and sulphuric acid, when, if fluorine is present, the hydrofluoric acid evolved by the action of the sulphuric acid on the fluoride at once attacks the silica of the sand, SiF_4 is evolved, and hence, if a moistened glass rod is held in the gas evolved, a film of silica is produced on it if fluorine is present :—

$$2RF + H_2SO_4 = 2HF + R_2SO_4$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O$$
$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4.$$
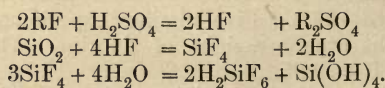
Estimation.—Insoluble metallic fluorides are fused with Na_2CO_3, whereby they are converted into soluble NaF. The product is extracted with water and nearly neutralised with HCl solution, care being taken, however, to leave a little free Na_2CO_3 in the solution. Next $CaCl_2$ solution is added, and a mixture of CaF_2 and $CaCO_3$ is precipitated. This is treated with acetic acid to remove the $CaCO_3$, washed with water, dried and ignited, and weighed as CaF_2.

In order to check the purity of the CaF_2 it may be warmed with concentrated sulphuric acid, and then heated until all the sulphuric acid is evaporated. There remains $CaSO_4$; e.g. CaF_2 yields 1·7409 grams $CaSO_4$. Sometimes the amount of fluorine is estimated volumetrically by adding to the substance to be analysed excess of pure SiO_2 and conc. sulphuric acid. On warming, all the fluorine is evolved as a gas, SiF_4, which is conducted from above into a Hempel's burette filled with mercury to a certain mark. The increase of volume gives the volume of SiF_4, whence the amount of F can be calculated.

FLUORINE AND HYDROGEN.

Only one compound is known, namely :—

HYDROFLUORIC ACID.

Formula, HF.   Molecular weight = 20·0.

Hydrofluoric acid is formed in many ways—for example, by the direct union of hydrogen and fluorine (see p. 28); by the action of hydrogen on many heated metallic and non-metallic fluorides (indeed, anhydrous HF has been prepared by heating AgF in a stream of H[1]); by blowing steam over red-hot metallic fluorides, whereby the oxide of the metal is produced and hydrofluoric acid formed; by the action of fluorine gas on hydrogen-rich organic substances; by the action of mineral acids on metallic fluorides; even weak organic acids like oxalic or tartaric or citric acid liberate hydrofluoric acid from certain fluorides.[2]

However, as regards the practical processes for preparing hydrofluoric acid, only two methods are employed, the one for making anhydrous pure hydrofluoric acid, and the other for making aqueous acid; we shall describe each in detail :—

(1) **Preparation of Anhydrous Hydrofluoric Acid.**[3]—Fremy[4] and Gore[5] obtain this volatile, very dangerous liquid by heating the double fluoride, KF.HF to redness in a platinum retort. The double salt, KF.HF, is first obtained as follows (Moissan) :—To 1 to 2 kilograms of pure aqueous hydrofluoric acid, containing 40–50 per cent. HF, and placed in a silver basin, the theoretical amount of pure potassium carbonate, K_2CO_3, is added in order to produce the substance KF.HF.

The double fluoride, on standing, gradually separates out from the solution in small transparent crystals. These are removed, pressed between filter-papers, and then dried *in vacuo*.

The dried salt is now rapidly transferred to a platinum retort (as no vessels of glass, porcelain, or substances containing SiO_2 can be employed, because hydrofluoric acid attacks them, thus—$SiO_2 + 4HF = SiF_4 + 2H_2O$). The platinum retort (A, fig. 5) is now gently heated so as to fuse the salt and drive off traces of water. The temperature is gradually raised, and acid begins to distil over—KF.HF = KF + HF. The first portion of the acid which distils is rejected, as it still contains some water. Next, the platinum retort is connected up to a platinum tube about 90 cm. long, which is surrounded by a freezing mixture of ice and calcium chloride, contained in B. The tube leads into a platinum receiver, c, likewise immersed in a freezing mixture, a platinum exit-tube, d, leading away from this. The apparatus is made air-tight at the joints by means of a lute of fused sulphur and lamp-black (in the hotter places), and by a lute of molten paraffin wax and lamp-black at the cooler joints. The hydrofluoric acid is evolved as a gas, condenses in the cooled platinum tube, and thence runs into the platinum receiver.

The heating is carried out very carefully and gradually, as towards the end of the operation "bumping" may occur. It is best to heat the walls

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[1] See Gore, *Trans. Chem. Soc.*, 1869, [ii.], **7**, 368.
[2] See Paternò and Alvisi, *Atti R. Accad. Lincei*, 1898, [iii.], **7**, i. 327 ; ii. 15 ; *Gazzetta*, 1898, **28**, ii. 18–24.
[3] An interesting historical account is given by F. D. Chattaway, *Chem. News*, 1913, **107**, 25, 26, 37–39.   [4] Fremy, *Ann. Chim. Phys.*, 1856, [iii.], **47**, 5.
[5] Gore, *Phil. Trans.*, 1869, **159**, 173.

of the retort and not the bottom for the same reason. The operation is finished when the bottom of the retort has been heated to redness.

The acid is redistilled from the water-bath under 39° C. in order to remove all traces of potassium fluoride which is often carried over by the gas coming from the decomposing salt ; all contact with air during the process must be avoided. Moissan[1] obtained 400 grams of anhydrous acid in one and a half hours by this method. According to the same authority, traces of moisture are still contained in the acid thus prepared, which can only be removed by electrolysing the liquid, when the water present is decomposed by the evolved fluorine, producing HF and ozone. The perfectly anhydrous acid thus obtained ceases to conduct the electric current once the water is completely destroyed.

Anhydrous hydrofluoric acid, thus obtained, is a most dangerous body. A drop in contact with the skin produces a sore which heals only after
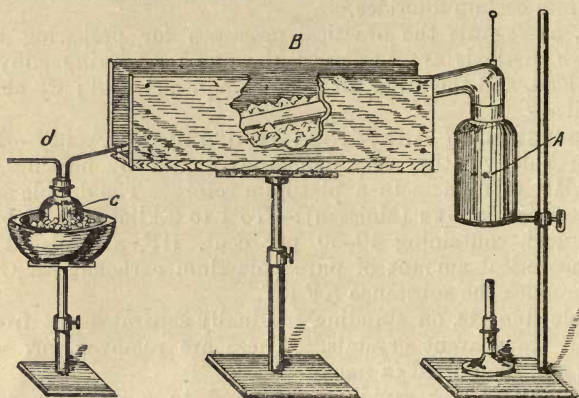
FIG. 5.—Preparation of anhydrous hydrofluoric acid.

months, while Professor Nickls of Nancy was killed in 1869 by accidentally breathing its vapour. Being exceedingly volatile, the water-free acid must be kept in platinum bottles with a flanged mouth, against which is securely clamped a platinum plate coated with paraffin wax. The bottle must be kept in a cool place, the temperature never being allowed to rise beyond 15° C. : otherwise the vessel may burst owing to the pressure developed by the volatile hydrofluoric acid ; for the same reason a freezing mixture should always be within reach when experimenting with the anhydrous acid (Gore).

(2) **Preparation and Manufacture of Aqueous Hydrofluoric Acid.**—In the laboratory this is usually carried out by heating fluorspar, CaF_2, with concentrated sulphuric acid in platinum or lead stills :—[2]

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
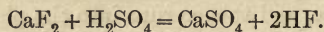
A nearly anhydrous acid distils over and may be condensed by passing through a **U**-tube immersed in a freezing mixture, or, if a dilute aqueous solution be required, into a little water placed in a platinum receptacle, and into which the neck of the flask just dips.

[1] Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **24**, 224.
[2] Gay-Lussac and Thénard, *Ann. Chim. Phys.*, 1809, [i.], **69**, 204.   See also H. J. Braun, *Ber.*, 1914, **47**, 646-56.

Illustrations of the apparatus used are shown in figs 6 and 7. A (fig. 6) is the retort (made of platinum or lead), B the still head, C the platinum U-tube which is immersed in a freezing mixture when the gaseous hydrofluoric acid has to be condensed. When, however, an aqueous solution has to be prepared, the second arrangement (fig. 7) is used. A is a leaden retort, with a leaden still head (B) leading into a vessel (C), also made of lead, and in this vessel is placed some pure water in a platinum dish (D). The acid vapours are absorbed by the water,[1] and thus a lead-free solution of hydrofluoric acid is obtained.

Any uncondensed hydrofluoric acid escapes by g.

Technically hydrofluoric acid is made[2] by heating calcium fluoride and sulphuric acid in large cast-iron vessels, and leading the evolved gas into water. The crude aqueous solution is transported in leaden vessels whose edges have been fused together by the blow-pipe.

Purification.—The aqueous acid of commerce contains,[3] as a rule, 39 to 55 per cent. HF, and impurities such as 2·7 to 14·9 per cent. H_2SiF_6,
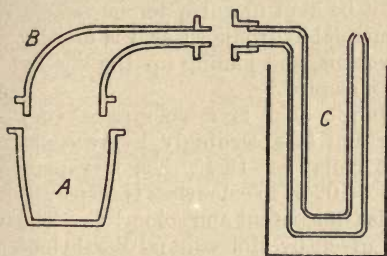
FIG. 6.—Preparation of aqueous hydrofluoric acid.
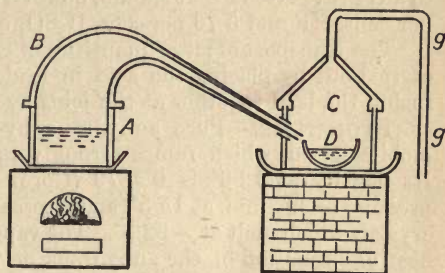
FIG. 7.—Preparation of aqueous hydrofluoric acid.

0·8 to 4 per cent. H_2SO_4, some SO_2, As, Fe, Ca, Pb. The silicofluoric acid, H_2SiF_6, is derived from the silica always contained in the native fluorspar, CaF_2, which is used in the manufacture of the acid, the silica present being acted on by hydrofluoric acid, thus—

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$
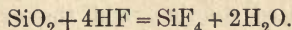
The SiF_4 distils over with the HF, and some collects in the aqueous acid—

$$2HF + SiF_4 = H_2SiF_6.$$
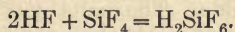
Similarly the iron, arsenic, SO_2, are derived from the fluorspar or from the sulphuric acid used in the manufacture, the lead usually coming from the vessels in which the acid is generated. When the fluorspar contains pyrites or lead sulphide, H_2S may be found in the acid.

The silicofluoric acid, H_2SiF_6, may be removed by adding a small amount of aqueous KOH solution, whereby K_2SiF_6 is precipitated. The clear supernatant solution is decanted and distilled.

[1] See Stromeyer, *Annalen*, 1856, **100**, 96 ; Briegler, *Annalen*, **111**, 380 ; Dexter, *Amer. J. Sci.* (Sill.), 1866, [ii.], **42**, 110 ; W. Hempel, *Ber.*, 1885, **18**, 1434.

[2] See Stahl, *Zeitsch. angew. Chem.*, 1896, **9**, 225 ; also L. Meyer, *D. R. Patent*, 142,931 (1900). A full account is given in Geoffrey Martin's *Industrial Inorganic Chemistry*.
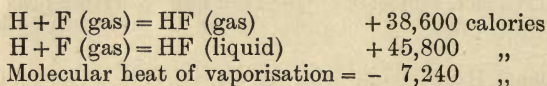
[3] Stahl, *loc. cit.*

According to Gore,[1] the best way to purify the acid is to dilute until it contains less than 40 per cent. HF, pass in H_2S until all the As and Pb, etc., are precipitated, add somewhat more K_2CO_3 than is required to neutralise the H_2SO_4 and H_2SiF_6 present, decant the liquid from the precipitated salts, remove any free H_2S still present by the cautious addition of Ag_2CO_3, AgF, or Ag_2O, and distil from a lead retort heated in an oil bath to 160°–240°, platinum condensing tubes and receiver being used. Contact with leaden vessels causes the acid to be contaminated with lead.[2]

Transport and Storage of the Aqueous Acid. — The pure acid is best kept in a platinum bottle with a platinum plate, covered with paraffin wax, securely clamped against it (Gore). However, the great cost of platinum makes this method, commercially, impossible. Pure aqueous acid for analytical purposes is therefore best kept in ceresine bottles.[3] Ordinary commercial acid may be kept in gutta-percha bottles, which is not much attacked even by fuming aqueous hydrofluoric acid, vulcanite bottles not being so suitable, and india-rubber, when vulcanised, also not being attacked to any great extent.[4] It should, however, be mentioned that acid containing 70 per cent. HF and 5·76 per cent. H_2SO_4 cannot be kept in gutta-percha vessels.

The transport of large quantities of commercial hydrofluoric acid is usually carried out by placing the acid in leaden vessels, and joining up the lids by fusing the lead together at the joins by the blowpipe.[5]

Properties.—Pure anhydrous hydrofluoric acid is a colourless, very mobile liquid, which fumes strongly in air and is exceedingly hygroscopic. Its density at 12·6° is 0·9879 (Gore). It boils[6] at 19·4°, has a vapour pressure of 394 mm. at 15·5°, and freezes[7] at − 102·5° to colourless transparent crystals which melt at − 92·3°. The vapour is transparent and colourless. The heat of formation of the anhydrous acid is given by Moissan and Berthelot[8] as follows :—

$$\text{H} + \text{F (gas)} = \text{HF (gas)} \qquad + 38{,}600 \text{ calories}$$
$$\text{H} + \text{F (gas)} = \text{HF (liquid)} \qquad + 45{,}800 \quad \text{,,}$$
$$\text{Molecular heat of vaporisation} = - 7{,}240 \quad \text{,,}$$

The perfectly anhydrous acid does not conduct the electric current,[9] and Moissan found that the last traces of water are best removed from it by electrolysing the liquid so long as it conducts, the water present being destroyed by the liberated fluorine, and the oxygen escaping as ozone. Liquid anhydrous hydrofluoric acid was shown by E. C. Franklin[10] to be a good solvent for salts such as NaF, NaBr, $NaClO_3$, $NaBrO_3$, $NaNO_3$, KF, KCl, K_2SO_4, urea, acetamide. The salts BaF_2, AgCN, $CuCl_2$ were only sparingly soluble, while CaF_2, $Cu(NO_3)_2$, $CuSO_4$, $FeCl_2$, HgO, PbF_2, and

[1] Gore, *Phil. Trans.*, 1869, **159**, 173.
[2] For other methods of purification see Thorpe and Hambly, *Trans. Chem. Soc.*, 1889, **55**, 103 ; Allen, *Analyst*, 1896, **21**, 87 ; Blount, *Analyst*, 1896, **21**, 87 ; Moissan, *Ann. Chim. Phys.*, 1891, [vi.], **24**, 224 ; Deussen, *Zeitsch. anorg. Chem.*, 1905, **44**, 303 ; W. Hempel, *Ber.*, 1885, **18**, 1438.
[3] See Stahl, *Zeitsch. angew. Chem.*, 1896, **9**, 225 ; E. Hart, *Zeitsch. anal. Chem.*, 1890, **29**, 444 ; Heräus, *Zeitsch. angew. Chem.*, 1895, **8**, 434.
[4] Städeler, *Annalen*, 1853, **87**, 137.
[5] Stahl, *loc. cit.*, also Eckelt, *Chem. Zeit.*, 1892, **16**, 17.
[6] Gay-Lussac and Thénard, *Ann. Chim. Phys.*, 1809, [i.], **69**, 204.
[7] Olszewski, *Monatsh.*, 1886, **7**, 371.
[8] Moissan and Berthelot, *Ann. Chim. Phys.*, 1891, [vi.], **23**, 570.
[9] L. Bleekrode, *Wied. Annalen*, 1878, **3**, 161.
[10] Franklin, *Zeitsch. anorg. Chem.*, 1905, **46**, 2.

metallic magnesium proved insoluble. The acid, when perfectly dry, does not act on glass, although the slightest trace of moisture causes it to become active in this respect, $SiO_2 + 2HF = SiF_4 + 2H_2O$, and of course once the action is started water is generated and so the acid soon becomes active. The anhydrous acid, also, scarcely acts upon non-metal or metals (with exception of the alkali metals) at ordinary temperatures. Thus Gore states that between $-29°$ C. and $-18°$ C. no action takes place when metals are brought into contact with the anhydrous acid, with the exception of sodium and potassium, which act on it as on water, dissolving with the simultaneous production of a flame. Zinc and cadmium act on the anhydrous acid at a red heat to produce fluorides, and reduced iron and chromium also attack it below a red heat, when they are converted into fluorides.

Aluminium is attacked at $1000°$ C., gold and platinum are unacted on at temperatures even higher than this, while copper is scarcely attacked at a red heat.[1] Crystallised silicon will catch fire in a heated stream of dry hydrofluoric acid gas. As regards the action on metals, however, the aqueous acid is far more active—as we shall see,—attacking practically all the metals to a greater or less extent, with the exception of platinum and the noble metals generally. Even copper and silver dissolve slowly in the aqueous acid, evolving hydrogen, while iron and zinc dissolve very rapidly, forming fluorides and generating hydrogen. The strong acid also dissolves silicon, tantalum, manganese, etc., forming fluorides and evolving hydrogen.

A mixture of nitric and hydrofluoric acids dissolves boron, silicon, niobium, and tantalum, but does not attack silicon carbide, the diamond, gold, or platinum.

The acid decomposes carbonates with effervescence, forming fluorides. Almost all metallic oxides are attacked by anhydrous or aqueous hydrofluoric acid.[2]

The acid unites with such oxides as P_2O_5, SO_3, MoO_3, V_2O_5, Nb_2F_5, WO_3, Sb_2O_5, Ta_2O_5.

Hydrofluoric acid decomposes some iodides, iodates, bromides, and bromates. However, such iodides as those of Zn, Cd, Pb, Hg, and Pt are not destroyed. Chlorides such as those of Ag, Hg, Pb, Cd, Mn, Ni, Co are not attacked. Also $KClO_3$ is not attacked by the aqueous acid.

This shows that the acid is considerably weaker than HCl, HBr, or even HI—a surmise borne out by measurements of the acid's inversion constant and electrolytic conductivity. See p. 40.

As regards the action of the anhydrous and aqueous acid on organic substances, it should be mentioned that methyl and ethyl alcohols are miscible with the substance, but are decomposed by it. Acids like oxalic, benzoic, etc., are not much affected. Benzene does not mix with the acid. Paraffin wax is not attacked. On the other hand, caoutchouc, amber, copal, gum-arabic, rosin, shellac, etc., are rapidly attacked, usually dissolving to form red liquids. Turpentine oil explodes and forms a red liquid. Seal oil, stearic acid, and myrtle wax are not attacked to any great extent. Silk, paper, cotton, gelatine, and pergament dissolve to sticky fluid masses. Horn swells up to a white mass, while flannel, sponge, and celluloid are only slowly attacked. Gaseous hydrofluoric acid (also the vapours from the aqueous acid) slowly carbonises cork, and acts on paper, silk, and wood in a similar manner
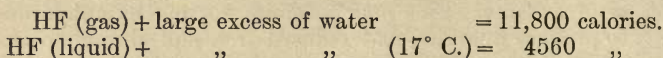
[1] Poulenc, *Ann. Chim. Phys.*, 1894, [vii.], **2**, 5.
[2] See, for example, van Haagen and E. F. Smith, *J. Amer. Chem. Soc.*, 1911, **33**, 1504.

to the aqueous acid, only rather more slowly. Coal, sulphur, and selenium are not altered, whereas ordinary sealing-wax absorbs the vapour, and becomes friable and soft. Caffein, indigo, milk sugar and other sugars are dissolved.

Hydrofluoric acid gas is extremely soluble in water, the anhydrous acid, in fact, possessing such an avidity for water that it rapidly attracts moisture from the air, fuming vigorously in so doing, and sometimes developing sufficient heat to cause ebullition.

Guntz[1] gives the following thermal data regarding the solution of the gas in water :—

$$HF \text{ (gas)} + \text{large excess of water} = 11,800 \text{ calories.}$$
$$HF \text{ (liquid)} + \quad \text{,,} \quad \text{,,} \quad (17° \text{ C.}) = \quad 4560 \quad \text{,,}$$

HEAT OF DILUTION OF THE AQUEOUS ACID.

Original Composition.	Final Composition.	Heat developed.
HF (0·00 H_2O)	HF.400H_2O	+ 4560 calories.
,, 0·50 H_2O	,,	+ 2050 ,,
,, 1·67 ,,	,,	+ 720 ,,
,, 2·25 ,,	,,	+ 450 ,,
,, 6·51 ,,	,,	+ 100 ,,
,, 12·03 ,,	,,	nearly 0 ,,

Thomsen[2] gives the heat of neutralisation of hydrofluoric acid as

$$(NaOH \text{ aq. } HF \text{ aq.}) = + 16,272 \text{ calories.}$$
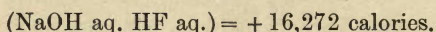
This is nearly 4 per cent. greater than that of sulphuric acid, and much greater than that of HCl, HBr, or HI—another point in which hydrofluoric acid departs in properties from those acids (see p. 11).

Thomsen showed that if a solution of caustic soda, NaOH, is exactly neutralised with hydrofluoric acid, thus

$$NaOH + HF = NaF + H_2O ;$$
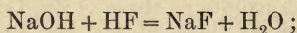
and to the neutral solution an excess of HF is added, a very considerable quantity of heat is *absorbed*, thus :—

$$(NaF \text{ aq., } HF \text{ aq.}) = - 288 \text{ calories.}$$
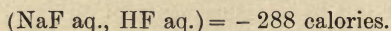
Hydrochloric acid does not exhibit this behaviour.

The heat of neutralisation of HF by NH_3 was determined by Guntz :—[3]

$$NH_3 \text{ (1 equiv. in 2 litres)} + HF \text{ (1 equiv. in 2 litres)} = NH_4F \text{ (solution)} + 15,200 \text{ calories.}$$
$$NH_3 \text{ (gas)} + HF \text{ (gas)} = NH_4F \text{ (solid)} + 37,300 \text{ calories.}$$
$$NH_3 \text{ (gas)} + HF \text{ (liquid)} = NH_4F \text{ (solid)} + 30,100 \quad \text{,,}$$
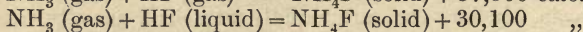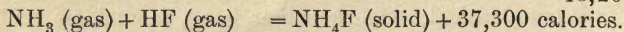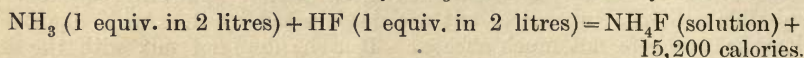
The heats of formation of various fluorides are discussed by Geoffrey Martin.[4]

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[1] Guntz, *Compt. rend.*, 1883, 96, 1659.
[2] Thomsen, *Thermochemische Untersuchungen*, i. 157.
[3] Guntz, *Ann. Chim. Phys.*, 1884, [vi.], 3, 5 ; *Compt. rend.*, 1883, 97, 1483. This author also determined the heat of formation of some other fluorides ; see Guntz, *Compt. rend.*, 1883, 97, 256, 1558 ; 1884, 98, 819.
[4] Geoffrey Martin, *Chem. News*, 1904, 89, 49 ; *Researches on the Affinities of the Elements*, p. 69.

When the concentrated aqueous acid is boiled it loses HF, until at 120° it attains a constant composition [1] of from 36 to 38 per cent. HF, the liquid thus obtained, however, not being a definite hydrate (see HCl, p. 104). When the aqueous acid is allowed to evaporate over slaked lime, $Ca(OH)_2$, it attains a constant composition of 32·6 per cent. HF. Conversely, when the diluted acid is distilled it concentrates, until at 120° a constant composition acid of 35·37 per cent. HF, and specific gravity 1·20 is attained.[2]

Gore[3] showed that by fractional distillation it is possible to get a fraction containing as much as 48·17 per cent. HF (boiling-point, 125–125·5°). Winteler[4] gives the following table of strengths of aqueous hydrofluoric acid. The percentage of HF in the solution was determined by titration with normal alkali, using as indicator phenolphthalein. Litmus and methyl orange were inapplicable. In order to determine the density, special pykno-meters made of vulcanite had to be used.

DENSITY AND COMPOSITION OF AQUEOUS HYDRO-FLUORIC ACID AT 20° C. (Winteler.)

% HF.	Sp. Gr.	° Bé.	% HF.	Sp. Gr.	° Bé.
1	1·003	0·5	26	1·092	12·0
2	1·007	1·0	27	1·095	12·4
3	1·011	1·5	28	1·098	12·7
4	1·014	2·0	29	1·101	13·1
5	1·018	2·5	30	1·104	13·4
6	1·023	3·0	31	1·106	13·7
7	1·027	3·5	32	1·109	14·1
8	1·030	4·0	33	1·112	14·4
9	1·035	4·5	34	1·114	14·7
10	1·038	5·0	35	1·117	15·0
11	1·041	5·5	36	1·120	15·4
12	1·045	6·0	37	1·122	15·7
13	1·049	6·5	38	1·125	16·0
14	1·052	7·0	39	1·127	16·3
15	1·055	7·5	40	1·130	16·5
16	1·059	8·0	41	1·133	16·8
17	1·062	8·4	42	1·136	17·2
18	1·066	8·8	43	1·138	17·5
19	1·069	9·3	44	1·141	17·8
20	1·072	9·7	45	1·143	18·1
21	1·076	10·1	46	1·146	18·4
22	1·079	10·5	47	1·149	18·7
23	1·082	10·9	48	1·152	19·0
24	1·086	11·3	49	1·154	19·3
25	1·089	11·7	50	1·157	19·5

A concentrated solution of hydrofluoric acid has a maximum density of 1·262 at 0° C. and contains 76·93 per cent. of HF; it fumes strongly in air, behaving in this respect like concentrated sulphuric acid.

[1] Bineau, *Ann. Chim. Phys.*, 1843, [iii.], **7**, 257.
[2] Roscoe, *Trans. Chem. Soc.*, 1861, 162.   [3] Gore, *Phil. Trans.*, 1869, **159**, 173.
[4] Winteler, *Zeitsch. angew. Chem.*, 1902, **15**, 33 ; see also Hill and Sirkar, *Proc. Roy. Soc.*, 1909, **A**, **83**, 130 ; and Eckelt, *Chem. Zeit.*, 1898, **22**, 225.

Aqueous hydrofluoric acid esterifies alcohols, and inverts sugar, acting in this respect like hydrochloric acid.

Hydrofluoric acid, judged from measurements of the inversion constant and its electrolytic conductivity, is a much weaker acid than hydrochloric acid. Thus its inversion constant[1] is only $\frac{1}{17}$th that of hydrochloric acid, being 5·7 for a N/1 solution, while that for N/1 monochloracetic acid is 4·7, and that for N/1 phosphoric acid is 6·0—so that the strength of hydrofluoric acid lies intermediate between that of monochloracetic acid and that of phosphoric acid. Determinations of the inversion constant of the greatly diluted acid, viz. 0·005 N to 0·10 N, showed that the inversion constant approached that of the weakly dissociated formic acid, rather than that of a strong mineral acid, such as dibasic sulphuric acid.

Measurements by Ostwald[2] on the electrolytic conductivity of the acid confirmed the above conclusions regarding the relative weakness of hydrofluoric acid as an acid. For example, Ostwald showed that solutions of hydrochloric acid containing 1 gram molecule in 4 litres solution had a conductivity no less than twelve times greater (viz. 78·9) than that of a hydrofluoric acid solution of the same relative dilution. The ionic mobility of the fluorine ion at 18° C. is 46·6, and at 25° C. is 54·4; the corresponding mobilities of the hydrogen ion being 314·5 and 350·0 respectively (see Volume I., p. 206). By Kohlrausch's law the molecular conductivity of hydrofluoric acid at infinite aqueous dilution at any particular temperature is the sum of the ionic mobilities of hydrogen and fluorine at that temperature. Thus at 25° C.

$$\mu_\infty = 350 \cdot 0 + 54 \cdot 4 = 404 \cdot 4.$$

The following table gives Deussen's[3] recent determination of the conductivity of aqueous hydrofluoric acid solutions:—

CONDUCTIVITY OF AQUEOUS HYDROFLUORIC ACID.

V = volume in which 1 gram molecule of HF is contained.
μ_0 = conductivity at 0°. μ_{25} = conductivity at 25°.

$\alpha_{25} = \dfrac{\mu_v}{\mu_\infty}$ = degree of dissociation.

V.	μ_0.	$\mu_{25}°$.	$\alpha_{25}°$.
1	18·94	24·46	0·060
2	20·42	26·17	0·065
4	23·57	29·88	0·074
8	28·30	36·21	0·090
16	36·60	46·37	0·114
32	47·39	60·8	0·150
64	61·55	80·7	0·20
128	81·2	106·7	0·26
256	105·8	140·8	0·35
512	135·8	181·5	0·45
1024	173	230	0·57

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[1] Deussen, *Zeitsch. anorg. Chem.*, 1905, **44**, 300, 408.
[2] See Ostwald, *J. prakt. Chem.*, 1885, [ii.], **32**, 303 ; R. Abegg, Fox, and Herz, *Zeitsch. anorg. Chem.*, 1903, **35**, 135.
[3] Deussen, *Zeitsch. anorg. Chem.*, 1905, **44**, 312, 315. See also Hill and Sirkar, *Proc. Roy. Soc.*, 1909, **A**, **83**, 130.

These numbers serve to show how weakly dissociated hydrofluoric acid is at a given concentration. The dissociation increases with the dilution, but even when the solution contains only 1 molecule HF in 1000 litres the acid is only half dissociated into ions.

The same fact regarding the relative weakness of hydrofluoric acid was confirmed by Thomsen [1] by a study of its thermal relations.

Thus by measurements of the heat evolved when one equivalent of HF acts on one equivalent of NaCl, and conversely when one equivalent of NaF acts on one equivalent of HCl, Thomsen showed that the "avidity" of hydrofluoric acid was only 5 to 6 per cent. of that of HCl. When 1 equivalent of HCl acts on 1 equivalent of NaF 95 per cent. of the NaF is converted into NaCl, and conversely when 1 equivalent of HF acts on 1 equivalent of NaCl only 5 per cent. of the NaCl is turned into NaF; from these results the "avidity" or hydrofluoric acid works out as 0·05. Now, this relative weakness of hydrofluoric acid compared with HCl, HBr, and HI is somewhat unexpected, as the avidity of the acids HCl, HBr, HI *increases* as the molecular weight *decreases*, and so we should have expected that HF would have been a *stronger*, not a weaker acid than hydrochloric acid—such, however, is not the case, as we have seen. The causes of this are discussed in Chapter I. p. 11.

Analogy between Water and Hydrofluoric Acid. — Martin [1] pointed out in 1905 that there exists a close analogy between *hydrofluoric acid* and *water*.

The following table was given [2] illustrating not only the physical but also the chemical resemblance between water and hydrofluoric acid :—

H_2O.	HF.	H_2O.	HF.
1. At an ordinary temperature water is a clear transparent mobile liquid. Boils at 100°. Freezes at 0°.	1. At an ordinary temperature HF is a clear, transparent, colourless, mobile liquid. Boils at 19·44°. Melts at −92·3°.	3. Liquid water at ordinary temperatures does not react as a rule on metals or non-metals. It, however, reacts with the alkali metals at ordinary temperature.	3. Liquid HF at −18° to −29° does not as a rule react on metals or non-metals except the alkali metals.
2. Water consists of complex molecules at ordinary temperatures. According to Ramsay and Shields the molecule is $(H_2O)_4$, according to other authors $(H_2O)_2$.	2. Complex molecules; probably varying in complexity from $(HF)_4$ to H_2F_2 and HF.	4. Liquid water reacts violently with many anhydrides, *e.g.* P_2O_5 and SO_3.	4. Liquid HF reacts violently with many anhydrides, *e.g.* P_2O_5 and SO_3.
		5. H_2O does not decompose the chlorides of the alkali metals, but it decomposes chlorides of P, Sb, Ti.	5. HF decomposes the chlorides of the alkali metals. And also the chlorides of P, Sb, and Ti.

Of all the halogen hydrides, HF is the one whose heat of formation most closely approaches that of water (34,000 calories to 37,200 calories);

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[1] See Thomsen, *Thermochemische Untersuchungen*, i. pp. 157, 158.
[2] Martin, *opus cit.*, p. 85. This volume, p. 8.

it is also the one that in most of its chemical properties most closely resembles water :—

(1) Its boiling-point lies nearest to that of water.

(2) Its range of fluidity (*i.e.* difference between boiling-point and melting-point) approaches nearest to that of water ($H_2O = 100°$, $HF = 111·74°$); while all the other hydrides, such as HCl, HBr, HI, are so volatile as to be gaseous at ordinary temperatures, water and HF are colourless mobile liquids.

(3) HF is a much weaker acid than HCl, HBr, or HI, and in this respect also tends to approach water, which is a practically neutral substance.

This analogy between water and hydrofluoric acid is only a particular instance of the analogy between oxides and fluorides (*vide infra*, p. 45).

Hydrates of Hydrofluoric Acid.—Many attempts have been made to isolate hydrates of hydrofluoric acid, corresponding to those of hydrochloric acid, but with little success. In 1894 Metzner[1] showed that while a 70 per cent. aqueous acid did not solidify at $-70°$ C., yet a 5 per cent. acid, when cooled to $-45°$ C., deposited crystals containing $52·3$ per cent. HF and corresponding to the formula $HF.H_2O$.

No other hydrate has been isolated.

Composition of Hydrofluoric Acid.—The composition by volume of anhydrous hydrofluoric acid was determined by Gore[2] by estimating the volume of hydrogen which combined with a calculated weight of fluorine contained in a given weight of silver fluoride. He found that when 1 volume of hydrogen was heated with the equivalent weight of silver fluoride (in which 19 parts by weight of fluorine were present) $2·005$ volumes of HF gas were obtained. Hence he concluded that 2 volumes of hydrofluoric acid gas are obtained from 1 volume of hydrogen gas, and that, moreover, for every 1 part by weight of hydrogen present there are 19 parts by weight of fluorine gas united with it.

This conclusion of Gore was confirmed by Moissan[3] in 1900, who determined the volumetric composition of hydrofluoric acid by measuring the volumes of hydrogen and of fluorine liberated by the electrolysis of hydrofluoric acid (see p. 24). The volume of hydrogen was directly measured in the ordinary way, whereas the volume of fluorine was estimated by leading it into water and measuring the volume of the liberated oxygen : $2F_2 + 2H_2O = 4HF + O_2$. On the assumption that 2 volumes of fluorine liberated 1 volume of oxygen, the amount of fluorine liberated was found to agree with the amount of liberated hydrogen. He also confirmed this result by the converse experiment. He took a measured volume of fluorine and allowed it to act on water, when hydrofluoric acid and oxygen gas were formed. The volume of oxygen liberated was measured, and the weight of hydrofluoric acid formed was estimated by titration. Knowing the density of anhydrous hydrofluoric acid, the volume of this weight of hydrofluoric acid could be calculated. The result confirmed that of Gore, namely, that 2 volumes of hydrofluoric acid gas were composed of 1 volume of hydrogen gas united with 1 volume of fluorine gas. The vapour density of hydrofluoric acid was accurately estimated by Thorpe and Hambly.[4] They showed that it varied rapidly with the temperature and pressure. The following table shows some of their results :—

[1] R. Metzner, *Compt. rend.*, 1894, **119**, 682.
[2] Gore, *Phil. Trans.*, 1869, **159**, p. 173.
[3] Moissan, *Compt. rend.*, 1900, **130**, 544.
[4] Thorpe and Hambly, *Trans. Chem. Soc.*, 1888, **53**, 765 ; 1889, **55**, 163.

Temperature, °C.	Vapour Pressure in mm.	Vapour Density (air=1).	Molecular Weight.
26·4	745	1·773	51·18
27·8	746	1·712	49·42
29·2	750	1·578	45·54
32·0	743	1·377	39·74
33·1	750 ·	1·321	38·12
33·8	758	1·270	36·66
36·3	739	1·115	32·20
38·7	751	1·021	29·46
39·2	743	1·002	28·94
42·8	741	0·910	26·26
47·3	745	0·823	23·76
57·5	750	0·737	21·28
69·4	746	0·726	20·96
88·1	741	0·713	20·58

These numbers show that the dissociation of hydrofluoric acid vapour is quite continuous, so that although at low temperatures the hydrofluoric acid molecules may be associated together, thus $(HF)_n$—where n is at least 2,— yet when the substance is perfectly gasified, viz. at temperatures over 70° C., the vapour then only seems to contain molecules of the formula HF.

Many authors have supposed that in a liquid state or at low temperatures molecules of constitution H_2F_2 exist. Thus Abegg,[1] in 1903, came to this conclusion from molecular weight determinations (by the cryoscopic method) of hydrofluoric acid and boric acid, while similar conclusions founded on similar experiments were put forward by Paternò and Peratoner[2] in 1895, although their conclusions are disputed by Pellini and Pegoraro[3] (1907, 1908). A. Jaeger[4] also (from experiments on the behaviour of hydrofluoric acid on mercuric oxide) thinks that H_2F_2 is the molecular weight of the acid, while R. Kremann and W. Decolle[5] came to the same conclusion from measurements of the electrolytic conductivities of HF solution. Blomstrand[6] (1869) assumes that fluorine is acting as a trivalent element in hydrofluoric acid, and gives it the formula H – F = F – H.

Walden,[7] however (1888), comes to the conclusion that in dilute aqueous solution the acid acts simply as a weak monobasic acid H – F, there being no evidence to show that it acts like a dibasic acid, as Blomstrand's formula would have it. Experiments on the electrolytic conductivity of the aqueous acid (see p. 40) seem to confirm Walden's conclusion, the acid resembling a weakly dissociated monobasic acid like formic acid, rather than a strong dibasic acid like sulphuric acid. The reader, however, should see Pellini and Pegoraro's paper in this connection,[3] and also the papers of Deussen[8] and Pick.[9]

[1] Abegg, *Zeitsch. anorg. Chem.*, 1903, **35**, 137.
[2] Paternò and Peratoner, *Atti R. Accad. Lincei*, 1895, [5], **6**, 606.
[3] Pellini and Pegoraro, *Zeitsch. Elektrochem.*, 1907, **13**, 621 ; *Gazz. Chim. ital.*, 1908, **38**, i. 1. [4] A. Jaeger, *Zeitsch. anorg. Chem.*, 1901, **27**, 28.
[5] R. Kremann and W. Decolle, *Monatsh.*, 1907, **28**, 917.
[6] Blomstrand, *Chemie der Jetzzeit*, 1869, pp. 210, 341.
[7] Walden, *Zeitsch. physikal. Chem.*, 1888, **2**, 61.
[8] Deussen, *Zeitsch. anorg. Chem.*, 1905, **44**, 300, 408.
[9] Hans Pick, *Festschrift W. Nernst*, 1912, 360–73.

Uses of Hydrofluoric Acid.—The chief use of hydrofluoric acid is the etching of glass.[1]   The divisions on the glass of eudiometers, thermometers, and scientific instruments generally are sometimes etched by hydrofluoric acid which is evolved from fluorspar and concentrated sulphuric acid placed in a long leaden trough, and above which are placed the glass tubes, covered with wax and having the wax scratched off where a mark is desired to appear on the glass.   A better plan is to carry out the etching in the cold by placing hydrofluoric acid in the trough and exposing the tube for some hours to the vapours arising therefrom, the trough being covered with folds of thick paper.

Pure hydrofluoric acid is used for smooth etchings, while its ammonium salt, NH_4F, is used for making matt etchings.

Another use is in the fermentation industries,[2] where it is added to the fermenting mashes in order to check the growth of wild yeasts, and also to prevent other sorts of fermentation, pure yeast being very insensitive to its action, while lactic acid fermentation is markedly hindered by its presence in the mash.   Not only is hydrofluoric acid used for this purpose, especially in distilleries, but also fluorides are used.

Hydrofluoric acid is made use of to some extent in causing the coagulation of rubber latex,[3] one preparation being known as " Purub."

A 1 to 2 per cent. solution of hydrofluoric acid is also used in engineering practice[4] for opening boring holes for petroleum or natural gas (the acid eating away siliceous matter), and also for removing sand from iron castings.

It is also used in the laboratory for analytical purposes, especially for the estimation of silica.[5]

Fluorides (for the individual fluorides see under the respective elements).—The fluorides of the metals are formed by acting on the metal, metallic oxide, hydroxide, or carbonate, with hydrofluoric acid.   Fluorine gas (which, however, is difficult to prepare) acts on numerous substances forming fluorides (p. 29).

The fluorides of the alkalies are soluble in water.   Silver fluoride is also soluble in water—differing markedly in this respect from silver chloride, bromide, or iodide.   The fluorides of the alkaline earths are insoluble in water—in which respect, again, hydrofluoric acid differs from hydrochloric acid. Many fluorides, especially those of non-metals, are gaseous at ordinary temperatures ; for example, we may mention BF_3, SiF_4, PF_3, PF_5, CF_4, AsF_5, SF_6. SbF_5 is a liquid which solidifies when cooled.

Most fluorides are stable bodies, not being decomposed by heating either alone or with carbon.

Even silver fluoride, AgF, and mercury fluoride, HgF_2, when heated, are not decomposed.   Silver fluoride, is, however, decomposed by hydrogen gas at a red heat, whereas calcium fluoride is unaffected.   Steam when passed

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[1] See Knight, *Chem. News*, 1905, **92**, 295.

[2] See W. Thomson, *Chem. News*, 1887, **56**, 132.   J. Effront, *Bull. Soc. chim.*, 1890, [iii.], **4**, 337 ; **5**, 734 ; **6**, 705 ; *Compt. rend.*, 1893, **117**, 559.   Märcher, *Zeitsch. f. spiritus-Ind.*, 1891, **13**, 217.   Heinzelmann, *ibid.*, 1891, **13**, 247.   A. Jörgensen and Holm, *Monit. scient.*, 1893, [4], **7**, 179.   H. Will and R. Braun, *Zeitsch. f. ges. Brauwesen*, 1904, **27**, 521.

[3] See D. Sandmann, *D.R.P.*, 189,235 (1906).   Geoffrey Martin, *Industrial Chemistry*, vol. i.

[4] Stahl, *Zeitsch. angew. Chem.*, 1896, **9**, 225.

[5] See R. Fried, *Zeitsch. angew. chem.*, 1903, **16**, 176.   L. Smith, *Compt. rend.*, 1878, **87**, 146.

over calcium fluoride heated to redness, however, completely decomposes it. Most metallic fluorides are completely decomposed by heating with conc. H_2SO_4, with evolution of hydrofluoric acid. Concentrated HNO_3 decomposes many, but fluorides such as CaF_2 withstand its action ; also HCl gas, when passed over fluorides heated to redness in a platinum tube, causes the evolution of HF. NaF and CaF_2 are thus decomposed by HCl gas, with evolution of HF and formation of the corresponding chlorides. However, CrF_3, ZnF_2, and AlF_3 withstand this action of HCl gas.

Martin[1] undertook an extended study of the physical and chemical properties of the fluorides as a class in order to compare them with the corresponding oxides and chlorides. He showed : (1) that the heats of forma-tion of the fluorides (so far as they are known) stand closer to the heats of formation of the oxides than to those of the corresponding chlorides ; (2) that when we contrast an oxide and the corresponding fluoride, on the one hand, with the same oxide and the corresponding chloride on the other, the oxide and the fluoride approach each other much more closely as regards their stability than do the oxide and chloride ; in fact, when the oxides of an element are unstable and the chlorides stable, the fluorides follow the oxides in being unstable ; (3) that the *non-metallic* fluorides (like the oxides) are *more volatile* than the non-metallic chlorides ; (4) that the *metallic* fluorides (like the oxides) are *less* volatile than the metallic chlorides. As the result of this comparative study, it is clear that a considerable analogy exists between the oxides and the fluorides.

Most of the fluorides unite with hydrofluoric acid to form crystalline com-pounds which are termed *acid fluorides*—we have, for example, already referred to the body KF.HF, which has been used for the preparation of pure HF. This capacity for forming acid fluorides has given rise to the idea that hydrofluoric acid was a dibasic acid, like sulphuric : —

$$H - F = F - H + NaOH = NaF.FH + H ;$$
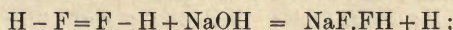
however, the evidence seems against this view (see p. 43).

Moissan brought to light a whole series of these acid potassium fluorides, the formation of which is attended with the evolution of considerable quantities of heat. Thus we have :—[2]

KF	(solid) + HF	(liquid)	= KF.HF	(solid) + 13·9	Calories.
KF	,, + 2HF	(gas)	= KF.2HF	,, + 35·2	,,
KF	,, + 3HF	,,	= KF.3HF	,, + 47·1	,,
KF.HF	,, + HF	(liquid)	= KF.2HF	,, + 6·5	,,
KF.KF	,, + 2HF	,,	= KF.3HF	,, + 11·6	,,
KF.2HF	,, + HF	,,	= KF.3HF	,, + 5·1	,,

Similar acid salts are produced by dissolving silver fluoride, AgF, in hydrofluoric acid by gently warming. On cooling the solution, crystals of the composition AgF.3HF separate. This latter compound, when dried in a stream of air at $0°$ C., decomposes, yielding the compound AgF.HF. Fluorides

[1] See Geoffrey Martin, *opus cit.* (1905), pp. 69–78, 85–86 ; see also *Chem. News*, 1904, **89**, 49. The analogy of the fluorides to the chlorides is discussed by P. Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, **31**, 192.
[2] Guntz, *Bull. Soc. chim.*, 1895, [iii.], **13**, 114.

such as NH_4F, NaF, RbF, CrF_3, UF_4 all dissolve in anhydrous hydro-fluoric acid, combining with it vigorously to form double acid fluorides.[1] The fluorides of Li, Ba, and Ag also react with anhydrous HF, but do not dissolve therein. The fluorides of Hg, Cu, Sb, Bi, Sn, Pb, Ni, Co, Mn, Fe, Mg, Al, Ce, Zn, Cd do not, apparently, either dissolve or react with anhydrous hydrofluoric acid.

Boron fluoride, BF_3, and silicon tetrafluoride, SiF_4, unite with hydro-fluoric acid to produce complicated acids, which, according to Werner,[2] are produced thus :—

$$FB \begin{matrix} F \\ \\ F \end{matrix} + HF \quad = \quad FB.FH \begin{matrix} F \\ \\ F \end{matrix} \quad \rightarrow \quad (BF_4)H$$

$$F.SiF \begin{matrix} F \\ \\ F \end{matrix} + 2HF \quad = \quad F\underset{F}{\overset{F}{Si}}\cdot\begin{matrix} FH \\ .FH \end{matrix} \quad \rightarrow \quad [SiF_6]H_2.$$
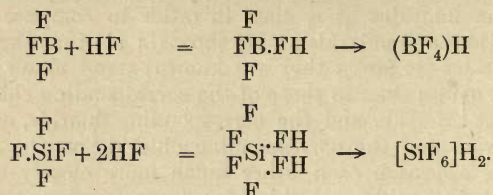
These substances are known, respectively, as borofluoric and silicofluoric acid.

Böhm[3] describes the whole series of complex acid fluorides which contain water of crystallisation thus :—

$$HgF_2.4H_2O.4HF \; ; \; CuF_2.5H_2O.5HF \; ; \; NiF_2.6H_2O.5HF \; ; \; CoF_2.6H_2O.5HF.$$
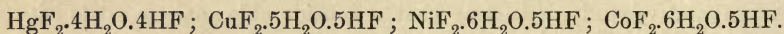
In addition to their capacity for uniting with hydrofluoric acid to produce "acid fluorides," the metallic fluorides possess, to a remarkable degree, the capacity for uniting among themselves[4] to produce *double fluorides*—which are often beautifully crystalline compounds.

As typical of these double salts may be mentioned the following: $SiF_4.2KF$; $AlF_3.3KF$; $AlF_3.3NaF$; $AlF_3.3NH_4F$; $AlF_3.3LiF$; $FeF_3.4KF$; $BF_3.KF$; $BeF_2.2KF$; $FeF_2.2KF$; $ZnF_2.2KF$; $CuF_2.2KF$. Many similar compounds have been described.

A complete list of all the known double fluorides was drawn up by Barteczko[5] in 1900, of which the following list gives a summary. Those fluorides enclosed in brackets [ ] consist of types only known as compounds of HF. In general, M stands for a metal :—

(1) *Monovalent elements* Li, Na, (NH_4), K, Rb, Cs, Ag, Hg, Tl.

Li	Na	NH$_4$	K	Rb	Cs	Ag	Hg	Tl
[LiF$_2$M]	[NaF$_2$M]	[NH$_4$F$_2$M]	[KF$_2$M]	[RbF$_2$M]	[CsF$_2$M]	[AgF$_2$M]	[HgF$_3$M$_2$]	[TlF$_2$M]
...	...	...	[KF$_3$M$_2$]	[RbF$_3$M$_2$]	...	[AgF$_3$M$_2$]	...	...
...	...	...	[KF$_4$M$_3$]	[RbF$_4$M$_3$]	...	[AgF$_4$M$_3$]	...	...

[1] See A. Ditte, *Compt. rend.*, 1896, **123**, 1281 ; Eggeling and Meyer, *Zeitsch. anorg. Chem.*, 1905, **46**, 174 ; F. C. Franklin, *Zeitsch. anorg. Chem.*, 1905, **46**, 2.
[2] A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (Braunschweig, 1913).
[3] E. Böhm, *Zeitsch. anorg. Chem.*, 1905, **43**, 326.
[4] See P. Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, **31**, 192.
[5] Paul Barteczko, *Dissertation* (Bern, 1900), 20.

(2) *Divalent elements* Ca, Mg, Be, Zn, Cd, Cu, Fe, Co, Ni, Sn.

$\ddot{C}a$	$\ddot{M}g$	$\ddot{B}e$	$\ddot{Z}n$	$\ddot{C}d$
... [CaF_4M_2]	MgF_3M MgF_4M_2	BeF_3M BeF_4M_2	... ZnF_4M_2	CdF_3M ...

$\ddot{C}u$	$\ddot{F}e$	$\ddot{C}o$	$\ddot{N}i$	$\ddot{S}n$
... CuF_4M_2 CuF_7M_5 ...	FeF_3M FeF_4M_2 ...	CoF_3M CoF_4M_2 CoF_7M_5 ...	NiF_3M NiF_4M_2 NiF_7M_5 ...	... SnF_4M_2 ... $Sn_3F_8M_2$

(3) *Trivalent elements* B, Al, Sb, Bi, Di, La, Fe, Cr, Mn, U, V, Ti.

$\dddot{B}$	$\dddot{A}l$	$\dddot{S}b$	$\dddot{B}i$	$\dddot{D}i$	$\dddot{L}a$
BF_4M BF_5M_2	AlF_4M AlF_5M_2 AlF_6M_3 AlF_7M_4 ... Al_2F_7M $Al_2F_9M_3$ $Al_2F_{11}M_2$ ... $Al_3F_{14}M_5$	SbF_4M SbF_5M_2 SbF_6M_3 ... Sb_2F_7M ... ... $Sb_3F_{10}M$ ... $Sb_4F_{13}M$ ... $Sb_7F_{25}M_4$	... ... BiF_6M_3	DiF_4M ... DiF_6M_3 ... ... Di_2F_7M ... ... $Di_4F_{15}M_3$ ...	... ... $La_2F_9M_3$ ... ...

$\dddot{F}e$	$\dddot{C}r$	$\dddot{M}n$	$\dddot{U}$	$\dddot{V}$	$\dddot{T}i$
FeF_4M FeF_5M_2 FeF_6M_3 ... ... $Fe_2F_9M_3$ ...	... CrF_5M_2 CrF_6M_3 ... ... $Cr_2F_9M_3$ ...	MnF_4M MnF_5M_2	... ... $UF_{11}M_8$	VF_4M VF_5M_2 VF_6M_3 ... ... $V_2F_{11}M_5$	... TiF_5M_2 TiF_6M_3 ... ...

(4) *Tetravalent elements* Te, Si, Ge, Sn, Ti, Zr, Ce, Mn, Pb, Th, U.

Te	Si	Ge	Sn	Ti	Zr
TeF_5M	...	...	...	...	ZrF_5M
...	SiF_6M_2	GeF_6M_2	SnF_6M_2	TiF_6M_2	ZrF_6M_2
...	SiF_7M_3	...	...	TiF_7M_3	ZrF_7M_3
...	...	...	SnF_8M_4	TiF_8M_4	ZrF_8M_4
...	...	...	...	...	Zr_2F_9M
...	...	...	...	...	$Zr_2F_{13}M_5$
...	...	...	...	...	...
...	...	...	...	...	$Zr_3F_{14}M_2$
...	$Si_3F_{17}M_5$	...	...	...	$Zr_3F_{17}M_5$

Ce	Mn	Pb	Th	U
...	...	...	ThF_5M	UF_5M
...	MnF_6M_2	...	ThF_6M_2	UF_6M_2
...	...	...	...	...
...	...	PbF_8M_4	..	...
...	...	...	..	...
...	...	...	...	...
$Ce_3F_{11}M_3$	...	...	...	...

(5) *Pentavalent elements,* As, Sb, Nb, Ta.

As	Sb	Nb	Ta
...	SbF_6M	...	TaF_6M
AsF_7M_2	SbF_7M_2	NbF_7M_2	TaF_7M_2
...	...	...	TaF_8M_3
...	...	$NbF_{10}M_5$	...
...	...	$NbF_{12}M_7$	...
...	...	...	$TaF_{20}M_{15}$

Werner [1] discusses the formation of these double salts according to his coordination theory. He explains the formation by formulæ such as these:—

$$\begin{matrix} F \\ FAl \\ F \end{matrix} + 3NaF = \begin{matrix} F\ .FNa \\ FAl.FNa \\ F\ .FNa \end{matrix} \longrightarrow [AlF_6]Na_3$$

$$\begin{matrix} F \\ F \end{matrix}Fe + 2KF = \begin{matrix} F \\ F \end{matrix}Fe\begin{matrix} .FK \\ .FK \end{matrix} \longrightarrow [FeF_4]K_2.$$
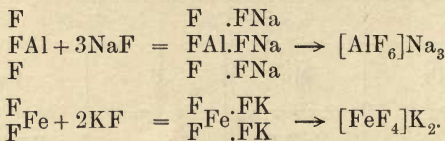
Proceeding in this manner, Werner arranges the double fluorides in types, such as the following :—

$[AlF_6]R_3$; $[FeF_6]R_3$; $[CrF_6]R_3$; $[TlF_6]R_3$; $[SnF_6]R_3$;
$[SiF_6]R_2$; $[TiF_6]R_2$; $[ZrF_6]R_2$;
$[CoF_4]R_2$; $[NiF_4]R_2$; $[CuF_4]R_2$;
$[BF_4]R.$
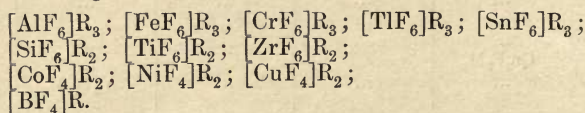
In these R stands for a monovalent metallic radicle.

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[1] A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (Braunschweig, 1913).

A large class of fluorides exist in which part of the fluorine is displaced by oxygen. These are termed "oxyfluorides," and as typical of these may be mentioned [1] the compounds WOF_4, VO_2F, VOF_2. These oxyfluorides also unite with other fluorides to give rise to double oxyfluorides; for example:—

$$2KF.VO_2F \; ; \; 3NH_4Cl.VOF_2.$$
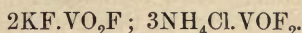
Barteczko [2] has compiled the following table of the principal types of these oxyfluorides:—

III. BiO—	IV. MnO=	IV. VO=	IV. TiO2=
$[(BiO)F_3M_2]$	$(MnO)F_4M_2$	$(VO)F_4M_2$	$(TiO_2)F_4M_2$
...	...	$(VO)F_5M_3$	$(TiO_2)F_5M_3$
...	...	$(VO)_3F_{13}M_4$	$(TiO_2)F_6M_2$
...	...	$(VO)_3F_{14}M_8$	$(TiO_2)F_7M_3$
...	...	$(VO)_4F_{15}M_7$	...

V. AsO≡	V. MoO≡	V. VO≡	V. VO2—	V. NbO≡	V. NbO2—	V. TaO≡
$(AsO)F_4M$	$(MoO)F_5M_2$	$(VO)F_5M_2$	$(VO_2)F_3M_2$	$(NbO)F_4M$	$(NbO_2)_3F_5M_2$	$(TaO)F_6M_3$
...	$(MoO)_3F_{14}M_5$	$(VO)_2F_9M_3$	$(VO_2)F_4M_3$	$(NbO)F_5M_2$	...	$(TaO)F_7M_4$
...	...	...	$(VO_2)F_5M_4$	$(NbO)F_6M_3$	...	...
...	...	...	...	$(NbO)F_7M_4$	...	...
...	...	...	...	$(NbO)_3F_{13}M_4$	...	...
...	...	...	...	$(NbO)_3F_{14}M_5$	...	...

VI. MoO=	VI. WO2=	VI. UO2=
$(MoO_2)F_3M$	$(WO_2)F_3M$	$(UO_2)F_3M$
$(MoO_2)F_4M_2$	$(WO_2)F_4M_2$	$(UO_2)F_4M_2$
$(MoO_2)F_5M_3$	$(WO_2)F_5M_3$	$(UO_2)F_5M_3$
$(MoO_2)_3F_{11}M_5$	...	$(UO_2)F_6M_4$
...	...	$(UO_2)_2F_7M_3$
...	...	$(UO_2)_2F_9M_5$
...	...	$(UO_2)_2F_{10}M_6$

[1] See Melikoff and Kasanezky, *Zeitsch. anorg. Chem.*, 1901, **28**, 242 ; Ephraim, *Zeitsch. anorg. Chem.*, 1903, **35**, 80 ; Miolati and Alvisi, *Atti R. Accad. Lincei*, 1898, [v.], **6**, ii. 376. The constitution of the oxyfluorides is discussed by A. Werner in his book *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (Braunschweig, 1913).
[2] Paul Barteczko, *Dissertation* (Bern, 1900).

FLUORINE AND OXYGEN.

No oxide of fluorine is known, and, apparently, none are capable of existing.

Recently Ruff and Zedner [1] tried to induce F and O to unite by heating them together to the temperature of the electric arc, but no combination took place.

Gallo [2] attempted to prepare an oxygen compound of fluorine by subjecting a mixture of the two gases to the action of an electric discharge in an apparatus similar to that employed for the preparation of ozone. A violent explosion took place, and no traces of an oxygen compound could be detected.

Fluorine, in fact, has only an extremely small chemical attraction for oxygen.

Moreover, no fluorine compounds corresponding to hypochlorites, chlorates, etc., are known. When fluorine gas is led into aqueous alkalies ozone and fluorides are generated, but no hypofluorites or similar compounds—which, if they are capable of existing at all, must be extremely unstable.

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[1] Ruff and Zedner, *Ber.*, 1909, 42, 1037–46.
[2] Gino Gallo, *Atti R. Accad. Lincei*, 1910, [v.], 19, i. 295, 753.

CHAPTER III.

CHLORINE AND ITS COMPOUNDS.

CHLORINE.

Symbol, Cl.   Atomic weight, 35·46 (O = 16).

Occurrence.—Chlorine is a very widely distributed element. In the form of its compounds enormous quantities occur locked up in the soil and the sea, while it is always present in living matter. In sea-water the average amount of chlorine is 2·07 per cent., while the solid crust of the earth contains about 0·01 per cent. of chlorine.[1]

Free chlorine never occurs in nature—no doubt on account of its great chemical activity. Combined with hydrogen, as hydrochloric acid, however, chlorine occurs in considerable quantities in the gases evolved from volcanoes, and in the waters which take their rise in volcanic regions : for example, the Rio Vinagre of Mexico yields daily 42,150 kg. of free hydrochloric acid.[2] Free hydrochloric acid also occurs in the stomachs of most animals : for example, the gastric juice of the dog contains about 0·6 per cent. of free hydrochloric acid.

By far the greatest amount of chlorine occurs combined with the metals sodium, potassium, and magnesium in the form of chlorides. For example, the solid components of sea-water[3] consist mainly of sodium, potassium, and magnesium chlorides,[3] and small quantities of salt also occur in rain water[4] and in the air.[5] Enormous deposits of rock salt (NaCl) occur in Tertiary formations in various parts of the earth's surface. For example, the mines at Wielicza, in Galicia, have been worked continuously for 600 years, and the salt deposits here are said to be 500 miles long, 20 miles broad, and 1200 feet thick. Vast deposits are also found at Stassfurt (Germany), Cheshire (England), Cardona (Spain), California, Utah, Kansas, Michigan, Virginia, and other places in the United States, also in Russia and China. Potassium chloride, KCl, although occurring less abundantly than sodium chloride, is also found in certain salt beds, as in the Stassfurt salt beds, both

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[1] See Vogt, *Zeitsch. prakt. Geol.*, **1898**, p. 226.
[2] Boussingault, *Compt. rend.*, 1874, **78**, 453, 526, 593.
[3] As regards the amount of chlorine in the various seas, see C. Schmidt, *Jahresber.*, **1877**, 1374 ; Moss, *Proc. Roy. Soc.*, 1878, **27**, 544 ; Berlund, *Ber.* 1885, **18**, 2888 ; v. Lill, *Jahresber.*, **1884**, 2031 ; van Laas, *Chem. Zentral.*, 1905, ii. 1047.
[4] Warrington, *Trans. Chem. Soc.*, 1887, **51**, 500 ; Miller, *J. of Agric. Science*, 1906, i. 280 ; Harrison and Williams, *J. Amer. Chem. Soc.*, 1897, **19**, 1.
[5] See Gautier, *Compt. rend.*, 1845, **21**, 715 ; Jorissen, *Chem. Zentral.*, 1906, ii. 1579.

in the pure state, as sylvine, KCl, and in the form of a double compound with magnesium chloride as carnallite, $KCl.MgCl_2 + 6H_2O$.

In small quantities the chlorides and oxychlorides of a great many metals are found in nature. For example, the following well-known minerals may be mentioned:—cotunite, $PbCl_2$; matlockite, $PbO.PbCl_2$; phosgenite, $Pb_2Cl_2CO_3$; coleite, $3(PbCl_2.Cu(OH)_2)$; molysite, $FeCl_3$; douglasite, $2KCl.FeCl_2.2H_2O$; lawrencite, $FeCl_2$; calomel, Hg_2Cl_2; terlinguaite, Hg_2ClO; eglestonite, $Hg_6Cl_3O_2$; hornsilver, kerargyrite, $AgCl$; nantokite, $CuCl$; atacamite, $Cu_2Cl(OH)_3$; scalite, $MnCl_2$; daubreite (a bismuth oxychloride); bischofite, $MgCl_2.6H_2O$; chlorine also often occurs in apatite, where it is stated to partially replace fluorine. It also occurs in certain silicates.

Chlorides also occur in the bodies of plants and animals, and are vital necessities.[1] Salt, NaCl, for example, occurs in the blood and in urine; potassium chloride, KCl, occurs in flesh; milk and albumin contain much KCl and only a little NaCl. 100 parts of human blood contain 0·259 part of chlorine; 100 parts of serum contain 0·333 part of Cl.[2] Human teeth contain 0·24 to 0·41 per cent. of Cl, against 0·17 per cent. Cl contained in the teeth of animals.[3]

History.—In 1774 Scheele[4] found that a yellowish-green gas, soluble in water, is evolved when hydrochloric acid is heated with the oxidising agent, manganese dioxide. This, we now know, is the element chlorine. In accordance with the views then prevailing, Scheele explained his observation by assuming that this yellow gas was simply hydrochloric acid ("muriatic acid") deprived of its phlogiston. Hence he christened it "dephlogisticated muriatic acid." Berthollet in 1785 came to the conclusion that it contained oxygen.[5] Some years afterwards Lavoisier put forward the theory that oxygen is a necessary constituent of all acids, and, applying this theory in 1789 to Scheele's observations, he came to the conclusion that "dephlogisticated muriatic acid," must be simply an oxide of muriatic acid (hydrochloric acid), the relation between muriatic acid and Scheele's yellow gas being similar to that between sulphurous and sulphuric acid. He called chlorine "oxymuriatic acid," and considered that both this and hydrochloric acid (muriatic acid) were compounds of oxygen with a hypothetical muriatic base, "murium." The mode of formation of chlorine (viz. by heating hydrochloric acid with an oxidising agent) and C. L. Berthollet's observation that an aqueous solution of chlorine in water gave off bubbles of oxygen gas, with the gradual formation of hydrochloric acid, made this view of Lavoisier appear very plausible.

In 1809 Gay-Lussac and Thénard[6] further investigated "oxymuriatic acid," as chlorine was now called. They tried to deoxidise it so as to isolate Lavoisier's hypothetical "muriatic base," by passing the dry gas over red-hot carbon, but failed to obtain from the oxymuriatic acid anything but itself. Reviewing their facts, Gay-Lussac and Thénard favoured Lavoisier's theory, but pointed out that the facts could also be explained on the hypothesis that oxymuriatic acid is an elementary body.

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[1] See Grünwald, *Zentr. physiol.*, 1908, **22**, No. 16.

[2] See Wanach, *Jahresber.*, 1889, p. 2159; Magnus-Levy, *Biochem. Zeitsch.*, 1910, **24**, 363; Rosemann, *Pflüger's Archiv*, 1911, **142**, 447, 459.

[3] Gassmann, *Zeitsch. physiol. Chem.*, 1908, **55**, 455.

[4] Scheele, *opus cit.*, i. 247.

[5] Berthollet, *Mém. de l'Acad. des Sciences* (Paris, 1785), p. 276.

[6] Gay-Lussac and Thénard, *Mémoires d'Arcueil*, **2**, 357; *Recherches*, **2**, 93. See also Gay-Lussac, *Ann. Chim.*, **91**, 96; *Schweigger's J.*, 1815, **14**, 79.

Davy,[1] in 1810, made repeated attempts to decompose oxymuriatic acid. He passed hydrochloric acid gas over heated metallic sodium and potassium, and found that only sodium or potassium chloride was formed along with free hydrogen gas. No water or free oxygen was obtained in these experiments, and so he came to the conclusion that, since from oxymuriatic acid nothing simpler than itself has ever been obtained, the substance must be an element. He proposed the name "chlorine" and the symbol Cl to denote this new elementary substance, deriving the name from chloros ($\chi\lambda\omega\rho\sigma$), greenish yellow.

Preparation for Laboratory Use : (1) *From Manganese Dioxide and Hydrochloric Acid.*—This is the usual method employed in the laboratory when a high degree of purity is not required. One part of manganese dioxide in the form of small lumps free from powder is placed in a flask (A, fig. 8), and four parts of concentrated hydrochloric acid are poured on, the quantity being insufficient to completely cover the manganese dioxide. The mixture is then gently heated, when chlorine is evolved, thus :—

$$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O.$$
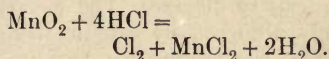
The gas is usually passed through a wash-bottle containing water, which absorbs any hydrochloric acid carried

Fig. 8.—Laboratory preparation of chlorine.

over, then through a wash-bottle containing concentrated sulphuric acid, to dry it, the last traces of moisture being removed by passing the gas through a long inclined tube filled with fragments of pumice moistened with sulphuric acid, which has been previously boiled.

The exact mechanism of the action is still a matter of dispute. A dark greenish-brown solution is first formed,[2] which undoubtedly contains an unstable higher chloride of manganese, such as $MnCl_4$ or $MnCl_3$, and the chlorine is evolved by the decomposition of the higher chloride.

According to one theory[3] manganese tetrachloride, $MnCl_4$, is first formed, which then decomposes, according to the equations :—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O,$$
$$MnCl_4 = MnCl_2 + Cl_2.$$
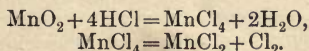
According to R. J. Meyer and H. Best,[3] the chloride $MnCl_4$ is not capable of existing in a free condition, but exists in solution or in the form of a double salt, such as $MnCl_4.2KCl$.

[1] Davy, *Phil. Trans.*, 1811, pp. 1 and 32 ; Bakerian Lecture for 1810.
[2] Berthelot, *Compt. rend.*, 1880, 91, 251.
[3] See Nicklès, *Compt. rend.*, 1865, 60, 479 ; Fischer, *Trans. Chem. Soc.*, 1878, 33, 409 ; Vernon, *Proc. Chem. Soc.*, 1890, 58 ; Meyer and Best, *Zeitsch. anorg. Chem.*, 1899, 22, 169 ; Wacker, *Chem. Zeit.*, 1900, 24, 285 ; Holmes and Manuel, *J. Amer. Chem. Soc.*, 1908, 30, 119 ; see also under Manganese Trichloride, p. 273.

According to another theory a chloride $MnCl_3$ or Mn_2Cl_6 is first formed by the action of hydrochloric acid on manganese dioxide, and chlorine is then evolved by the breakdown of this trichloride into the dichloride ; [1] thus :—

$$2MnO_2 + 8HCl = 4H_2O + 2MnCl_3 + Cl_2 ;$$
then $$2MnCl_3 = 2MnCl_2 + Cl_2.$$
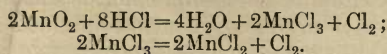
G. Neumann [2] actually prepared the double salts $2KCl.MnCl_3$ and $2NH_4Cl.MnCl_3$, and assumes the existence of $MnCl_3$ in solution. Christensen [3] assumes that the following actions take place when concentrated HCl acts on MnO_2 :—

(1) $MnO_2 + 6HCl = MnCl_4.2HCl + 2H_2O.$
(2) $MnCl_4.2HCl = Cl_2 + MnCl_2 + 2HCl.$
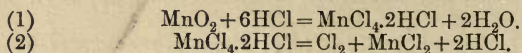
In the presence of a sufficient quantity of $MnCl_2$ further complications ensue, the $MnCl_4.2HCl$ uniting thus :—

(3) $MnCl_2 + H_2(MnCl_6) = Mn(MnCl_6) + 2HCl.$
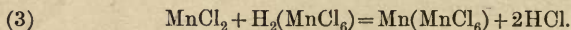
The product then is decomposed by water, thus :—

(4) $Mn(MnCl_6) + 4H_2O = MnO_2.Mn(OH)_2 + 6HCl.$
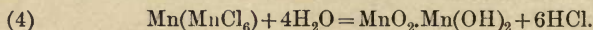
This higher oxide is then decomposed by the free hydrochloric acid present into $MnCl_2$ and $MnO_2.H_2O.$

In order to obtain a continuous stream of chlorine by this process many different methods have been proposed. Thus L. L. de Koninck [4] generates chlorine in a Kipp's apparatus by means of manganese dioxide and dilute hydrochloric acid, the whole kipp being immersed to the neck in a heated water bath. Later he proposed the passing of gaseous hydrochloric acid gas upwards through a drying tower containing manganese dioxide. The gas is known to be free from air when it is completely absorbed by caustic soda. A washing with water alone is not sufficient to free the issuing gas from all traces of hydrochloric acid, and Moissan and Du Jassoneix [5] recommend passing the gas over a layer of manganese dioxide heated to 50°, while Hampe [6] passes it through a concentrated $KMnO_4$ solution. As crude manganese dioxide frequently contains calcium carbonate, which causes the chlorine to be contaminated with carbon dioxide, it is advisable to moisten the dioxide with warm dilute nitric acid, and then wash free from acid. In order to remove traces of carbon dioxide, the gas may be passed through dilute nitric or sulphuric acid, and then washed until free from acid. Traces of oxides of chlorine are removed [7] by passing the gas through a tube filled with asbestos and heated to redness. Chlorine is dried by passing through concentrated sulphuric acid or calcium chloride.[8] For ordinary laboratory work the gas may be collected by upward displacement of air in the fume cupboard, or by collecting over hot water saturated with salt. The gas attacks mercury, and so is not collected over that liquid. It is also soluble in water, and the solution is difficult to work with.

[1] Forchhammer, *Ann. Phil.*, 1850, [ii.], i. 50 ; Pickering, *Trans. Chem. Soc.*, 1879, **35**, 654.

[2] Neumann, *Ber. Wien. Akad.*, 1894, July. See also Franke, *J. prakt. Chem.*, 1887, [ii.], **36**, 31, 451.

[3] Christensen, *Jahresber.*, 1886, 419, 496 ; *J. prakt. Chem.*, 1887, [ii.], **35**, 57.

[4] de Koninck, *Zeitsch. anal. Chem.*, 1878, **17**, 181. For other apparatus for generating chlorine see also Brugnatelli, *Zeitsch. anal. Chem.*, 1867, **6**, 389 ; Orlowski, *Zeitsch. anal. Chem.*, 1872, **11**, 38.   [5] Moissan and Du Jassoneix, *Compt. rend.*, 1903, **137**, 1198.

[6] Hampe, *Chem. Zeit.*, 1890, **14**, 1777.

[7] Treadwell and Christie, *Zeitsch. angew. Chem.*, 1905, **18**, 1931.

[8] Ditz (*Zeitsch. angew. Chem.*, 1901, **14**, 6) made a careful study of the conditions necessary to prepare chlorine free from HCl, CO_2, and H_2O.

(2) *Preparation of Chlorine from Manganese Dioxide, Salt, and Sulphuric Acid.*—One part of manganese dioxide and one part of salt are placed in a flask containing a cold mixture of two parts of strong sulphuric acid and two of water. On gently warming chlorine is evolved. The equation usually given for the reaction is this :—

$$MnO_2 + 2NaCl + 3H_2SO_4 = Cl_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$$
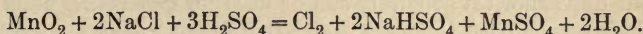
According to this equation, the whole of the chlorine is evolved. Klason,[1] however, shows that the following equation more closely approximates to what actually takes place :—

$$4NaCl + MnO_2 + 3H_2SO_4 = Cl_2 + 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O.$$
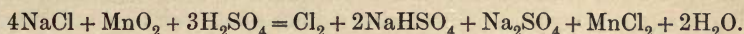
Harker[2] prepares pure chlorine by heating a mixture of 400 parts MnO_2, 900 parts NaCl, and 1200 parts H_2SO_4, mixed with 600 parts of water. The gas is passed into cold water, whereby the hydrate $Cl_2.10H_2O$ separates. It will keep at a temperature under $9°$ C. in the dark. On warming gently very pure chlorine (with a maximum impurity of $0·2$ per cent.) is evolved.

(3) *Preparation of Chlorine from Potassium Permanganate and Hydrochloric Acid.* —A very convenient oxidising agent for preparing chlorine is potassium permanganate,[3] chlorine being quantitatively evolved according to the equation :—

$$2KMnO_4 + 16HCl = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O.$$
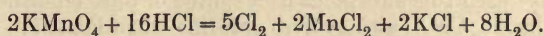
10 grams of pure crystallised permanganate are placed in a flask, which is fitted with a leading tube and bent dropping funnel. 60–65 c.c. of concentrated hydrochloric acid of sp. gr. $1·17$ are placed in the dropping funnel and allowed to run in drop by drop. The chlorine is evolved at ordinary temperatures.

(4) *Preparation of Chlorine from Potassium Dichromate and Hydrochloric Acid.*—Fairly pure chlorine is evolved by heating together potassium dichromate and hydrochloric acid,[4] the reaction taking place according to the equation :—

$$K_2Cr_2O_7 + 14HCl = 3Cl_2 + Cr_2Cl_6 + 2KCl + 7H_2O.$$
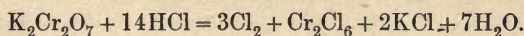
(5) *Preparation of Chlorine from Bleaching Powder and Hydrochloric Acid.*—It has long been known[5] that bleaching powder forms a convenient method of obtaining chlorine. The bleaching powder may be bought for this purpose compressed into cubes, either mixed with[6] or without[7] plaster of Paris, and is best used in a Kipp's apparatus[6] with hydrochloric acid (free from sulphuric acid) solution (1 part HCl of density $1·124 + 1$ part water). After use a certain amount of air is blown in, which forms a non-absorbable gaseous layer between the bleaching powder cubes and the free acid, and so prevents the gradual exhaustion of the cubes. Since commercial bleaching powder

[1] Klason, *Ber.*, 1890, **23**, 330.
[2] Harker, *Zeitsch. physikal. Chem.*, 1892, **9**, 673.
[3] See Lassar-Cohn, *Arbeitsmethoden f. organisch-chem. Laboratorien* (1901) ; Graebe, *Ber.*, 1902, **35**, 43 ; Wedekind and Lewis, *Proc. Chem. Soc.*, 1909, 59.
[4] Roscoe, *Annalen*, 1855, **95**, 357.
[5] Boissenot, *J. Pharm.*, 1849, [iii.], **15**, 185 ; Mermet, 1874, *Bull. Soc. chim.*, 1874, [ii.], **21**, 541 ; Kämmerer, *Ber.*, 1876, **9**, 1548.
[6] Winkler, *Ber.*, 1887, **20**, 184 ; 1889, **22**, 1076.
[7] Thiele, *Annalen*, 1889, **253**, 239.

always contains some calcium carbonate, the evolved chlorine will contain some carbon dioxide, but for most purposes this does not matter. Within the last few years a great many proposals and pieces of apparatus have been suggested for generating chlorine by this method. See, for example, Vosmaer,[1] Klason,[2] Graebe,[3] Merck,[4] Kreis,[5] Eckart,[6] Geisel,[7] Rupp,[8] Huss.[9] Not only bleaching powder but hypochlorites generally can be used for generating chlorine.

(6) *Preparation from Chlorates and Hydrochloric Acid.*—Several authors have described methods of obtaining chlorine by the action of hydrochloric acid on potassium chlorate,[10] but the gas so evolved contains ClO_2 and other oxides of chlorine, which can be destroyed by passing the gas through a hot concentrated solution of $MnCl_2 + HCl$, the last traces of ClO_2 being removed by passing the gas through tubes filled with red-hot asbestos. 1 grm. $KClO_3$ gives about $\frac{1}{2}$ litre of chlorine. G. Graebe[11] proposes the use of sodium chlorate.

(7) *Other Methods of preparing Chlorine for Laboratory Purposes.*—Very pure chlorine gas may be prepared by the electrolysis of fused silver chloride in a V-shaped tube by means of a current of 2·8 ampères. Gaseous impurities and moisture are removed by repeatedly reversing the current and exhausting the tube with a Sprengel's mercury pump.[12]

Very pure chlorine may also be obtained by heating gold or platinum chlorides, *e.g.* Shenstone and Beck[13] heated $PtCl_2$ to 360° C. in order to prepare pure chlorine, and Victor Meyer, in his work on the vapour density of chlorine, also used this substance as a source of pure chlorine.

Cupric chloride, $CuCl_2$ also evolves chlorine when heated :—

$$2CuCl_2 = 2CuCl + Cl_2.$$
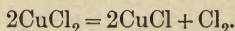
Where considerable quantities of chlorine are required in the chemical laboratory it is better and cheaper to use a cylinder of liquid chlorine (p. 63) than to prepare the chlorine in the laboratory.

Manufacture of Chlorine.[14]

Chlorine is prepared industrially on a very large scale, being used for the manufacture of bleaching powder, bleaching solutions, chlorates, and similar substances. Large quantities of chlorine are used in the coal-tar dye industry for the purpose of chlorinating various organic products, and for this purpose

[1] Vosmaer, *Zeitsch. anal. Chem.*, 1888, **27**, 638.
[2] Klason, *Ber.*, 1890, **23**, 330.   [3] Graebe, *Ber.*, 1901, **34**, 645.
[4] Merck, *Pharm. Zeit.*, 1903, **48**, 894.   [5] Kreis, *Chem. Zeit.*, 1903, **27**, 281.
[6] Eckart, *Zeitsch. anal. Chem.*, 1905, **44**, 398.
[7] Geisel, *Chem. Zeit.*, 1905, **29**, 726.
[8] Rupp, *Zeitsch. anorg. Chem.*, 1902, **32**, 359.
[9] Huss, *Zeitsch. Untersuchungen Nahr.-Genussm.*, 1906, **12**, 221.
[10] For example, see Gooch and Kreider, *Zeitsch. anorg. Chem.*, 1894, **7**, 17 ; Graebe, *Ber* , 1901, **34**, 645.   [11] Graebe, *loc. cit.*
[12] Shenstone, *Trans. Chem. Soc.*, 1897, **71**, 471 ; Mellor and Russell, *Proc. Chem. Soc.*, 1902, **18**, 166 ; Tolloczko, *Zeitsch. anorg. Chem.*, 1904, 41, 407.
[13] Shenstone and Beck, *Chem. News*, 1893, **67**, 116.
[14] For a full account of the subject, including literature, see Lunge, *Sulphuric Acid and Alkali Industry* ; Geoffrey Martin, *Industrial Chemistry*, vol. ii., *Inorganic* (Crosby, Lockwood & Son, 1915); Hölbing, *Fabrikation der Bleichmaterialien*, 1902 ; Teichmann, *Komprimierte Gase* (Halle, 1908); Hölbing, *Fortschritte in der Fabrikation der anorganischen Sauren, der Alkalien, des Ammoniaks und Verwandter Industriezweige* (Berlin, 1845) ; Kershaw, *Die elektrolytische Chlorit-Industrie* (Halle, 1905) ; Engelhardt, *Hypochlorite und elektrische Bleiche* (Halle, 1903) ; Förster, *Elektrochemie wässriger Lösungen* (Leipzig, 1905)

the chlorine is brought on to the market as a liquid enclosed in strong steel cylinders.

The ultimate source of industrial chlorine is the naturally occurring chlorides, such as sodium or potassium chloride, also magnesium and calcium chloride. The chlorides are not used directly except when the chlorine is manufactured electrolytically. More usually hydrochloric acid is first prepared from them, and the chlorine in it is then liberated from this.

We shall give a brief account of the methods in vogue, fuller details being available in the works mentioned on p. 56.

Chlorine from Hydrochloric Acid.—Several processes are known. The two most important are (1) Weldon's process, (2) Deacon's process. The other processes will be only very briefly alluded to, as they are not technically important.

Weldon's Process.—This is based on the oxidation of hydrochloric acid with manganese dioxide and the subsequent recovery of the manganese dioxide: $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$.

The manganese dioxide used for the purpose is called "pyrolusite," and is extensively mined in Spain and in the Caucasus. It invariably contains iron, and its value for the manufacture of chlorine depends entirely upon its "available oxygen," *i.e.* the amount of oxygen which is active in liberating chlorine when the pyrolusite is distilled with hydrochloric acid. The manganese dioxide is always recovered from the waste liquors, so that it is obvious that chlorine is mainly obtained from "recovered" manganese dioxide, and only that amount of fresh manganese dioxide is used to cover the working losses of the recovery process. Technologists usually allow a loss of 3 parts manganese dioxide on every 100 parts of bleaching powder produced. The only acid in use is hydrochloric acid, as if much sulphuric acid is present in the hydrochloric acid it converts the manganese chloride largely into sulphate and so hinders the regeneration of the manganese dioxide. The chlorine produced by the Weldon process is very concentrated, usually amounting to 90 per cent. by volume.

The chlorine *generators* or *stills* (A, fig. 9) [1] are tanks composed of 6 to 8 granite slabs fastened together so as to form a vessel about 9 feet high by 6 feet diameter. The inlet and exit tubes are composed of acid-resisting earthenware. The calculated charge of hydrochloric acid is run into the vessel, and then the calculated amount of "Weldon mud" (*i.e.* recovered manganese dioxide) is gradually allowed to run in, so that chlorine is evolved in a regular stream. Finally the mixture is heated by steam driven in through a sandstone tube, until the mixture boils. When 18° to 19° Bé hydrochloric acid is used, the reaction proceeds, practically, to completion—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

| Manganese dioxide. | Hydrochloric acid. | Manganese chloride. | Chlorine gas. | Water. |
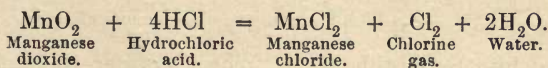
The manganese chloride liquors are run off through a pipe at the bottom of the still into a cement-lined tank B (fig. 9).

When native manganese dioxide is used, it is broken into pieces and placed in a different generator on a grating made of sandstone, hydrochloric acid is added, and the action is completed by driving in steam.

Some small factories (such as bleachers) generate their own chlorine in earthenware generators or stills, such as that illustrated in fig. 10.[1] More usually, however, these small users buy chlorine in the liquid state in steel cylinders (see p. 63).

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[1] G. Martin, *Industrial Chemistry*, vol. ii.

As a rule, several generators are used in succession, one being filled while the other is in use, so that the evolution of chlorine becomes practically continuous. When a generator becomes exhausted it is cut out of the series by means of such an arrangement as that shown in fig. 11.[1] Between the main conducting pipe A (wherein the chlorine from the several generators is conducted away) and a branch pipe B connecting A with a particular generator, a U-tube DDD is placed, being connected with A and B by means of water seals at cc. When the generator connected with B is to be cut off from A,
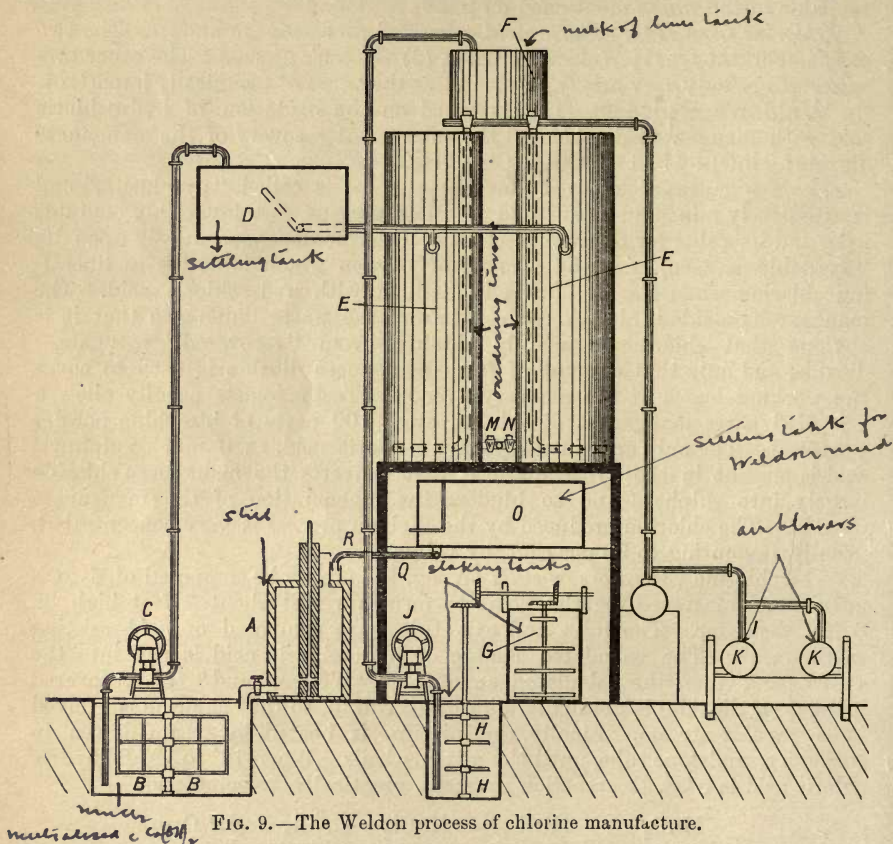
FIG. 9.—The Weldon process of chlorine manufacture.

water is filled into the U-tube by e. When, however, connection between B and A is to be re-established, the water is let out of the U-tube by means of f.

Recovery of the Manganese Dioxide.—The waste liquors rich in manganese chloride, $MnCl_2$, are run from the exhausted generators into a receptacle, and excess of milk of lime is run in, whereby manganese hydroxide, $Mn(OH)_2$, is precipitated : $MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$. Air at $50°$-$55°$ C. is now blown in, and, in the presence of excess of $Ca(OH)_2$ (also of NaOH) the manganese hydroxide oxidises to the peroxide state, the resulting " Weldon mud " having a composition varying from $CaO.MnO_2$ to $CaO.2MnO_2$

—all the manganese being in the peroxide state. If excess of lime is not present, the $Mn(OH)_2$ will only oxidise to the $Mn(OH)_3$ state. Fig. 9 shows Weldon's plant for performing this operation, which has been operated on a very large scale since 1866.

A is the chlorine generator. From it the spent liquor rich in manganese chloride is run into the cemented basin B and is here neutralised with $Ca(OH)_2$, which just precipitates the iron hydroxide $Fe(OH)_3$. The liquor is pumped by the pump C into the depositing tank D, where the iron hydroxide settles out. The clear manganese chloride solution is next run into the oxidising towers EE, which are usually 30 feet high and 6–7 feet in diameter. By means of steam the temperature of the liquids is raised to 55° C. and a measured amount of milk of lime is gradually run in from the tank F into the towers. The milk of lime is prepared in the lime-slaking tanks G and H, and is thence forced by means of the pump J into the tank F. The air is
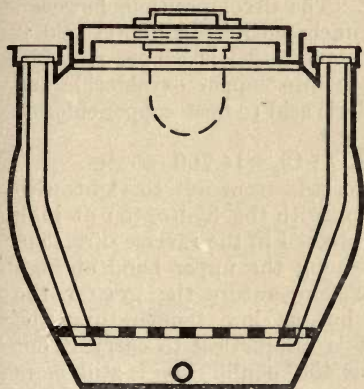
Fig. 10.—Small chlorine still.
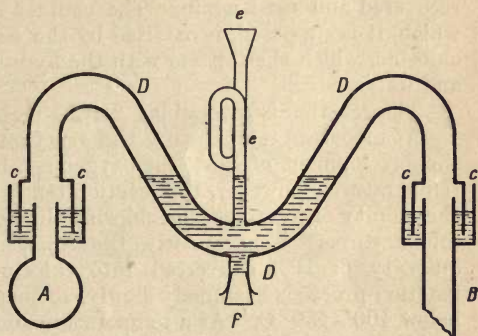
Fig. 11.—Connection of chlorine still with main conducting pipes.

pumped in at the base of the tower, the compressed air coming from the air-tanks K through the double blower into a tube placed at the base of the towers and provided with a number of small holes. The progress of the oxidation is controlled by repeatedly withdrawing samples of the blackening mud and titrating it with ferrous sulphate and potassium permanganate. Towards the end of the reaction the manganese chloride liquors are added so long as manganese hydroxide is precipitated by the lime still in the water.

The operation is conducted with the object of obtaining a mud as rich in manganese dioxide as possible, and consequently as poor in lime as is compatible with efficiency. A mud having the composition $CaO.MnO_2$ gives with 6 molecules of HCl about 2 molecules of chlorine, while a mud having the composition $CaO.2MnO_2$ gives with 10 molecules of HCl 4 molecules of chlorine. The oxidising process lasts 4–5 hours, and the presence of a certain amount of calcium chloride liquor is necessary in order to allow the oxidation to take place efficiently.

The "Weldon mud" is run out of the towers by MN into the settling tank O, and thence by means of the tube QR into the chlorine generator A. The calcium chloride solution is siphoned off from the settled mud ; it contains

about 70 per cent. of the total chlorine of the original hydrochloric acid, and is either run to waste or worked up in the manufacture of chlorates, etc.

Industrial Position of the Weldon Process.—The process at the present time is run at a loss owing to the great waste of hydrochloric acid—70 per cent. of the chlorine going over into the comparatively valueless calcium chloride. Consequently, at the present time the Weldon process is only employed in districts where no market exists for hydrochloric acid and where the calcium chloride generated can be economically utilised.

The Deacon process, described below, is still gaining ground.

Deacon Process of Manufacture.—The oxygen of the air can be used to oxidise hydrochloric acid to chlorine and water; when a mixture of hydrochloric acid and air is led over a heated suitable "contact" substance, the following change takes place :—

$$2HCl + O = Cl_2 + H_2O.$$
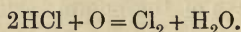
This is the process of Deacon and Hurter. The decomposition, however, is by no means a quantitative one, and the unchanged hydrochloric acid is recovered and used again. The contact substance used is copper chloride, which, it is supposed, is oxidised by the oxygen into copper oxychloride and chlorine, which then reacts with the hydrochloric acid to form copper chloride and water.

The reaction is reversible : $2HCl + O \rightleftharpoons H_2O + Cl_2 \pm 14,700$ calories.

At moderate temperature the reaction proceeds from left to right with the development of heat, the oxygen combining with the hydrogen; at high temperatures, however, the reaction tends to proceed in the reverse direction, the affinity of hydrogen for chlorine thus obtaining the upper hand at high temperatures. Consequently the lower the temperature the greater the quantity of HCl converted into chlorine; but at low temperatures the reaction proceeds extremely slowly, so that it is unpractical to carry it out below $400°$–$430°$ C. At a temperature such as $450°$ equilibrium is still more rapidly attained, but the yield of chlorine is seriously diminished, and at temperatures above this notable amounts of copper chloride are lost by volatilisation.

For example, investigations carried out by Haber[1] showed that, using the ordinary mixture of HCl and air, at $430°$ from 75–80 per cent. of the HCl is transformed into chlorine, whereas at $577°$ barely 50 per cent. was so transformed. In its original form the Deacon process could not (in 1870) compete with the Weldon process, principally because the HCl gases, mixed with air, were led directly from the salt-cake furnaces into the contact apparatus. The gaseous hydrochloric acid was thus contaminated with sulphuric acid, ferric chloride, and arsenic, and had a variable HCl content. Consequently the contact substance was very soon spoilt, and the yield of chlorine rapidly diminished.

It was only when Hasenclever (Rhenania) purified the hydrochloric acid gases that financial success was attained. The gases coming from the salt-cake furnaces are, according to the improved process, first absorbed, usually in water, and a concentrated hydrochloric acid solution is thus obtained. From this a regular stream of pure HCl gas is obtained by allowing concen-

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[1] See Haber, *Thermodynamik technischer Gasreaktion*, 1905, p. 89. A recent investigation on the equilibrium of the Deacon's process has been published by Vogel von Falckenstein, *Zeitsch. physikal. Chem.*, 1907, **59**, 313 ; 1909, **65**, 371–79.

trated sulphuric acid (60° Bé) to flow in, finishing up by blowing in air.   The evolved HCl, mixed with the proper amount of air, is then led into the contact apparatus, while the sulphuric acid is recovered by evaporating to 60° Bé.

Fig. 12 [1] shows the usual Deacon plant, after Lunge.   A is the salt-cake furnace, C a condenser used for collecting the aqueous HCl and H_2SO_4, E is the preheater, and F the contact tower.   The latter consists of a cylindrical iron tower, surrounded with a masonry shell $m\,m$, whereby it can be heated by hot air.   Inside the iron tower are layers of clay or earthenware balls, previously soaked in copper chloride solution and dried.   In order to avoid loss of $CuCl_2$ by volatilisation, the stream of gas is first admitted at the bottom of the apparatus, and comes out at the top ; then it is sent in the reverse direction, so that an even balance is maintained.   In most works about 65 per cent. of the HCl is transformed into chlorine.   The chlorine leaves the contact tower through H, passes into a series of condensing tubes J, and finally passes into a tower K, where it is washed by a descending
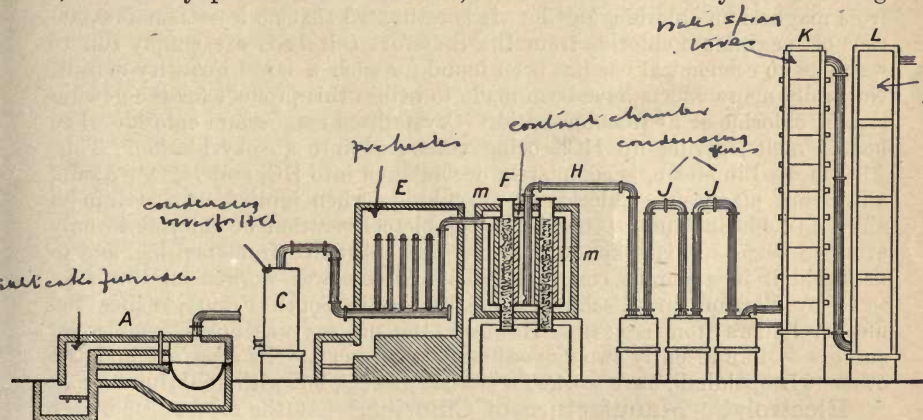
FIG. 12.—The Deacon process of chlorine manufacture.

spray of water ; here most of the hydrochloric acid (on account of its great solubility) is washed out, only a small amount of chlorine being absorbed. Finally the moist chlorine gas passes up a tower L, where it is sprayed with sulphuric acid, which removes the moisture.   The recovered hydrochloric acid from K is freed from chlorine by merely blowing in air.

The evolved chlorine finally obtained contains only 8–12 per cent. by volume of Cl.   This method has for many years been successful even against electrolytic processes for making chlorine.   Quite recently (1909) at Mannheim the process has been restored to its original simplicity by obtaining in mechanical salt-cake furnaces a 30 per cent. by volume HCl gas, free from arsenic ; this is freed from dust and H_2SO_4 by passing it through a series of water-cooled condensing vessels ; then it is heated to 220° C. and directly led into the contact apparatus, where a temperature of 400°–450° prevails, owing to the heat given out during the reaction (see above).

Now for the chamber process of manufacture of "bleaching powder" a very concentrated chlorine is necessary, whereas the gas as it comes from the last drying tower of Deacon's apparatus only contains about 8–12 per cent. by

[1] Martin, *Industrial Chemistry*, vol. ii.

volume. Consequently the chlorine can only be utilised by employing a special apparatus designed by Hasenclever, which is described in Vol. III. dealing with bleaching powder.

Chlorine from Magnesium Chloride, Calcium Chloride, and Ammonium Chloride.—Calcium chloride is produced as a by-product in very large quantities in certain chemical processes, *e.g.* in the Weldon process, the ammonia soda process, potassium chlorate manufacture, etc. Many attempts have been made to use it as a source of chlorine (principally by Solvay), one process consisting of heating $CaCl_2$ with sand or clay in a stream of air ; another process consisted in heating with magnesium sulphate and steam. All these attempts, however, have been commercially unsuccessful.

Many efforts have also been made, principally by Mond, to obtain chlorine from the ammonium chloride liquors obtained in the ammonia soda process, likewise without commercial success.

More important are the efforts which have been made to obtain chlorine from magnesium chloride, $MgCl_2$. It is estimated that no less than 500,000 tons of magnesium chloride from the Stassfurt salt beds are simply run to waste as no economical use has been found for such a large quantity of salt. Naturally many efforts have been made to utilise this product for the generation of chlorine or hydrochloric acid. Crystallised magnesium chloride when heated melts, giving up HCl, being converted into an oxychloride. This, when heated in steam, is completely decomposed into HCl and MgO. Again, anhydrous magnesium chloride or oxychloride when ignited in a stream of air yields chlorine and magnesia, but complete liberation of chlorine is only attained when care is taken to prevent the substance from melting, and to maintain it in a porous condition. This process was worked on the large scale by Weldon and Pechiney at Salindres in South France, using the mother liquors from sea-salt. However, the process was not a commercial success. More recently two potassium works, one at Neustassfurt and the other at Leopoldhall, have worked a similar process, but with doubtful success.

Electrolytic Manufacture of Chlorine.[1]—At the present time over half the amount of chlorine manufactured is obtained by the electrolysis of the chlorides of sodium, potassium, and magnesium. Chlorine was first manufactured electrolytically about 1890, but at the present time the industry is still increasing as very valuable products are simultaneously produced.

When an electric current is sent through an aqueous solution of common salt the substance is decomposed, the negatively charged chlorine ion is liberated at the positive pole, while the positively charged sodium ion is liberated at the negative pole, thus :—

$$NaCl = \overset{+}{\underset{\substack{\text{sodium ion} \\ (-\text{pole})}}{Na}} + \overset{-}{\underset{\substack{\text{chlorine ion} \\ (+\text{pole})}}{Cl}}$$
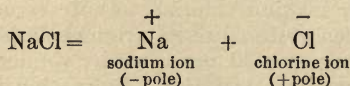
The sodium, when liberated, immediately reacts with water—$2Na + 2H_2O = 2NaOH + H_2$ forming a solution of caustic soda at the negative pole, while at the positive pole the chlorine ions unite to give ordinary chlorine gas, Cl_2. Hence for the preparation of chlorine and caustic alkalies the electrolysis must be so carried out that the cathodic product (NaOH) is separated as

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[1] See references to Forster, Hölbing, etc., p. 56 ; also Martin, *opus cit.*, vol. ii., gives a full account.

completely as possible from the anodic product (chlorine); otherwise the two will simply unite and destroy each other. This result is attained by three different methods:—

(1) *Diaphragm Process.*—Here the anode is separated from the cathode by means of a porous diaphragm. The first technically successful diaphragm was made out of Portland cement. Carmichael proposes porous asbestos as a suitable material. Among other materials which have been proposed may be mentioned chalk and alkaline earth oxides mixed with cement.

(2) *The Quicksilver Process.*—Here the cathode consists of quicksilver, which dissolves the alkali metal as it is liberated, while the chlorine is evolved at the anode. When the quicksilver is sufficiently charged with the alkali metal, it is run off.

(3) *The Bell Process.*[1]—Here no quicksilver or diaphragms are used, but the anodic and cathodic liquids are kept separate by means of their different specific gravity, by help of a series of "bells."

However, as these processes are more particularly described under the manufacture of caustic soda and potash, we must refer the reader to Vol. II. for details.

The anode used when chlorine is liberated consists almost invariably of carbon, which is not appreciably attacked by nascent chlorine.

Several attempts have been made to electrolyse fused chlorides, but the difficulties for an extended manufacture of chlorine by these processes have prevented the development of the industry.

Electrolytic chlorine consists of 80–90 per cent. chlorine, and so can be directly utilised for the chamber process of bleaching powder manufacture.

Liquid Chlorine.—In 1888, R. Knietsch, of the Badische Aniline und Soda Fabrik, discovered that iron is not attacked by anhydrous liquid chlorine, and since that time liquid chlorine has become an important article of commerce.[2] The liquid chlorine is transported on the large scale in iron tanks mounted on wheels; from these it is run out from underneath in a liquid state into the vessels used for storing it; from the storage vessels it is obtained for use in a gaseous form, being drawn off from above. Users of small quantities of chlorine obtain it condensed in steel cylinders.

In this manner the element chlorine is obtainable in a convenient form for use, and now finds general application both on a small and on a large scale. It is especially used for chlorinating purposes in the manufacture of chloracetic acid, for indigo, chloroform, chloral, carbon tetrachloride, chlorbenzene, chlortoluene, for generating bromine, and for bleaching works. Liquid chlorine cannot be conveniently made from Deacon chlorine, as this is too dilute; it is always made by condensing the concentrated electrolytic or Weldon chlorine.

The process is carried out as follows: The chlorine as it comes from the generators is passed through earthenware tubes in order to cool the gas and condense any water and hydrochloric acid present: then the gas is dried by passing through concentrated sulphuric acid, and is then pumped into a gas-holder (A, fig. 13), the sealing liquid being concentrated sulphuric acid, whence it is drawn off to be liquefied. Chlorine, under ordinary atmospheric pressure, liquefies at − 34° C.; and consequently can be condensed to a liquid

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[1] Besides the authorities quoted above, see Brochet, *Chem. Zeit.*, 1908, **32**, 1117.
[2] See *Chemische Industrie*, 1893, **16**, 373; 1905, **28**, 698; 1906, **29**, 105; also Lunge, *Zeitsch. angew. Chem.*, 1907, **20**, 2013; Martin, *opus cit.*

merely by cooling to $-50°$ with liquid CO_2. Since, however, chlorine boils at $+15°$ C. under a pressure of 5·8 atmospheres, more usually the chlorine is liquefied under a pressure of 8 atmospheres, using ordinary water-cooling.

Fig. 13 shows one form of apparatus employed.[1] The dry chlorine passes from the gas-holder A through the tube *bcd* into the compressing pump D. This latter is filled from *e* to *f* with concentrated sulphuric acid, which at *f* is covered with a layer of petroleum. The jacket H contains warm water. The chlorine gas is drawn out of *d* and forced by the pump through the valve F, and is thence forced through the pipe *g* into the condenser K, where it liquefies under the pressure and runs first into V, and then into the steel cylinder H which stands on a weighing machine, and is thus filled with the proper weight of liquid chlorine. Usually a steel cylinder will contain 50 kg. of chlorine, and every two years it must be tested under 22 atmospheres pressure. Also
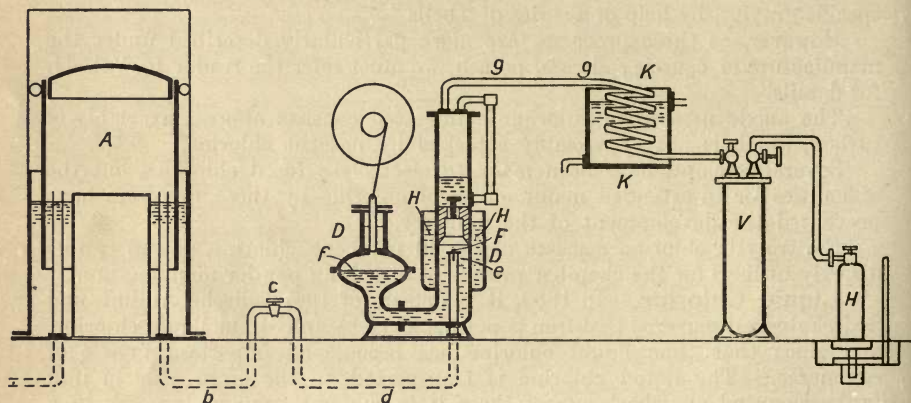
Fig. 13.—Manufacture of liquid chlorine.

to every litre cubic contents of the steel cylinder no more than 1·25 kg. chlorine may be added.

One litre of the liquid chlorine corresponds to 300 litres of gas.[2]

Solid Chlorine.—At $-102°$ C. yellow crystals begin to form in liquid chlorine, and at a still lower temperature the whole liquid solidifies to a yellow crystalline mass.[3]

Physical Properties.—Chlorine is at ordinary temperatures a greenish yellow gas, whose colour becomes deeper with rise of temperature.[4] It has a most disagreeable smell, which in the case of a very diluted gas somewhat resembles that of seaweed. The concentrated gas has a suffocating, excessively irritating action when breathed, producing coughing, inflammation of the passages of the nose and throat, and even death.

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[1] See Kausch, *Zeitsch. comp. flüss. Gase*, 1903, **7**, 58; *D.R.P.*, 50,329 (1888); *U.S. Pat.*, 491,699. See also Teichmann, *Komprimierte Gase* (Halle, 1908); Martin, *Industrial Chemistry*, vol. ii.

[2] Fribourg, *Bull. Soc. chim.*, 1893, [ii.], **9**, 351.

[3] Olszewski, *Monatsh.*, 1884, **5**, 127. Wahl (*Proc. Roy. Soc.*, 1913, **A**, **88**, 348–53) gives an account of the optical properties of these crystals.

[4] Schönbein, *J. prakt. Chem.*, 1852, **55**, 154. See also Ferentzy, *Chem. Zeit.*, 1908, **32**, 285.

The density [1] of the gas is given by the following numbers (air = 1), Gay-Lussac's law being only obeyed at temperatures above 200° :—

Temperature, °C. .	0°.	20°.	50°.	100°.	150°.	200°.
Density . .	2·491	2·4807	2·4783	2·4685	2·4609	2·4502

It will be seen that chlorine is about 2·5 times heavier than air, and 2·3 times heavier than oxygen gas. The density at 200° corresponds to a molecular weight 35·26, so that at 200° chlorine exists as Cl_2. This density is maintained up to a white heat, above which it decreases. It is evident, therefore, that at a high temperature the diatomic molecule Cl_2 has become partially dissociated into monatomic molecules.[2]

These results were confirmed by an elaborate investigation on the density of gaseous chlorine, undertaken by M. Pier [1] in 1908. He showed that the density of chlorine is normal between 300° C. and 1450°, amounting to 2·4494 (air = 1). Above 1450° C. the chlorine begins to dissociate into atoms.

The specific heat of chlorine [3] between 16° and 343° is $C_p = 0·1155$, $C_v = 0·08731$, $K = \dfrac{C_p}{C_v} = 1·323$. The molecular heat of chlorine at constant volume can, according to Pier,[1] be expressed by the formula $C_v = 5·431 + 0·0005t$, which is valid up to 1400° C. The compressibility of gaseous chlorine has been studied by Richards.[4]

The atomic refraction has been studied by Eisenlohe, Zecchini, and Brühl.[5] The refractive index at N.T.P.[6] $n = 1·000773$ for the D line ; the viscosity [7] of chlorine is $1·297 \times 10^{-4}$ in C.G.S. units, at 12·7°, and $1·688 \times 10^{-41}$ at 99·1° C. Cl dissolved in nitrobenzene is deposited on the anode.[8]

Liquid Chlorine is a transparent, dark greenish yellow, very mobile liquid, immiscible with water, which boils at − 33·6° C. at 760 mm. ;[9] it does not conduct the electric current, and no inorganic substance is known [10] which dissolves in it with ionisation, although a mixture of HCl and ether enables the liquid to conduct well. The following table gives the density of liquid chlorine, according to Knietsch :— [11]

Temp. °C.	Sp. Gr.	Temp. °C.	Sp Gr.	Temp. °C.	Sp. Gr.	Temp. °C.	Sp. Gr.
− 80	1·6602	+ 9·70	1·4434	+ 26·37	1·3930	+ 55·5	1·3000
− 33·6	1·5560	11·10	1·4359	27·63	1·3891	63	1·274
− 9·5	1·4931	13·85	1·4314	30·90	1·3786	67	1·258
0	1·4689	14·50	1·4278	36·20	1·3621	69	1·250
+ 5·25	1·4541	19·00	1·4156	40·00	1·3490	77	1·216
+ 7·73	1·4481	21·80	1·4065	51·3	1·3160		

[1] Leduc, *Compt. rend.*, 1897, **125**, 571 ; Pier, *Zeitsch. physikal. Chem.*, 1908, **62**, 385.
[2] Langer and Meyer, *Pyrochemische Untersuchungen*, p. 46 (Vieweg, 1885).
[3] Strecker, *Wied. Annalen*, 1881, [ii.], **13**, 20 ; Petrini, *Zeitsch. physikal. Chem.*, 1895, **16**, 97.   [4] Th. W. Richards, *Zeitsch. Elektrochem.*, 1907, **13**, 519.
[5] Eisenlohe, *Zeitsch. physikal. Chem.*, 1910, **75**, 585 ; Zecchini, *Gazz. chim. ital.*, 1892, **22**, ii. 592 ; Brühl, *Zeitsch. physikal. Chem.*, 1891, **7**, 191.
[6] Bleekrode, *Proc. Roy. Soc.*, 1884, **37**, 339.
[7] O. Rankine, *Proc. Roy. Soc.*, 1912, **A**, 86, 162.
[8] Bruner and Galecki, *Zeitsch. physikal. Chem.*, 1913, **84**, 513–57.
[9] See Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 96.
[10] Johnston and M'Intosh, *J. Amer. Chem. Soc.*, 1909, **31**, 1138.
[11] Knietsch, *Annalen*, 1890, **259**, 100.   See also Johnston and M'Intosh, *J. Amer. Chem. Soc.*, 1909, **31**, 1138–44.

The following formula gives the density of liquid chlorine :—

$$D = 1{\cdot}6583346 - 0{\cdot}002003753x - 0{\cdot}0000045596743.x^2,$$ where $x = t° + 80$.

The coefficient of expansion with heat of liquid chlorine increases with the temperature. The mean coefficient between -80 and $-33{\cdot}6°$ C is $0{\cdot}001409$; from -30 to $0°$ it is $0{\cdot}001793$; for $50°$ to $60°$ it is $0{\cdot}002690$; for $+70°$ to $+80°$ it is $0{\cdot}003460$. At $90°$ the expansion equals that of gaseous chlorine (Knietsch). The latent heat of evaporation at $-22°$ C is $67{\cdot}38$ Cal.[1]

The following table is due to A. Lange :—[2]

Temp. °C.	Sp. Gr.	Relative Specific Volume. $v_0 = 1$.	Mean Coefficient of Expansion.	Temp. °C.	Sp. Gr.	Relative Specific Volume. $v_0 = 1$.	Mean Coefficient of Expansion.
-50	$1{\cdot}5950$	$0{\cdot}9207$		30	$1{\cdot}3799$	$1{\cdot}0642$	$0{\cdot}00226$
-45	$1{\cdot}5829$	$0{\cdot}9277$	$0{\cdot}00151$	35	$1{\cdot}3640$	$1{\cdot}0766$	$0{\cdot}00234$
-40	$1{\cdot}5709$	$0{\cdot}9348$	$0{\cdot}00153$	40	$1{\cdot}3477$	$1{\cdot}0896$	$0{\cdot}00242$
-35	$1{\cdot}5589$	$0{\cdot}9420$	$0{\cdot}00155$	45	$1{\cdot}3311$	$1{\cdot}1032$	$0{\cdot}00250$
-30	$1{\cdot}5468$	$0{\cdot}9494$	$0{\cdot}00158$	50	$1{\cdot}3141$	$1{\cdot}1175$	$0{\cdot}00259$
-25	$1{\cdot}5342$	$0{\cdot}9572$	$0{\cdot}00162$	55	$1{\cdot}2967$	$1{\cdot}1325$	$0{\cdot}00268$
-20	$1{\cdot}5216$	$0{\cdot}9651$	$0{\cdot}00165$	60	$1{\cdot}2789$	$1{\cdot}1482$	$0{\cdot}00278$
-15	$1{\cdot}5088$	$0{\cdot}9733$	$0{\cdot}00169$	65	$1{\cdot}2607$	$1{\cdot}1648$	$0{\cdot}00289$
-10	$1{\cdot}4957$	$0{\cdot}9818$	$0{\cdot}00175$	70	$1{\cdot}2421$	$1{\cdot}1823$	$0{\cdot}00301$
-5	$1{\cdot}4823$	$0{\cdot}9907$	$0{\cdot}00181$	75	$1{\cdot}2228$	$1{\cdot}2009$	$0{\cdot}00314$
0	$1{\cdot}4685$	$1{\cdot}0000$	$0{\cdot}00187$	80	$1{\cdot}2028$	$1{\cdot}2209$	$0{\cdot}00333$
5	$1{\cdot}4545$	$1{\cdot}0096$	$0{\cdot}00192$	85	$1{\cdot}1821$	$1{\cdot}2423$	$0{\cdot}00351$
10	$1{\cdot}4402$	$1{\cdot}0196$	$0{\cdot}00199$	90	$1{\cdot}1602$	$1{\cdot}2657$	$0{\cdot}00376$
15	$1{\cdot}4257$	$1{\cdot}0300$	$0{\cdot}00205$	95	$1{\cdot}1374$	$1{\cdot}2911$	$0{\cdot}00402$
20	$1{\cdot}4108$	$1{\cdot}0409$	$0{\cdot}00212$	100	$1{\cdot}1134$	$1{\cdot}3189$	$0{\cdot}00430$
25	$1{\cdot}3955$	$1{\cdot}0523$	$0{\cdot}00219$				

The critical temperature of liquid Cl is $141°$ (Dewar),[3] $146°$ (Knietsch), $148°$ (Ladenburg).[4] The critical pressure[5] $= 83{\cdot}9$ atmospheres. Melting-point[6] $= -102°$ C. The coefficient of compression[7] is $0{\cdot}000225$ at $35{\cdot}4°$, $0{\cdot}000366$ at $64{\cdot}9°$ C., and $0{\cdot}000637$ at $91{\cdot}4°$ C. The specific heat[6] is $0{\cdot}2262$ between 0 and $24°$, $0{\cdot}2230$ between $-80°$ and $15°$.[7] The refractive index of liquid chlorine[8] is given as $1{\cdot}367$ (D line at $14°$ C.) by Bleekrode, and $1{\cdot}385$ (D line at $20°$ C.) by Dechant.

The vapour tension of liquid chlorine is given by Knietsch[9] as follows :—

[1] See Beckmann, *Zeitsch. anorg. Chem.*, 1906, 51, 96.
[2] Lange, *Zeitsch. angew. Chem.*, 1900, 684.
[3] Dewar, *Chem. News*, 1885, 51, 27.
[4] Ladenburg, *Ber.*, 1878, 11, 822.
[5] Olszewski, *Monatsh.*, 1884, 5, 127.
[6] Lange, *Zeitsch. angew. Chem.*, 1900, 13, 683 ; Th. W. Richards, *Zeitsch. Elektrochem.*, 1907, 13, 519 ; A. Grüneisen, *Ann. Physik*, 1908, [iv.], 26, 393.
[7] Knietsch, *Annalen*, 1890, 259, 100 ; Estreicher and Staniewski, *Bull. Acad. Sci. Cracow*, 1910, 349.
[8] Bleekrode, *Proc. Roy. Soc.*, 1884, 37, 339 ; Dechant, *Monatsh.*, 1884, 5, 615.
[9] Knietsch, *Annalen*, 1890, 259, 100. See also Johnson and M'Intosh, *J. Amer. Chem. Soc.*, 1909, 31, 1138 ; E. Marchand, *J. Chim. phys.*, 1913, 11, 573-76.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
	atmos.		atmos.		mm. Hg.		mm. Hg
146	93·5	13·12	5·433	− 34·4	710	− 54	305
130	71·6	9·62	4·885	− 34·9	720	− 58	236
120	60 4	0	3·660	− 37	628	− 58·5	232
110	50·8	− 9·5	2·662	− 38	632	− 60	217
100	41·7	− 33·6	1·000	− 40	544	− 61	198
90	34·5	...	...	− 41	528	− 65	160
80	28·4	...	...	− 42·5	498	− 66	155
70	23·0	...	...	− 43	490	− 73	100
60	18·6	...	...	− 43·5	475	− 75	90
50	14·7	...	...	− 44	470	− 76	82
40	11·50	...	...	− 44·2	459	− 77	80
38·72	10·889	...	...	− 44·8	461	− 80	62·5
33·16	9·470	...	...	− 45	442	− 83	50
29·70	8·652	...	...	− 46	424	− 85	45
21·67	6·960	...	...	− 47	402	− 87	40
20·85	6·791	...	...	− 49·5	365	− 88	37·5

The molecular surface energy of liquid chlorine has been determined by Johnson and M'Intosh,[1] and Marchand,[1] between − 61·5° and − 28·7° C., and from the results the formula of liquid chlorine is found to be Cl_2.

Solid Chlorine.—Yellow crystals, which melt at − 102° C.[2] or − 103·5° C.[3] The specific heat[3] of solid chlorine between − 192° C. and − 108° C. is 0·1446. This gives 5·13 for the atomic heat of solid chlorine. The latent heat of liquefaction of solid chlorine is 22·96 calories per gram. The optical properties of solid chlorine crystals were investigated by W. Wahl.[4]

Action of Light on Chlorine.[5]—Draper,[6] in 1843, discovered that chlorine which had been exposed to light unites more readily with hydrogen than that which has been kept in the dark. Although this was denied by Bunsen and Roscoe[7] in 1857, more recently Bevan, Burgess, and Chapman[8] have shown that *moist* chlorine does exhibit a difference, but that this increased activity is destroyed when the gas is bubbled through water (as was done by Bunsen and Roscoe).

The cause of this action is not known with certainty. Some authors assume that the light has partially dissociated the chlorine into a more active allotropic modification, consisting of single chlorine atoms. Roscoe, however, believes that under the action of light the chlorine reacts with the moisture present, with formation of an active compound, which facilitates the union of the chlorine and the hydrogen. The phenomenon is even yet by no means clearly explained, although nearly three-quarters of a century have elapsed since the effect was first observed.

In 1870 Budde[9] discovered that when chlorine is exposed to light rays of high refrangibility a slight increase of volume occurs. This is not due to

[1] Johnson and M'Intosh, *loc. cit.*; Marchand, *loc. cit.*
[2] Olszewski, *Monatsh.*, 1884, **5**, 127.
[3] Estreicher and Staniewski, *Bull. Acad. Sci. Cracow*, 1910, 349.
[4] W. Wahl, *Proc. Roy. Soc.*, 1913, **A, 88**, 348-53.
[5] See also under Direct Union of Hydrogen and Chlorine, p. 81.
[6] Draper, *Phil. Mag.*, 1845, [iii.], **27**, 327 ; 1857, [iv.], **14**, 161.
[7] Bunsen and Roscoe, *Phil. Trans.*, 1857, ii. 355.
[8] Bevan, Burgess, and Chapman, *Proc. Chem. Soc.*, 1904, **52**.
[9] Budde, *Phil. Mag.*, 1871, [v.], **42**, 290.

the heating effects of the rays, as the same increase occurs when all the heat rays are filtered out by passing them first through a water screen ; the effect only occurs with moist chlorine, not with dry.[1] The explanation suggested by Budde is that some of the Cl_2 molecules are dissociated into single atoms.[2] Mellor, however, finds that the increase of volume is exactly proportional to the rise of temperature which takes place, and that therefore the increase of temperature is due to a slight chemical action taking place between the moisture present and the chlorine under the influence of light, producing an active compound which, according to Kümmell,[3] is hydrogen chloride.

A continuously recording actinometer, constructed by Richardson,[4] is founded on this property of chlorine. Two bulbs, connected by a narrow tube, are filled one with dry air and the other with chlorine, a little sulphuric acid separating the two gases. The bulbs are attached to the beam of a balance in such a manner that the flow of acid from one arm to the other causes the beam to move, this movement being communicated by means of a lever to a pen, and so is traced on a rotating drum. The expansion caused by heat rays is eliminated by a special compensating device.

Weigert[5] showed that chlorine does not decompose ozone in the dark, but does so in the light, while Ludlam[6] investigated the action of ultra-violet light on chlorine.

As regards the solubility of chlorine in water, see under Chlorine Water, p. 71. One of the best solvents for chlorine is carbon tetrachloride,[7] which takes up about 10 per cent. Tetra- and penta-chlorethane are also good solvents for Cl.[8] Chlorine is strongly absorbed by blood charcoal.[9] Chlorine cannot be collected over cold water, as it dissolves in about half its volume of that liquid, but since its solubility in boiling water is zero, and in hot water the solubility is slight, it may be collected over hot water. Since it attacks mercury, it cannot be collected over that liquid. As explained above, chlorine, owing to the fact that it is about two-and-a-half times heavier than air, is usually collected simply by displacing the air from a vessel.

Chemical Properties.—The chemical properties of chlorine are decided largely by its strong chemical attraction for hydrogen and its feeble attraction for oxygen.

So great is its attraction for hydrogen that it burns in that gas, and even decomposes many hydrocarbons, setting free carbon. On this same attraction for hydrogen rests the capacity of Cl for decomposing water, liberating nascent oxygen, to which circumstance chlorine owes its exceptional bleaching power. Chlorine, therefore, is a very chemically active element, combining directly with most elements, especially metals, with the exception of oxygen, nitrogen, and the argon group of elements. The chemical activity of chlorine, however, seems considerably greater in the presence of light or under the influence of a silent electric discharge. For example, when a mixture of oxygen,

[1] See Mellor, *Trans. Chem. Soc.*, 1902, **81**, 1284 ; Richardson, *Phil. Mag.*, 1891, [v.], **32**, 277 ; Recklinghausen, *Zeitsch. physikal. Chem.*, 1894, **14**, 494.
[2] Kümmell and Wobig (*Zeitsch. Elektrochem.*, 1909, **15**, 252) find no dissociation takes place from measurement of density.
[3] See also Kümmell, *Zeitsch. Elektrochem.*, 1911, **17**, 408.
[4] A. Richardson, *Phil. Mag.*, 1891, [v.], **32**, 283.
[5] F. Weigert, *Zeitsch. Elektrochem.*, 1908, **14**, 591.
[6] Ludlam, *Phil. Mag.*, 1912, [vi.], **23**, 757.
[7] W. H. Perkin, *Trans. Chem. Soc.*, 1894, **65**, 20.
[8] Konsortium, F., "Elektrochem. Ind.," *Chem. Zeit.*, 1907, **31**, 1095.
[9] H. Freundlich, *Zeitsch. physikal. Chem.*, 1906, **57**, 385.

chlorine, and a trace of nitrogen is subjected to a silent electric discharge, Hautefeuille and Chappuis[1] state that a compound $N_2Cl_2O_{13}$ is formed; again, a mixture of chlorine and hydrogen violently explodes in the light, but only combines gradually in the dark. Since chlorine will not combine directly with oxygen, it obviously is not inflammable in air.

The combustion of hydrogen in chlorine may be easily observed by plunging a jet of burning hydrogen into a jar filled with chlorine (fig. 14), when the hydrogen will continue to burn, while fumes of hydrochloric acid will be seen arising :—

$$H_2 + Cl_2 = 2HCl.$$
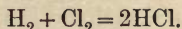
Conversely, a jet of chlorine may be caused to burn in hydrogen.

Another experiment is to fill two equal-sized jars, one with hydrogen and the other with chlorine, place them mouth to mouth, and withdraw the glass plates closing each. The gases thus mix, and if a flame is brought near the mouths of the cylinders, the gases unite with a noise, dense fumes of HCl gas being simultaneously formed. This experiment, however, must be made either by gas- or candle-light, or in a darkened room, as bright sunlight, or even daylight, may cause the combination to take place with explosion.

The following experiments illustrate the power chlorine possesses of withdrawing hydrogen from its combination with carbon :—

A piece of filter-paper is moistened with warm turpentine oil, $C_{10}H_{16}$, and plunged into a jar of chlorine. The paper bursts into flame, and clouds of soot are simultaneously deposited :—

$$C_{10}H_{16} + 8Cl_2 = 16HCl + 10C.$$
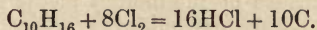
When a burning candle or taper is plunged into a jar of chlorine, it continues to burn with a red, smoky flame, the chlorine combining with the hydrogen in the wax or stearic acid of the candle, leaving the carbon, which appears as

FIG. 14.—Combustion of hydrogen in chlorine.

soot. The flame appears red for the same reason that the sun setting on a misty day looks red—the longer light-waves, viz. red ones, get through the surrounding cloud of carbon particles, while the shorter blue and yellow rays are absorbed.

A similar experiment may be made by mixing one volume of olefiant gas, C_2H_4, with two volumes of chlorine and lighting the mixture with a taper. The mixture burns, evolving a thick smoke, composed of liberated carbon, while fumes of HCl gas simultaneously appear :—

$$C_2H_4 + 2Cl_2 = 4HCl + 2C.$$
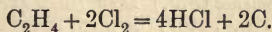
Not only will chlorine abstract hydrogen from combination with carbon, but it will also remove it from union with sulphur. For example, when sulphuretted hydrogen, H_2S, is passed through chlorine water, the sulphur is set free as a yellowish precipitate, while HCl is formed :—

$$H_2S + Cl_2 = 2HCl + S.$$
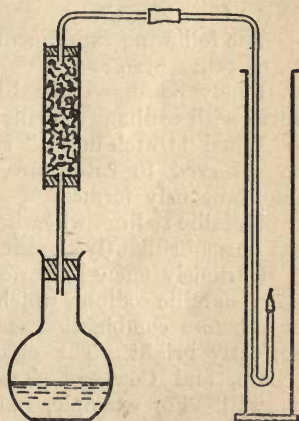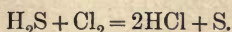
[1] Hautefeuille and Chappuis, *Compt. rend.*, 1884, **98**, 626.

Another good laboratory experiment is the burning of phosphorus in chlorine gas. A small piece of phosphorus is placed in a deflagrating spoon and immersed in the gas; it soon melts and then catches fire, burning to form phosphorus pentachloride and also phosphorus trichloride. Arsenic also inflames in chlorine.

Although pure carbon is not attacked by chlorine, yet when porous charcoal is left in contact with chlorine a very large amount of gas is absorbed. One molecule of chlorine when absorbed by charcoal evolves 13,570 calories.[1] According to Mixter,[2] chlorine is absorbed by carbon which contains chemically combined hydrogen, not mechanically, but rather by the chlorine actually replacing hydrogen, and so remaining chemically united with the carbon.

Chlorine unites directly with nitric oxide, yielding nitrosyl chloride, $NOCl$.[3] The reaction has recently been made the subject of investigation by Miss Arpád,[4] J. E. Coates and Miss Finney,[5] and by M. Trautz,[6] who show that the reaction is termolecular, proceeding according to the equation $2NO + Cl_2 = 2NOCl$.

The following experiments show the chemical attraction chlorine possesses for certain metals :—

Finely powdered metallic antimony when thrown into a jar of chlorine burns with brilliant scintillations, forming $SbCl_3$.

When "Dutch metal" is plunged into a jar of chlorine, the metal may be observed to catch fire, dense yellow fumes of cupric chloride being simultaneously formed.

Metallic sodium when heated in a metal spoon and plunged into chlorine gas burns brilliantly, forming sodium chloride, $NaCl$.

Curiously enough, perfectly *dry* or *pure* chlorine has no action at all upon metallic sodium, which, as Wanklyn[7] observed, can be actually melted in it before combination ensues, the surface of the molten metal remaining perfectly bright. The chlorine must be slightly moist before combination occurs, and Cowper[8] showed that the same holds true for other metals as well. For example, imitation gold leaf can be kept for months in dry chlorine gas without any action taking place. On adding a drop of water, however, an immediate combination ensues. Similarly dry chlorine does not attack zinc foil or magnesium; silver is attacked, but slowly, bismuth superficially, while tin is rapidly chlorinated with the evolution of heat. A piece of brass wire cannot be burnt in dry chlorine, whereas it readily burns in moist chlorine. Iron[9] may be heated to 90° and above before dry chlorine attacks it, although it is readily attacked by the moist gas. On the other hand, Shenstone[10] showed that even perfectly dry chlorine instantly

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[1] Berthelot and Guntz, *Compt. rend.*, 1884, **99**, 7 ; *Ann. Chim. Phys.*, 1886, [vi.], **7**, 138.
[2] W. G. Mixter, *Amer. J. Science* (*Sill.*), 1893, [iii.], **45**, 363.
[3] Gay-Lussac, *Ann. Chim. Phys.*, 1848, [iii.], **23**, 203.
[4] Miss Arpád, "A nitrogen oxyd és chlor egymásra hatásának sebességéről," *Dissertation*, Budapest und Magyar-Chemikusok, Lapja, 1913, Évi 7–8.
[5] Coates and Miss Finney, *Trans. Chem. Soc.*, 1914, **105**, 2444.
[6] Trautz, *Zeitsch. Elektrochem.* (abstract), 1914, **20**, 325 ; from *Sitzungsber. Heidelberger Akad. Wiss.*, Abt. A., Abh. 1, Jan. 1914.
[7] Wanklyn, *Chem. News*, 1869, **20**, 271 ; see also Ferentzy, *Chem. Zeit.*, 1908, **32**, 285.
[8] Cowper, *Trans. Chem. Soc.*, 1883, **43**, 153.
[9] See Lange, *Zeitsch. angew. Chem.*, 1900, **13**, 683.
[10] Shenstone, *Trans. Chem. Soc.*, 1897, **71**, 471.

attacks mercury. Gold is attacked by chlorine,[1] whereas at ordinary temperatures platinum [2] seems unaffected.

When chlorine is dissolved in carbon tetrachloride it acts very energetically on many metallic oxides.[3]

Bleaching Properties of Chlorine Gas.—Chlorine is used on a very large scale for bleaching purposes, especially in the paper and cotton trades. Its bleaching power depends upon its power of withdrawing hydrogen from water, thus setting free nascent oxygen,[4] which then attacks the organic colouring matter and destroys it :—$Cl_2 + H_2O = 2HCl + O$.

Dry chlorine has no bleaching action. For example, a piece of dry litmus paper or a piece of dry cloth dyed turkey-red when immersed in dry chlorine remains unaltered in appearance for hours, but on adding a small amount of water the colour rapidly disappears.

Since the bleaching action of chlorine depends upon a process of oxidation, it is not surprising that neither mineral colours nor black tints produced by free carbon are, in general, bleached by chlorine. Printers' ink, for example, which contains lamp-black or finely divided carbon, is not attacked, whereas ordinary writing-ink, which consists of organic compounds of iron or of aniline dyes, is rapidly bleached. An effective experiment is to cover a printed card with ordinary writing-ink, so as to render the printed matter indistinguishable, and then immerse the whole in moist chlorine gas. The writing-ink is rapidly bleached, and the characters in printers' ink become visible.

Chlorine is also a powerful disinfectant and deodoriser—properties which depend upon its oxidising activities.

Chemical Properties of Liquid Chlorine.[5]—Potassium and sodium when immersed in liquid chlorine at − 80° retain their metallic lustre. Magnesium also is not attacked. Aluminium, however, when immersed in liquid chlorine, catches fire at − 20° C., but is unchanged at − 33·6° C. (the boiling-point of liquid chlorine). Liquid chlorine unites explosively with yellow phosphorus, while red phosphorus is also attacked. Arsenic, even at − 90°, unites with liquid chlorine, catching fire after a time, and burning to $AsCl_3$. Antimony and bismuth are not attacked by liquid chlorine at its boiling-point (− 33·6° C.), but combination ensues at higher temperatures. Tin, gold, and iodine, bromine, sulphur, selenium, and tellurium are all attacked by liquid chlorine. Iron is not attacked by dry liquid chlorine (Lange)—a fact of great technical importance, as upon it depends the possibility of transporting large masses of liquid chlorine in steel boilers and bombs.

Chlorine Water. Chlorine Hydrate.—The maximum solubility of chlorine in water [6] occurs at 9·6° C., when the partial pressure of the chloride is equal to one atmosphere. Below that temperature the solubility decreases

[1] See Krüss and Schmidt, *Zeitsch. anorg. Chem.*, 1893, **3**, 421.
[2] Haber, *Zeitsch. anorg. Chem.*, 1906, **51**, 356.
[3] See Michael and Murphy, *Amer. Chem. J.*, 1910, **44**, 365–84.
[4] Popper (*Annalen*, 1885, **227**, 167) suggests the formation of $HClO_3$ and $HOCl$ as playing an important part in the reaction :—$3Cl_2 + 3H_2O = 5HCl + HClO_3$; $3Cl_2 + 3H_2O = 3HCl + 3HOCl$. Other authorities suggest the formation of a *cellulose peroxide* plays an important part, while the condensation of nascent oxygen on the surface of the fibres is held by others to account for the oxidising action, as by condensation the oxygen would be brought into a state of high concentration. See Cross and Bevan, *Zeitsch. angew. Chem.*, 1907, **20**, 570, 1280 ; Ditz, *Chem. Zeit.*, 1907, **31**, 833, 844, 857.
[5] See Gautier and Charpy, *Compt. rend.*, 1891, **113**, 597 ; Thomas and Dupuis, *Compt. rend.*, 1906, **143**, 282 ; Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 96 ; Lange, *Zeitsch. angew. Chem.*, 1900, **13**, 683. [6] Schönfeld, *Annalen*, 1855, **93**, 26 ; **95**, 8.

owing to the formation of hydrate,[1] and above that temperature the solubility also decreases, becoming zero at 100° at 760 mm.

The usual apparatus employed for making chlorine water is shown in fig. 15 ; the water should be at 9·6° C., and the chlorine should be as air-free as possible. Another method consists in leading chlorine gas into an inverted retort filled with water, as illustrated in fig. 16.

Saturated chlorine water is a yellowish-green liquid, which smells, tastes, and bleaches like chlorine. It should not be acid when freshly
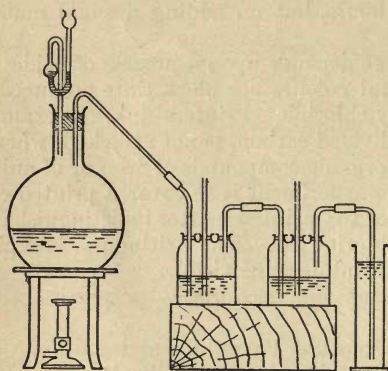
FIG. 15.—Preparation of chlorine water.   FIG. 16.—Preparation of chlorine water.
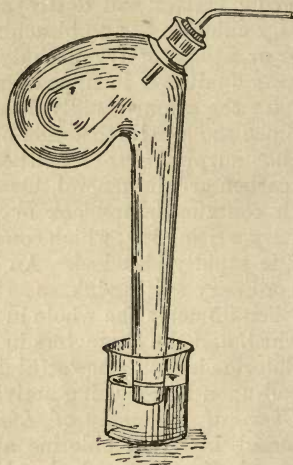
made. It freezes at 0°, separating into chlorine hydrate and into chlorine-free ice. Water saturated with chlorine possesses at 6° C. a density of 1·003.

1 volume of water absorbs, according to Winkler, the following volumes of chlorine measured at 0° and at a total pressure (*i.e.* partial pressure of chlorine and of water vapour) of 760 mm. :—

Temp. ° C.	Solubility.	Temp. ° C.	Solubility.	Temp. ° C.	Solubility.
10	3·095	21	2·200	35	1·575
11	2·996	22	2·143	40	1·414
12	2·900	23	2·087	45	1·300
13	2·808	24	2·035	50	1·204
14	2·720	25	1·985	60	1·006
15	2·635	26	1·937	70	0·848
16	2·553	27	1·891	80	0·672
17	2·474	28	1·848	90	0·380
18	2·199	29	1·808		
19	2 325	30	1·767		
20	2·260				

[1] The solubility increases with fall of temperature below 9·6° provided chlorine hydrate does not separate out ; but the system is metastable.

The absorption of chlorine in water is not a mere process of solution. For example, Roscoe[1] showed that chlorine, when mixed with a gas such as carbon dioxide or hydrogen, dissolves in water between 11° and 38° in greater quantities than it should according to Dalton and Henry's law of partial pressures. Also Richardson[2] showed that when chlorine water is distilled, we get hypochlorous acid passing over, together with free chlorine, while hydrochloric acid is left in the residual liquid. When, however, the condensed products are made to continuously flow back into the flask, the chlorine water remains practically unchanged at the boiling-point.

These remarkable results are explained by Jakowkin[3] as due to a reversible change, represented by the equation—

$$Cl_2 + H_2O + Aq. \rightleftharpoons HCl.Aq + HClO.Aq.$$
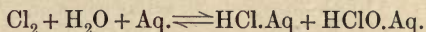
The reaction proceeds with the absorption of heat, which decreases with rise of temperature and becomes zero between 75° and 95°. The solution warmth of chlorine in water is given by T. J. Baker[4] as 4970 calories per gram-molecule against 4870 calories given by Thomsen.

Water saturated with KCl absorbs at 15° one-third less chlorine than pure water.[5] A saturated solution of NaCl absorbs[6] at 14·5°, 29°, 60°, and 82°, 0·3607, 0·3125, 0·1332, and 0·0586 volumes respectively of chlorine (reduced to 0° and 760 mm.). Goodwin[7] states that LiCl and HCl increase the solubility of chlorine in water.

The depression of the solubility of chlorine in water containing sodium chloride is well expressed by the following results obtained by Kumpf :— [8]

Brine, NaCl = 9·97 per cent.

Temperature	7·9°	11·9°	15·4°	18·8°
Solubility coeff.	1·8115	1·5879	1·2785	1·0081

NaCl = 16·01 per cent.

Temperature	6°	11·6°	16·4°	21·4°	26·9°
Solubility coeff.	1·5866	1·2227	1·0121	0·8732	0·7017

NaCl = 19·66 per cent.

Temperature	0°	9·2°	14·8°	15·4°	20·4°	21·9°
Solubility coeff.	1·6978	1·2145	0·9740	0·9511	0·7758	0·7385

When chlorine water is exposed to light, oxygen is liberated :—

$$Cl_2 + 2H_2O = 4HCl + O_2.$$
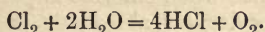
[1] Roscoe, *J. Chem. Soc.*, 1856, **8**, 14.
[2] A. Richardson, *Trans. Chem. Soc.*, 1903, **83**, 380.
[3] Jakowkin, *Zeitsch. physikal. Chem.*, 1899, **29**, 613. See also Mumm, *Zeitsch. physikal. Chem.*, 1907, **59**, 459.
[4] T. J. Baker, *Proc. Roy. Soc.*, 1901, **68**, 9.
[5] Dettmar, *Annalen*, 1841, **38**, 35.
[6] C. A. Kohn and O'Brien, *J. Soc. Chem. Ind.*, 1898, **17**, 1100.
[7] Goodwin, *Ber.*, 1882, **15**, 3039.
[8] Kumpf, *Wied. Ann. Beibl.*, 1882, **6**, 276.

Curiously enough, if the chlorine water is too concentrated, no decomposition occurs in light. For example, it was long ago observed by Wöhler[1] that when chlorine hydrate is placed in a sealed tube and exposed for a whole summer to the sunlight (the chlorine hydrate naturally decomposing in the warmth to chlorine water and chlorine), there was practically no decomposition ; and as soon as the winter came the chlorine hydrate re-formed again in the tube. Again, Pedler[2] showed that chlorine water containing one molecule of chlorine to 64 of water could be exposed to tropical sunlight for two months without decomposition, whereas more dilute solutions were decomposed according to the following table :—

Mols. H_2O for 1 mol. Cl_2.	Percentage of Cl acting on water.
64	no action
88	29
130	46
140	29
412	78

When the solutions are very dilute and are placed in direct sunlight, the reaction appears to take place in accordance with the equation—

$$Cl_2 + 2H_2O = O_2 + 4HCl.$$
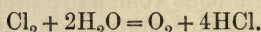
A small amount of chloric acid is also formed. When, however, the solution is placed in diffuse daylight, much chloric acid is formed and the reaction appears to take place mainly according to the equations :—[3]

$$Cl_2 + H_2O = HCl + HClO ; \quad 8HClO = 2HClO_3 + 6HCl + O_2.$$
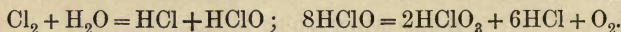
Traces of $HClO_4$ are also formed.

These irregularities in the evolution of oxygen make it very difficult to utilise the volume of oxygen evolved as a measure of the chemical action of light.

In fact, the photochemical decomposition of chlorine water is not even approximately proportional to the intensity of the light and the time of illumination. The varying amounts of HCl, HClO, $HClO_3$, and $HClO_4$, which are formed, each influence the velocity of the reaction, and thus complicate the effect.

Indeed, under certain conditions the reverse change can take place, causing the formation of free chlorine from a mixture of HCl and oxygen (see, for example, Deacon's process, p. 60). Klimenko and Pekatoros[4] showed that the addition of alkali chlorides and other chlorides to chlorine water decreased very perceptibly the rate of decomposition.

Chlorine hydrate is formed when chlorine is passed into water maintained at a temperature only a few degrees above 0°. Beautiful crystals, composed of regular octahedra, separate out, which, according to Faraday,[5] contain 27·70 per cent. of chlorine, and have the composition $Cl_2 + 10H_2O$. The

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[1] Wöhler, *Annalen*, 1853, **85**, 375.

[2] A. Pedler, *Trans. Chem. Soc.*, 1890, **57**, 613.

[3] Popper, *Annalen*, 1885, **227**, 161.

[4] Klimenko and Pekatoros, *Zeitsch. physikal. Chem.*, 1889, **4**, 483. See also Klimenko, *Ber.*, 1895, **28**, 2558. Milbauer (*Zeitsch. physikal. Chem.*, 1914, **86**, 564–66) tried the effect of such bodies as I, Br, H_2SO_4, Au, Cd, Hg, etc., etc.

[5] Faraday, *Quart. Journ. of Science*, **15**, 71.

composition is a matter of dispute, as Roozeboom [1] gives the composition $Cl_2 + 8H_2O$, while de Forcrand [2] gives the formula $Cl_2 + 7H_2O$. The hydrate decomposes at $9.6°$ in the air and at $28.7°$ in a closed vessel, forming two layers, one of liquid chlorine and the other of aqueous chlorine water. Faraday in 1823 first liquefied chlorine in this way. He placed some crystals of the hydrate in a bent sealed tube, immersed one end in a freezing mixture, and the other end was warmed. Liquid chlorine condensed as an oily liquid in the cooled end (fig. 17).

It is related that while Faraday was thus operating with chlorine hydrate in a sealed tube, Dr Paris called at the laboratory of the Royal Institution, where Faraday was at work, and, noticing some oily matter in the tube, he commented on "the carelessness of employing soiled vessels." Faraday later attempted to open the tube by filing the sealed end, when an explosion took place and the oil vanished. On repeating the experiment Faraday proved that the "oil" was really liquid chlorine, and Dr Paris next morning received a curt note: "Dear Sir,—The *oil* you noticed yesterday turned out to be liquid chlorine. — Yours faithfully, Michael Faraday." The pale yellow crystals of chlorine hydrate have a specific gravity of 1·2. Their colour fades as the tem-

FIG. 17.—Faraday's experiment.

perature decreases, and at $-50°$ the crystals appear to be almost white.

The crystals may be sublimed from one part of the tube to another, do not conduct electricity, are without action on polarised light, and act on ammonia and ammonium salts in the same manner as free chlorine. The dissociation tension of the hydrate has been measured. The following numbers are given by Roozeboom :—[1]

Temperature, °C.	0°	4°	8°	9°	14°
Dissoc. tension	249 mm.	398 mm.	620 mm.	701 mm.	1240 mm.

The critical temperature of decomposition in an open vessel is $9.6°$ C.—in other words, the dissociation pressure is 760 mm. at this temperature.

According to de Forcrand [2] the heat of formation is given by

$$Cl_2 \text{ (gas)} + nH_2O \text{ (liquid)} = Cl_2, \, nH_2O \text{ (solid)} + 1857 \text{ calories.}$$
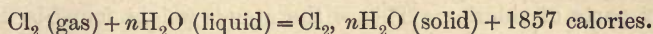
Valency of Chlorine.—Chlorine can act with a valency of 1, 3, 4, 5, and 7. In most of its compounds, especially with metals, it acts as a monovalent element. The oxides and oxy-acids of chlorine, however, show that it can act with a higher valency than unity. Meldola [3] in 1888 described a compound of methyl oxide, in which he assumed chlorine to be trivalent and oxygen tetravalent : $(CH_3)_2 = O = Cl - H$; and the question of the valency of chlorine was discussed at length by Heyes.[4] A similar discussion was given by Stanley.[5]

In chlorine peroxide, ClO_2, chlorine is, apparently, acting as a tetravalent element.

[1] Roozeboom, *Rec. Trav. Chim.*, 1884, 3, 29, 59, 73, 84 ; 1885, 4, 216.
[2] de Forcrand, *Compt. rend.*, 1901, 133, 1304, 134, 991.
[3] R. Meldola, *Phil. Mag.*, 1888, [v.], 26, 403.
[4] Heyes, *Phil. Mag.*, 1888, [v.], 25, 297.   [5] Stanley, *Chem. News*, 1902, 85, 133.

Mathews[1] deduces the valency of chlorine in various compounds from the molecular cohesion of chlorine compounds.

Physiological Action.—Chlorine has a very irritating action on the lungs and mucous membrane of the nose and throat, and when breathed causes violent coughing, sometimes attended with asthma and the spitting up of blood, especially if breathed for some time. Many fatal accidents have occurred with chlorine ; death appears to be due to heart paralysis ; it has been proved that an average man can only breathe without injury one part of chlorine mixed with two or three million parts of air. Workers, however, used to chlorine can often breathe without injury a value as high as one part in 100,000 parts of air.

In cases of chlorine poisoning various authorities recommend the breathing of sulphuretted hydrogen, alcohol vapour, ether vapour, aniline, or steam inhalation.

Workmen who have to deal with electrolytic chlorine often suffer from an illness accompanied by swellings in various parts of the body, coughing, and giddiness.[2] These effects appear to be due rather to the oxides of chlorine contained in electrolytic chlorine than to chlorine itself ; these oxides are often present to the extent of 0·5 to 0·8 per cent. When the cells used for making electrolytic chlorine are coated with tar, certain organic chlorinated products are stated to cause a peculiar skin disease among the workmen.[3]

Chemically combined chloride (*i.e.* chlorides) are vital constituents of both plant and animal juices, and deficiency in chlorides may lead to death. When an animal is deprived of all chlorides, but its food contains bromides, the bromine takes the place of chlorine, both in the blood serum and in the other tissues.[4]

Atomic Weight.—Berzelius[5] determined the atomic weight of chlorine, together with those of silver and potassium, by the following method : viz. (1) $KClO_3$ was transformed into KCl by heating. The loss of weight = oxygen. He found that 100 parts $KClO_3$ gave 39·15 of oxygen ; whence $KCl = 74·605$ if $O = 16$. (2) Potassium chloride was precipitated with silver nitrate solution. He found that 100 parts of KCl gave 192·4 parts of $AgCl$, whence the molecular weight of $AgCl = 143·54$. (3) He next transformed a known weight of silver into silver chloride, and found that 100 parts of Ag gave 132·75 $AgCl$; consequently in a molecular weight of $AgCl$ (143·54) there are 35·412 parts of chlorine. This is the atomic weight found by Berzelius for chlorine, on the basis $O = 16$.

Penny[6] in 1839, by evaporating $KClO_3$ to dryness with hydrogen chloride, found that the percentage of $O = 39·177$, $KCl = 74·521$, and 100 parts Ag gave 132·84 parts of $AgCl$.

Marignac,[7] in 1844, and Maumené,[8] in 1846, carried out similar experiments.

In 1859 Dumas[9] made two syntheses of $AgCl$, and found that 108 parts

[1] Mathews, *J. Physical Chem.*, 1913, **17**, 183–204 ; 252–63.
[2] Herxheimer, *Zeitsch. angew. Chem.*, 1899, **12**, 310.
[3] Leymann, *Chem. Zeit.*, 1907, **31**, Rep. 250. See also Lunge, *Sodaindustrie*, 1896, **3**, 237, 416 ; Jurisch, *Gefahren für die Arbeiter in chemischen Fabriken*, p. 11 ; Holtzmann, *Chem. Zeit.*, 1908, **32**, Rep. 192.
[4] Böninger, *Zeitsch. exp. Path.*, 1907, **4**, 414.
[5] Berzelius, *Pogg. Annalen*, 1826, **8**, 1.
[6] Penny, *Phil. Trans.*, 1839, p. 13. [7] Marignac, *Annalen*, 1844, **44**, 11.
[8] Maumené, *Ann. Chim. Phys.*, 1846, [iii.], **18**, 41.
[9] Dumas, *Ann. Chim. Phys.*, 1859, [iii.], **55**, 134.

of silver united with 35·499 and 35·512 parts of chlorine. He came to the conclusion that the atomic weight of Cl = 35·5.

Stas [1] now took up the work and made numerous experiments. He decomposed $KClO_3$ both by heat and by evaporating with hydrogen chloride, synthesised AgCl by four different methods, decomposed $AgClO_3$ to estimate the oxygen, and converted sodium and potassium nitrates into chlorides. He obtained numbers for the atomic weight of chlorine varying from 35·455 to 35·460 (O = 16). Stas, taking into account Marignac and Penny's results, came to the conclusion that the correct atomic weight of Cl was 35·457 on the basis of O = 16. Clearly, however, the value obtained depends upon that deduced for the atomic weight of silver, and Stas' results have been re-calculated by van der Plaats [2] and by Ostwald, [3] whereby the following values have been adduced (O = 16) :—

Computer.					Cl.	Ag.
Stas	.	.	.	.	35·457	107·930
van der Plaats		.	.	.	35·456	107·930
Ostwald .	.	.	.	.	35·453	107·938

In 1905 Richards and Wells [4] concluded that the ratio

$$Ag : Cl = 1 : 0·328445$$

as given by Stas is not quite correct. Their own experimental result was

$$Ag : Cl = 1 : 0·32867,$$

according to which the atomic weight of chlorine is 35·473, if that of silver is taken at 107·930.

Within the last decade a great deal of valuable research has been done on this subject, with the result that the value given by Stas for the atomic weight of silver has been proved to be incorrect (see Vol. II.), whilst, curiously enough, the value given for chlorine is almost exactly correct, although based on slightly inaccurate data.

In 1905 Dixon and Edgar [5] synthesised hydrogen chloride, determining the weights of hydrogen and chlorine that combined together. Their results lead to the value Cl = 35·463. Three years later Edgar [6] gave the results of a similar series of experiments in which, however, all three substances, viz. hydrogen, chlorine, and hydrogen chloride, were weighed.

From the relationship H : Cl, the value Cl = 35·462 was obtained, and from H : HCl the value Cl = 35·461. All of these results are based on the assumption that H = 1·00762 when O = 16 (Morley).[7]

[1] Stas, "Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels," *Mém. Acad. roy. Belg.*, 1865, **35**, 3. A good account of this work will be found in the Stas Memorial Lecture of the Chemical Society (*Trans. Chem. Soc.*, 1893, **63**, 1). See also Stas, *Œuvres Complètes* (Brussels), 1894, vol. i.
[2] J. D. van der Plaats, *Ann. Chim. Phys.*, 1886, [vi.], **7**, 499.
[3] Ostwald, *Lehrbuch der allgemeinen Chemie* (Leipzig, 1891), vol. i.
[4] Th. W. Richards and Wells, *J. Amer. Chem. Soc.*, 1905, **27**, 459.
[5] Dixon and E. C. Edgar, *Phil. Trans.*, 1905, **205**, 169.
[6] Edgar, *Proc. Roy. Soc.*, 1908, **A, 81**, 216 ; *Phil. Trans.*, 1908, **A, 209**, 1.
[7] The alternative value H = 1·00787, due to W. A. Noyes (1907), cannot be regarded as having the same accuracy as Morley's number, and when adopted as the basis of calculation in the experiments of Dixon and Edgar, of Edgar, and of Burt and Gray, the results obtained for the atomic weight of chlorine diverge considerably from those furnished by the most accurate modern gravimetric analyses.

Noyes and Weber,[1] in 1908, also made a series of determinations. They determined the relation H : Cl by absorbing the hydrogen in palladium, and then leading the gas evolved over a weighed amount of K_2PtCl_6. The loss of weight of the palladium gave the hydrogen, and the loss of weight of the K_2PtCl_6 gave the chlorine. Taking $H = 1 \cdot 00762$, this gave $Cl = 35 \cdot 452$.

Guye and Fluss[2] determined the atomic weight of chlorine in respect to oxygen by distilling a known weight of nitrosyl chloride, NOCl, over silver in order to absorb the chlorine, then over heated copper to absorb the oxygen, and finally over metallic calcium to retain the nitrogen. From the direct weights of the oxygen and the chlorine they obtained $Cl = 35 \cdot 468$ ($O = 16$).

In 1909 Richards, Koethner, and Tiede[3] measured the ratio $AgCl : NH_4Cl$, and by combining the result with those for Ag : Cl (Richards and Wells) and Ag : $AgNO_3$ (Richards and Forbes),[4] it is possible to calculate the atomic weights of chlorine, silver, and nitrogen. The results are as follows :—

	Ag.	Cl.	N.
$H = 1 \cdot 00762$ (Morley) . .	$107 \cdot 880$	$34 \cdot 457$	$14 \cdot 008$
$H = 1 \cdot 00787$ (Noyes) . .	$107 \cdot 878$	$35 \cdot 456$	$14 \cdot 007$

The only atomic weight other than $O = 16$ that has to be assumed is that of hydrogen, but the present uncertainty of that has practically no influence on the result.

In 1910 Richards and Willard[5] determined the ratios $LiClO_4 : LiCl$, . $LiCl : AgCl$, and $LiCl : Ag$. By combining these results with the ratio Ag : Cl (Richards and Wells) the atomic weights of lithium, chlorine, and silver admit of calculation on the basis $O = 16$. The results lead to the values $Cl = 35 \cdot 454$ and $Ag = 107 \cdot 871$.

Gray and Burt,[6] by decomposing hydrogen chloride, HCl, by red-hot aluminium and measuring the volume of hydrogen evolved, obtained $Cl = 35 \cdot 459$ ($H = 1 \cdot 00762$), using their own value for the density of hydrogen chloride, and Morley's value for that of hydrogen. From the density and compressibility of hydrogen chloride they found, by the method of limiting densities (see Vol. I. p. 133), $Cl = 35 \cdot 461$. The mean value is $Cl = 35 \cdot 460$.

Baume and Perrot[7] combined gaseous hydrogen chloride with a weighed amount of liquid ammonia and found $Cl = 35 \cdot 465$ (taking $N = 14 \cdot 009$).

Wourtzel,[8] synthesising nitrosyl chloride, NOCl, from weighed amounts of nitric oxide and chloride, found $Cl = 35 \cdot 460$ ($N = 14 \cdot 008$). One other determination remains to be mentioned, namely, the modern repetition of the method of Berzelius. The necessary data are furnished by the ratios Ag : Cl (Richards and Wells), KCl : Ag, and KCl : AgCl (Richards and Stähler),[9] and

[1] W. A. Noyes and H. C. P. Weber, *J. Amer Chem. Soc.*, 1908, **30**, 13.

[2] Guye and Fluss, *J. Chim. phys.*, 1908, **6**, 732 ; Guye, *J. Chim. phys.*, 1913, **11**, 275–318 ; Boubnoff and Guye, *ibid.*, 1911, **9**, 290. See also this Series, Vol. I., Chap. VII.

[3] Richards, Koethner, and Tiede, *J. Amer. Chem. Soc.*, 1909, **31**, 6 ; Richards and Willard, *J. Amer. Chem. Soc.*, 1910, **32**, 4.

[4] Richards and Forbes, *J. Amer. Chem. Soc.*, 1907, **29**, 808.

[5] Richards and Willard, *J. Amer. Chem. Soc.*, 1910, **32**, 4 ; *Carnegie Institution Publications*, 1910, No. 125.

[6] T. W. Gray and Burt, *Trans. Chem. Soc.*, 1909, **95**, 1633 ; *Chem. News*, 1911, **103**, 161, 170 ; *Trans. Faraday Society*, 1911, **7**, 30–41. Compare Guye and Ter-Gazarian, *Compt. rend.*, 1907, **143**, 1233 ; D. Berthelot, *loc. cit.*, 1907, **144**, 269 ; Scheuer, *Zeitsch. physikal. Chem.*, 1909, **68**, 575.

[7] G. Baume and F. Louis Perrot, *Compt. rend.*, 1912, **155**, 461–64.

[8] Eugène Wourtzel, *Compt. rend.*, 1912, **155**, 345–46 ; *J. Chim. phys.*, 1913, **11**, 214–48.

[9] Richards and Stähler, *J. Amer. Chem. Soc.*, 1907, **29**, 623.

finally $KClO_3$: KCl (Stähler and Meyer).[1] By combining these values the value $Cl = 35\cdot458$ ($O = 16$) is arrived at.

The International Commission on Atomic Weights in 1909 decided on the atomic weight $Cl = 35\cdot46$ ($O = 16$), which value is still (1915) held to be the most probable one.

The preceding sketch of the attempts which have been made to determine the atomic weight of chlorine with precision can give no idea of the enormous labour and rigorous accuracy which has been brought to bear on the subject in a series of masterly researches.[2] In fact, about the atomic weight of chlorine has centred some of the most accurate research work ever undertaken in chemistry, and an accurate knowledge of this constant is of fundamental importance in settling the atomic weights of large numbers of other elements, and in deciding whether Prout's hypothesis or Dumas's modification of it (namely, that the atomic weights of all the elements are multiples or submultiples of that of hydrogen) is founded on an experimental basis. The experiments above discussed have decided against Prout's hypothesis. At the same time the tendency of atomic weights to approximate whole numbers seems to be a most remarkable fact which needs explanation.

Uses of Chlorine.—Chlorine is mainly used for manufacturing bleaching powder, hypochlorites[3] (bleaching liquids), and chlorates.

Considerable quantities of liquid chlorine were formerly used in the extraction of gold from its ores,[4] but the chlorination process for gold is now practically obsolete, having been superseded, mainly by the cyanide process. Chlorine also finds a considerable use as a disinfecting agent.

Large quantities of chlorine are used in the manufacture of certain chlorinated organic substances;[5] thus over 3000 tons of chloracetic acid are produced yearly for making synthetic indigo, the chlorine being obtained electrolytically for this purpose.

Other important chlorinated chemicals are chloral, phosgene gas, carbon tetrachloride, dichlorethylene, trichlorethylene, perchlorethylene, tetrachlorethane, pentachlorethane, and hexachlorethane. These compounds are used as extraction agents, and have the advantage of being non-inflammable, so that there is no danger of explosion when they are used.[6]

Chlorinated benzene and naphthalene derivatives are much used in the making of dyes; while recently chlorinated indigoid dyes have been placed on the market.

CHLORINE AND HYDROGEN.

Only one chloride of hydrogen has been isolated with certainty. This is HCl—hydrogen chloride, hydrochloric acid gas, or muriatic acid gas. Its aqueous solution is the well-known substance "hydrochloric acid solution."

Besides the chloride HCl, there is some evidence for the existence in solution of a perchloride HCl_3, analogous to HI_3.

The existence of HCl_3 is briefly discussed on p. 118.

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[1] Stähler and Meyer, *Zeitsch. anorg. Chem.*, 1911, **71**, 378.

[2] A full account of the determination of the ratio LiCl : AgCl, one of the ratios mentioned in the text, is given in Vol. I. Chap. VII., and illustrates the extreme care necessary in accurate atomic weight researches.

[3] See H. S. Duckworth, *J. Soc. Chem. Ind.*, 1906, **24**, 1157.

[4] Harrison, *Eng. Min. J.*, 1907, **83**, 137.

[5] See Askenasy, *Zeitsch. angew. Chem.*, 1907, **20**, 1166 ; F. Ullmann, *Chem. Ind.*, 1908, **31**, 405.

[6] See Konsortium F., " Elektrochem. Ind.,"*Chem. Zeit.*, 1907, **31**, 1095 ; " Chem. Fabrik Griesheim-Elektron," *Chem. Zeit.*, 1908, **32**, 256.

HYDROCHLORIC ACID.

(Hydrogen Chloride.   Muriatic Acid.)

Formula, HCl.   Molecular weight = 36·46.

Occurrence.—Considerable quantities of hydrochloric acid occur in the gases evolved from volcanoes. For example, D. Franco[1] found that the emanations arising from Vesuvius, and the gases given off by flowing lava in the process of solidification, contain large amounts of hydrochloric acid gas. Bunsen,[2] in 1847, proved the same thing as regards the fumaroles on Hecla. Enormous quantities of hydrochloric acid gas are belched forth by the volcanoes of South America, and much of this finds its way into the waters of brooks and rivers taking their rise in volcanic districts. Thus, the water of the Rio Vinagre in Mexico contains no less than 0·091 per cent. of free HCl,[3] and there flows to waste daily in this river 42,150 kg. of HCl together with 46,873 kg. of sulphuric acid.

The origin of this volcanic hydrochloric acid is believed to be due to the decomposition of salt and other chlorides contained in rocks by highly heated water. Many authorities believe that volcanic activity is largely determined by sea-water (which contains much salt and other chlorides such as magnesium chloride) gaining access to the interior hot regions of the earth, the pressure of the resulting steam causing volcanic eruptions.

Now, very hot water acts like an acid in decomposing chlorides, and this explanation readily accounts for the evolution of HCl.

Free hydrochloric acid also occurs in the gastric juice of man[4] and other animals ; the gastric juice of dogs, for example, contains on an average ·6 per cent. and that of man[5] 0·2 to 0·4 per cent.

History.—Hydrochloric acid was known to Geber (in the Middle Ages) in the form of a mixture with nitric acid, known as *aqua regia* on account of its property of dissolving gold. This aqua regia was obtained by distilling a mixture of nitre, sal-ammoniac, and vitriol.

The pure acid, however, is first mentioned in the works of Basil Valentine under the name of *spiritus salis*, which was prepared from *guter vitriol* and *sal commune.*

Glauber, about 1648, obtained the acid by the action of sulphuric acid on common salt. Stephan Hales, in 1727, in a book on *Vegetable Staticks*, remarks on the evolution of large quantities of a gas soluble in water when ammonium chloride is heated with oil of vitriol. Priestley,[6] in 1772, collected this gas over mercury in a pneumatic trough, this being probably the first preparation of gaseous hydrochloric acid. Priestley called the gas " marine acid air," since it was derivable from sea-salt. The gas was at first thought to be an oxygen compound, but Davy in 1810 proved that it consisted of chlorine and hydrogen alone.

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[1] Franco, *Ann. Chim. Phys.*, 1873, [iv.], **30,** 87 ; Palmieri, *The Late Eruption of Vesuvius*, 1872, p. 136 ; Matteuci, *Compt. rend.*, 1899, **129,** 65.

[2] Bunsen, *Annalen*, 1847, **62,** 1 ; see also " Pseudo-Volcanic Phenomena of Iceland," *Cavend. Soc. Mem.*, p. 327.

[3] Boussingault, *Compt. rend.*, 1874, **78,** 453, 526, 593.

[4] See for Cahn and Mering, *Jahresber.*, **1887,** 2320 ; Danneel, *Pflüger's Arch.*, 1906, **114,** 108.

[5] Sommerfeld, *Biochem. Zeitsch.*, 1908, **9,** 352 ; see also Christiansen, *Biochem. Zeitsch.*, 1912, **46,** 24, 50, 71, 82.

[6] Priestley, *Observations on Different Kinds of Air* (1772), vol. iii. p. 208.

Formation of Gaseous Hydrogen Chloride.—(1) *By Direct Union of Hydrogen and Chlorine.* —When equal volumes of hydrogen and chlorine are mixed together and exposed to sunlight they unite with a violent explosion,[1] but without change of volume, to give gaseous hydrochloric acid :—

$$\underset{\text{1 volume}}{H_2} \quad + \quad \underset{\text{1 volume}}{Cl_2} \quad = \quad \underset{\text{2 volumes.}}{2HCl}$$
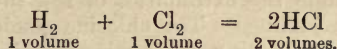
No combination whatever occurs so long as the mixture remains at ordinary atmospheric temperature in the dark. But diffused daylight causes a gradual union of the gases, while a bright light rich in chemical rays, such as magnesium light, acts like sunlight in causing almost instantaneous explosion. Other intense artificial lights usually explode it, although sometimes some minutes elapse before the action takes place. Thus the Drummond limelight causes an explosion after some minutes' exposure. Also if a flame be brought near the mouth of the jar containing the gases, or if an electric spark be passed through the gaseous mixture, a sudden combination takes place, and the heat evolved is sufficient to generate an explosive wave in the mixture.

Even when the mixture is expanded to twenty-four times its volume, or when the gas is mixed with eighteen times its volume of oxygen, an electric spark still causes the mixture to unite with a bright flash of light.

This remarkable action of light may be experimentally shown in several ways.[2] A small thin flask placed in a darkened room is filled half with chlorine (by displacement over hot water) and half with hydrogen gas. It is then corked and covered up. When the flask is exposed to bright sunlight, or when a piece of magnesium ribbon is burnt near it, the flask is shattered with a loud explosion, and fumes of hydrochloric acid fill the air.

An easier method of proceeding is to electrolyse aqueous hydrochloric acid, thus obtaining a mixture of exactly equivalent volumes of hydrogen and chlorine.

Fuming hydrochloric acid (30 per cent. HCl) is placed in the glass tube A (fig. 18), fitted as shown with two carbon electrodes (usually arc lamp carbons are employed), which are secured in the tubulures in the sides by means of rubber stoppers. The whole apparatus is brought into a darkened room or into a room whose only source of light is a small gas- or candle-flame, and the carbon poles are connected with a powerful current (such as that evolved by four Bunsen cells).

When the current passes through the hydrochloric acid, hydrogen and chlorine are evolved, thus :—

$$2HCl = \underset{\text{(− pole)}}{H_2} \quad + \quad \underset{\text{(+ pole)}}{Cl_2,}$$
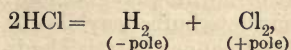
and the gases, thus evolved in exactly equivalent quantities, mix on their way out. At first the chlorine is absorbed by the liquid, but after the evolution of gas has been going on for two or three hours, the liquid becomes saturated with chlorine, and after this hydrogen and chlorine are evolved in equal quantities. When this state of equilibrium is attained, the evolved gas is

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[1] Gay-Lussac and Thénard, *Recherches*, **2**, 93. H. B. Dixon (*J. Soc. Chem. Ind.*, 1906, **25**, 145) gives a complete review of the work on this subject which has been carried out since 1801.

[2] See Roscoe, *J. Chem. Soc.*, 1856, **8**, 16.

washed by being passed through a little water contained in the bulb tube B ground into the neck of A, and then passes into a bulb C, the size of a hen's egg, which has been blown in a piece of easily fusible glass tubing. At each end the tubing is drawn out very thin and should have an internal diameter under one millimetre, while the extremities of the tube are wider, so as to fit ordinary rubber tube joinings. The chlorine coming off at the free end of the bulb is absorbed by passing the issuing gas into a jar D filled with granulated soda lime. The gas so evolved contains no oxides of chlorine, but only 0·009 per cent. of oxygen.[1] When the gas has been passed into the bulb-tube at the rate of two bubbles per second for about ten minutes, the tube is disconnected from the generator, the ends being closed by pieces of glass rod. When it is required to keep the gaseous mixture for any length of time (as the mixture undergoes no change in the dark), the bulb is covered
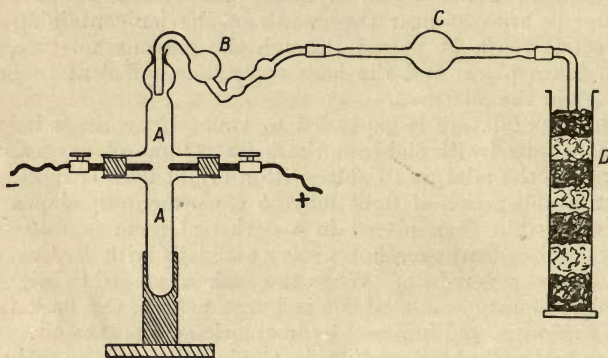
Fig. 18.—Method of obtaining a mixture of equivalent volumes of hydrogen and chlorine.

with a cloth to guard against damage from explosion, and the thinnest part of the tube is brought a little distance above a very small flame from a Bunsen burner. The glass softens below a red heat, and the ends are drawn out and sealed hermetically. As soon as one bulb has been removed, a second is placed on the generator, and after ten minutes is likewise removed and sealed off. Sixty [2] such bulbs may be thus prepared from about 120 c.c. of pure fuming 30 per cent. HCl, and the bulbs thus obtained should be numbered in succession, and the first and last tested by exposing them to a strong light such as sunlight or burning magnesium ribbon. If they explode when this is done, the intermediate bulbs may also be considered good.

The exact mechanism of the manner in which hydrogen and chlorine unite, and the part played by light rays in furthering the reaction, has been the subject of repeated investigation during the last seventy years.

In 1843 [3] Draper showed that when light from an electric spark falls on

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[1] Mellor, *Trans. Chem. Soc.*, 1901, **79**, 216. Regarding the liberation of oxygen during the electrolysis of hydrochloric acid, see also Pfleiderer, *Zeitsch. physikal. Chem.*, 1909, **68**, 49 ; also Gooch and Gates, *Amer. J. Sci.*, 1909, [iv.], **28**, 435 ; *Zeitsch. anorg. Chem.*, 1909, **64**, 273.

[2] Roscoe, *Proc. Manch. Lit. and Phil. Soc.*, Feb. 1865.

[3] Draper, *Phil. Mag.*, 1843, [iii.], **23**, 388, 401 ; 1844, [iii.], **25**, 1 ; 1845, [iii.], **26**, 465 ; **27**, 327.

a mixture of equal volumes of hydrogen and chlorine, a sudden expansion occurs, and the mixture then returns to its original volume. This is called the "Draper effect." In 1902 Mellor and Anderson [1] showed that the expansion is due solely to light rays; they filtered out the heat rays by passing the incident light through water, and concluded that the Draper effect only takes place when light rays fall on an approximately equal volume of hydrogen and chlorine, but not on chlorine alone. It is exhibited both under diminished and ordinary pressures and at temperatures between 15° and 100° C. The effect is not shown when chlorine is mixed with steam, air, nitrogen, marsh gas, carbon dioxide, or monoxide. The explanation is as follows : the light rays bring about the formation of hydrochloric acid in limited quantity, which causes the evolution of a certain amount of heat and a consequent expansion of the gaseous mixture; finally, when the heat is dispersed, the gases return to their original volume, as the hydrogen chloride gas formed occupies the same volume as the hydrogen and chlorine which have disappeared. P. V. Bevan [2] comes to the same conclusion. When the effect reaches a certain value the heat is generated more rapidly than it is dispersed, an explosive wave is generated, and the mixture explodes.

When diffused daylight acts on a mixture of hydrogen and chlorine, combination only gradually takes place, the rate of formation of hydrogen chloride increasing with an increasing proportion of shorter light wavelengths.

Bunsen and Roscoe,[3] in 1857, found that the action of light is at first very slow, a definite length of time being required in order for it to reach its maximum activity. These authors found, for example, that when a mixture of these gases was exposed to the light of a small petroleum lamp burning at a fixed rate, the amount of hydrochloric acid formed in each minute increased during the first nine minutes, and then became constant. This phenomenon is known as *Photochemical induction.*

In 1887 Pringsheim [4] proved that when the mixed gases are carefully dried, the action of light is much less marked than in the case of moist gases. He concluded that the hydrogen does not unite directly with chlorine, but that an intermediate compound is formed by the action of light causing a reaction between the moisture present and the chlorine, and it is this intermediate compound which then reacts with the hydrogen, yielding hydro· chloric acid and re-forming water, which is again acted on with re-formation of the intermediate compound.

The "period of induction" is, according to Pringsheim, due to the fact that during the first period of the action of light the formation of the hydrogen chloride is slow, because the formation of the acid can only take place after a certain quantity of the intermediate compound has been formed ; after a short time, however, the quantity of intermediate compound forming per unit time is equal to the quantity decomposing per unit time, and consequently the amount of intermediate compound in the mixture remains constant, and so the rate of formation of hydrochloric acid also remains constant. It is pre-

[1] Mellor and Anderson, *Trans. Chem. Soc.*, 1902, **81**, 414 ; *Proc. Chem. Soc.*, 1902, **18**, 32.
[2] Bevan, *Phil. Trans.*, 1903, **A**, **202**, 71 ; *Proc. Camb. Phil. Soc.*, 1902, **11**, 264.
[3] Bunsen and Roscoe, *Phil. Trans.*, 1857, **147**, 355, 381, 601.
[4] Pringsheim, *Wied. Annalen*, 1887, [ii.], **32**, 421.

supposed that during the whole time the mixture is subjected to a light of constant intensity, but insufficiently intense to start an explosion.

H. B. Baker,[1] in 1894, apparently confirmed this hypothesis when he proved that when the mixture of hydrogen and chlorine is very highly dried, the combination in daylight proceeds exceedingly slowly, so that 25 per cent. of the gas remained uncombined after exposure to diffused daylight for two days, and bright sunlight for an equal time.

However, no direct proof of the existence of this compound has as yet been given, and, if formed at all, it must be present in only very small amounts. The following facts speak for the formation of an intermediate compound of chlorine and oxygen :—

Draper[2] found in 1843 that moist chlorine which has been exposed to light combines more readily with hydrogen than unexposed chlorine.

Consequently it was assumed that the moisture reacts with the chlorine to form the intermediate compound, and not the hydrogen. This conclusion was apparently supported by Mellor's[3] observation in 1904 that when electrolytic chlorine is exposed to a silent electric discharge or to an acetylene light, and is then mixed with hydrogen, the period of "induction" is less than two minutes against six minutes with a similar gas which has not been previously exposed to the light or electric discharge before mixing.

Pringsheim[4] suggested that the intermediate compound is chlorine monoxide, and explains the reactions thus :—

$$(1) \quad H_2O + Cl_2 = Cl_2O + H_2.$$
$$(2) \quad 2H_2 + Cl_2O = 2HCl + H_2O.$$
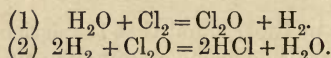
Other authors[5] suggested hypochlorous acid as the intermediate compound :—

$$(1) \quad H_2O + Cl_2 = HClO + HCl.$$
$$(2) \quad HClO + H_2 = H_2O + HCl.$$
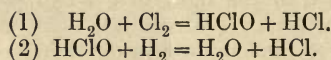
If either of these theories is correct, the introduction of chlorine monoxide or hypochlorous acid should shorten the period of induction. That such is not the case was proved by Mellor[6] in 1902, while Burgess and Chapman[7] actually showed that a mixture of hydrogen and chlorine which has passed through the period of induction is rendered *inactive* again by mixing with hypochlorous acid, chlorine water, hydrochloric acid, water, nitrogen peroxide, or chlorine peroxide. There can be no doubt, therefore, that neither chlorine monoxide nor hypochlorous acid can be the intermediate compound. Bevan[8] put forward the suggestion that the intermediate compound had the constitution

$$\begin{matrix} Cl \\ \\ Cl \end{matrix} \Big\rangle O \Big\langle \begin{matrix} H \\ \\ H \end{matrix} \, ,$$
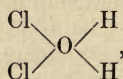
[1] H. B. Baker, *Trans. Chem. Soc.*, 1894, **65**, 611 ; see also Mellor and Russell, *ibid.*, 1902, **81**, 1272.
[2] Draper, *Phil. Mag.*, 1843, [iii.], **23**, 403, 415.
[3] Mellor, *Proc. Chem. Soc.*, 1904, **20**, 140.
[4] Pringsheim, *Ann. Phys. Chem.*, 1887, [ii.], **32**, 384.
[5] See Becquerel, *Wurtz Dict.*, 1879, **2**, 255 ; Veley, *Phil. Mag.*, 1894, [v.], **37**, 170 ; Gautier and Hélier, *Compt. rend.*, 1897, **124**, 1268–76.
[6] Mellor, *Trans. Chem. Soc.*, 1902, **81**, 1292.
[7] Burgess and Chapman, *Proc. Chem. Soc.*, 1904, **20**, 52, 164.
[8] Bevan, *Phil. Trans.*, 1903, **A**, **202**, 71.

being formed by the direct union of chlorine with water. Mellor [1] investigated the influence of temperature on the period of induction in 1904. He showed that between 3° and 50° the higher the temperature the shorter the period, while over 38° side reactions apparently take place, hiding the effect due to temperature alone. In 1906 Burgess and Chapman [2] definitely disproved the intermediate compound theory by showing that mixtures of moist hydrogen and chlorine, in the absence of impurities, exhibit no period of photochemical induction. Bunsen and Roscoe in 1857 observed that oxygen caused inhibition, a fact that has been confirmed by Luther and Goldberg,[3] and by Chapman and M'Mahon,[4] although, according to the latter investigators, oxygen is not nearly so powerful an inhibitor as nitrogen trichloride. Other inhibitors are ozone, chlorine peroxide, and the gases produced by the interaction of moist nitric oxide and chlorine. Nitrous oxide, chlorine monoxide, and nitrogen simply serve as diluents. In the experiments of earlier workers it is probable that the impurities responsible for inhibition were derived from traces of ammonia or nitrogenous matter in the water present. D. L. Chapman and Underhill [5] studied the effect of varying the partial pressure of the hydrogen upon the rate of union of hydrogen and chlorine in the presence of light. Bevan [6] has shown that the temperature coefficient of the velocity of this photochemical change is smaller than is usually found for purely thermal reactions.

As regards the specific action of light on chlorine, there is no doubt that it does act in some remarkable way on the molecules. It is well to call to mind in this connection how in organic chemistry chlorination is often greatly facilitated by taking place in the action of light; also how water is only decomposed rapidly by chlorine in sunlight; also, in photography, the action of light on silver chloride, which contains combined chlorine. Such instances may be multiplied, and the only conclusion which can be drawn from them is that light in some way undoubtedly causes the chlorine atoms or molecules to undergo some change whereby they become more chemically active. The influence of moisture in helping this increased activity of chlorine may be analogous to the influence of traces of moisture in aiding chemical reactions generally, as shown by the work of Baker, Dixon, and others.[7]

The influence of temperature on the union of moist hydrogen and chlorine has also been investigated, but the conditions of union seem to depend largely upon the conditions under which the experiment is carried out. For example,[8] if the gases are heated together in a closed vessel, explosion may take place at any temperature between 240° and 270°; if, however, the mixture is passed in a stream through a heated vessel, the explosion does not take place until the temperature reaches 430°–440°. A piece of brick heated to 150° C. causes the mixture to explode.[9]

[1] Mellor, *Proc. Chem. Soc.*, 1904, **20**, 53.
[2] Burgess and Chapman, *Trans. Chem Soc.*, 1906, **89**, 1399.
[3] Luther and Goldberg, *Zeitsch. physikal. Chem.*, 1906, **53**, 43.
[4] Chapman and M'Mahon, *Trans. Chem. Soc.*, 1909, **95**, 135, 959, 1717 ; 1910, **97**, 845.
[5] Chapman and Underhill, *Trans. Chem. Soc.*, 1913, **103**, 496–508.
[6] Bevan, *Phil. Trans.*, 1903, **A**, **202**, 71.
[7] See Baker, *Phil. Trans.*, 1888, **A**, **179**, 571 ; *Trans. Chem. Soc.*, 1894, **65**, 614. Dixon, *Phil. Trans.*, 1893, **A**, **184**, 97. R. Cowper, *Trans. Chem. Soc.*, 1883, **43**, 153. Wanklyn, *Chem. News.*, 1869, **20**, 291. For a bibliography see Mellor and Russell, *loc. cit.*
[8] Freyer and V. Meyer, *Zeitsch. physikal. Chem.*, 1893, **11**, 28 ; see also H. Sirk, *Zeitsch. physikal. Chem.*, 1908, **61**, 545.
[9] Gay-Lussac and Thénard, *Recherches*, **2**, 93.

According to Coehn and Wassiljewa,[1] ultra-violet light, acting on pure HCl gas placed in a quartz tube, splits it up to an appreciable extent into hydrogen and chlorine.[2]   In the presence of charcoal in the dark a complete union of hydrogen and chlorine takes place.

The rays evolved from radium [3] only cause a very weak union of the hydrogen and chlorine.   In thirty-three hours two radium preparations only caused $1\cdot13$ c.cm. of the gas to unite to form HCl.

(2) *By the Action of Chlorine on Various Compounds of Hydrogen.*— Chlorine has such a powerful chemical attraction for hydrogen that it withdraws this element from every one of its compounds with the sole exception of hydrofluoric acid.   For example, it decomposes such compounds as PH_3, AsH_3, H_2S, HI, NH_3, BH_3; and it also attacks most organic compounds, removing their hydrogen in the form of hydrogen chloride.   Thus turpentine is attacked at ordinary temperatures with inflammation, liberating carbon, thus :—

$$C_{10}H_{16} + 8Cl_2 = 10C + 16HCl.$$
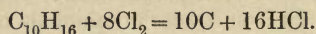
Other organic compounds are also attacked by chlorine.   According to Mitscherlich, all organic compounds are decomposed at a red heat by chlorine, all the hydrogen being liberated as hydrogen chloride and all the oxygen in the form of oxides of carbon.

We have already seen that water is decomposed by chlorine in the light, but not in the dark—

$$H_2O + Cl_2 = 2HCl + O.$$
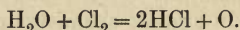
When a mixture of water and chlorine is heated to a red heat, the action takes place fairly rapidly (also the reverse action, see Deacon's process), and if an oxidisable substance (*e.g.* B, P, S, etc.) is present to remove the oxygen from the sphere of action as rapidly as it is liberated, the reaction proceeds very rapidly.

(3) *By the Action of Hydrogen on Chlorides.*—Many chlorides are decomposed by heating with hydrogen.   For example, metallic chlorides, such as those of sodium or potassium, are decomposed by hydrogen at a red heat.[4] Phosphorus pentachloride is similarly decomposed.

(4) *By the Action of Water on Various Chlorides.*—Provided that the temperature be high enough, water will decompose almost all chlorides. For example, both sodium and potassium chloride are partially decomposed by water at 400°, with formation of caustic alkalies.   The reaction, however, does not proceed to completion at temperatures below a red heat.[5]   Hydrochloric acid has actually been manufactured by heating magnesium chloride in steam—

$$MgCl_2 + H_2O = MgO + 2HCl.$$
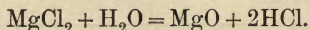
Aluminium chloride, tin chloride, and the chlorides of the non-metals (carbon excepted) are decomposed by water either at ordinary temperatures or on gently warming.

[1] Coehn and Wassiljewa, *Ber.*, 1909, **42**, 3183.
[2] See note 7, p. 85.
[3] See Jorissen and Ringer, *Chem. Weekbl.*, 1905, **2**, 41 ; *Ber.*, 1905, **38**, 899 ; 1906, **39**, 2093 ; *Archiv. Néerland*, 1907, [ii.], **12**, 157.
[4] Favre and Silbermann, *Ann. Chim. Phys.*, 1852, [iii.], **34**, 357.
[5] Spring, *Ber.*, 1885, **18**, 344.

Laboratory Preparation of Hydrochloric Acid Gas.—The usual method is to place common salt in a flask fitted with a thistle funnel and delivery tube. Next a quantity of sulphuric acid is taken, diluted with one-third its weight of water, cooled, and added to the salt, so that the proportion exists, $1NaCl : 1H_2SO_4$. On warming, hydrochloric acid gas is evolved, and the gas may be dried by passing through concentrated sulphuric acid. The reaction which takes place is this :—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$
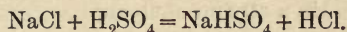
A much more convenient method than this for obtaining a steady stream of dry gas is as follows :—

At the bottom of a stout, large filter flask A is placed a quantity of ordinary salt, which is then well covered with fuming hydrochloric acid. Ordinary concentrated sulphuric acid is placed in the tap-funnel D and is allowed to enter A drop by drop. A steady stream of hydrochloric acid gas is thus evolved at ordinary temperatures, which may be dried by bubbling through concentrated sulphuric acid contained in the wash-bottle B.[1]

Although common salt is usually used in the above preparation—on account of its cheapness—yet other chlorides can also be used as well. For example, ammonium chloride, NH_4Cl, and carnallite, $KCl.MgCl.6H_2O$, have both been proposed for the preparation of hydrochloric acid.

Technical Preparation of Hydrochloric Acid.[2]—Hydrochloric acid is obtained on a very large scale industrially as a by-product in the manufacture of "salt-cake" (sodium sulphate). As this manufacture is described in detail in Vol. II., we will merely mention that the method consists in heating two molecular proportions of

Fig. 19.—Laboratory preparation of hydrochloric acid gas.

salt with one molecular proportion of concentrated sulphuric acid. The practice in English works is to place a charge of 10 cwt. of salt in large hemispherical iron pans set in brickwork and heated by a fire underneath. Next, an equal weight of concentrated sulphuric acid of specific gravity 60° Bé (1·7, specific gravity) is run on to it from a leaden cistern placed above the furnace. The first action then takes place, about 70 per cent. of the hydrogen chloride escaping—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$
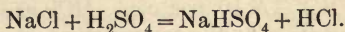
The iron pan is covered with a dome of brickwork through which the hydro-chloric acid gas escapes, and is condensed as subsequently described. The action is completed by raking the fused mass into another part of the furnace, where it is heated to redness, when the action completes itself, thus :—

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$
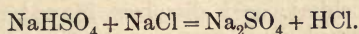
The hydrogen chloride is led off through a separate flue, and is condensed in a special apparatus.
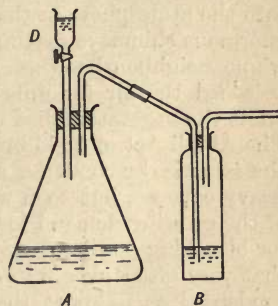
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[1] See also Küster and Abegg, *Zeitsch. f. chem. Apparatenkunde*, 1905, i. 89.

[2] A full account of the subject is given in George Lunge's *Sulphuric Acid and Alkali*, vol. ii. See also Th. Meyer, *Die Fabrikation von Sulfat und Salzsäure* (Halle, 1907); G. Martin, *Industrial Chemistry*, vol. ii.

Hydrochloric acid is also obtained as a by-product in Hargreave's and Robinson's process for the manufacture of salt-cake, Na_2SO_4, which takes place according to the equation :—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$
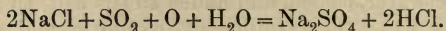
The process is described in Vol. II., under Sodium Sulphate.

Some hydrochloric acid has been prepared technically by heating magnesium chloride, $MgCl_2$, in a stream of steam,

$$MgCl_2 + H_2O = MgO + 2HCl,$$
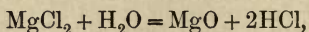
or by merely heating magnesium oxy-chloride, MgOCl, to 750° C., when it decomposes thus :—[1]

$$2MgOHCl = MgO + HCl.$$
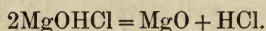
Condensation of Hydrochloric Acid Gas.—The hydrochloric acid gas evolved in the salt-cake process was at one time allowed to escape directly into the atmosphere in the neighbourhood of alkali factories ; and, in spite of enormous chimneys reaching to the height of 450 feet and more, caused the whole neighbourhood of the factory to be enveloped in dense smoke, and poisoned the air for miles around, so that in the alkali-manufacturing districts the vegetation died and the greatest distress was caused among farmers. The Alkali Act of 1863 brought this evil to an end in England by compelling the factories to condense all except 5 per cent. of HCl. This was at first a heavy expense, but soon was turned into an actual source of gain, on account of the growing demand for hydrochloric acid for the manufacture of chlorine for bleaching powder. At the present time so complete is the condensation that very often over 99·27 per cent. of the hydrochloric acid in the gases is condensed as follows : the hydrochloric acid escaping in the gases from the flues is allowed to pass through long earthenware tubes, and then through a series of earthenware vessels, where they are caused to pass through water.

The problem facing chemical technologists at the present time is not so much the absorption of all the gaseous hydrogen chloride as the absorption of the gas so as to produce only *concentrated* acid solutions.[2] This is by no means an easy problem. In the first place, the strength of the hydrochloric acid obtainable by the absorption of the gas in water depends largely upon the temperature and the concentration of the gas. Thus a 100 per cent. gas at 0° C. can yield a 45·2 per cent. HCl solution ; whereas a gaseous mixture containing only 5 per cent. HCl can, under the same conditions, only yield (at 0° C.) a 36 per cent. HCl solution (22° Bé). A 10 per cent. HCl gas yields a 39 per cent. HCl solution (24° Bé) at 0°. As the temperature rises a weaker acid results, *e.g.* a 5 per cent. HCl gas can at 20° only give an acid of 20° Bé.

Now the gases coming from the salt-cake furnaces contain very variable amounts of HCl, ranging from 10 per cent. by volume downwards. The gases obtained by Hargreave's process are much more dilute than this ; moreover, when hydrochloric acid dissolves in water a very considerable amount of heat is evolved, and, consequently, this also causes considerable difficulty in absorbing the gas, as the absorbing water must be pumped directly against the warm gases.

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[1] See, for example, *D.R.P.*, 203,080 (1906).
[2] Hurter (*J. Soc. Chem. Ind.*, 1885, p. 639 ; 1887, p. 707 ; 1893, p. 226) discusses this subject. See also Lunge, *loc. cit.*

Acid pumps, however, cause the continual circulation of the water, so that now, even out of a very dilute gas such as that coming from Hargreave's process, a hydrochloric acid solution of 20° Bé is obtained.

Fig. 20 [1] shows a typical condensation plant for HCl from a salt-cake furnace. The gas coming from the furnaces is led away through two separate pipes, B and B_1—the one B leading the gas from the "pan" A, and the other pipe (B_1) conducting the gas coming from the "muffle" or calcining part of the furnace A_1. The gas first passes through two condensation towers (C, C_1), made out of sandstone plates tarred over, and then through two series of earthenware pots (D, D_1), and finally through two sprinkling towers (E, E_1), where the last traces of hydrochloric acid are removed, and the two streams of gas then unite and pass away to the chimney through FF, an earthenware pipe.

The first part of B_1, the tube leading from the hot muffle furnace A_1, is made of sandstone tarred over. The sandstone towers (C, C_1) serve to cool the gas and to free it from flue dust and sulphuric acid vapours carried over from the furnace. The fifty-three or so earthenware vessels following are simply enlarged "Woulff's bottles," about 3 feet high and having the section shown in fig. 21.[1] Through them flows a stream of water in a direction opposite to that of the incoming gases. The saturated hydrochloric acid solution is run off into the vessels G and G_1.

More effective than the air-cooled Woulff's bottles referred to above are the water-cooled "Cellarius" condensing vessels, shown in fig. 22.[1] They possess a larger surface and are placed in vats filled with cold water. A very effective condensation is thus effected. The gas enters at C and passes out at D, while the water enters at a, pours over the saddle, and escapes by b. This device causes the water to exhibit a good surface, and effectively mixes with and cools the gas. The last portions of the hydrochloric acid are removed by the two towers E, E_1. They consist of a series of earthenware rings, about 3 feet in diameter, filled below with acid-fast plates, and above with coke. Water from a tank H is sprinkled over the coke by a sparger, whence it flows down the tower and escapes from the basement to the earthenware condensing vessels above described, being forced through them by means of special pumps. The gases enter at I and pass out at K. This is one of the most efficient arrangements. However, many works employ a simple tower, 60–100 feet high, made out of sandstone which has been boiled in tar, and filled with coke, down which water runs.

The pumping of hydrochloric acid from one part of the works to another is done by means of acid pumps composed of vulcanite or earthenware, while pumps having membranes of vulcanite closed by valves of india-rubber are also used. Metals such as iron or lead are badly attacked by hydrochloric acid, and so are not usually used for pumping the acid. Very often the acid is elevated by compressed air from a stoneware vessel shown in section in fig. 23.[1] The compressed air enters at c and forces the liquid contained in b up the tube ba. Ingenious automatic air lifts are now in use.

Purification.—The chief impurities in hydrochloric acid obtained as above described are sulphuric acid, sulphur dioxide, and chlorides of arsenic and iron. The purification takes place in special factories. The greater part of the sulphuric acid is removed in the absorption process, but the last traces are got rid off by means of barium chloride : $BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$.
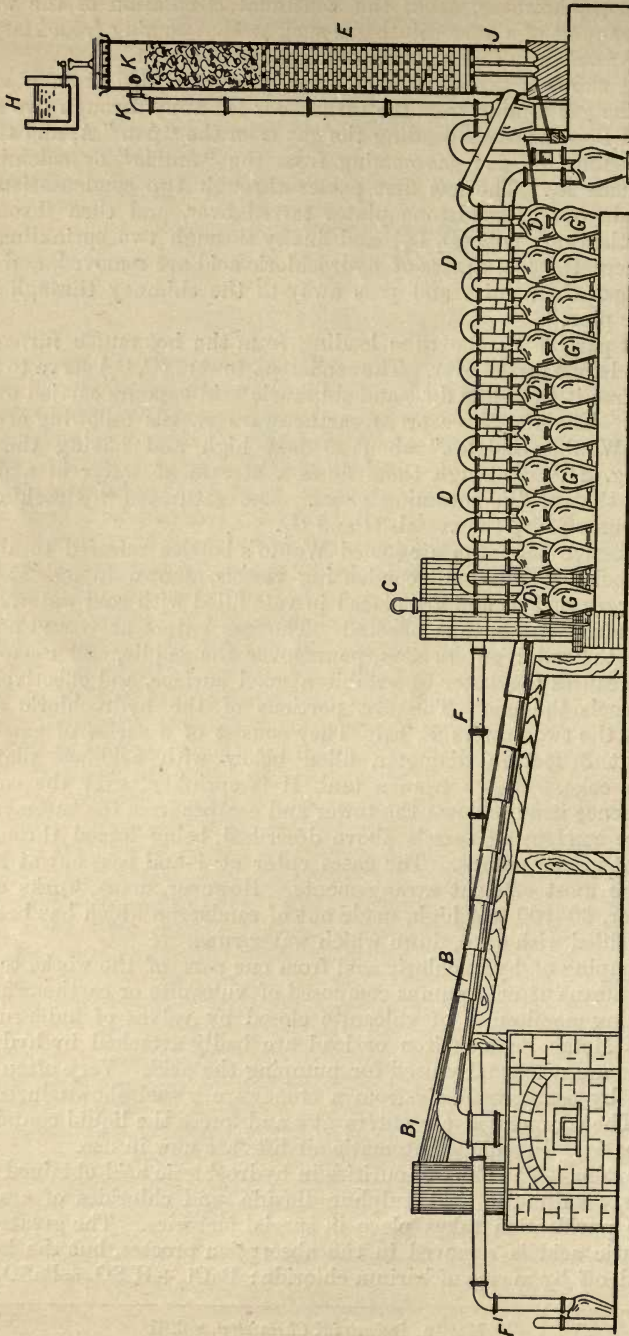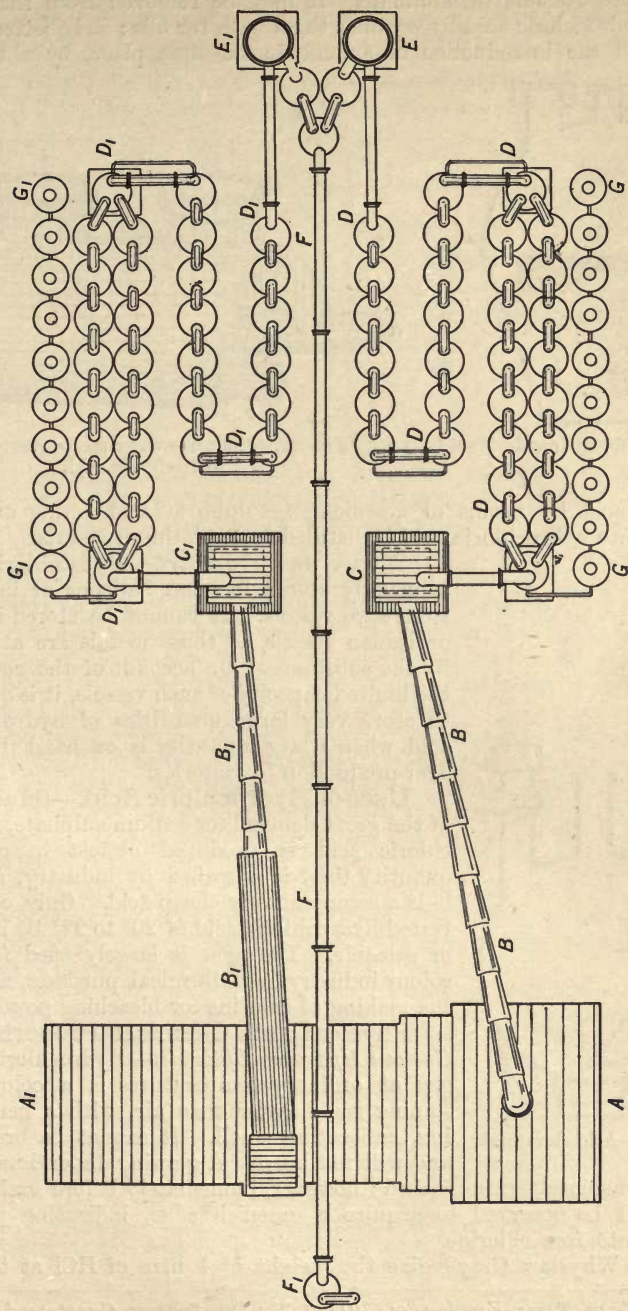
Elevation.

Fig. 20.—Manufacture of hydrochloric acid.

Arsenic is more difficult to eliminate. It may be removed from the gases containing hydrochloric acid by washing them with tar oils ; it is better, however, to avoid the introduction of arsenic in the first place, by obtaining
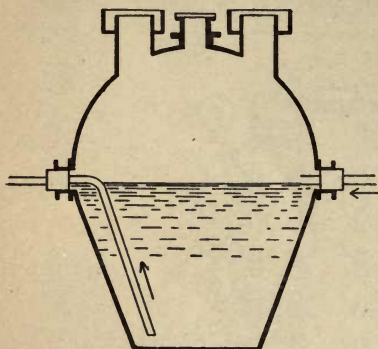
FIG. 21.—Receiver for hydrochloric acid.
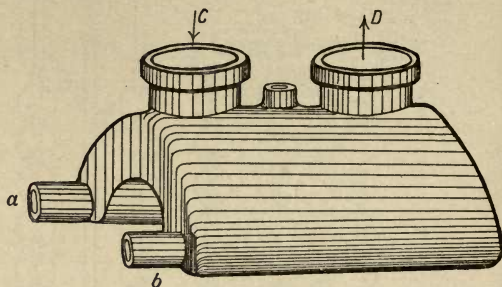
FIG. 22.—Cellarius water-cooled receiver for hydrochloric acid.

hydrochloric acid by means of arsenic-free sulphuric acid acting on salt. Chemically pure hydrochloric acid is distilled from platinum vessels.

FIG. 23.—Acid elevator.

Storage and Transport.—Hydrochloric acid is usually stored in glass balloons or in large stoneware vessels. It cannot be stored in iron or leaden vessels, as these metals are attacked by the substance. On account of the cost and the limited capacity of such vessels, it is difficult to store very large quantities of hydrochloric acid when a large quantity is on hand through over-production in factories.

Uses of Hydrochloric Acid.—On account of the great demand for sodium sulphate, hydrochloric acid is produced almost in greater quantity than is absorbed by industry, and so it is a comparatively cheap acid. Only concentrated hydrochloric acid of 20° to 22° Bé is used or saleable. The acid is largely used for the colour industry, metallurgical purposes, and for the making of chlorine for bleaching powder.

Physical and Chemical Properties.—*Gaseous Hydrogen Chloride.*—Hydrochloric acid gas at ordinary temperatures is a colourless, fuming gas, heavier than air, with a penetrating, suffocating smell. It cannot be breathed and will not burn. A glowing taper immersed therein is immediately extinguished ; however, immediately before extinction the flame will be observed to acquire a greenish edge, indicating partial dissociation into free chlorine.

Burt and Whytlaw Gray [1] give the weight of 1 litre of HCl at 0° and

[1] Burt and Gray, *Trans. Faraday Soc.*, 1911, **7**, 30 ; Otto Scheuer, *Compt. rend.*, 1909, **149**, 599. See A. Leduc, *Compt. rend.*, 1897, **125**, 571 ; *Ann. Chim. Phys.*, 1898, [vii.],
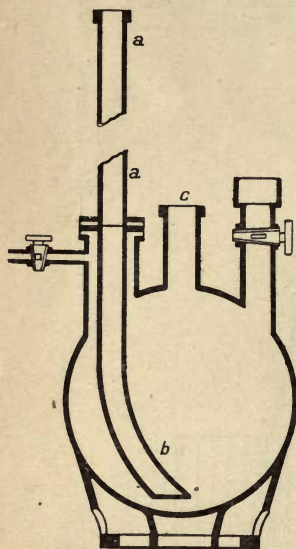
760 mm. and in lat. 45° as 1·63915 grams. O. Scheuer arrives at the value 1·6394 g. for 1 litre, but this value is slightly too high owing to neglect of the error due to absorption.

The density (grams per c.c.) of the *vapour* of HCl in equilibrium with liquid HCl was determined by Rupert [1] as follows :—

Temp. °C.	Density (Grams. per c.c.).	Temp. °C.	Density (Grams. per c.c.).
51	0·278	20	0·0974
50	0·247	0	0·0539
45	0·215	− 15	0·0343
40	0·181	− 30	0·0238
35	0·152	− 50	0·0125
30	0·130		

Pure hydrogen chloride placed in a quartz tube and subjected to ultraviolet light is split up to an appreciable extent into hydrogen and chlorine.[2] The gas is very stable towards heat, being practically unchanged at 1500°, but at 1700° dissociation begins to be marked.[3] The passage of electrical sparks through the gas scarcely changes it—at most only 1/35 being resolved into hydrogen and chlorine. When heated to about 1500°, it begins to dissociate into hydrogen and chlorine, and Deville [4] detected traces of free chlorine and hydrogen in samples of the gas which had been suddenly cooled from 1500° to ordinary temperatures. According to Bodenstein and Geiger,[5] the amount of HCl dissociated at 2000° is only 0·8 per cent., at 1000° only 0·002 per cent., while at ordinary temperatures less than $6·6 \times 10^{-15}$ parts are dissociated. The heat of formation of hydrogen chloride is 22·00 Cals. (Thomsen),[6] 23·78 Cals. (Favre and Silbermann).[7]

The specific heat of the gas (water = 1) at constant pressure (22° to 214° C.) is 0·1852 (Regnault),[8] while the ratio of the specific heats [9] $C_p/C_v = 1·389$ at 20° and 1·400 at 100°, while $C_v = 0·175$, taking air = 0·1684.

The refractive index of the gas [10] for the D line at N.T.P. is 1·000447. It possesses much more pronounced absorption bands in the ultra-red light than chlorine,[11] and indeed absorbs heat rays to a very considerable extent. The maximum absorption is at $\lambda = 3·41\mu$.

15, 1 ; Guye and Ter-Gazarian, *Compt. rend.*, 1907, **143**, 1233 ; Whytlaw Gray, *Proc. Chem. Soc.*, 1908, **23**, 119 ; Gray and Burt, *Trans. Chem. Soc.*, 1909, **93**, 1634.

[1] Rupert, *J. Amer. Chem. Soc.*, 1909, **31**, 851.

[2] A. Coehn and A. Wassiljewa, *Ber.*, 1909, **42**, 3183.

[3] Langer and V. Meyer, *Pyrochemische Untersuchungen* (Vieweg), p. 67.

[4] H. St.-Claire Deville, *Compt. rend.*, 1865, **60**, 317 ; *Annalen*, **135**, 94.

[5] Bodenstein and Geiger, *Zeitsch. physical. Chem.*, 1904, **49**, 70. See also Haber, *Thermodynamik technischer Gasreaktionen* (1905), p. 92, who calculates that at 2000° C. 100 vols. of HCl gas contain 0·2 vol. of free hydrogen and 0·2 vol. free chlorine.

[6] J. Thomsen, *Thermochemische Untersuchungen*, 1882, ii. 20.

[7] Haber, *Thermo-dynamik technischer Gasreaktionen*, 1905, p. 89.

[8] Regnault, *Mém. de l'acad. de scienc.*, 1863, **26**, 1.

[9] See Müller, *Wied. Annalen*, 1883, **18**, 94 ; Strecker, *Wied. Annalen*, 1882, **17**, 85.

[10] Bleckrode, *Proc. Roy. Soc.*, 1884, **37**, 339.

[11] K. Ångström and W. Palmer, *Oefvers. af. K. Vetensk. Akad.*, Förh., 1893, 389. See also Tyndall, *Phil. Trans.*, 1862, **152**, i., 59.

The gas is extremely soluble in water or ice, forming a solution of aqueous acid (see p. 88). The gas fumes in the air uniting with atmospheric moisture: 1 c.cm. of water at 8° absorbs 525 c.c. of gas, at 18° 451·2 c.c. (760 mm.). As regards its solubility in water, however, see the table, p. 101. A very effective method of exhibiting its great solubility in water is shown in fig. 24. A large dry glass globe placed on a stand is filled with the gas by displacement. Next, a glass tube, very slightly drawn out at the upper end, is passed air-tight through a rubber stopper fitted into the upper flask, the end of the tube just reaching to the middle of the flask as shown.

Below this is another equal globe fitted as shown, the piece of rubber tubing joining the two flasks being closed with a clip. The lower globe is filled with water coloured blue with litmus. When the screw clip is opened and the side-tube is blown through in order to force a little water into the upper flask, a vacuum is formed in the upper flask by the rapid absorption of the gas in the water and the liquid rushes up in a fountain and at the same time changes from blue to red.

The gas is also soluble in methyl, ethyl, isopropyl, and other alcohols; in benzene, xylol, hexane, acetone, ether, etc. One volume of ethyl alcohol [1] of density $= 0·836$ dissolves 327 volumes of the gas at 17°, expanding to 1·324 of its original volume in so doing and then acquiring the density $D = 1·005$. 100 parts of benzol at 18° dissolve 2 parts by weight of the gas. [2]

FIG. 24.—Solubility of hydrochloric acid gas

Dissolved in benzol or in nitrobenzol, the gas is associated [3] from 5 to 2·8 times its molecular weight, HCl.

At a temperature T°, and with the partial pressure of the hydrogen chloride equal to 760 mm., 1 gram of the solution in ether contains the following quantities of hydrogen chloride in grams:— [4]

Temperature, ° C.	HCl, grams.	Temperature, ° C.	HCl, grams.
− 9·2	0·3751	+ 10	0·3035
− 6	0·3718	+ 15	0·2762
− 2	0·3630	+ 20	0·2490
0	0·3560	+ 25	0·2218
+ 5	0·3310	+ 30	0·1947

A considerable quantity of heat is evolved when the gas dissolves in various solvents. For example, when 1 gram-molecule dissolves in the following solvents, the following quantities of heat are evolved [5] (molecular heat of solution):—

[1] Pierre, Ann. Chim. Phys., 1851, [iii.], 31, 135.
[2] Falk and Waters, Amer. Chem. J., 1904, 31, 398.
[3] Bechmann and Lockemann, Zeitsch. physikal. Chem., 1907, 60, 385.
[4] Schuncke, Zeitsch. physikal. Chem., 1894, 14, 331.
[5] Timofejew and Brylik, Chem. z. centr., 1905, ii. 431.

Solvent.				Per cent. HCl in Solution formed. Cals.	Molecular Heat of Solution. Cals.
Methyl alcohol	.	.	.	0·26 to 11·03	1·649 to 1·105
Ethyl ,,	.	.	.	0·24 ,, 9·88	1·713 ,, 1·113
Proply ,,	.	.	.	0·27 ,, 4·61	1·921 ,, 1·068
Isobutyl ,,	.	.	.	0·40 ,, 3·49	1·794 ,, 1·185

The heat evolved is mainly an adhesion effect. Only 3 to 4 per cent. of this heat is due to electrolytic dissociation of the molecule.[1]

Kablukoff[2] made a number of very interesting determinations of the electrolytic conductivity of solutions of the gas in various solvents. He showed, for example, that the solution in methyl alcohol possessed the greatest conductivity; that the ethyl alcohol solution had its conductivity greatly increased by the addition of water, and that in a solution of 60 per cent. alcohol the acidity of the hydrogen chloride was three times as much as that of sulphuric acid; that, on the other hand, the solutions in benzene, xylene, and hexane were extremely bad conductors. Nitrobenzene acts like benzene in this respect.[3]

When investigations were undertaken to see whether any parallelism existed between the chemical activity of hydrogen chloride solutions in organic solvents and the electrolytic dissociation as measured by its electrolytic conductivity, several curious facts were brought to light. Thus Zecchini[4] investigated the action on zinc of solutions of hydrogen chloride gas in various organic solvents; he showed that the gas dissolved in ether acted more vigorously than the same gas dissolved in methyl, ethyl, and amyl alcohol; so that the rapidity of the chemical action did not, here, stand in relationship to the ionic dissociation of the acid. Dry zinc is only very feebly attacked by hydrogen chloride gas when dissolved in benzol.[5]

An alcoholic solution of the gas acts on calcium carbonate, but not on potassium carbonate, presumably because potassium chloride is insoluble in alcohol.[6]

Marble is attacked by a solution of hydrogen chloride in methyl alcohol about forty times more slowly than it is attacked by an aqueous solution of the same strength.[7]

When silver nitrate, $AgNO_3$, is dissolved in anhydrous organic solvents, such as anhydrous alcohol, or in benzene, a stream of dry hydrogen chloride gas when passed through the solution only precipitates traces of silver chloride, even on heating. However, when a trace of water is added to the alcoholic solution, the silver nitrate is completely decomposed, with a voluminous precipitate of silver chloride, $AgCl$.[8]

According to Kablukoff,[9] in ethereal solution hydrogen chloride appears to lose its acid properties almost completely; for example, it would not evolve

[1] Timofejew and Brylik, *Chem. z. centr.*, 1905, ii. 431.
[2] J. Kablukoff, *Zeitsch. physikal. Chem.*, 1889, **4**, 429; *Wied. Annalen Beibl.*, 1891, **15**, 775. See also Lapworth and Partington, *Trans. Chem. Soc.*, 1911, **99**, 1426; Partington, *Trans. Chem. Soc.*, 1911, **99**, 1937.
[3] Beckmann and Lockemann, *Zeitsch. physikal. Chem.*, 1907, **60**, 385.
[4] Zecchini, *Gazz. chim. ital.*, 1897, **27**, i. 466.
[5] Falk and Waters, *J. Amer. Chem. Soc.*, 1904, **31**, 398.
[6] Warren, *Chem. News*, 1889, **59**, 221.
[7] Geiger, *Gazz. chim. ital.*, 1899, **29**, i. 421.
[8] Hughes, *Phil. Mag.*, 1893, [v.], **35**, 531.
[9] Kablukoff, *Ber.*, 1892, **25**, 152. (Referate.)

carbon dioxide from marble, while magnesium and even sodium were so inert towards the dissolved gas that no hydrogen was evolved !

Patten[1] and Kahlenberg made some extensive investigations on this point ; solutions of dry hydrogen chloride in dry $CHCl_3$, CCl_4, C_2H_5Cl, $SiCl_4$, $SnCl_4$, PCl_3, $AsCl_3$, $SbCl_5$, S_2Cl_2, $SOCl_2$ were found to act very differently on metals such as Mg, Al, Cr, Mn, Zn, Fe, Co, Ni, Pb, Cd, Sn, Bi, Cu, Ag, Sb, Au, Pt, As, Te, and Pd ; and, generally speaking, the action was much less intense than with the aqueous solutions containing the same percentage of dissolved gas.

However, in some cases a marked reaction took place—a fact which showed that the presence of water is not always necessary in order to cause the hydrogen chloride to react.

Charcoal absorbs considerable quantities of the gas, the exact amount varying with the nature of the charcoal. One c.c. of charcoal takes up about 165 c.c. of gas.[2] The heat given out by each gram-molecule of hydrogen chloride in thus condensing is about 10,000 calories.

Direct sunlight has no action on a dry mixture of hydrochloric acid gas and oxygen ; when, however, more moisture is present than is needed for the complete saturation of the gas, decomposition in sunlight gradually takes place :—

$$2HCl + O = H_2O + Cl_2.$$
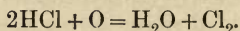
Hypochlorous acid also appears to be formed. The action, however, varies much with the proportion of oxygen present ; for example, a mixture of 4 volumes of hydrochloric acid gas and *one volume* of oxygen only gave 0·34 per cent. of free chlorine after 24 days' exposure ; whereas 8 volumes of oxygen liberated 73·81 per cent. of the chlorine.[3] Also when hydrochloric acid gas is mixed with one-fourth its volume of oxygen, and the mixture is subjected to an electric discharge, chlorine and water are formed. When platinum-black is heated to 121° C. in the mixture, the same action takes place, while a mixture of gaseous hydrogen chloride and oxygen sent through a red-hot tube forms water and chlorine. See Deacon's process (p. 60), which is an extension of this action.

Sulphur trioxide, SO_3, absorbs a large volume of hydrogen chloride, producing a liquid known as chlorosulphuric acid. Both phosphorus and phosphorus pentoxide act on hydrogen chloride. One gram of phosphorus pentoxide absorbs[4] no fewer than 227 c.c. of the gas, while an aqueous solution of concentrated acid when heated to 200° C. in a tube with amorphous phosphorus, causes the formation of much phosphine.[5]

Dry hydrogen chloride when passed over chromic oxide, CrO_3, attacks it,[6] with the development of much heat, forming chromyl chloride, CrO_2Cl_2.

Liquid and Solid Hydrogen Chloride.—Davy and Faraday[7] were the first to liquefy hydrochloric acid gas by allowing sulphuric acid to act on ammonium chloride in a sealed bent tube.

The pressure finally developed caused the gas to condense to a colourless

[1] H. Eastman Patten, *J. Physical Chem.*, 1903, **7**, 153.
[2] Favre, *Ann. Chim. Phys.*, 1874, [5], i. 209.
[3] A. Richardson, *Trans. Chem. Soc.*, 1887, **51**, 801 ; M'Leod, *Trans. Chem. Soc.*, 188 , **49**, 591.
[4] Bailey and Fowler, *Trans. Chem. Soc.*, 1888, **53**, 755.
[5] Oppenheim, *Bull. Soc. chim.*, 1864, [ii.], **1**, 163.
[6] Autenrieth, *Ber.*, 1902, **35**, 2057.
[7] Davy and Faraday, *Phil. Trans.*, 1823, **113**, 164.

liquid, which by gentle warming could be caused to distil over into the empty limb of the tube.

It is a colourless liquid, the density of which varies very considerably with the temperature. Ansdell,[1] also M'Intosh and Steele,[2] has investigated the density of liquid hydrogen chloride, and the following table is compiled from their results :—

Temp. ° C.	Density. (Grams per c.c.)	Temp. ° C.	Density. (Grams per c.c.)
+ 47·8	0·619	− 83·1	1·1842
+ 41·6	0·678	− 85·8	1·1937
+ 33·0	0·748	− 89·8	1·2038
+ 22·7	0·808	− 92·9	1·2127
+ 15·85	0·835	− 97·2	1·2242
+ 11·67	0·854	− 101·2	1·2347
+ 7·5	0·873	− 104·5	1·2438
0	0·908		

Rupert[3] gives the following figures for the density of liquid hydrogen chloride :—

Temp. ° C.	Density. (Grams per c.c.)	Temp. ° C.	Density. Grams per c.c.)
51	0·572	20	0·839
50	0·597	0	0·929
45	0·658	− 15	0·984
40	0·707	− 30	1·032
35	0·749	− 50	1·090
30	0·783		

It will be seen that the density diminishes rapidly as the temperature increases—i.e. the expansion of the liquid with rise of temperature is very great.

Liquid hydrochloric acid boils at − 82·9° C. (M'Intosh and Steele), and − 83·1 according to Ladenburg and Krügel.[4] The molecular volume at the boiling-point is calculated to be 30·8.

The critical temperature[5] is about 52° C. (Dewar gives 52·3°, and later authors give 51·5° and 52°), while the critical pressure given varies, namely,

[1] Ansdell, *Proc. Roy. Soc.*, 1880, **30**, 117.
[2] M'Intosh and Steele, *Zeitsch. physikal. Chem.*, 1906, **55**, 141 ; *Proc. Roy. Soc.*, 1904, **73**, 450.
[3] Rupert, *J. Amer. Chem. Soc.*, 1909, **31**, 851.
[4] Ladenburg and Krügel, *Ber.*, 1900, **33**, 637.
[5] See Dewar, *Chem. News*, 1885, **51**, 27 ; Estreicher, *Zeitsch. physikal. Chem.*, 1897, **20**, 603 ; Leduc and Sacerdote, *Ann. Chim. Phys.*, 1898, [vii.], **15**, 1 ; Briner, *J. Chim. phys.*, 1906, **4**, 476.

86 atmos. (Dewar), 83 (Leduc), and 83·6 (Briner).   The following table gives the vapour pressure at different temperatures :— [1]

Temp. ° C.	Vapour Pressure.	Temp. ° C.	Vapour Pressure.	Temp. ° C.	Vapour Pressure.
− 109·9	141 mm.	− 47·5	5·83 atmos.	+18·1	41·80 atmos.
− 101·3	245 ,,	− 41	7·4 ,,	+22·0	45·75 ,,
− 92·9	430 ,,	− 36	8·53 ,,	+26·75	51·00 ,,
− 85·9	648 ,,	− 30	10·66 ,,	+33·4	58·85 ,,
− 82·9	1 atmos.	− 20·5	13·88 ,,	+39·4	66·95 ,,
− 80·5	1·14 ,,	− 4	23·08 ,,	+44·8	75·20 ,,
− 69	2·28 ,,	0	26·2 ,,	+48·0	80·80 ,,
− 64	2·9 ,,	+ 4	29·8 ,,	+49·4	84·75 ,,
− 60·5	3·37 ,,	+ 9·25	33·9 ,,	+50·56	85·33 ,,
− 55	4·26	+13·8	37·75 ,,		

Liquid hydrochloric acid has its molecules somewhat associated, the association factor being 1·5. The refractive index [2] is 1·254 for the D line at 10·0°. Although aqueous hydrochloric acid is a good electrical conductor, liquid hydrochloric acid scarcely conducts the electric current, the conductivity at its boiling-point being [3] only $0·167 \times 10^{-6}$. Many organic substances dissolve in the liquid, some producing conducting solutions, while others produce solutions almost as bad conductors as the original acid. Tin chloride, $SnCl_4$, also dissolves in liquid hydrogen chloride to give a non-conducting solution. [4] The molecular surface energy and viscosity of liquid hydrogen chloride have been determined by Steele, M'Intosh, and Archibald. [5]

The molecular latent heat of evaporation is given as 3600 gram-calories at the boiling-point. [6]

Liquid hydrochloric acid turns dry litmus extract a deep red colour, a little of the extract dissolving and colouring the liquid a pale purple or blue-black colour. [7]

Many organic substances combine directly with liquid hydrochloric acid, forming addition products. This is especially the case with alcohols ; [8] e.g. methyl alcohol unites to form the substance $(CH_3OH)_3(HCl)_2$, melting-point, − 64°; acetaldehyde give the substance $(CH_3CHO)_2(HCl)_3$, melting-point, − 18°; acetic acid and acetic ester give respectively with hydrogen chloride the compounds $(CH_3COOH)_2(HCl)_3$ and $(CH_3COOC_2H_5)(HCl)_2$, which have the respective melting-points − 53° and − 75° C.

Gore [7] made extensive experiments on the action of liquid hydrochloric acid on various substances ; he showed that the liquid had, in general, but a feeble solvent power, and was fairly inert, scarcely attacking the metals, with

[1] Compiled from the results of G. Ansdell (Proc. Roy. Soc., 1880, 30, 117) and M'Intosh and Steele (Proc. Roy. Soc., 1904, 73, 450). For the density of the vapour see Rupert, p. 14.
[2] L. Bleekrode, Proc. Roy. Soc., 1884, 37, 339.
[3] Helbig and Fausti, Atti R. Accad. Lincei, 1904, [v.], 13, 30 ; see also Bleekrode, Wied. Annalen, 1878, 3, 161 ; Hittorf, Wied. Annalen, 1878, 4, 374.
[4] See Archibald, Chem. Zeit., 1906, 30, 910 ; J. Amer. Chem. Soc., 1907, 29, 1416.
[5] Helbig and Fausti, loc. cit. ; see also Steele, M'Intosh, and Archibald, Zeitsch. physikal. Chem., 1906, 55, 129 ; Baly, Burke, and Marsden, Trans. Chem. Soc., 95, 1103.
[6] Elliot and M'Intosh, J. Physical Chem., 1908, 12, 163.
[7] Gore, Phil. Mag., 1865, [iv.], 29, 541.
[8] M'Intosh, J. Amer. Chem. Soc., 1906, 28, 588.

the exception of aluminium. He showed, for example, that charcoal, boric acid, phosphorus, sulphur, and selenium remained unchanged in liquid hydrochloric acid; iodine, however, dissolved to form a purple liquid.

The carbonates of ammonium, sodium, potassium, calcium, strontium, and barium were all gradually converted by the liquid into the corresponding chlorides, without effervescence or the evolution of gas being noticed. Metallic potassium and sodium became coated over with a layer of the chloride, which remained undissolved in the liquid. Aluminium, however, dissolved rapidly, evolving gas. Arsenic, antimony, and cadmium remained unchanged. Tin changed slowly, without the development of gas, into a white mass, which was insoluble in water. Polished thallium went black superficially, while lead was also slowly attacked, forming a white mass. Iron and copper were only superficially attacked. Silver and platinum were unattacked.

Most metallic oxides remained undissolved, but arsenic oxide and antimony oxide readily passed into solution, while zinc oxide very slowly dissolved.

Many sulphides were slowly attacked, without evolution of gas, however. Thus sodium sulphide gradually changed into chloride; antimony sulphide dissolved; lead sulphide turned white, without dissolving. Iron sulphide evolved no gas and was unchanged.

Many chlorides were undissolved; for example, ammonium chloride, sodium and potassium chloride, nickel chloride, $NiCl_2$, silver chloride, etc., etc.

Solid hydrochloric acid is obtained by slowly cooling the liquid; it then solidifies to a crystalline mass, which melts at $-112 \cdot 5°$ according to Olszewski, and at $-111 \cdot 3°$ according to Ladenburg and Krügel. The solid is a non-conductor of electricity.

Composition of Hydrochloric Acid Gas.—

The composition of the gas may be shown as follows:—

(1) *To show that two volumes of HCl gas contain one volume of hydrogen.*

A eudiometer of the shape shown in fig. 25 has both limbs completely filled with dry mercury. Dry hydrochloric acid gas is next introduced into the closed limb AB, by attaching the end carrying the stopcock A, by means of a piece of rubber tubing, with a flask from which pure hydrochloric acid gas is being slowly evolved from a mixture of dry salt and concentrated sulphuric acid (all air must have been previously driven out of the flask).

Fig. 25.—Composition of hydrochloric acid gas.

By turning the stopcock A, and opening the stopcock C, the mercury will run out, and dry gas will enter the limb AC, while air fills the other tube DC to the same level. When the hydrochloric acid gas reaches a mark on the tube indicating that it is two-thirds full, the stopcocks are closed, and liquid sodium amalgam (prepared by pressing a few pieces of metallic sodium under mercury contained in a mortar) is poured into DC so as to completely fill it. The end of the tube is now firmly closed by the thumb, and the gas is transferred to the limb DC containing the amalgam,
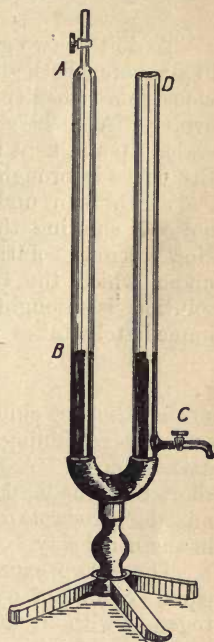
and well shaken so as to cause the gas to come into intimate contact with it. The following action takes place :—

$$2Na + 2HCl = 2NaCl + H_2$$
<div align="center">2 vols.   1 vol.</div>
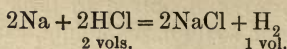
The gas is next passed back into the closed limb AB, and the pressure equalised by allowing mercury to run out at C. The hydrogen now in the limb AB will be found to occupy exactly half the volume of the original gas. By opening the stopcock A and lighting the emerging gas, it may be shown to consist of hydrogen.

(2) *To show that two volumes of hydrochloric acid gas contain one volume of chlorine.*

To do this two glass tubes are taken, each about 50 cm. long by $1\frac{1}{2}$ cm. in diameter, both drawn out to a fine thread at each end and filled as previously described (p. 82) with the gaseous mixture of hydrogen and chlorine evolved from the electrolysis of hydrochloric acid solution. The tubes are sealed up and kept in the dark. To show the composition of the gas, one of the tubes is brought into a dimly lighted room, and one of the drawn-out ends is broken under mercury. No alteration in the bulk of the gas is noticed, showing that the gas in the tube is under atmospheric pressure. Now a strong solution of potassium iodide is made to replace the mercury under which the tube dips, and by shaking the tube longitudinally, the solution is brought into contact with the gas. The following change immediately takes place :—

$$2KI + Cl_2 = 2KCl + I_2,$$
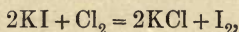
so that the free chlorine in the mixture is rapidly absorbed, iodine being set free and remaining dissolved in the iodide solution, which therefore becomes dark-coloured. A diminution of bulk of the gas in the tube occurs, and in a short time the liquid half fills the tube, proving that half the volume of the mixed gas consists of chlorine : the residual half may be proved to be hydrogen in the usual way.

These two experiments show that hydrochloric acid gas is made up of equal volumes of hydrogen and chlorine, and that these two gases combine together without change of volume to produce hydrochloric acid gas. This latter conclusion may be further verified by exposing the second tube for a few minutes first to dim and then to strong daylight, until the greenish colour of the chlorine contained therein has entirely disappeared. The gases will have gradually united :—

$$H_2 + Cl_2 = 2HCl.$$
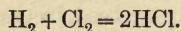
On breaking the end of the tube under mercury, no alteration of volume will be observed, while the enclosed gas may be proved to be nothing but hydrochloric acid gas by the simple process of adding water to the mercury and bringing the broken end of the tube into this, when complete absorption will ensue and the tube will be completely filled with mercury.

More accurate results than are possible with the above volumetric methods may be obtained by quantitatively estimating the chlorine in a given volume of gas by ordinary methods for estimating free chlorine.

Aqueous Hydrochloric Acid.—As above mentioned, hydrochloric acid

is very soluble in water, and the solution is very largely used for laboratory and commercial purposes. The manufacture of the aqueous acid has been described on p. 87.

A very considerable quantity of heat is absorbed when hydrochloric acid dissolves in water, amounting, according to Thomsen,[1] to as much as 17,314 calories per gram-molecule (17,430 calories, according to Berthelot and Louguinine).[2]

The pure saturated aqueous acid is a colourless liquid which fumes strongly in air. Many commercial samples are coloured faintly yellow owing to the presence of iron and other impurities.

A saturated solution may be prepared by the apparatus shown in fig. 16 (p. 72). One volume of water at 0° and 760 mm. absorbs 503 times its volume of hydrochloric acid gas. At −12·0° C., 1 volume of gas dissolves[2] 560 volumes of HCl.

Roscoe and Dittmar[3] give the following data for the weight of gas dissolved by one gram of water at different temperatures, when the partial pressure of the hydrogen chloride plus that of the water equals 760 mm.

Temp. ° C.	Gram HCl.	Temp. ° C.	Gram HCl.	Temp. ° C.	Gram HCl.
0	0·825	24	0·700	48	0·603
4	0·804	28	0·682	52	0·589
8	0·783	32	0·665	56	0·575
12	0·762	36	0·649	60	0·561
16	0·742	40	0·633		
20	0·721	44	0·618		

The following table, also due to Roscoe and Dittmar,[3] shows the weight of hydrochloric acid gas absorbed by 1 gram of water at 0° C. under different partial pressures of hydrogen chloride :—

Partial Pressure in mm. of Hg.	Gram HCl absorbed by 1 gram H_2O at 0° C.	Partial Pressure in mm. of Hg.	Gram HCl absorbed by 1 gram H_2O at 0° C.	Partial Pressure in mm. of Hg.	Gram HCl absorbed by 1 gram H_2O at 0° C.
60	0·613	400	0·763	1000	0·856
100	0·657	500	0·782	1100	0·869
150	0·686	600	0·800	1200	0·882
200	0·707	700	0·817	1300	0·895
250	0·724	800	0·831		
300	0·738	900	0·844		

[1] Thomsen, *Thermochemische Untersuchungen*, 1882, ii. 19.
[2] Berthelot and Louguinine, *Compt. rend.*, 1873, **76**, 679. See Richards, Rowe, and Burgess, *J. Amer. Chem. Soc.*, 1910, **32**, 1176.
[3] Roscoe and Dittmar, *J. Chem. Soc.*, 1860, **12**, 128.

The solubility of the gas in water does not follow Dalton and Henry's law; *i.e.* the amount dissolved under constant temperature but varying pressure does not vary proportionally as the pressure. For example, taking the above results, under 1000 mm. of mercury 1 gram of water absorbed 0·856 gram of the gas; therefore, if Dalton and Henry's law be strictly obeyed by the gas, the solubility at one-tenth this pressure (*i.e.* at 100 mm. of mercury) should be exactly one-tenth of the solubility at 1000 mm.

In other words, the solubility should be 0·0856 gram hydrogen chloride at 100 mm. Hg; whereas experiment showed that it was 0·657 gram.

The vapour tensions of concentrated hydrogen chloride solutions at 18·4° were recently determined by Allan [1] as follows:—

Per cent. HCl:—
36·40　　35·90　　35·10　　34·85　　33·90　　32·85　　31·75　　30·20　　28·10

Pressure in mm. Hg:—
138·1　　109·8　　75·8　　66·6　　46·0　　32·7　　21·9　　11·8　　5·5

It will be seen that the tensions are not strictly proportional to the amount of undissociated acid present in solution.

The density and the coefficient of expansion of aqueous solutions of hydrogen chloride have been investigated by various authors. Thus Kolb [2] found that the coefficient of expansion of the concentrated acid (43·09 per cent. HCl) is 0·058, or nine times greater than that of water. The coefficient of expansion of ordinary commercial acid (36·61 per cent. HCl) is about eight times smaller than that of water. Marignac [3] gave the following table for the density and coefficient of expansion of solutions of hydrogen chloride:—

　　D = density,
　　n = number of water molecules to 1 molecule of HCl,
　　t = temperature (centigrade),
　　a = coefficient of expansion.　　Density of water = 0·99826.

n.	D.	D. at 20°.	a at 20°.
6·25	$1·13040 - 0·0005049t + 0·00000005t^2$	1·12030	0·0004546
12·5	$1·07367 - 0·0003001t - 0·000001666t^2$	1·06700	0·0003460
25	$1·03946 - 0·0001580t - 0·000003253t^2$	1·03500	0·0002799
50	$1·02065 - 0·0000673t - 0·000004378t^2$	1·01755	0·0002394
100	$1·01071 - 0·0000313t - 0·000004845t^2$	1·00815	0·0002240
200	$1·00560 - 0·0000173t - 0·000004847t^2$	1·00330	0·0002107

The following table gives the specific gravities of aqueous hydrochloric acids of various strengths:—

[1] F. B. Allan, *J. Physical Chem.*, 1898, **2**, 120.
[2] J. Kolb, *Compt. rend.*, 1872, **74**, 737.
[3] Marignac, *Arch. Sci. phys. nat.*, 1870, **39**, 273.

SPECIFIC GRAVITY OF HYDROCHLORIC ACID SOLUTIONS AT 15°.

(Lunge and Marchlewski.[1])

Sp. Gr. 15°/4°.	Degrees Baumé.	Degrees Twaddle.	Per cent. HCl present in 100 Parts by Weight.	Sp. Gr. 15°/4°.	Degrees Baumé.	Degrees Twaddle.	Per cent. HCl present in 100 Parts by Weight.
1·000	0·0	0·0	0·16	1·105	13·6	21	20·97
1·005	0·7	1	1·15	1·110	14·2	22	21·92
1·010	1·4	2	2·14	1·115	14·9	23	22·86
1·015	·2·1	3	3·12	1·120	15·4	24	23·82
1·020	2·7	4	4·13	1·125	16·0	25	24·78
1·025	3·4	5	5·15	1·130	16·5	26	25·75
1·030	4·1	6	6·15	1·135	17·1	27	26·70
1·035	4·7	7	7·15	1·140	17·7	28	27·66
1·040	5·4	8	8·16	1·145	18·3	29	28·61
1·045	6·0	9	9·16	1·150	18·8	30	29·57
1·050	6·7	10	10·17	1·155	19·3	31	30·55
1·055	7·4	11	11·18	1·160	19·8	32	31·52
1·060	8·0	12	12·19	1·165	20·3	33	32·49
1·065	8·7	13	13·19	1·170	20·9	34	33·46
1·070	9·4	14	14·17	1·175	21·4	35	34·42
1·075	10·0	15	15·16	1·180	22·0	36	35·39
1·080	10·6	16	16·15	1·185	22·5	37	36·31
1·085	11·2	17	17·13	1·190	23·0	38	37·23
1·090	11·9	18	18·11	1·195	23·5	39	38·16
1·095	12·4	19	19·06	1·200	24·0	40	39·11
1·100	13·0	20	20·01				

When a saturated solution of hydrochloric acid in water (sp. gr. 1·22) is distilled under ordinary atmospheric pressure, the distillate obtained is richer in hydrogen chloride than the original liquid.

Consequently the residual liquid from a concentrated acid on heating becomes weaker as the distillation proceeds. But, conversely, when a weak aqueous acid is distilled, the distillate is weaker than the residue, so that the residue becomes more concentrated as the heating proceeds. It will therefore be seen that both the weak and the strong acid when evaporated ultimately reach the same strength, and the acid of this final strength when boiled distils over unchanged in composition.

The acid thus obtained, which boils unchanged at 760 mm. pressure, contains 20·24 per cent. HCl and boils at 110° C. (760 mm.). It has been proposed to utilise this fact for preparing standard solutions of the acid of known strength.[2]

When the pressure is altered, however, the composition of the acid which distils over unchanged also alters. The following table[3] shows this :—

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[1] Lunge and Marchlewski, *Zeitsch. angew. Chem.*, 1891, **4**, 133.
[2] Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 390.
[3] Roscoe and Dittmar, *J. Chem. Soc.*, 1860, **12**, 128.

Pressure in mm. Hg.	Per cent. HCl in Acid of Constant Boiling Point.	Pressure in mm. Hg.	Per cent. HCl in Acid of Constant Boiling-Point.	Pressure in mm. Hg.	Per cent. HCl in Acid of Constant Boiling-Point.
50	23·2	800	20·2	1700	18·8
100	22·9	900	19·9	1800	18·7
200	22·3	1000	19·7	1900	18·6
300	21·8	1100	19·5	2000	18·5
400	21·4	1200	19·4	2100	18·4
500	21·1	1300	19·3	2200	18·3
600	20 7	1400	19·1	2300	18·2
700	20·4	1500	19·0	2400	18·1
760	20·24	1600	18·9	2500	18·0

From this table it will be seen that the percentage of the acid in the distillate of constant composition is 23·2 per cent. HCl when the distillation is carried out at 50 mm., whereas it is 18·0 per cent. HCl when the distillation is carried out under a pressure of 2500 mm.

These solutions in water, having a constant boiling-point, are physical mixtures, not true chemical compounds, since they change in composition when the pressure under which they are distilled is altered in ever so slight a degree.   A true chemical compound preserves its constant composition throughout a definite range of temperature and pressure.

When dry air is passed through an aqueous solution of hydrochloric acid, practically the same results are obtained as in the case of distillation.   Part of the acid is vaporised, and finally a residue is obtained which for each given temperature remains of constant composition.   No matter whether the original acid is stronger or weaker, it ultimately attains this same composition, provided that the temperature be kept constant.

The following table is due to Roscoe and Dittmar :— [1]

Temperature, ° C.	Per cent. HCl after leading Air through Solution.	Temperature, ° C.	Per cent. HCl after leading Air through Solution.
0	25·0	60	23·0
10	24·7	70	22·6
20	24·4	80	22·0
30	24·1	90	21·4
40	23·8	100	20·7
50	23·4		

Comparing this table with the preceding one, it will be seen that the constant acid obtained by passing dry air through aqueous acid maintained at a particular temperature contains the same percentage of acid as an

[1] Roscoe and Dittmar, *J. Chem. Soc.*, 1860, **12**, 128.

aqueous acid which boils unaltered at the same temperature under a given pressure. For example, when the pressure is lowered so that the hydrochloric acid boils unchanged at, say, 62° (which occurs when the partial pressure of the hydrogen chloride is 100 mm.), the composition of the acid boiling unchanged is 22·9 per cent. HCl. If, now, air be passed through hydrochloric acid maintained at 62° C., the constant point is reached when the liquid also contains 22·9 per cent. HCl.

The conductivities of aqueous solutions of hydrochloric acid were determined by Kohlrausch [1] in 1888 :—

Per cent. HCl.	Sp. Gr. 15°.	Specific Conductivity at 18° in reciprocal ohms per cm. cube.
5	1·0242	0·3948
10	1·0490	0·6302
15	1·0744	0·7453
20	1·1000	0·7615
25	1·1262	0·7225
30	1·1524	0·6620
35	1·1775	0·5910
40	1·2007	0·5152

The variation of the molecular conductivity of hydrochloric acid with temperature and dilution has been determined by various experimenters. A summary of the results for 0°, 18°, and 25° is given in the accompanying table :—[2]

MOLECULAR CONDUCTIVITY OF AQUEOUS HYDRO-CHLORIC ACID.

n = normality of solution.
V = volume in litres that contains one gram-molecule of hydrochloric acid.
Conductivities given in C.G.S. units.

n.	V.	Molecular Conductivity of HCl at		
		0° C.	18° C.	25° C.
0·000	00	...	...	424
0·001	1000	...	375·9	...
0·005	200	...	372·6	415·3
0·01	100	...	370	411·6
0·05	20	249	360	398·4
0·1	10	244	351	390·4
0·5	2	226	327	362
1	1	214	301	331
5	0·20	...	152·2	168
10	0·10	...	64·4	70·9

[1] Kohlrausch, Pogg. Annalen, 1876, **159**, 233.
[2] Based on the data given by Kohlrausch and Holborn, Das Leitvermögen der Elektrolyte (Leipzig, 1898) ; Goodwin and Haskell, Proc. Amer. Acad., 1904, **40**, 399 ; Physical Rev., 1904, **19**, 369 ; Bray and Hunt, J. Amer. Chem. Soc., 1911, **33**, 781 ; Green, Trans.

Fick,[1] in 1885, also investigated the influence of pressure on the conductivity for electricity, and showed that it steadily increased at a rate proportional to the pressure until 300 atmospheres was reached, and at higher pressures slowly decreased again.

The *specific heats* of hydrochloric acid solutions of different concentrations were determined by Hammerl,[2] who showed that while a 32·37 per cent. HCl solution had a specific heat of 0·6260, this increased with dilution, so that an acid with 4·8 per cent. HCl had a specific heat of 0·9310. The refractive index of aqueous hydrochloric acid increases with the density of the acid. If the refractive index of water = 1, we have the following results :—

Density	.	.	.	1·055	1·087	1·121	1·146	1·177
Refractive index		.		1·053	1·088	1·121	1·138	1·180

The *refractive index*[3] of a concentrated solution of density 1·1630 is 1·4071 (D ray at 16° C.). An N/1 solution[4] has a refractive index = 1·3414, and an N/2 solution has refractive index = 1·3374 for sodium light at 18° C.

Isambert[5] investigated the *compressibility* of solutions of hydrochloric acid, and came to the conclusion that the hydrochloric acid was chemically united to the water, since the compressibility was less than that of pure water. He determined the coefficient of compressibility to be 0·0000366 at 20·5°.

The *coefficient of diffusibility*[6] is 490×10^{-7} cm.^{2}/sec., while the *coefficient of friction*[7] is 0·000156 at 10°–20°.

Hydrochloric acid is a very strong[8] monobasic acid, and, if we set the *avidity* of nitric acid as 100, we obtain the value of the "avidity" of hydrogen chloride as 100 (Thomsen), 98 (Ostwald), or 92 (calculated by Arrhenius). The heat of neutralisation[9] by NaOH is 13,700 calories.

Freezing-Point of Hydrochloric Acid Solutions.   Hydrates.—A saturated solution of hydrochloric acid freezes below − 40° to a buttery mass. An acid containing 30·3 per cent. HCl does not crystallise at − 83° C. Richards and Jackson[10] investigated the freezing-points of aqueous solutions of hydrochloric acid.

Chem. Soc., 1908, **93**, 2023 ; Jones, *Zeitsch. physikal. Chem.*, 1906, **55**, 420 ; Jones and Pearce, *Amer. Chem. J.*, 1907, **38**, 683 ; Jones and Douglas, *ibid.*, 1901, **26**, 428.   See also Ostwald, *J. prakt. Chem.*, 1885, [ii.], **31**, 433 ; Landolt and Bornstein, *Physikalisch-chemische Tabellen* (Berlin, 3rd edition, 1912).   The conductivities have been measured up to 306° C. by Noyes and others, *Carnegie Institution Publications*, 1907, No. 63 ; *Zeitsch. physikal. Chem.*, 1910, **70**, 335.

[1] Fick, *Wied. Annalen*, 1885, **26**, 481.
[2] H. Hammerl, *Compt. rend.*, 1879, **89**, 902.
[3] H. Becquerel, *Ann. Chim. Phys.*, 1877, [v.], **12**, 5.
[4] J. Conroy, *Proc. Roy. Soc.*, 1899, **64**, 308.
[5] F. Isambert, *Compt. rend.*, 1887, **105**, 375.
[6] Umoff, *J. Russ. phys. Ges.*, 1892, **23**, 2, 335.
[7] O. E. Meyer and Springmühl, *Pogg. Annalen*, 1873, **148**, 526.
[8] See Thomsen, *Thermochemische Untersuchungen*, 1882, i. 151 ; Ostwald, *J. prakt. Chem.*, 1878, **18**, 362 ; Arrhenius, "Untersuchungen über die galvanische Leitfähigkeit der Elektrolyte," Ostwald's *Klassiker der exakten Naturwissenschaften*, Nr. 160 ; see also Kühling, *Ber.*, 1901, **34**, 3941 ; Sackur, *Ber.*, 1902, **35**, 99 ; Bodländer, *Ber.*, 1902, **35**, 99, 1255.
[9] Regarding the heat of neutralisation of HCl with various oxides, see Berthelot, *Compt. rend.*, 1872, **75**, 435, 480, 538, 584 ; 1882, **94**, 172, 664 ; see also Thomsen, *Thermochemische Untersuchungen* ; Kablukoff, *J. Russ. physik. Ges.*, 1892, **23**, i. 459.
[10] T. W. Richards and F. G. Jackson, *Zeitsch. physikal. Chem.*, 1906, **56**, 362.

Richards and Jackson propose to use the various freezing-points of solutions of hydrochloric acid for standardising thermometers without the use of a normal thermometer, since a solution of hydrochloric acid of definite strength possesses a quite definite freezing-point.

Several definite hydrates of hydrochloric acid exist.

Thus Rupert [1] has isolated a monohydrate $HCl.H_2O$, of density 1·48 and melting-point $-15·35°$ C. It is very soluble in water, but only slightly in liquid HCl, and has a vapour pressure at its melting-point nearly equal to that of liquid HCl—namely, 17·3 atmospheres.

A hydrate $HCl.2H_2O$ separates out when a saturated solution of hydrochloric acid is cooled below $-40°$ C. It also separates from solutions containing 43·93 to 48·81 per cent. at temperatures between $-26·25°$ and $-17·5°$. Pierre and Puchot [2] obtained the same hydrate by leading dry HCl gas into a concentrated HCl solution maintained between $-25°$ and $-30°$. This hydrate is unstable in air, evolving white fumes and melting at $0°$, evolving gas. Roozeboom [3] investigated the dissociation of the hydrate, and found that it followed Debray's law. He gave the following dissociation vapour tensions :—

Temperature. ° C.	Tension of Dissociation.	Temperature. ° C.	Tension of Dissociation.
$-23·4$	193 mm.	$-18·2$	791 mm.
$-20·5$	376 „	$-17·83$	990 „
$-19·2$	534 „	$-17·7$	1080 „

The critical temperature of decomposition is $-18·3$ in open vessels, while in closed vessels it is $-17·7°$. The heat of formation of the hydrate $HCl.2H_2O$ is 11,600 calories [4] when liquid, and 14,100 calories when solid, while its density (water = 1) is 1·46.

A hydrate $HCl.3H_2O$ exists (Pickering).[5] It separates out from solutions containing 25·1 to 42·5 per cent. HCl between $-80°$ and $-25·65°$. It contains 40·33 per cent. HCl.

Hydrates having the composition $HCl.6·5H_2O$ and $HCl.10H_2O$ are also said to exist.

Chemical Properties of Aqueous Hydrochloric Acid.—To a great extent these have already been discussed under gaseous hydrochloric acid. It suffices to say that the acid is a strong monobasic acid, which when electrolysed gives rise to equal volumes of hydrogen and chlorine (see p. 81). Concentrated solutions of hydrochloric acid when permanently exposed to the light gradually decompose [6] to some extent with the liberation of free chlorine, so that a piece of gold-leaf placed in the liquid is, after a few hours, attacked

[1] Rupert, *J. Amer. Chem. Soc.*, 1909, **31**, 851.
[2] See Pierre and Puchot, *Compt. rend.*, 1876, **82**, 45.
[3] Roozeboom, *Rec. trav. chim.*, 1884, **3**, 29, 59, 73, 84.
[4] Berthelot, *Compt. rend.*, 1878, **86**, 279.
[5] Pickering, *Ber.*, 1893, **26**, 277.
[6] See N. W. Fischer, *J. prakt. Chem.*, 1849, **48**, 70 ; L'Hôte, *Ann. chim. anal. appl.*, 1900, **5**, 208.

by the nascent chlorine. Sufficient chlorine sometimes accumulates in the liquid to be detectable by odour alone. Dilute acid is much more stable towards light.

When a concentrated solution of hydrochloric acid is heated with red phosphorus to 200° in a sealed tube, a considerable amount of phosphine gas, PH_3, is produced.[1]

Mercury is not attacked to any great extent by aqueous hydrogen chloride. Antimony dissolves in the solution only in the presence of oxygen. Platinum-black [2] appears to be slowly attacked by concentrated hydrogen chloride solution at ordinary temperatures, forming H_2PtCl_6, whereas platinum-foil is not attacked at ordinary temperatures, but is when heated with concentrated hydrogen chloride solution in the presence of oxygen at 170°. Gold is also attacked under some circumstances. According to Berthelot,[3] at ordinary temperatures both gold and platinum are quite unattacked by fuming hydrogen chloride solution when kept in the dark. In the presence of light, however, they are attacked to some extent, especially in the presence of a catalyser such as manganous chloride. Many salts [4] take up considerable quantities of hydrochloric acid owing to the formation of an acid salt and a chloride : examples of these salts are Na_2SO_4 and Na_2HPO_4.

CHLORIDES.

As above mentioned, hydrochloric acid is a strong monobasic acid which generates a very numerous series of salts known as chlorides. For the purposes of classification we may divide the chlorides into :—

    (1) Normal chlorides.
    (2) Acid chlorides.
    (3) Double chlorides.
    (4) Other compounds of chlorine.

We will take each series in succession.

(1) NORMAL CHLORIDES.

General formula, R–Cl.

The normal chlorides are the usual products of the replacement of the hydrogen in hydrochloric acid by a metal.

Methods of Formation.—(1) *By Direct Action of Chlorine Gas.*—With the exception of carbon, nitrogen, oxygen, and the argon group of elements, all the elements can be made to unite directly with chlorine. Many metals unite with chlorine gas with incandescence. For example, the following metals at ordinary temperatures take fire and burn in chlorine gas : potassium, arsenic, antimony, bismuth, tin, brass foil, reduced copper or nickel ; while the following metals burn in chlorine when heated : sodium, zinc, thallium, indium, tungsten, tellurium, iron, nickel, and mercury maintained at its boiling-point. Gold, silver, lead, and platinum also unite when heated in chlorine, but the heat evolved by the act of union is

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[1] Oppenheim, *Bull. Soc. chim.*, 1864, [ii.], **1**, 163.
[2] G. Matignon, *Compt. rend.*, 1902, **134**, 1497.
[3] Berthelot, *Compt. rend.*, 1904, **138**, 1297 ; Mallet, *Amer. Chem. J.*, 1901, **25**, 430.
[4] J. W. Thomas, *Trans. Chem. Soc.*, 1878, **33**, 72.

not sufficiently intense to cause incandescence. For experiments on combustion in chlorine, see p. 70.

It is not always necessary to use the free metal; for chlorine also attacks various compounds, producing chlorides. For example, very often the metallic oxides are decomposed when heated in chlorine gas.

Silver oxide, Ag_2O, at ordinary temperatures, is converted into chloride with liberation of oxygen, while the oxides of the alkaline earths, CaO, BaO, SrO, are decomposed on heating, with the formation of the corresponding chlorides and the liberation of oxygen gas, whose volume amounts to half the volume of the absorbed chlorine.

CaO, BaO, SrO, when heated red-hot and plunged into chlorine, are actually decomposed with the production of incandescence. MgO is also decomposed when highly heated in chlorine gas, but without incandescence appearing. Also the oxides of zinc, cadmium, lead, copper, and nickel are easily decomposed by hot chlorine, while cobalt and iron oxides are decomposed only with difficulty. Aluminium oxide and silica are not decomposed, even at a white heat only small amounts of chlorides being formed. The trioxides Cr_2O_3, MoO_3, WO_3 form oxychlorides. SnO, Sb_2O_5, As_2O_3, when strongly ignited in the gas, are completely converted into chlorides.

Several oxides which are only slightly attacked in the presence of hot chlorine are readily decomposed if mixed with charcoal, and then the mixture is ignited in a stream of chlorine. For example, $SiCl_4$, $SnCl_4$, $AlCl_3$, $ThCl_4$, etc., may be prepared by this method from the corresponding chlorides.

Chlorine also acts on most bromides and iodides of metals, displacing bromine or iodine and producing chlorides. Many sulphides are decomposed when heated in a stream of chlorine, and this provides a method of producing chlorides of many metals.

A modification of this method consists in passing a stream of chlorine charged with vapours of disulphur dichloride over heated oxides and oxygen salts. Many anhydrous chlorides have been obtained in this manner. SiO_2, for example, at a dull red heat yields $SiCl_4$; Al_2O_3 gives $AlCl_3$, while ThO_2 at a red heat yields $ThCl_4$. WO_3 gives WO_2Cl_2 at a high temperature, and $WOCl_4$ at a lower temperature. NiO, CoO at 400° give the chlorides, while Cr_2O_3 and Fe_2Cl_3 give $CrCl_3$ and $FeCl_3$ even below redness.

Similarly the oxy-salts of calcium, strontium, and barium (e.g. the sulphates), are transformed into chlorides by this method. In the application of this, however, care must be taken not to have excess of disulphur dichloride if the chlorides to be prepared are volatile. When, however, the chlorides to be prepared are fairly non-volatile, the action is accelerated by excess of the sulphur chloride.

(2) *By the Action of Hydrochloric Acid.*—Many metals when heated in a stream of HCl gas directly unite with the chlorine, liberating hydrogen, thus:—

$$2HCl + 2M = 2MCl + H_2.$$
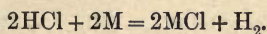
This action often occurs at ordinary temperatures, while many metals such as zinc, iron, magnesium, etc., dissolve in an aqueous solution of the gas, producing chlorides and hydrogen:—

$$Zn + 2HCl = ZnCl_2 + H_2.$$
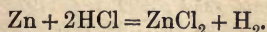
Hydrogen chloride, either in the form of a gas or as an aqueous solution, also acts on metallic oxides, carbonates, and sulphides, producing chlorides :—

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$
$$FeS + 2HCl = FeCl_2 + H_2S.$$
$$ZnO + 2HCl = ZnCl_2 + H_2O.$$
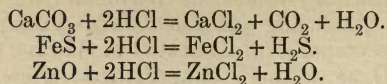
Many substances which are scarcely affected by hydrochloric acid under ordinary conditions are readily attacked when heated in a sealed tube with concentrated aqueous hydrochloric acid in *the presence of oxygen*. For example, platinum foil is hardly attacked at all—or only with extreme slowness in the presence of air and light—by ordinary concentrated hydrochloric acid solution. When, however, the foil is heated at 170° C. for many hours in a sealed glass tube with concentrated hydrochloric acid and oxygen, it is gradually dissolved, with formation of H_2PtCl_6. The same takes place with gold foil—amorphous gold actually being attacked by hydrogen chloride and oxygen at ordinary temperatures. Tellurium heated with hydrogen chloride and oxygen to 100° C. in a sealed tube is likewise attacked, forming the tetrachloride $TeCl_4$. It will thus be seen that Pt, Au, and Te are attacked by the mixture at a temperature far below that at which gaseous hydrogen chloride is oxidised by oxygen.

C. Matignon,[1] who made extensive researches on the subject in 1902–04, showed that all the metals of the platinum group were completely transformed into chlorides by heating with the mixture of concentrated hydrogen chloride and oxygen in sealed tubes ; palladium dissolving slowly at ordinary temperatures to form palladium dichloride, ruthenium dissolving at 125° C., iridium at 150° C., rhodium rapidly at 200° C., and osmium at 150° C.

(3) *By the Action of Other Chlorine Compounds.*—Many chlorine compounds besides hydrochloric acid possess the property of yielding up chlorine and producing chlorides under suitable conditions.

For example, the chlorides of phosphorus are well-known chlorinating agents, their use being especially widely extended in organic chemistry. Vapours of carbon tetrachloride, CCl_4, and also phosgene gas, $COCl_2$ (or mixtures of $CO + Cl_2$ gases), when passed over red-hot oxides of metals such as Ni, Co, Al, Ti, Cr, Nb, Ta, Zr, W, convert them into chlorides. On the other hand, SiO_2 and B_2O_3 are not attacked thus.

Another method which has been successfully worked is the passing of petroleum previously saturated with chlorine or HCl over ignited oxides. For example, Warren[2] converted Al_2O_3 into $AlCl_3$ by igniting the oxide in a stream of low-boiling petroleum which had been previously saturated with Cl or HCl gas. He also used for the same purpose naphthalene chloride.

(4) *By Double Decomposition.*—This is one of the most usual methods of preparing certain chlorides, and a few examples may be given here.

When mercury chloride, $HgCl_2$, is heating with antimony, we get

$$2Sb + 3HgCl_2 = 2SbCl_3 + 3Hg,$$
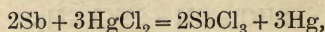
and with antimony sulphide,

$$Sb_2S_3 + 3HgCl_2 = 2SbCl_3 + 3HgS.$$

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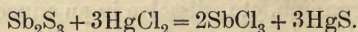
[1] Matignon, *Compt. rend.*, 1902, **134**, 1497 ; 1903, **137**, 1051.
[2] Warren, *Chem. News*, 1887, **55**, 192.

Ammonium chloride, NH_4Cl, when heated with a great many substances causes their total or partial conversion into chloride.

(5) If two or more chlorides exist, the compound containing the most halogen may be usually prepared by heating the one containing less with chlorine. Examples are afforded by the following equations :—

$$2FeCl_2 + Cl_2 = 2FeCl_3,$$
$$2HgCl + Cl_2 = 2HgCl_2,$$
$$SnCl_2 + Cl_2 = SnCl_4.$$
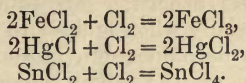
(6) *By heating the higher chloride*, in certain cases, chlorine is evolved and the lower chloride is left. For example, when thallic chloride, $TlCl_3$, is heated, $TlCl$ is formed :—

$$TlCl_3 = TlCl + Cl_2 ;$$
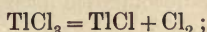
similarly $AuCl_3$ yields $AuCl$:—

$$AuCl_3 = AuCl + Cl_2.$$
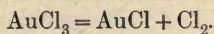
In a similar manner bodies like $GaCl_3$, $InCl_3$, $ScCl_4$, when heated to a high temperature, yield lower chlorides such as $GaCl_2$, $InCl$, $InCl_2$, Sc_2Cl_6.

Cases are known where the lower chloride, on heating, decomposes into the higher chloride and the metal :—

$$3BiCl_2 = 2BiCl_3 + Bi.$$
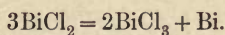
Lower chlorides of such elements as titanium, molybdenum, tungsten, chromium, etc., may be prepared by the action of hydrogen on the higher chlorides at a red heat.

Sometimes the removal of halogen from the higher halide may be obtained by reducing it in solution. Thus the operations of "reducing" ferric chloride in solution by means of hydrogen generated from zinc and hydrochloric acid, sulphur dioxide, or stannous chloride, are examples in point. Sulphuretted hydrogen also acts as a mild reducing agent, reducing $FeCl_3$ and $RhCl_3$ to lower chlorides.

Physical Properties of the Chlorides.—The chlorides of the metals are almost invariably more volatile than the metals themselves. A few metallic chlorides, indeed, are actually volatile liquids at ordinary temperatures —examples are the chlorides of arsenic, antimony, and tin. Others are solids at ordinary temperatures, but easily melt, and when strongly heated readily volatilise—examples are $MgCl_2$, $AlCl_3$, chlorides of zinc, antimony, and bismuth.

The great majority of metallic chlorides are readily soluble in water, the most notable exceptions being $AgCl$, $HgCl$, $PbCl_2$, $CuCl$, $TlCl$.

Some chlorides which are very sparingly soluble in water are dissolved more easily by concentrated hydrochloric acid. For example, $CuCl$ and $AgCl$ dissolve in concentrated HCl, while $PbCl_2$ and $HgCl$ are taken up to a greater extent in hot HCl than by hot water.

Chemical Properties of the Chlorides.—A few chlorides decompose when heated into the metal and chlorine gas. These are principally the chlorides of "noble" metals like gold and platinum. Thus by heating $PtCl_4$ pure chlorine is liberated. Even copper chloride, $CuCl_2$, when heated to a high temperature, loses part of its chlorine. Lead chloride when heated in a stream of nitrogen to 400°–500° gradually decomposes with evolution of chlorine.

Many chlorides which appear stable enough when heated in an inactive gas decompose readily enough when heated in dry oxygen gas. Thus aluminium chloride at a dark red heat in oxygen gas evolves part of its chlorine, while such a stable chloride as that of sodium when heated very intensely in dry air also evolves chlorine.[1]

A great many chlorides otherwise exceedingly stable are completely decomposed by water, especially when ignited in a current of steam. Thus $AlCl_3$, $SnCl_4$, and $SiCl_4$ are decomposed by water at ordinary temperatures, and, with the exception of the alkali chlorides, barium chloride and mercuric chloride, practically all the known chlorides are decomposed by igniting in a stream of water vapour. Of the chlorides of the alkaline metals LiCl is decomposed with difficulty by this treatment, so also are $SrCl_2$ and $CaCl_2$. $MgCl_2$ is easily decomposed (see p. 62). As regards the decomposition of NaCl see below.

Many chlorides are decomposed when heated in a stream of hydrogen. AgCl is decomposed by this treatment, although not easily. Iron chloride, $FeCl_3$, is easily reduced to iron. Many chlorides, however, do not seem to be sensibly attacked when subjected to this process, even cadmium chloride, for example, being only very slowly reduced by heating to redness in hydrogen.

Most involatile chlorides which are not decomposed by heating to redness in air are also not, as a rule, decomposed by heating, even to whiteness, with carbon. However, when a chloride is heated to a high temperature with carbon, and steam is passed over the hot mass, even difficultly reducible chlorides, like AgCl and $HgCl_2$, are easily reduced to a metallic condition.

Gay-Lussac and Thénard made some extensive experiments on this point. As regards the action of steam they showed, for example, that chlorides quite stable even at very high temperatures (such as NaCl, AgCl, $HgCl_2$) are also not decomposed in the absence of moisture when heated to whiteness with such substances as SiO_2, Al_2O_3, B_2O_3, acid phosphates of calcium, etc. Nevertheless, when steam is driven through the incandescent mass, the chloride is hydrolysed with formation of the oxide of the metal, hydrogen chloride being liberated. Heating with sulphur, also, does not usually decompose the chlorides, but heating with phosphorus often has that effect.

P_2O_5 decomposes NaCl, $POCl_3$ being formed.

Many anhydrous chlorides are decomposed by the electric current when maintained in a molten condition, and many metals are now prepared on a large scale by the electrolytic decomposition of the fused chloride—e.g. Na, Mg, Ca, etc. Aqueous solutions of chlorides are also decomposed with formation of metallic hydroxides and free chlorine (see Chlorine, p. 62).

Most chlorides when heated with concentrated sulphuric acid are completely decomposed into sulphates of the metals and gaseous hydrochloric acid. This change takes place at ordinary temperatures in the case of the chlorides of Na, K, Rb, Cs, NH_4, Fe, Co, Zn, Mn ; but the chlorides of Sb, Bi, and Cu require a high temperature to bring about the complete change, and a few metallic chlorides—e.g. $AsCl_3$, $SnCl_2$, $SnCl_4$, and $HgCl_2$—are at no temperature completely decomposed by concentrated H_2SO_4.

The chlorides of Na, K and NH_4, Ag and Ba absorb a large amount of sulphur trioxide without the development of any gas ; apparently union takes

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[1] de Sanderval, *Compt. rend.*, 1893, **116**, 641.

place, and it is only on heating that sulphur di-oxide and chlorine are evolved. The following change takes place :—

$$NaCl + 2SO_3 = NaOS_2O_5Cl.$$
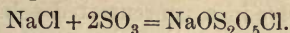
On gently heating sodium chloride with sulphur tri-oxide the action which takes place is represented by :—

$$2NaCl + 4SO_3 = Na_2S_2O_7 + S_2O_5Cl_2,$$
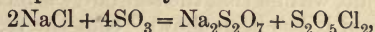
while when sulphur tri-oxide vapour is led over red-hot sodium chloride the following change takes place :—

$$2NaCl + 2SO_3 = Na_2SO_4 + Cl_2 + SO_2.$$
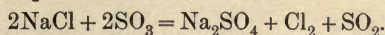
Nitric acid decomposes almost all the metallic chlorides, converting them into nitrates—with the exception of silver chloride, AgCl, and mercuric chloride, $HgCl_2$.

Also such acids as boric, arsenic, and phosphoric usually decompose chlorides, especially on heating, with liberation of hydrogen chloride and formation of the metallic salts of the acids.

Nearly all chlorides are decomposed by fusing with the alkali carbonates, the chlorine combining with the alkali metal, thus :—

$$2NaKCO_3 + 4AgCl = 2KCl + 2NaCl + 4Ag + O_2 + 2CO_2.$$
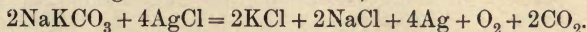
Most metallic chlorides, when mixed with MnO_2 or PbO_2 and heated with concentrated sulphuric acid, evolve chlorine gas (see p. 55).

When metallic chlorides are mixed with CrO_3 or $K_2Cr_2O_7$, and then distilled with concentrated sulphuric acid, a dark blood-red distillate of chromyl chloride, CrO_2Cl_2, is obtained, thus :—

$$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 3H_2O.$$
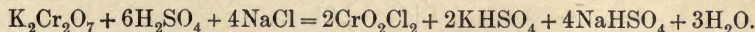
The distillate, when treated with water, decomposes thus :—

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$
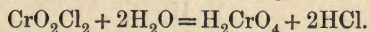
An entirely different reaction takes place if *dilute* sulphuric acid is used instead of *strong*.

$$K_2Cr_2O_7 + 11H_2SO_4 + 6NaCl = 6NaHSO_4 + 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Cl_2.$$
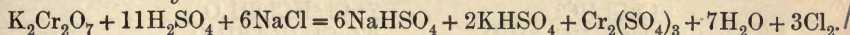
(2) Acid Chlorides.

Alkali chlorides and also the chlorides of other metals absorb in the cold considerable quantities of hydrogen chloride, the absorption being attended with the evolution of heat, which apparently points to the formation of acid salts. These acid salts, however, are apparently completely decomposed in solution, as was shown by the experiments of Berthelot and Martin.[1]

These authors mixed solutions containing equivalent quantities of HCl and metallic chlorides, but the amount of heat evolved or absorbed was too small to allow of the conclusion being drawn of chemical combination of any sort. For example, the following numbers were observed :—

$$NaCl + HCl = -0.03 \text{ calories.}$$
$$KCl + HCl = -0.03 \quad ,,$$
$$NH_4Cl + HCl = -0.04 \quad ,,$$
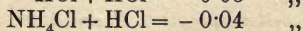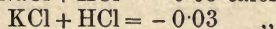
They therefore came to the conclusion that, in contradistinction to dibasic acids, monobasic acids do not form acid salts capable of existing in solution.

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[1] Berthelot and L. de Saint Martin, *Compt. rend.*, 1869, **69**, 464 ; 1872, **75**, 207, 263.

Certain facts, however, indicate that in some cases a definite chemical combination with hydrogen chloride takes place in solution ; for example, chlorides in general dissolve in a concentrated solution of hydrochloric acid much less readily than in water—as is to be expected according to the ordinary conceptions of physical chemistry regarding solubility. Nevertheless, in the case of mercuric chloride, we find that the solubility is increased by the addition of hydrochloric acid, and it has been shown [1] that the freezing-points of dilute solutions of hydrogen chloride are progressively depressed by the addition of $HgCl_2$, until the solution has the composition corresponding, approximately, to $HgCl_2.2HCl$.

Indications also exist [2] of a compound with cuprous chloride and hydrochloric acid, such as $CuCl.HCl$ or $CuCl.2HCl$.

Also a double chloride $PtCl_4.2HCl$ has been obtained, to which Werner [3] gives the constitution :—
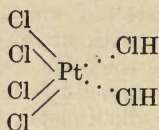
and Friend :—

Pfeiffer [4] gives the following list of acid chlorides which have been prepared :—

$CuCl.HCl$	$ZnCl_2.HCl.2H_2O$
$CuCl_2.HCl.3H_2O$	$2ZnCl_2.HCl.2H_2O$
$CuCl_2.2HCl.5H_2O$	$SnCl_2.HCl.3H_2O$
$CuCl_2.3HCl$	$HgCl_2.HCl$
$PtCl_2.HCl.2H_2O$	$CdCl_2.2HCl.7H_2O$
$AuCl_3.HCl.4H_2O$	$SnCl_4.2HCl.6H_2O$
$2SbCl_3.HCl.3H_2O$	$PtCl_4.HCl$
$2BiCl_3.HCl.3H_2O$	$PtCl_4.2HCl.6H_2O$

(3) Double Chlorides.

A great many metallic chlorides unite [5] to form double halides, a list of which is given below. The chlorides of the alkalies, however, do not thus unite

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[1] See M. le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 385 ; Berthelot, *Ann. Chim. Phys.*, 1881, [v.], **23**, 85.

[2] M. le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 385.

[3] A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (Braunschweig, 1905) ; Friend, *Trans. Chem. Soc.*, 1908, **93**, 1006. See Vol. IX.

[4] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, **31**, 202.

[5] See a discussion by A. Werner, *Zeitsch. anorg. Chem.*, 1899, **19**, 158 ; *Ber.*, 1907, **40**, 4441.

—at least, no true double compounds have been described. The same applies to the halides of Ca, Sr, and Ba, also to those of Sc, Y, La among the metals.

The chlorides (and halides generally) of the strong electronegative elements, nitrogen, phosphorus, and sulphur, do not form addition products with the chlorides of the alkalies, although the one group of elements belongs to the most strongly marked electropositive elements, and those of the other to very strongly marked electronegative elements.

Boron, carbon, and silicon halides also do not, in general, give rise to double halides. On the other hand, the tendency to form double salts is quite highly developed in the case of elements such as Cd, Au, Pt, Al, Sn, Pb, As, Sb, Bi, Se, Te—all of which are the higher analogues of elements which do not form double salts. Apparently increase of atomic weight in a series of related elements brings out the tendency to produce double salts. Curiously enough, although the halides of phosphorus do not combine with the halides of the alkali metals to form double halides, they readily unite with the halides of platinum (*e.g.* $PtCl_2$) and gold (AuCl) to produce very stable addition compounds.

The following list of the various known types of double salts is due to Pfeiffer,[1] who arranges the elements whose chlorides are capable of acting as the acid component of the union in the order of their valency, as follows (M stands for a monovalent metallic radicle) :—

1. *Monovalent Elements.*—Cu, Ag, Au.

Cu	Ag	Au
$CuCl_2M$	$AgCl_3M$	$AuCl_2M$
$CuCl_3M_2$		
$CuCl_4M_3$		
Cu_2Cl_3M		
$Cu_2Cl_5M_3$		
$Cu_3Cl_5M_2$		

2. *Divalent Elements.*—Cu, Mg, Zn, Cd, Hg, Sn, Pb, Mn, Fe, Co, Ni, Mo, Pd, Pt :—

Cu	Mg	Zn	Cd	Hg	Sn	Pb
$CuCl_3M$	$MgCl_3M$	$ZnCl_3M$	$CdCl_3M$	$HgCl_3M$	$SnCl_3M$	$PbCl_3M$
$CuCl_4M_2$		$ZnCl_4M_2$	$CdCl_4M_2$	$HgCl_4M_2$	$SnCl_4M_2$	$PbCl_4M_2$
$CuCl_5M_3$		$ZnCl_5M_3$	$CdCl_6M_4$	$HgCl_5M_3$		
$Cu_2Cl_7M_3$		Zn_2Cl_5M	Cd_2Cl_5M	Hg_2Cl_5M		$PbCl_6M_4$
			$Cd_2Cl_7M_3$	Hg_3Cl_7M		Pb_2Cl_5M
				$Hg_3Cl_8M_2$		
				$Hg_3Cl_{10}M_4$		
				Hg_4Cl_9M		
				$Hg_5Cl_{11}M$		
				$Hg_5Cl_{12}M_2$		
				$Hg_5Cl_{14}M_4$		
				$Hg_6Cl_{13}M$		

[1] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, **31**, 230. See also A. Werner, *Zeitsch. anorg. Chem.*, 1899, **19**, 158 ; *Neuere Anschauungen auf dem Gebiete der anorganischem Chemie* (Braunschweig, 1905), p. 71 ; Wells, *Amer. Chem. J.*, 1901, **26**, 389 ; Weinland and Pupils, *Ber.*, 1903, **36**, 246 ; *Zeitsch. anorg. Chem.*, 1905, **44**, 37, 81 ; *Ber.*, 1905, **38**, 1080, 3784 ; *Ber.*, 1906, **39**, 4042 ; *Zeitsch. anorg. Chem.*, 1907, **54**, 223.

2. *Divalent Elements.*—continued.

$\overset{..}{\text{Mn}}$	$\overset{..}{\text{Fe}}$	$\overset{..}{\text{Co}}$	$\overset{..}{\text{Ni}}$	$\overset{..}{\text{Mo}}$	$\overset{..}{\text{Pd}}$	$\overset{..}{\text{Pt}}$
$MnCl_3M$ $MnCl_4M_2$	$FeCl_4M_2$	$CoCl_3M$ $CoCl_4M_2$ $CoCl_5M_3$	$NiCl_3M$	$Mo_3Cl_8M_2$	$PdCl_4M_2$	$PtCl_3M$ $PtCl_4M_2$

3. *Trivalent Elements.*—Al, In, Tl, As, Sb, Bi, Cr, Mn, Fe, Au, Ru, Rh, Os, Ir.

$\overset{...}{\text{Al}}$	$\overset{...}{\text{In}}$	$\overset{...}{\text{Tl}}$	$\overset{...}{\text{As}}$	$\overset{...}{\text{Sb}}$	$\overset{...}{\text{Bi}}$	$\overset{...}{\text{Mn}}$
$AlCl_4M$ $AlCl_5M_2$	$InCl_5M_2$ $InCl_6M_3$	$TlCl_4M$ $TlCl_5M_2$ $TlCl_6M_3$ $Tl_2Cl_9M_3$	$As_2Cl_9M_3$	$SbCl_4M$ $SbCl_5M_2$ $SbCl_6M_3$ Sb_2Cl_7M $Sb_2Cl_9M_3$ $Sb_3Cl_{14}M_7$ $Sb_3Cl_{16}M_7$	$BiCl_4M$ $BiCl_5M_2$ $BiCl_6M_3$ Bi_2Cl_7M $Bi_2Cl_9M_3$ $Bi_3Cl_{16}M_7$	$MnCl_5M_2$

$\overset{...}{\text{Fe}}$	$\overset{...}{\text{Au}}$	$\overset{...}{\text{Ru}}$	$\overset{...}{\text{Rh}}$	$\overset{...}{\text{Os}}$	$\overset{...}{\text{Ir}}$
$FeCl_4M$ $FeCl_5M_2$ $FeCl_6M_3$	$AuCl_4M$ $AuCl_5M_2$ Au_2Cl_7M	$RuCl_5M_2$	$RhCl_4M$ $RhCl_5M_2$ $RhCl_6M_3$	$OsCl_5M_4$ $OsCl_6M_3$	$IrCl_6M_3$

4. *Tetravalent Elements.*—Ti, Th, Sn, Pb, Sb, Te, U, Mn, Ru, Pd, Os, Ir, Pt.

$\overset{....}{\text{Ti}}$	$\overset{....}{\text{Th}}$	$\overset{....}{\text{Sn}}$	$\overset{....}{\text{Pb}}$	$\overset{....}{\text{Sb}}$	$\overset{....}{\text{Te}}$	$\overset{....}{\text{U}}$
$TiCl_6M_2$ $TiCl_8M_4$	$ThCl_6M_2$ $ThCl_7M_3$	$SnCl_6M_2$ $SnCl_8M_4$	$PbCl_6M_2$ ...	$SbCl_6M$ $SbCl_6M_2$ ... $Sb_2Cl_{13}M_3$	$TeCl_6M_2$	UCl_6M_2

$\overset{....}{\text{Mn}}$	$\overset{....}{\text{Ru}}$	$\overset{....}{\text{Pd}}$	$\overset{....}{\text{Os}}$	$\overset{....}{\text{Ir}}$	$\overset{....}{\text{Pt}}$
$MnCl_6M_2$	$RuCl_6M_2$	$PdCl_6M_2$	$OsCl_6M_2$	$IrCl_6M_2$	$PtCl_5M$ $PtCl_6M_2$

As regards a general discussion of these compounds and their causes of formation, and the light they throw upon the theory of valency, the reader is

referred to Pfeiffer, Werner, and Wells' papers. No simple conclusions appear to have been reached, although Werner's co-ordination theory appears to account for their formation in a satisfactory manner.

(4) Other Compounds of Chlorine.

Ammonium Addition Compounds — Water of Crystallisation. — A large number of addition compounds are produced by the addition of ammonia, NH_3. Well-known compounds of this type are represented by the formulæ :—

$$Cl_4Pt \cdot \cdot \cdot \begin{matrix} NH_3 \\ \\ NH_3, \end{matrix} \qquad Cl_2Pt \cdot \cdot \cdot \begin{matrix} NH_3 \\ \\ NH_3. \end{matrix}$$
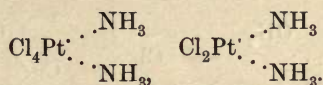
According to Thomsen,[1] the majority of chlorides which contain water of crystallisation may be expressed by one or other of the formulæ :—

$$RCl_2 . 2H_2O, \quad RCl_2 . 4H_2O, \quad RCl_2 . 6H_2O, \quad RCl_2 . 8H_2O.$$
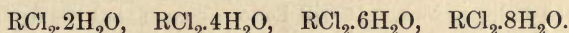
Here R represents either an atom of a divalent element or two atoms of a monovalent element.

Werner [2] discusses the constitution of these substances according to his co-ordination theory. For example, to the substance $PtCl_4 . 2H_2O$ he attributes acidic properties, and gives it the constitution :—

$$\begin{matrix} Cl & & Cl \\ & \diagdown & \diagup & OH_2 \\ & & Pt & \\ & \diagup & \diagdown & OH_2 \\ Cl & & Cl \end{matrix}$$
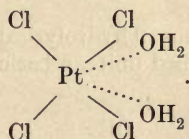
When this body is dissolved in water, Werner asserts that it dissociates electrolytically, thus :—

$$\left[Pt_{(OH)_2}^{Cl_4} \right]^{--} + 2H^+,$$
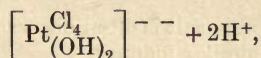
and behaves as a dibasic acid; for example, it reacts thus with silver nitrate :—

$$\left[Pt_{(OH)_2}^{Cl_4} \right] H_2 + 2AgNO_3 = \left[Pt_{(OH)_2}^{Cl_4} \right] Ag_2 + 2HNO_3.$$
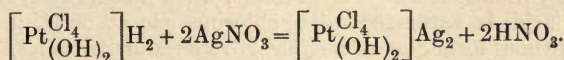
Gold chloride, $AuCl_3$, and all other chlorides which do not electrolytically dissociate in solution behave in a somewhat similar manner. When the chlorides undergo partial electrolytic dissociation in solution, the actually dissociated molecules behave in a normal manner, being split up into halogen ions and metal ions; whereas the hydrate of that part of the salt which is not so dissociated behaves like an acid, and gives off H ions like the $PtCl_4 . 2H_2O$

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[1] Thomsen, *Thermochemische Untersuchungen*, 1882, **2**, 430.
[2] A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (1905), p. 82.

discussed above. So that in aqueous solution such salts will dissociate electrolytically and simultaneously into H ions, halogen ions, and metal ions. Cupric chloride, $CuCl_2.2H_2O$, is a very good example of this behaviour, dissociating electrolytically in solution in the following manner :—

(1)
$$\begin{array}{cc} Cl & OH_2 \\ & >Cu \\ Cl & OH_2 \end{array} \quad \underset{\rightarrow}{\leftarrow} \quad \begin{array}{cc} Cl & \overset{-}{OH} & \overset{+}{H} \\ & >Cu< & + \\ Cl & \underset{-}{OH} & \overset{+}{H}. \end{array}$$

(2)
$$\begin{array}{cc} Cl & OH_2 \\ & >Cu \\ Cl & OH_2 \end{array} \quad \underset{\leftarrow}{\rightarrow} \quad \overset{-}{Cl} \quad + \quad \overset{++}{Cu} \begin{array}{c} OH_2 \\ < \\ OH_2. \end{array}$$
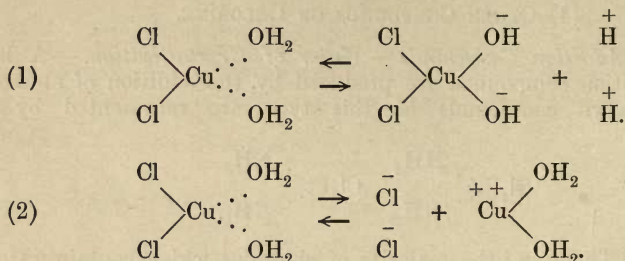
Solutions of such salts react acid, and at the same time they show the reactions of the halogen ions. It will hence be seen that an aqueous solution of copper chloride contains, besides H ions and Cl ions, two complex ions, namely :—

$$++Cu \begin{array}{c} OH_2 \\ \\ OH_2 \end{array} \quad \text{and} \quad \begin{array}{cc} Cl & \overset{-}{OH} \\ & Cu< \\ Cl & \underset{-}{OH}. \end{array}$$
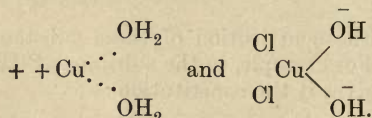
The copper chloride is thus "hydrolytically" dissociated, and when the two complex ions last mentioned unite, a basic salt is precipitated :—

$$\begin{array}{cc} Cl & \overset{-}{OH} \\ & Cu< \\ Cl & \underset{-}{OH} \end{array} + \begin{array}{c} + & OH_2 \\ & Cu \\ + & OH_2 \end{array} = \begin{array}{ccc} Cl & OH & OH_2 \\ & Cu & >Cu \\ Cl & OH & OH_2. \end{array}$$
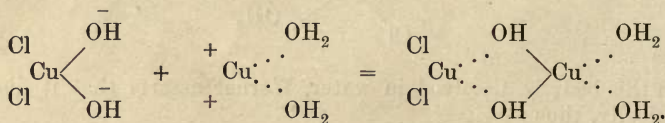
This precipitation of a basic salt is often observed in the case of hydrolysed salts, and is explained in a similar manner.

Hydrogen Perchloride, HCl_3.—Several authors have pointed out indications of the existence of this body, which would correspond to HI_3 (iodine dissolved in hydriodic acid). For example, when a concentrated solution of hydrochloric acid is saturated with chlorine gas at 0° C. it is absorbed, apparently, without formation of a chlorhydrate; and Berthelot,[1] who investigated the matter thermochemically, came to the conclusion that the heat evolved agreed with what would be expected for the formation of such a body :—

$$HCl \text{ (solution)} + Cl_2 \text{ (gas)} = HCl_3 \text{ (solution)} + 9400 \text{ calories.}$$
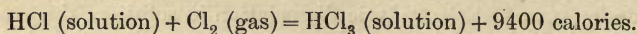
Mellor[2] showed that strong solutions of HCl absorbed chlorine in a manner which suggested the formation of a compound between HCl and Cl_2, probably HCl_3.

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[1] Berthelot, *Compt. rend.*, 1880, **91**, 195.
[2] Mellor, *Trans. Chem. Soc.*, 1901, **79**, 216 ; see also Jakowkin, *Ber.*, 1897, **30**, 518.

<center>CHLORINE AND OXYGEN.</center>

Chlorine and oxygen do not directly unite, but by indirect methods three distinct oxides have been isolated, while four oxy-acids are known, as shown :—

Oxides.			Oxy-acids.		
Chlorine monoxide	.	Cl_2O	Hypochlorous acid	.	HClO
Chlorine peroxide	.	ClO_2	Chlorous acid	. .	$HClO_2$
Chlorine heptoxide	.	Cl_2O_7	Chloric acid	. .	$HClO_3$
			Perchloric acid .	.	$HClO_4$

Millon[1] thought that he had isolated chlorine trichloride, Cl_2O_3. This oxide, however, appears to have been proved[2] to be chlorine perchloride, ClO_2, mixed with free chlorine, Cl_2.

The oxides and oxy-acids of chlorine are very unstable bodies, some of them being violently explosive, being resolved into their component elements when heated or when subjected to percussion. They are all powerful oxidising agents. It is very remarkable that of the four oxy-acids of chlorine mentioned above, the one containing the most oxygen, viz. $HClO_4$, is by far the most stable.

CHLORINE MONOXIDE.

<center>Formula, Cl_2O.</center>

Preparation.—Chlorine monoxide is prepared[3] by passing dry chlorine gas over cold dry mercuric oxide, HgO, contained in a tube which is cooled in a stream of cold water or in ice. The chlorine monoxide coming over may be condensed in a tube which is immersed in a freezing mixture at $-20°$ C. The following reaction takes place :—

$$2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O.$$
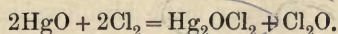
The mercuric oxide used for the purpose must be the precipitated variety, which, after careful washing, must be dried at 300° to 400°. When the precipitated oxide is dried at ordinary temperatures, chlorine acts on it with the evolution of heat and light, forming crystals of mercuric chloride and a mixture of oxygen and chlorine monoxide ; whereas when the mercuric oxide is previously heated to 300° to 400° and cooled before subjecting it to the action of the chlorine, it is attacked by the chlorine much more slowly, and the evolved gas consists of oxygen-free chlorine monoxide. Mercuric oxide prepared by the dry method is attacked so slowly by chlorine gas at ordinary temperatures that it is unsuitable for the purpose.

Properties.—Chlorine monoxide is a brownish-yellow gas, with a smell somewhat resembling that of chlorine ; it attacks the eyes in a very irritating manner ; the density at ordinary temperatures is about[4] 43·5, that for Cl_2O requiring 43·35 (if H = 1). The gas can be collected over mercury, but cannot be kept over it for any great length of time, as it gradually decomposes. Thomsen[5] gives $-17,929$ calories for its heat of formation, while

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[1] Millon, *Ann. Chim. Phys.*, 1843, [iii.], **7**, 298 ; *Annalen*, 1843, **46**, 281.

[2] Garzarolli-Thurnlackh, *Annalen*, 1881, **209**, 184.

[3] V. Meyer, *Ber.*, 1883, **16**, 2999 ; Ladenburg, *Ber.*, 1884, **17**, 157. See also Gay-Lussac, *Compt. rend.*, 1842, **14**, 927 ; Balard, *Ann. Chim. Phys.*, 1834, **57**, 225.

[4] See Garzarolli-Thurnlackh and Schacherl, *Annalen*, 1885, **230**, 273.

[5] Thomsen, *Thermochemische Untersuchungen*, vol. ii. p. 126.

Berthelot[1] gives $-15,100$ calories. When cooled, the gas condenses to an orange liquid, boiling at $+5°$ under $739·9$ mm. pressure. The liquid is heavier than water.[2]

This liquid explodes violently when an attempt is made to seal it up in the glass tube in which it has been prepared. Scratching the tube with a file may cause it to explode even when the liquid is cooled to $-20°$ at the same time. Also pouring it from one glass tube to another, or heating suddenly, will cause explosion, so that the substance is very dangerous to work with. The following is the change which takes place on explosion :—

$$2Cl_2O = 2Cl_2 + O_2.$$
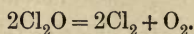
Garzarolli-Thurnlackh and Schacherl (loc. cit.) state that chlorine monoxide does not decompose in direct sunlight in a short time. Older observers, e.g. Balard, state that a few minutes' exposure to direct sunlight causes complete decomposition without explosion, and that diffuse daylight does not cause decomposition even after some hours.

If all organic matter be carefully excluded, the liquid may be distilled without explosion under ordinary pressures.

The gas, when mixed with hydrogen, explodes violently when a light is applied, forming a white cloud of hydrochloric acid,

$$Cl_2O + H_2 = 2HCl + O.$$
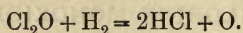
Most easily oxidisable substances, and many finely divided metals, inflame in the gas, causing it to explode. For example, sulphur catches fire at ordinary temperatures in the gas, causing explosion ; sulphur di-oxide and disulphur di-chloride and free chlorine are formed. Sulphuretted hydrogen and carbon di-sulphide both cause the gas to explode, and selenium also has the same effect.

Phosphorus burns in chlorine monoxide, forming P_2O_5 and PCl_5, and usually, though not always, causes the gas to explode. Charcoal explodes the gas at ordinary temperatures, but only very little carbon di-oxide is thereby produced. Carbon monoxide gradually unites with the gas, forming phosgene gas or carbonyl chloride, $COCl_2$.

Chlorine monoxide is decomposed by hydrochloric acid into free chlorine and water, thus :—

$$2HCl + Cl_2O = 2Cl_2 + H_2O.$$
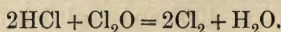
Iodine is oxidised to iodic acid and chloriodide, while an unstable orange-red substance, ICl_3O, is stated[3] to be formed.

Potassium burns in both the liquid and gaseous chlorine monoxide, very often producing an explosion. Arsenic behaves similarly. Finely divided antimony also catches fire in the gas, but solid lumps of antimony are scarcely attacked superficially at $20°$. Silver foil forms silver chloride, and oxygen is liberated. Mercury gradually absorbs the gas, forming mercury oxychloride. Among other substances which cause the gas to explode are calcium phosphide, sulphides of barium, mercury, antimony, and lead.

When the gas is led over calcium chloride it is decomposed ; chlorine is evolved, and the calcium chloride is transformed into a mass of calcium hypochlorite $Ca(OCl)_2$ mixed with unchanged calcium chloride.

[1] Berthelot, Ann. Chim. Phys., 1875, [v.], 5, 338.
[2] Pelouze, Ann. Chim. Phys., 1843, [iii.], 7, 176.
[3] Schützenberger, Ber., 1869, 2, 219.

Chlorine monoxide is readily soluble in water. At 0° C. about 200 volumes of gas are absorbed [1] by 1 volume of water, or 1 gram of water takes up 0·78 gram of gas at 0°, forming an orange-yellow solution. The solution forms what is known as hypochlorous acid, and is discussed below, p. 124.

CHLORINE PEROXIDE.
Formula, ClO_2.

This substance is a dangerously explosive gas, so that great care is necessary in its preparation.

Preparation.—The usual method of preparation is as follows :— [2]

Powdered potassium chlorate is added gradually to concentrated sulphuric acid contained in a small retort. The salt dissolves, and the retort is then gradually warmed by warm water, first to 20° C. and later to 30° or 40°. The escaping heavy gas is either collected in dry flasks, or else it is led into a tube immersed in a freezing mixture, where it condenses into a liquid ; while chlorine and oxygen gas, which are mixed with it, pass on, not being condensed at that temperature. The reaction which takes place may be expressed by the following equations :—

$$KClO_3 + H_2SO_4 = KHSO_4 + HClO_3$$
$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$
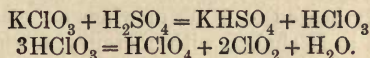
The purer and drier the potassium chlorate used, the less is the danger of explosion. Even the presence of water or potassium chloride—apparently inert substances—increases the danger of explosion.

All traces of organic matter must be rigorously excluded. For this reason the whole apparatus must be of glass, no rubber or cork stoppers being used. Also, if the heating during the preparation is too vigorous, a violent explosion will occur.

In the presence of light the gas is more liable to explode than in the dark. When liquid ClO_2 is being prepared the condenser must be changed every hour or so, in order to avoid the collection of too much of the explosive fluid in one receptacle. A few drops of the liquid when exploding—apparently often spontaneously—shatter the glass receptacle in which they are contained into a fine dust.

Where only a dilute solution of the gas is required, a dish containing 12 grams potassium chlorate and 44 c.c. concentrated sulphuric acid diluted with 10 c.c. water, is floated for some hours on 220 grams of water contained in a larger vessel, and containing ice, the whole being covered with a bell jar. [3] The chlorine peroxide evolved from the chlorate dissolves in the water of the larger dish.

Instead of using sulphuric acid for acting on the chlorate, several authors have proposed the use of an organic acid, notably oxalic acid. Thus, Calvert and Davies [4] warmed a mixture of 2 gram-molecules of pure potassium chlorate and 9 gram-molecules of crystallised oxalic acid to about 70° on the water-bath, and led the evolved gas (which contained CO_2) into water. This method is an easy and safe one of preparing the substance. [5] More recently

[1] Pelouze, *Ann. Chim. Phys.*, 1843, [iii.], **7**, 176.
[2] Millon, *Ann. Chim. Phys.*, 1843, [iii.], **7**, 298.
[3] Reychler, *Bull. Soc. chim.*, 1901, [iii.], **25**, 659.
[4] Calvert and Davies, *J. Chem. Soc.*, 1859, **11**, 193 ; Schacherl, *Annalen*, 1881, **206**, 68.
[5] H. L. Cohn, *J. prakt. Chem.*, 1861, **83**, 53.

Bray [1] modified the method by using a mixture of 40 grams $KClO_3$, 20 c.cs. water, and 150 grams crystallised oxalic acid. On heating to 60°, chlorine peroxide was evolved in a very regular stream.

Properties.—The gas is decomposed by mercury and dissolved by water, and consequently it is collected by displacement, as previously described. It is a dark-yellow heavy gas, with a smell somewhat similar to that of chlorine, but recalls to mind that of nitric acid ; very diluted the gas smells like ozone. When cooled, the gas condenses to a dark-red liquid, which boils [2] at $+9\cdot9°$, and freezes [3] at $-79°$ to orange-coloured crystals. These melt at $-76°$, the liquid floating on the still unmelted crystals. When the liquid is thrown into water, it sinks to the bottom and rapidly dissolves with the evolution of much gas. It sometimes explodes. The density of the gas is $2\cdot3894$ (air $=1$) (Schacherl), which corresponds to the formula [4] ClO_2. Bray [5] confirmed this by a molecular weight determination in carbon tetrachloride and in water. The spectrum of the gas shows strong absorption bands [6] in the blue and violet only, and in the liquid form the blue and violet parts of the spectrum are completely absorbed. Towards the ultra-violet region the gas seems to be transparent.

Chlorine peroxide can be kept unchanged in the dark. It is, however, gradually decomposed into its component elements when exposed to light. When the gas is rapidly heated to 100°, or when an electric spark is passed through, or even when it is shaken with mercury, a violent explosion occurs and the gas is decomposed thus :—

$$2ClO_2 = Cl_2 + 2O_2.$$
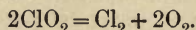
Liquid chlorine peroxide may be distilled without decomposition if every trace of organic matter be excluded [7] (Schacherl).

Chlorine peroxide is an extremely powerful oxidising agent, e.g. when phosphorus, sulphur, sugar, or other easily combustible substance is thrown into the gas, they spontaneously inflame and usually cause the gas to explode with violence. The following is a safe method of showing the oxidising action of the gas :—equal parts of powdered potassium chlorate, $KClO_3$, and white sugar are mixed together by means of a feather or writing-paper (grinding in a mortar may occasion explosion). The mixture is placed on a slate, and a drop of concentrated sulphuric acid is added. The material immediately takes fire. The sulphuric acid acting on the chlorate liberates the peroxide, which then inflames the sugar.

An effective experiment showing the combustion of phosphorus under water by the gas is made by throwing some crystals of potassium chlorate and a few small pieces of yellow phosphorus into a test-tube half filled with water. A small quantity of strong sulphuric acid is now allowed to flow through a tube funnel on to a lower part of the tube where the solids lie. When the acid comes into contact with the chlorate, chlorine peroxide is

[1] Bray, *Zeitsch. physikal. Chem.*, 1906, **54**, 463, 569, 731 ; *Zeitsch. anorg. Chem.*, 1906, **48**, 216.
[2] L. Pebal, *Annalen*, 1875, **177**, 1 ; Schacherl, *Annalen*, 1881, **206**, 68.
[3] Faraday, *Ann. Chim. Phys.*, 1845, [iii.], **15**, 357.
[4] Pebal and Schacherl, *Annalen*, 1882, **213**, 113.
[5] Bray, *Zeitsch. physikal. Chem.*, 1906, **54**, 575.
[6] See Gernez, *Compt. rend.*, 1872, **74**, 465 ; Liveing and Dewar, *Chem. News*, 1883, **47**, 121 ; W. A. Miller, *Phil. Mag.*, 1845, [iii.], **27**, 81.
[7] Schacherl, *loc. cit.*

evolved, which, coming into contact with the phosphorus, oxidises it with the evolution of bright flashes of light.

Gaseous ClO_2 (3 vols.) mixed with hydrogen (8 vols.) and exploded by means of an electric spark, yields water and hydrogen chloride.

Bromine and iodine are scarcely altered by the gas. However, an acid solution of potassium iodide is decomposed, thus :—

$$2ClO_2 + 10HI = 2HCl + 4H_2O + 5I_2.$$
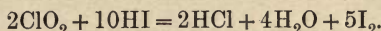
Ammonia gas is decomposed by chlorine peroxide at ordinary temperatures. Potassium permanganate solution is decomposed thus :—

$$3ClO_2 + KMnO_4 + H_2O = MnO_2 + KClO_3 + 2HClO_3.$$
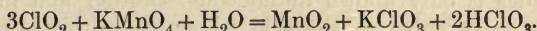
Mercury absorbs the gas slowly, forming $HgCl_2$ and $HgClO_3$.

Organic substances cause the gas to explode. The gas bleaches indigo solution and also moist litmus.

Water at 4° C. dissolves[1] nearly twenty times its volume of the gas, a bright yellow solution being produced. When the solution is cooled below 4° while the gas is being led into the liquid, a yellow crystalline hydrate is produced, which, on melting, loses a large volume of gas. According to Bray,[2] this hydrate has the formula $ClO_2.8H_2O(\pm 1H_2O)$. In a similar manner carbon tetrachloride may be made to combine with the gas to produce a yellow crystalline double compound.

When the aqueous solution of chlorine peroxide is treated with alkali both chlorite and chlorate are produced :—[3]

$$2KOH + 2ClO_2 = KClO_2 + KClO_3 + H_2O.$$
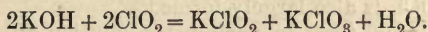
The yellow gas evolved when potassium chlorate is treated with hydrochloric acid is a mixture of free chlorine and chlorine peroxide in varying proportions.

This mixture has more powerful oxidising properties than chlorine gas, and has been used for disinfecting purposes. The mixture is the "Euchlorine" of Davy,[4] its true nature being established by Pebal.

CHLORINE HEPTOXIDE.[5]
Formula, Cl_2O_7.

Preparation.—Phosphorus pentoxide, P_2O_5, is cooled in a retort to below 10°, and perchloric acid (see below, p. 132) is slowly added. The mixture is allowed to stand some hours at a temperature below 10°, and is then warmed gradually until chlorine heptoxide distils over at 85°. The phosphorus pentoxide acts by withdrawing the water from the perchloric acid, thus :—

$$2HClO_4 + P_2O_5 = Cl_2O_7 + P_2O_5.H_2O.$$
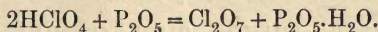
Properties.—Colourless volatile oil, boiling at 82° under ordinary pressure. It can be distilled without danger at ordinary pressure, but, on standing, it gradually decomposes, turning greenish yellow. When rapidly heated by

[1] Millon, *Ann. Chim. Phys.*, 1843, [iii.], **7**, 298.
[2] Bray, *Zeitsch. anorg. Chem.*, 1906, **48**, 221.
[3] See, however, Reychler, *Bull. Soc. chim.*, 1901, [iii.], **25**, 663.
[4] See Pebal, *Annalen*, 1875, **177**, 1.
[5] Michael and Conn, *Amer. Chem. J.*, 1900, **23**, 444 ; 1901, **25**, 89.

contact with a flame, or when subjected to percussion, it explodes with great violence. It reacts with iodine, apparently forming I_2O_7, a white solid, which, when heated under reduced pressure at 100°, left a residue of I_2O_5. Chlorine is evolved when the heptoxide acts on iodine. Chlorine heptoxide dissolves in water, forming perchloric acid. It also dissolves in benzene, slowly attacking it.

HYPOCHLOROUS ACID.
Formula, HClO.

This substance is only known in aqueous solution and in the form of salts. It must be regarded as the acid whose anhydride is chlorine monoxide, Cl_2O.

Formation.—(1) Water dissolves at 0° C. and 700 mm. more than 200 volumes of chlorine monoxide, Cl_2O. Liquid chlorine monoxide sinks in water, and then gradually dissolves. The solution of the gas must be regarded as an aqueous solution of hypochlorous acid :—

$$Cl_2O + H_2O = 2HClO.$$
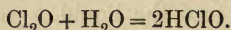
(2) An aqueous solution is best prepared by shaking chlorine water with precipitated mercuric oxide,[1] the oxide dissolving and the yellow colour of the chlorine simultaneously disappearing :—

$$HgO + 2Cl_2 + H_2O = HgCl_2 + 2HClO.$$
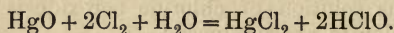
Brown insoluble $HgOCl_2$ is also largely formed.

On distilling the liquid (best in vacuum), a solution of hypochlorous acid, free from mercuric chloride, is obtained.

By fractional distillation the solution may be concentrated, the hypochlorous acid coming over with the first portions of the distillate.

Carius [2] prepared aqueous hypochlorous acid suitable for acting on organic compounds by shaking 15 grams precipitated mercuric oxide (which had, after washing, been heated to 300° C., see p. 119) with a little water and a litre of chlorine gas.

(3) An easy method [3] of obtaining aqueous hypochlorous acid is to add to bleaching powder solution the exact amount of dilute nitric or other mineral acid necessary to liberate the hypochlorous acid, but not sufficient to liberate free hydrochloric acid from the calcium chloride :—

$$\underbrace{CaCl_2 + Ca(OCl)_2}_{\text{Bleaching powder solution.}} + 2HNO_3 = CaCl_2 + Ca(NO_3)_2 + 2HOCl.$$
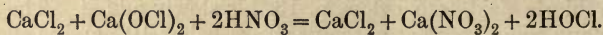
If more nitric acid than this is added, hydrochloric acid is liberated :—

$$CaCl_2 + 2HNO_3 = 2HCl + Ca(NO_3)_2,$$
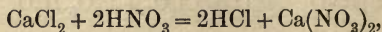
and the free hydrochloric then decomposes the hypochlorous acid, liberating chlorine :—

$$HClO + HCl = H_2O + Cl_2.$$

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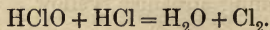
[1] Gay-Lussac, *Annalen*, 1842, **43**, 158 ; Ballard, *Ann. Chim. Phys.*, 1834, **57**, 225.
[2] Carius, *Annalen*, 1863, **126**, 196.
[3] Gay-Lussac, *Compt. rend.*, 1842, **14**, 927, 1843, **7**, 43 ; V. Meyer, *Ber.*, 1883, **16**, 2998.

Hence the method of procedure is as follows : Into a filtered solution of bleaching powder the calculated amount of a 5 per cent. nitric acid solution is allowed to flow from a burette. To avoid local supersaturation (which would cause liberation of hydrogen chloride and hence decomposition of the HOCl into water and chlorine) the liquid is kept rapidly stirred. The liquid is now distilled.

Lauch [1] recommends the use of boric acid for liberating hypochlorous acid from its salts.

(4) When chlorine gas is led into a cold solution or suspension of a carbonate, free hypochlorous acid is formed,[2] thus :—

$$CaCO_3 + 2Cl_2 + H_2O = 2HClO + CaCl_2 + CO_2.$$
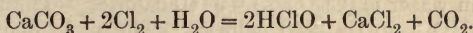
The salts of hypochlorous acid are decomposed by CO_2 gas, setting free the HClO.

The same liberation of hypochlorous acid occurs when chlorine is led through cold aqueous solutions of other salts of alkali metals, especially in the case of sodium sulphate and phosphate (Williamson):—

$$Na_2SO_4 + H_2O + Cl_2 = NaCl + NaHSO_4 + HClO,$$
$$Na_3PO_4 + 2Cl_2 + 2H_2O = 2HOCl + NaH_2PO_4 + 2NaCl.$$
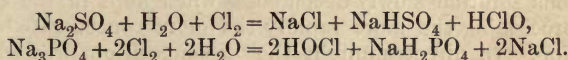
Alum, ferric sulphate, zinc sulphate, $MnSO_4$, $CuSO_4$, $PbSO_4$ (the last with difficulty) are also decomposed by chlorine gas, liberating hypochlorous acid.

When chlorine gas is led into a solution of potassium acetate, chlorine is absorbed, free acetic acid liberated, and a strong bleaching solution is produced.

(5) A solution of hypochlorous acid may also be obtained by saturating a bleaching powder solution with chlorine, then passing air through the solution in order to expel uncombined chlorine, and finally distilling the liquid :—

$$Ca(OCl)_2 + 2Cl_2 + 2H_2O = CaCl_2 + 4HClO.$$
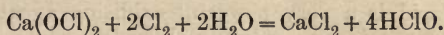
Baryta water, $Ba(OH)_2$, may also be saturated with chlorine, when barium hypochlorite is formed, which is then decomposed thus (Williamson):—

$$Ba(OCl)_2 + 2Cl_2 + 2H_2O = BaCl_2 + 4HClO.$$
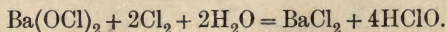
(6) Fluorine oxidises chlorine water thus :—[3]

$$H_2O + Cl + F = HF + HOCl.$$
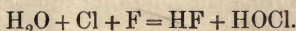
Oxygen is usually evolved by the excess of fluorine decomposing the water.

(7) A mixture of hydrochloric acid gas and air, when passed through solutions containing strong oxidising agents (e.g. $KMnO_4 + H_2SO_4$, or $MnO_2 + H_2SO_4$), is oxidised [4] to hypochlorous acid.

(8) Excess of hydrogen peroxide added to chlorine water oxidises the chlorine to hypochlorous acid :—[5]

$$Cl_2 + H_2O_2 = 2HOCl.$$

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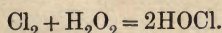
[1] Lauch, *Ber.*, 1885, **18**, 2287.
[2] Williamson, *Chem. Soc. Mem.*, 1850, **2**, 234 ; *Annalen*, 1845, **54**, 133. See also A. Richardson, *Trans. Chem. Soc.*, 1908, **93**, 280.
[3] Lebeau, *Compt. rend.*, 1906, **143**, 425.
[4] Odling, *Pharm. J.*, 1860, [ii.], **1**, 449.
[5] Fairley, *Brit. Assoc. Reports*, 1874, **44**, 57.

Properties. — Concentrated aqueous solutions of the acid possess an orange or golden colour, a penetrating smell resembling that of bleaching powder, and a strong, but not acid, taste. The liquid has a very corrosive action on the skin, a drop on the hand destroying the epidermis within thirty seconds, staining it a deep brown, and corroding it worse than nitric acid itself.

Hypochlorous acid is a very weak one, the constant of dissociation being determined by Sand [1] as $3 \cdot 7 \times 10^{-8}$ at 17°. The heat of formation in aqueous solution is $(Cl,O,H,aq.) = 29,930$ calories, according to Thomsen,[2] and 31,600 calories according to Berthelot.[3] The heat of solution of the anhydride Cl_2O in water is $(Cl_2O,aq.) = 9440$ calories. The heat of neutralisation $(NaOH \; aq., HOCl \; aq.) = 9980$ calories. The molecular weight of hypochlorous acid is normal in aqueous solution.[4]

Only dilute solutions of hypochlorous acid can be distilled without decomposition, but the acid can be concentrated by fractional distillation, the strongest acid coming over first. During the process of distillation with the concentrated acid, chlorine, oxygen, and chloric acid, $HClO_3$, are formed. The aqueous solution slowly decomposes when kept in the dark, the decomposition proceeding the more rapidly the more concentrated and the hotter the solution. In direct sunlight the decomposition proceeds very rapidly. When a solution is exposed to air the acid gradually volatilises. The acid is slowly decomposed by platinum black,[5] forming hydrochloric and chloric acids. The aqueous acid dissolves iron and aluminium, evolving hydrogen and chlorine; magnesium yields pure hydrogen;[6] copper, nickel, and cobalt evolve chlorine and oxygen. Potassium burns on the acid, forming KCl and KOCl. Mercury is turned into oxy-chloride and silver into AgCl with rapid evolution of oxygen. The acid attacks tin, lead, zinc, bismuth, or antimony; gold and platinum are not attacked by it, even when nitric or sulphuric acid is added.

Hypochlorous acid is a very powerful oxidising agent; thus sulphur is oxidised to sulphuric acid and sulphur chloride; while sulphur dioxide is oxidised to sulphuric acid and chlorine is set free, and the same applies to sulphuretted hydrogen. Carbon disulphide is oxidised to carbon di-oxide and sulphuric acid.

Hypochlorous acid has a bleaching power twice as great as that of the same amount of chlorine dissolved [7] in water.

The reason is obvious from the following equations :—

$$(1) \; 2Cl_2 + 2H_2O = 4HCl + O_2. \quad (2) \; 2HClO = 2HCl + O_2.$$
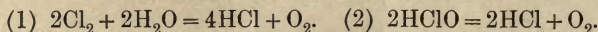
Since the bleaching action is due solely to the oxygen set free, the first equation shows that four atoms of Cl set free two atoms of oxygen; the second equation shows that two atoms of chlorine combined in hypochlorous acid sets free the same amount of oxygen, viz. two atoms, as the four atoms of chlorine gas dissolved in water, and therefore two atoms of chlorine in hypochlorous

[1] Sand, *Zeitsch. physikal. Chem.*, 1904, **48**, 610.
[2] Thomsen, *Thermochemische Untersuchungen*, vol. ii. pp. 126, 399.
[3] Berthelot, *Ann. Chim. Phys.*, 1875, [v.], **5**, 318.
[4] Jakowkin, *Zeitsch. physikal. Chem.*, 1899, **29**, 613.
[5] Foerster and Müller, *Zeitsch. Elektrochem.*, 1902, **8**, 515.
[6] White, *J. Soc. Chem. Ind.*, 1903, **22**, 132.
[7] Gay-Lussac, *Annalen*, 1842, **43**, 153.

acid have the same bleaching (or oxidising effect) as four atoms of chlorine gas dissolved in water.

Hypochlorous acid (also hypochlorites) is decomposed by hydrogen peroxide, evolving free oxygen :—

$$HClO + H_2O_2 = HCl + H_2O + O_2.$$
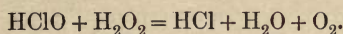
Hypochlorites.—The salts of hypochlorous acid form a technically very important series of bodies ; in most cases these are very unstable substances, and few have been isolated in a pure state. The most important of all is *calcium hypochlorite*, $Ca(ClO)_2$, which is formed when bleaching powder is dissolved in water. The substance is treated under *Calcium* in Vol. III. Other very important technical bleaching solutions are formed by the hypochlorites of sodium and potassium, NaClO and KClO. These, however, are treated in Vol. II., under the salts of sodium and potassium.

Hypochlorites are formed when chlorine acts on *cold* solutions of alkalies :—

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O.$$
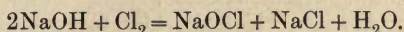
When the solution is *hot*, chlorates are formed :—

$$6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O.$$
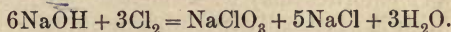
Constitution of Hypochlorous Acid.—The constitution of hypochlorous acid has been discussed by Vorländer,[1] who decides for H—O—Cl, giving for his reasons the very weak acid properties of the substance, its great tendency to oxidise into acids richer in oxygen, such as $HClO_3$, and finally the ease with which it is decomposed into Cl and OH. The alternative formula H—Cl = O, in which chlorine is represented as trivalent, has little if any evidence in its favour.[1]

CHLOROUS ACID.
Formula, $HClO_2$.

The pure acid is unknown in the free state, and its anhydride, the so-called chlorine trioxide, Cl_2O_3, also appears incapable of existence, the gas previously supposed to be this substance being a mixture [2] of Cl_2O and ClO_2 of the composition $Cl_2O + 4ClO_2 = 3Cl_2O_3$.

Chlorites, however, can be prepared by treating an aqueous solution of chlorine peroxide with potassium hydroxide :—[3]

$$2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O.$$
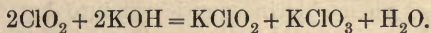
A mixture of potassium chlorite and chlorate is thus produced.

However, according to Reychler,[4] if sodium peroxide is used, oxygen is evolved and only sodium chlorite is produced :—

$$Na_2O_2 + 2ClO_2 = 2NaClO_2 + O_2.$$
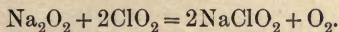
Lasègue [5] obtains chlorous acid in dilute aqueous solution by acting on $Ba(ClO_2)_2$ with H_2SO_4, the $Ba(ClO_2)_2$ being obtained by the interaction of $Pb(ClO_2)_2$ with $BaCO_3$.

[1] Vorländer, *Ber.*, 1901, **34**, 1632 ; see also Barker, *Amer. Chemist*, 1871, [ii.], **2**, 1.
[2] Garzarolli-Thurnlackh, *Annalen*, 1881, **209**, 184.
[3] Garzarolli-Thurnlackh and v. Hayn, *Annalen*, 1881, **209**, 203.
[4] Reychler, *Bull. Soc. chim.*, 1901, [iii.], **25**, 659.
[5] Lasègue, *Compt. rend.*, 1912, **155**, 158.

Chlorous acid is monobasic, forming normal salts $MClO_2$ with alkali hydroxides and $Ba(OH)_2$, and also red acid salts which cannot be isolated in a dry condition. The acid is very unstable, decomposing according to the equations :—[1]

$$3HClO_2 = 2HClO_3 + HCl ; \quad 4HClO_2 = 3ClO_2 + Cl + 2H_2O.$$
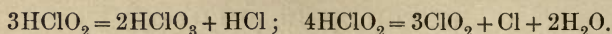
The salts of the alkali metals and alkaline earth metals are colourless, very soluble in water, and hygroscopic. They are all very unstable, and from their solutions yellow crystalline chlorites of lead and silver may be precipitated, as these salts are only sparingly soluble. If the lead salt be heated for some time to 100° C., it may explode with a loud detonation. When rubbed in a mortar with sulphur, metallic sulphides, and other oxidisable substances, ignition or even explosion may ensue. H_2S, when passed over it, first causes the formation of black PbS, which then oxidises to white $PbSO_4$. The soluble chlorites have a caustic taste and bleach vegetable colouring matters, even after adding arsenious oxide, As_2O_3. This distinguishes them[2] from solutions of hypochlorites, which also bleach vegetable colouring matters, but not after the addition of As_2O_3.

Chlorous acid and chlorites may be estimated[3] by precipitating the acid as lead chloride, which is practically insoluble in 80 per cent. alcohol.

CHLORIC ACID.
Formula, $HClO_3$.

Chloric acid is a most important member of the chlorine oxy-acids. The acid itself has been obtained only in aqueous solution. Its salts, however, have been obtained pure, and are well-known bodies. It occurs naturally in very small quantities in the form of sodium or potassium chlorate in Chili saltpetre.

Chloric acid is formed when the lower chlorine oxy-acids or aqueous solutions of the chlorine oxides are exposed to light or heat. Thus, when an aqueous solution of chlorine peroxide, ClO_2, is exposed to sunlight, the colour is soon discharged, and when the free chlorine has been expelled by warming the solution in the air, only chloric acid remains in solution. Again, a solution of chlorine peroxide in water may be oxidised to chloric acid by some oxidising agent[4] such as potassium permanganate. Hypochlorites, when warmed or exposed to light, break down into chlorates (see p. 126), and chlorates are formed when chlorine gas is led into hot solutions of caustic alkalies or alkaline earths ; cold solutions treated in this manner yielding hypochlorites (p. 127). Chlorates are also formed when hot aqueous solutions of chlorides are electrolysed (see p. 131), and silver chlorate is produced when silver fluoride in aqueous solution is acted on by chlorine :—[5]

$$6AgF + 3H_2O + 3Cl_2 = AgClO_3 + 5AgCl + 6HF.$$
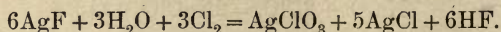
Laboratory Preparation.—Several methods exist :—

[1] See Bray, *Zeitsch. anorg. Chem.*, 1906, **48**, 217 ; *Zeitsch. physikal. Chem.*, 1906, **54**, 569–608. See also Lasègue, *loc. cit.*
[2] Millon, *Ann. Chim. Phys.*, 1843, [3], **7**, 298.
[3] G. Lasègue, *Bull. Soc. Chim.*, 1912, [iv.], **11**, 884.
[4] Fürst, *Annalen*, 1881, **206**, 75.
[5] Gore, *Chem. News*, 1871, **23**, 13.

(1) Barium chlorate is decomposed [1] with the equivalent quantity of dilute sulphuric acid :—

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$
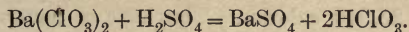
The barium sulphate precipitates, and the clear solution of chloric acid is decanted off and evaporated *in vacuo* over sulphuric acid. The aqueous residue thus obtained has a composition corresponding to $HClO_3 + 7H_2O$, 40 per cent. of pure chloric acid being present. When attempts are made to concentrate further than this, the chloric acid spontaneously decomposes with rapid evolution of oxygen and chlorine and formation of perchloric acid, $HClO_4$.

(2) A hot solution of potassium chlorate, $KClO_3$, is treated with excess of hydrofluosilicic acid, H_2SiF_6, when insoluble K_2SiF_6 is precipitated, and chloric acid remains [2] in solution together with excess of the hydrofluosilicic acid :—

$$2KClO_3 + H_2SiF_6 = K_2SiF_6 + 2HClO_3.$$
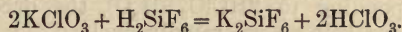
The excess of silicofluoric acid is removed by adding some silica and evaporating at 30° in air or *in vacuo* over sulphuric acid and potassium hydroxide so long as the liquid concentrates. The silicofluoric acid escapes as silicon tetrafluoride :—

$$2H_2SiF_6 + SiO_2 = 3SiF_4 + 2H_2O \; ;$$
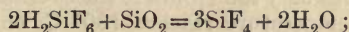
thus there remains in solution only pure chloric acid, which is poured off from the excess of silica and potassium silicofluoride, which settles out as a precipitate at the bottom of the vessel.

Properties.—The pure aqueous solution when dilute is colourless, but when concentrated takes on a yellowish tinge.

The liquid has a very sour taste ; when dilute and cold it has no perceptible odour. On warming, however, a penetrating odour (somewhat resembling that of nitric acid) is noticeable, especially with the concentrated solution. Chloric acid has a strong acid reaction, and forms a powerful monobasic acid.

Ostwald [3] determined its molecular conductivity at 25° C. as follows :—

Molecular Conductivity.	Dilution (No. of Litres in which a Gram-molecule of $HClO_3$ is dissolved).	Molecular Conductivity.	Dilution (No. of Litres in which a Gram-molecule of $HClO_3$ is dissolved).
353	2	391	·64
364	4	399	128
373	8	402	256
381	16	402	512
387	32	402	1024

It will be noticed that chloric, perchloric, and nitric acids have almost identical molecular conductivities near together, so that they are almost equally

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[1] See, for example, Bernard, *Zeitsch. f. Chem. Apparatenkunde*, 1906, i. 81 ; *Ann. Chim. anal.*, 1906, **11**, 81.
[2] See Serullas, *Ann. Chim. Phys.*, 1830, **45**, 204, 270.
[3] Ostwald, *J. prakt. Chem.*, 1885, [ii.], **31**, 433.

strong acids.   Thomsen [1] gives the heat of formation $(Cl_2,O_5,aq.) = -20,480$ calories, while he gives the heat of formation of the hydrate in water solution as $(Cl,O_3,H,aq.) = +23,940$ calories.   The heat of neutralisation is given as $(KOH,HClO_3,aq.) = +13,760$ calories.   When three molecules act on KOH solution, the heat evolved when $KClO_3$ is formed is 97,945 calories, while that when KOCl is formed is 73,855 calories, so that the difference in these two values expresses the heat set free when an aqueous solution of the constitution $3KCl + 3KOCl$ turns into one of the composition $5KCl + KClO_3$.

According to Ostwald,[2] the heat of formation of the ions ClO_3 is $+23\cdot4$ calories.

The acid may be concentrated [3] until it acquires the composition $HClO_3.7H_2O$, the liquid then having 40·1 per cent. $HClO_3$ present.   When the concentration has proceeded further than this, decomposition sets in, with evolution of a greenish gas ; when the concentration reaches 51·86 per cent. $HClO_3$ (corresponding to $2HClO_3.9H_2O$), the decomposition becomes almost violent, the gas being very rapidly evolved.

The dilute solution, however, is moderately stable at ordinary temperatures, but on standing some months exposed to light perchloric acid is found in the liquid.   The perfectly pure acid is so stable [4] in dilute solution that it may be heated to 95° with only the minutest traces of decomposition occurring, while even when the temperature reaches 100° C. only a small amount of acid undergoes decomposition.

The concentrated solutions of acid at $-20°$ C. become viscous, but do not crystallise out.

The acid is an extremely powerful oxidising agent.   Thus organic bodies such as wood and paper very rapidly decompose the acid ; the oxidation occurs with such vigour that inflammation usually ensues.[4]   The acid reddens litmus paper, and then bleaches it—as would be expected from its oxidising properties.

Many metals (e.g. Zn, Cd, Cu, Fe, etc.) rapidly dissolve in the acid ; usually the acid is reduced by the evolved hydrogen.[5]   Silver acts thus on the acid :—

$$6Ag + 6HClO_3 = 5AgClO_3 + AgCl + 3H_2O.$$
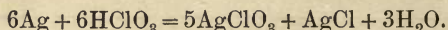
Aluminium reduces it quantitatively to chloride.[6]

Salts of Chloric Acid.—Chloric acid is a powerful monobasic acid, and generates a series of salts of the type $MClO_3$.

Of these salts **potassium chlorate**, $KClO_3$, is one of the best known, and is formed by the action of chlorine on a *hot* solution of caustic potash :—

$$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O.$$
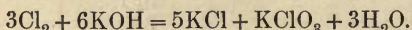
The properties and methods of formation of this substance are considered in Vol. II., under Potassium.

Other chlorates are, in general, produced in the same way.   Thus we have :—

$$6Cl_2 + 6Ca(OH)_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

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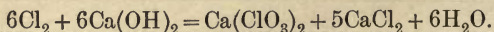
[1] Thomsen, *Thermochemische Untersuchungen*, 1882, vol. ii. pp. 137–45.
[2] Ostwald, *Grundriss der allgemeinen Chemie*, 1899, p. 281.
[3] Kämmerer, *Pogg. Annalen*, 1869, **138**, 399, 404.
[4] Serullas, *Ann. Chim. Phys.*, 1830, **45**, 204 and 270.
[5] Hendrixson, *J. Amer. Chem. Soc.*, 1904, **26**, 747 ; 1903, **25**, 637.
[6] Venditori, *Gazz. chim. ital.*, 1907, **37**, ii. 383.

Chlorates are also produced by the electrolysis of solutions of alkali chlorides.[1]

All the chlorates are strong oxidising agents, and many, indeed, are dangerous explosives. When treated with concentrated sulphuric acid, chlorine peroxide is evolved as a greenish gas : a series of violent cracklings, often attended with slight explosions, takes place. Chlorates, being powerful oxidising agents, are at once reduced to chlorides by such reducing agents as hydrogen (from zinc and acid, but not from sodium amalgam and water [2]) or sulphur dioxide.

Analytically, chlorates differ from chlorides in that they give no precipitates with silver nitrate. The following reactions are typical of chlorates :—

(1) Solution yields no precipitate with silver nitrate.

(2) Ignition of a dry chlorate decomposes it thus :—

$$2KClO_3 = 2KCl + 3O_2.$$
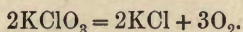
The oxygen may be recognised in the usual way by its power of lighting a glowing splinter, while the residual chloride gives a precipitate with silver nitrate, soluble in ammonia and insoluble in nitric acid.

(3) A solution of a chlorate, coloured blue with indigo, and then acidified with sulphuric acid and a little sulphurous acid, rapidly loses its colour owing to the oxidation of the indigo.

(4) Dry chlorates treated with concentrated sulphuric acid yield a yellow explosive gas (ClO_2), and violent "cracklings," attended with mild explosions, occur when the chlorate is warmed in a test-tube with concentrated sulphuric acid.

Constitution of Chloric Acid.—Several formulæ have been put forward to explain the constitution of chloric acid.

Kekulé gave the formula Cl—O—O—OH. Against this view may be urged the fact that substances containing oxygen linked together in this manner become more unstable the longer the chain, so that chloric acid, H—O—O—O—Cl, should be more unstable than either chlorous acid H—O—O—Cl, or hypochlorous acid, H—O—Cl, which is the exact reverse of what is actually the case, chloric acid being more stable than either chlorous or hypochlorous acid.

Blomstrand [3] gives the more probable formula

$$\begin{array}{c} O \\ O \end{array}\!\!\!\Big\rangle Cl—OH,$$
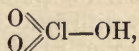
an hypothesis supported by Vorländer [4] and opposed by Spring,[5] on the ground that the chlorine atoms in all these chlorine oxy-acids have the same function ; whereas Blomstrand's formula shows the chlorine to be functioning as a pentad, which would cause it to behave differently from, say, the monovalent chlorine of hypochlorous acid.

[1] See, for example, E. & O. Müller, *Festschrift w. Nernst*, 1912, p. 319.
[2] Hendrixson, *J. Amer. Chem. Soc.*, 1904, **26**, 747 ; 1903, **25**, 637.
[3] Blomstrand, *Chemie der Jetztzeit* (Heidelberg, 1869), p. 259.
[4] Vorländer, *Ber.*, 1901, **34**, 1632.
[5] Spring, *Bull. Acad. Belg.*, 1875, **39**, 882.

H. Stanley,[1] from an examination of the products of decomposition of the acid, gives it the formula

$$H—Cl \begin{array}{c} O \\ | \\ O \end{array} = O$$
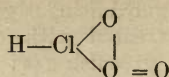
a formula which has several facts in its favour, and easily explains the transition into hypochlorous acid, and *vice versa*. In this latter formula the presence of tetravalent oxygen and trivalent chlorine is assumed. Oddo[2] also discusses the constitution of the acid.

PERCHLORIC ACID.
Formula, $HClO_4$.

This acid occurs in the form of its sodium salt in small quantities in Chili saltpetre.[3]

It is formed by the decomposition of chloric acid on exposure to light or heat :—

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O.$$
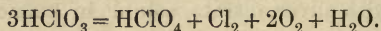
It is also produced by electrolysing water containing HCl or Cl_2, or by passing ozonised air through a solution of sodium hypochlorite, and in several other ways as well.

Preparation.—(1) The acid is usually obtained[4] from potassium perchlorate, $KClO_4$, which is prepared from potassium chlorate by heating it until it fuses and gives off oxygen slowly; finally, the whole mass becomes almost solid, owing to the formation of potassium perchlorate, $4KClO_3 = 3KClO_4 + KCl$, while simultaneously another reaction, $2KClO_3 = 2KCl + 3O_2$, also proceeds to some extent. When the previously fused mass becomes almost solid, it is cooled, powdered, and washed with water in order to remove most of the potassium chloride, KCl, which has been formed, the sparingly soluble potassium perchlorate remaining behind. Next, the powder is gently warmed with hydrochloric acid until all unchanged chlorate is converted into chloride, which occurs when chlorine and chlorine peroxide cease to be evolved. The mass is again washed with water to remove the chloride thus formed, when pure potassium perchlorate is left.

The acid is now liberated from the pure dry potassium perchlorate by placing the latter in a small retort with four times its weight of concentrated sulphuric acid, recently boiled (to expel water) and gradually heating ; at 110° the first traces of perchloric acid, $HClO_4$, begin to come over, accompanied by dense white clouds ; it condenses as a faint yellow liquid ; it is usually contaminated by a little sulphuric acid.

As the distillation continues, the substance coming over changes in character from a thin liquid, $HClO_4$, to a white crystalline mass of monohydrated perchloric acid, $HClO_4.H_2O$, which is produced by the partial de-

[1] H. Stanley, *Chem. News*, 1902, **85**, 133.
[2] Oddo, *Atti R. Accad. Lincei*, 1907, [v.], **15**, ii. 500.
[3] Selckmann, *Zeitsch. angew. Chem.*, 1898, p. 101 ; Fresenius and Bayerlein, *Zeitsch. anal. Chem.*, 1898, **37**, 501.
[4] Roscoe, *J. Chem. Soc.*, 1863, **16**, 82.

composition of the perchloric acid into oxides of chlorine, water, and oxygen, thus :—

$$8HClO_4 = 4H_2O + 4ClO_2 + 2Cl_2O + 9O_2 ;$$
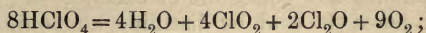
the water thus set free at once combines with excess of perchloric acid, to produce the hydrate.

However, the pure anhydrous acid may be obtained by heating the hydrate. The pure $HClO_4$ distils over, while in the retort there remains an aqueous acid which boils at 203°. More recently it has been shown that the yield of acid is greatly improved if the distillation of the perchlorate with sulphuric acid is carried out under diminished pressure, as the decomposition of the pure perchloric acid is thereby, to a great extent, avoided.

Thus Michael and Conn [1] distil at 10–20 mm. pressure. Vorländer and v. Schilling [2] proceed thus : 50 grams of powdered $KClO_4$ and 150 to 175 grams of concentrated sulphuric acid (96-97·5 per cent.) are placed in a fractionating flask of 300 c.c. capacity, which is immersed in an oil-bath, and the whole is distilled under reduced pressure, using an air condenser of 75 cm. length, which mouths into a glass condenser immersed in a freezing mixture of ice and salt. The gases escaping from the condenser, containing oxides of chlorine, are passed through a tube filled with soda lime rendered air-tight at the joints by means of asbestos and waterglass. At 50–70 mm. pressure the perchloric acid, $HClO_4$, begins to distil over at 135°–145° C., and the heating is gradually carried on until the temperature reaches 180° or 190° C. The crude acid is then rectified under a pressure of 45–50 mm., when 18–21 grams of pure anhydrous acid is obtained. See also van Wyk's, Mathers', and Richards and Willard's modifications [3] of this method.

(2) An aqueous solution of the acid is easily prepared by dissolving potassium perchlorate (prepared as above) in seven times its volume of warm water. Slight excess of hydrofluosilicic acid, H_2SiF_6, is added, the liquid is heated for one hour, the cooled solution is filtered from precipitated K_2SiF_6, more silicofluoric acid and water are added, and the liquid is again boiled, concentrated as far as possible on the water-bath, cooled, and separated from the K_2SiF_6 and the little $KClO_4$ which crystallises out. The little silicofluoric acid which remains in the liquid is now removed by adding the slightest excess of barium chloride, evaporating the clear solution until fumes due to $HClO_4$ begin to arise, diluting with water, adding a very little sulphuric acid (to remove $BaCl_2$), allowing the liquid to stand for several days, and then filtering from deposited solid. Caspari [4] thus obtained a nearly pure aqueous solution of perchloric acid.

(3) Concentrated hydrochloric acid (25-30 c.c.) is added [5] to sodium perchlorate (20 grams) ; the sodium chloride is collected on an asbestos filter and washed with ten successive portions of hydrochloric acid, each of 1 c.c. ; the filtrate and washings are heated to 135° C., in order to expel the hydrochloric acid. The perchloric acid thus obtained is free from chlorides, but

[1] Michael and Conn, *Amer. Chem. J.*, 1900, **23**, 444.
[2] Vorländer and Schilling, *Annalen*, 1900, **310**, 369.
[3] van Wyk, *Zeitsch. anorg. Chem.*, 1906, **48**, 1 ; F. C. Mathers, *Chem. Zeit.*, 1913, **37**, 363 ; Richards and Willard, *Carnegie Institution Publications*, 1910, No. 125.
[4] Caspari, *Zeitsch. angew. Chem.*, 1893, **6**, 68 ; see also Serullas, *Ann. Chim. Phys.*, 1830, **45**, 270 ; 1831, **46**, 294, 297, 323.
[5] F. C. Mathers, *J. Amer. Chem. Soc.*, 1910, **32**, 66 ; see also Kreider, *Zeitsch. anorg. Chem.*, 1895, **9**, 342.

contains about 4 per cent. of sodium perchlorate. The method cannot be employed with perchlorates of potassium or barium.

(4) Willard [1] prepares the acid by distilling ammonium perchlorate with nitric acid and hydrochloric acid.

Properties.—Pure anhydrous perchloric acid is a volatile, colourless, very mobile liquid, which fumes strongly in air, combining with the moisture present to form the monohydrate. The liquid boils at 19° under 11 mm. pressure,[2] and does not solidify when immersed in a freezing mixture of ether and solid carbon dioxide,[3] but freezes at − 112° (van Wyk); it has a specific gravity of 1·764 at 22° C. When the pure acid comes into contact with the skin it produces a painful and serious wound, which does not heal for months.[4] A few drops thrown upon organic material such as paper or wood causes an almost explosive sudden inflammation of these bodies. When dropped upon dry charcoal, a drop of the pure acid explodes as violently as nitrogen chloride.

The pure acid is partially decomposed when distilled under ordinary atmospheric pressure; when the temperature reaches 72° the liquid takes on a darker tinge, while at 92° dense white clouds arise, while a yellow-tinged gas, smelling like chlorine peroxide, escapes, and a few drops of a dark bromine-like liquid distils over, which contains 94·77 per cent. $HClO_4$; on heating further a violent explosion occurs, which shatters the apparatus. The composition of the substance here formed is quite unknown.

Pure colourless perchloric acid also spontaneously decomposes when kept even in the dark, the liquid becoming dark and spontaneously exploding after one or two weeks.[5]

The pure acid is soluble in chloroform, but on exposure to air the solution turns yellow, and when it is poured on to phosphorus pentoxide a violent explosion occurs. The acid is insoluble in carbon tetrachloride and also in benzene, C_6H_6, but reacts violently with them. In some cases attempts to dissolve in dry ether and also in alcohol caused a violent explosion, although in other cases the liquids mixed quietly. Iodine dissolves in perchloric acid, forming a yellow crystalline substance of the composition HI_7O_3 (Michael and Conn), from which, on cooling, iodine separates and a residue of iodic acid, HIO_3, is left.

When pure perchloric acid is dropped into water it dissolves, combining with the water so vigorously as to produce a loud hissing sound and the evolution of much heat. The aqueous solution of the acid reddens litmus without subsequently bleaching it. In solution the acid appears to be very stable, remaining undecomposed when subjected to the action of sunlight, sulphur di-oxide, sulphuretted hydrogen, or hydrogen chloride. The acid, however, is decomposed by the addition of either bromine or iodine.

The heat of neutralisation of the acid is determined by Berthelot [6] as $HClO_4$ (dilute) $+ \frac{1}{2}BaO$ (dilute) $= 13,800$ calories. Thomsen [7] gives :—(NaOH aq., $HClO_4$ aq.) $= + 14,080$ calories.

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[1] Willard, *J. Amer. Chem. Soc.*, 1912, **34**, 1480.
[2] Michael and Conn, *Amer. Chem. J.*, 1900, **23**, 444 ; 1901, **25**. 89.
[3] Vorländer and v. Schilling, *Annalen*, 1900, **310**, 369.
[4] Roscoe, *J. Chem. Soc.*, 1863, p. 82.
[5] Vorländer and v. Schilling, *loc. cit.*
[6] Berthelot, *Bull. Soc. chim.*, 1878, [ii.], **29**, 4.
[7] Thomsen, *Thermochemische Untersuchungen*, vol. i. p. 243.

The following thermal data regarding the heat of formation, etc., of $HClO_4$ are given by Berthelot :—[1]

$$Cl + O_4 + H = HClO_4 \text{ (liquid)} \quad +19,100 \text{ calories.}$$
$$Cl + O_4 + H + Aq. = HClO_4 \text{ (dilute)} \quad +39,350 \text{ calories.}$$
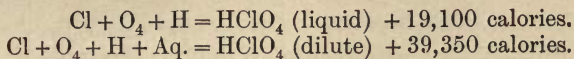
The heat of formation [2] of the ClO_4 ions is $-39,000$ calories.

Hydrates of Perchloric Acid.—Perchloric acid unites with water to form several distinct hydrates.

The formation of the monohydrate, $HClO_4.H_2O$, has already been described on p. 132 ; and it may always be obtained from anhydrous perchloric acid by adding the calculated amount of water which combines with the acid with the evolution of a considerable amount of heat ; according to Berthelot :—

$$HClO_4 \text{ (liquid)} + H_2O = HClO_4.H_2O + 1260 \text{ calories.}$$
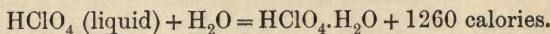
The heat of dilution of the anhydrous acid, when added to excess of water, is given as 20,300 calories by the same author. This is as large as the heat of dilution of P_2O_5. The substance forms colourless needle-shaped crystals, which are often several inches long, which melt at 50° C. (Roscoe), and solidify again at 49·5–50°, with a marked expansion. The density of the liquefied crystals is 1·811 at 50° (Roscoe), or 1·7756 (van Wyk), while the latent heat of fusion is 33·7 calories per gram.[3] The liquefied hydrate emits dense white fumes on exposure to air, and inflames both wood and paper. The solid crystals dissolve in water with the evolution of heat (see above).

When the monohydrate, $HClO_4.H_2O$, is heated to over 110° C., it decomposes into the pure acid $HClO_4$, and a thick oily fluid which much resembles concentrated sulphuric acid, boiling at 203°, having a specific gravity of 1·82 (see p. 133), and a composition corresponding to 71·6 per cent. $HClO_4$. When a dilute aqueous solution of $HClO_4$ is distilled, first of all pure water comes over at 100° C., then the temperature rises, and the distillate begins to contain $HClO_4$, until finally the distilling liquid comes over unchanged at 203°, having the same composition (viz. 71·6–72·2 per cent. $HClO_4$) as the acid distilling over when the concentrated acid was distilled.[4] Aqueous perchloric acid, therefore, behaves like hydrochloric and other aqueous acids (see p. 103) in this respect.

van Wyk,[5] from a study of the melting-point curve of mixtures of perchloric acid and water, came to the conclusion that besides the above-mentioned *monohydrate* $HClO_4.H_2O$, the following hydrates exist :— $HClO_4.2H_2O$ (melting-point $-20·6°$); $HClO_4.3H_2O$ $(-47°)$; $HClO_4.4H_2O$ $(-40°$ C.), and $HClO_4.6H_2O$ $(-45°)$; also the presence of an unstable hydrate (melting-point $-64°$) was indicated ; while later work indicates the presence of hydrates $2HClO_4.5H_2O$, $3HClO_4.7H_2O$, and *two* distinct hydrates of the composition $HClO_4.3H_2O$. For details the original papers must be consulted.

The specific gravities of aqueous solutions of perchloric acid of different strengths were investigated by van Wyk.

[1] Berthelot, *Compt. rend.*, 1881, **93**, 240, 291.
[2] Ostwald, *Grundriss. der allgemeinen Chemie*, 1899, p. 281.
[3] van Wyk, *Zeitsch. anorg. Chem.*, 1906, **48**, 1.
[4] Roscoe, *J. Chem. Soc.*, 1863, **16**, 82.
[5] van Wyk, *Zeitsch. anorg. Chem.*, 1902, **32**, 115 ; 1906, **48**, 1.

The following is an extract from his table :—

Specific Gravity.		Percentage of HClO$_4$ by Weight.	Molecular Per cent. HClO$_4$.
20° C.	50° C.		
1·7676	1·7098	100	100
1·8059	1·7531	94·67	76·15
1·6471	1·6110	68·42	27·96
1·4078	1·3779	50·51	15·46
1·1778	1·1574	27·07	6·23

Van Emster[1] gives a more extended table, of which the following is an extract :—

Specific Gravity 15° C. H$_2$O at 4° = 1.	Per cent. HClO$_4$.	Specific Gravity 15° C. H$_2$O at 4° = 1.	Per cent. HClO$_4$.	Specific Gravity 15° C. H$_2$O at 4° = 1.	Per cent. HClO$_4$.
1·005	1·00	1·150	22·99	1·330	42·97
1·020	3·61	1·200	29·26	1·400	49·23
1·045	7·68	1·255	35·49	1·500	57·06
1·070	11·58	1·270	37·08	1·600	64·50
1·090	14·56	1·290	39·10	1·675	70·15
1·115	18·16				

The molecular conductivity of solutions of perchloric acid at 25° C. was determined by Ostwald[2] as follows :—

Molecular Conductivity.	Dilution (HClO$_4$ in v Litres).	Molecular Conductivity.	Dilution (HClO$_4$ in v litres).	Molecular Conductivity.	Dilution (HClO$_4$ in v litres).
358·	2	399	32	407	512
372	4	404	64	407	1024
383	8	406	128		
390	16	407	256		

According to Ostwald, perchloric acid is one of the strongest of known acids, nitric, chloric, and perchloric acids being in this respect nearly equal.

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[1] van Emster, *Zeitsch. anorg. Chem.*, 1907, **52**, 270.
[2] Ostwald, *J. prakt. Chem.*, 1885, [ii.], **31**, 433.

Perchlorates.—Perchloric acid is a powerful monobasic acid, which generates a series of salts of the type $MClO_4$, termed *perchlorates*.

These salts are all soluble in water, but among the least soluble of the perchlorates are, strangely enough, those of the alkali metals. Thus 1 part of potassium perchlorate, $KClO_4$, requires 58 parts of water to dissolve it, while 1 part of rubidium perchlorate, $RbClO_4$, requires no less than 92 parts of water for solution at 21°. Since both salts are practically insoluble in absolute alcohol, they have been employed in the quantitative estimation of these metals.

Both normal salts, $M—O—ClO_3$, and basic salts (*e.g.* with $Pb(OH)_2$), are known, but no acid salts have been isolated.

The perchlorates as a class differ from the chlorates in the following respects :—

(1) They are not decomposed by hydrochloric acid.
(2) They are not reduced to chlorides by SO_2, and in general are far more stable towards reducing agents than chlorates.
(3) They do not yield the explosive gas ClO_2 when warmed with concentrated sulphuric acid.
(4) They are more stable towards heat than the chlorates.

The individual perchlorates are described under the respective metals (which see).

Constitution of Perchloric Acid.—On account of the great stability of perchloric acid and perchlorates as compared with the other oxy-acids of chlorine, such a formula as $H—O—O—O—O—Cl$ is out of the question, as a series of oxygen atoms linked up in this manner would exhibit the greatest instability.

The formula now generally accepted is that proposed by Blomstrand :— [1]

$$O=Cl—O—H,$$
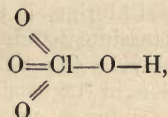
in which chlorine functions as a heptad.

This formula readily explains the constitution of the hydrate $HClO_4.H_2O$, which may be represented thus :—

$$
\begin{array}{c}
HO \quad O \\
\backslash \; \| \\
Cl—O—H, \\
/ \; \| \\
HO \quad O
\end{array}
$$
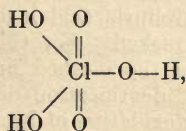
although no salts corresponding to this latter formula appear to have been isolated.

These formulæ are analogous to those proposed for per-iodic acid, and the fact that such oxides as ClO_2, Cl_2O_7, and Cl_2O exist is strong presumptive

[1] Blomstrand, *Ber.*, 1883, **16**, 183 ; see also Vorländer, *Ber.*, 1901, **34**, 1632 ; W. Ramsay, *Chem. Zeit.*, 1908, **32**, 437.

evidence that the valency of chlorine varies in its different compounds with oxygen and consequently also in the oxy-acids of chlorine ; these latter may therefore be attributed the constitutional formulæ :—

$$
\text{Cl—O—H} \qquad \text{O} = \text{Cl—OH} \qquad \overset{\text{O}}{\underset{\text{O}}{\diagdown\!\!\diagup}}\text{Cl—O—H} \qquad \text{O} = \overset{\text{O}}{\underset{\text{O}}{\diagup}}\text{Cl—O—H.}
$$

Hypochlorous acid. Chlorous acid. Chloric acid. Perchloric acid.
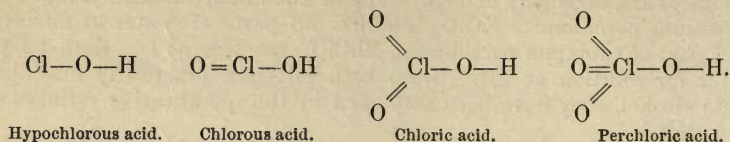
See also p. 131, under Chloric Acid.

Uses of Perchloric Acid.—According to Willard,[1] perchloric acid forms an excellent standard solution for use in acidimetry, especially where a non-volatile acid is necessary and sulphuric acid is unsuitable ; it may be employed as a substitute for sulphuric acid in permanganate titrations, and it may be added to ferric chloride solutions, instead of sulphuric acid, to ensure the complete removal of chloride by evaporation.

According to Hendrixson,[2] also Golblum [3] and Terlikowski,[3] the electrolytic estimation of copper, silver, cadmium, nickel, and cobalt from perchloric acid solutions give good results.

Estimation.—Perchloric acid may be titrated with N/10 alkali, with phenolphthalein as indicator.[3]

Alkali perchlorates may be estimated gravimetrically by converting them into chlorides by heating and estimating the chloride,[4] and volumetrically by reducing to chlorides with titanous sulphate.[3]

DETECTION AND ESTIMATION OF CHLORINE.

Detection of Chlorine.—Chlorine, if in the free state, may be estimated by adding excess of potassium iodide solution, when the equivalent weight of iodine is set free—$KI + Cl = KCl + I$—and then titrating the iodine with thiosulphate solution in the usual way (see under Estimation of Iodine). The presence of free chlorine may be detected by its bleaching action and smell.

If combined with a metal (chlorides), the presence of chlorine may be detected by the formation in aqueous or acid solution of a white precipitate of silver chloride, AgCl, with silver nitrate solution. The silver chloride is soluble in ammonia solution, insoluble in concentrated HNO_3, and when warmed with concentrated sulphuric acid it does not evolve brown or violet fumes, and is only slowly attacked. For the detection of chloride in the presence of bromide and iodide, the method first worked out by Caven [5] is rapid and convenient. This identification depends upon the oxidation of iodide by nitrous acid, and the oxidation of bromide by dilute nitric or iodic acid. The following is Caven's table :—

---

[1] Willard, *J. Amer. Chem. Soc.*, 1912, **34**, 1480.

[2] W. S. Hendrixson, *J. Amer. Chem. Soc.*, 1912, **34**, 389.

[3] Rothmund, *Zeitsch. anorg. Chem.*, 1909, **62**, 108. See also H. Golblum, *Zeitsch. anal. Chem.*, 1911, **50**, 741 ; *Bull. Soc. chim.*, 1912, [iv.], **11**, 103.

[4] Lamb and Marden, *J. Amer. Chem. Soc.*, 1912, **34**, 812.

[5] R. M. Caven, *Systematic Qualitative Analysis* (1909), p. 184 ; *J. Soc. Chem. Ind.*, 1909, **28**, 505. For further convenient methods see Benedict and Snell, *J. Amer. Chem. Soc.*, 1903, **25**, 809 ; Noyes, *ibid.*, 1912, **34**, 626.

Acidify the neutral or alkaline solution of the mixed halides with dilute sulphuric acid ; add sodium nitrite solution ; boil till the liquid is colourless, and coloured fumes have disappeared.

A brown solution or black precipitate on addition of nitrite shows presence of iodide. This is confirmed by holding in the moistened vapour a rod dipped in powdered starch. A purple colour proves *iodide*.	Add a little more nitrite, and again boil to expel the last traces of iodide. Neutralise with sodium carbonate, and evaporate just to dryness in a dish. Add 5 c.c. of dilute nitric acid, and heat just to boiling.

A brown colour shows the presence of bromide. Confirm by cooling part of the solution and shaking with CS_2 or chloroform. A brown layer proves *bromide*.	Boil rest of solution till colourless, adding more dilute nitric acid if necessary to keep volume of solution up to about 3 c.c. Then add silver nitrate. White precipitate, soluble in NH_3, insoluble in concentrated HNO_3, shows chloride.

Estimation of Chlorine.—This may be carried out by adding excess of silver nitrate solution to a solution of a chloride (acidified with HNO_3), when silver chloride is precipitated. This is filtered off, ignited to just under its fusing-point (very dull red heat), and weighed as such.

Volumetrically, the estimation may be carried out by taking a *neutral* solution of a chloride, adding to it a few drops of potassium chromate solution as indicator, and then running in N/10 silver nitrate solution until a faint red colour appears. As the silver nitrate enters, it precipitates all the chloride as AgCl, thus : $AgNO_3 + NaCl = AgCl + NaNO_3$. As soon as all the chloride is used up the free chromate then reacts with an additional drop of $AgNO_3$, producing a red-coloured silver chromate, thus : $2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3$, and so the end of the reaction is very delicately indicated by the appearance of a reddish tint in the liquid.

The ammonium thiocyanate method (Volhard) is somewhat similar, and has the advantage of being usable in acid solutions. The solution of chloride is acidified with dilute nitric acid and precipitated by addition of an accurately measured excess of N/10 $AgNO_3$ solution. The solution is briskly shaken and the silver chloride filtered off from the solution,[1] 5 c.c. of ferric alum solution are added, and then standard ammonium thiocyanate solution, NH_4CNS, is run in, until the liquid acquires a faint reddish colour. The silver nitrate first reacts with the ammonium sulphocyanide present, thus :—

$$AgNO_3 + NH_4CNS = AgCNS + NH_4NO_3.$$
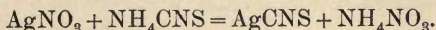
When all the free silver nitrate has been precipitated as silver thiocyanate, AgCNS, a drop of the ammonium salt in excess at once reacts with the ferric salt present to give a red colour of ferric-thiocyanate, $Fe(CNS)_3$.

By knowing the value of the N/10 silver nitrate solution in terms of the standard ammonium thiocyanate (by means of a previous titration), we can, by difference, obtain the amount of silver nitrate solution used up in precipitating the chloride, and hence obtain the amount of chlorine present in the solution.

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[1] Rosanoff and Hill, *J. Amer. Chem. Soc.*, 1907, **29**, 269.

As regards the *estimation of chloride in the presence of bromide* the method worked out by Caven [1] is rapid and accurate. A measured volume of the solution of mixed halides is placed in a 200-c.c. distilling-flask, 25 c.c. of concentrated nitric acid are added, the liquid in the flask being so diluted that the volume does not exceed 100 c.c. The nitric acid of most suitable strength is made by taking 1 vol. of 1·42 acid with 3 vols. water. If the acid is weaker, then evaporation is necessary before all the bromine is liberated ; and if stronger, some chlorine is lost.

The solution in the flask is heated while a current of air is passed in and the bromine is set free, boiling for one minute sufficing to complete the reaction. The liquid is then titrated for chloride in the usual way by Volhard's method.

When the liquid contains chloride *as well as bromide and iodide*, Caven (*loc. cit.*) recommends (1) titration of the total halide by Volhard's thiocyanate method (see above) ; (2) estimation of iodide by titrating with dichromate the ferrous iron produced on boiling the mixed halide solution with iron alum ; (3) titration of the chloride in nitric acid solution after successively eliminating iodide by hydrogen peroxide in presence of acetic acid, and bromide by dilute nitric acid ; (4) estimation of bromide by difference.

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[1] Caven, *J. Soc. Chem. Ind.*, 1909, **28**, 505.

BROMINE AND ITS COMPOUNDS.

BROMINE.

Symbol, Br.   Atomic weight, 79·92 (O = 16).

Occurrence. — Like chlorine, bromine never occurs in the free state in nature, on account of the readiness with which it reacts with other bodies. Matteucci [1] has found it, combined with hydrogen as hydrogen bromide, in volcanic gases, but it nearly always exists in combination with metals in the form of bromides, the most common compounds being those of sodium, potassium, and magnesium.   Silver bromide or bromyrite and silver chloro-bromide are found in Chili, Mexico, and Honduras, and also at Huelgoeth in Brittany.   Small quantities of the element are contained in some phosphates from France, in Silesian zinc ores, in English rock-salt, in Chili saltpetre, and in coal.   The Stassfurt deposits contain notable amounts of bromine, crude carnallite containing from 0·15 to 0·25 per cent.   These deposits are the chief source of the element at the present time.   Bromine is also found in many salt springs and mineral waters, among which may be mentioned those of Schönebeck and Kreuznach, in Germany ; Bex, in Switzerland ; Hall, in Austria ; Csiz, in Hungary ; the salines of the department of the Jura, in France ; Capo d'Istria, in Italy ; Anderton, Cheltenham, and Harrogate, in England. The salt springs of Ohio and other parts of the United States of America contain comparatively large amounts of bromine, and are only second in importance to the Stassfurt deposits as a commercial source of the element, practically the entire world's supply coming from these two sources.   Bromine is found in small quantities in sea-water, thus Berglund [2] found an average of 0·06 per cent. of the element.   According to Terreil,[3] the Dead Sea contains 0·7093 per cent. of bromine at a depth of 300 metres, and from 0·0176 to 0·4568 per cent. at the surface ; and Fresenius [4] has found 0·2124 per cent. of bromine in Dead Sea water of specific gravity 1·1555.   Marchand [5] found traces of bromine in many drinking waters, and even in rain water and melted snow. Marine animals and plants frequently contain the element ; thus, the ashes of the bladder wrack (*Fucus vesiculosus*) contain 0·682 per cent. of bromine, and many marine worms, crustaceans, and molluscs contain small amounts.   It is an essential constituent of Tyrian purple, which was obtained from a species

[1] Matteucci, *Compt. rend.*, 1899, **129**, 65.
[2] Berglund, *Ber.*, 1885, **18**, 2888.
[3] Terreil, *Compt. rend.*, 1866, **62**, 1329.
[4] Fresenius, *Verh. Ges. deut. Naturfirch. Aerzte*, 1913, p. 118.
[5] Marchand, *Compt. rend.*, 1850, **31**, 495.

of purpura, or "dog whelk," and is also found in sponges, in salted herrings, and in cod-liver oil.

History.—This element was discovered in 1826 by Balard [1] in the mother liquors from the salines of Montpellier. He gave it its name on account of its powerful and irritating odour ($\beta\rho\tilde{\omega}\mu o\varsigma$, a stench). It had already been observed by Joss, who, however, mistook it for selenium, and also by Liebig, who considered it to be a chloride of iodine. The earliest investigations of the element and its compounds were carried out by Balard, who was the first to obtain hydrogen bromide, hypobromous acid, and bromic acid, and also by Serullas and Löwig.

Preparation.—Bromine was first obtained commercially as a by-product from the salines of Kreuznach, Schönebeck, and other places, and also from the waters of the North Sea. It was afterwards obtained from kelp ashes (see p. 191), and from the salt springs of Ohio and Virginia. The mother liquors from the Stassfurt deposits first began to be used as a source of bromine in 1865, and at the present time they furnish by far the greater portion of the whole world's production, America supplying most of the remainder. The liberation of the bromine from these liquors is carried out in various ways which nearly all depend upon the displacement of the element by chlorine. The chlorine for this purpose may be generated within the mother liquor by means of hydrochloric acid and manganese dioxide, and in the early days of the industry this intermittent method was always used, although it involved the loss of time and material. The disadvantages of the method, however, have led to the introduction of various continuous processes in which the chlorine is prepared in a separate generator, or obtained compressed in steel cylinders, and passed into the liquor.

Laboratory Methods. — Bromine is prepared in the laboratory by passing a stream of chlorine into liquors containing bromides until the yellow colour imparted to the liquid ceases to increase in intensity. The reaction with magnesium bromide, for example, takes place according to the equation :—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$
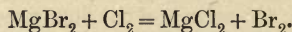
It is necessary to avoid using an excess of chlorine, as this would combine with the liberated bromine to form bromine chloride. The liquid is then shaken up with ether, chloroform, or carbon bisulphide, in order to dissolve out the bromine. On standing for a short time the two liquids separate into an aqueous layer and a brown solution of bromine in the organic solvent. The layers are separated, and aqueous potash is added to the bromine solution, when the colour at once disappears. The bromine reacts with the potash to form a mixture of potassium bromide and bromate, thus :—

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$
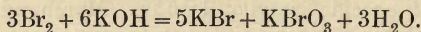
The solution is then concentrated and distilled with sulphuric acid and manganese peroxide, when the bromine is liberated and distils over.

It is also readily prepared by distilling potassium bromide with manganese dioxide and sulphuric acid in a tubulated retort and keeping the receiver cold by means of ice. The reaction takes place according to the equation :—

$$2KBr + MnO_2 + 2H_2SO_4 = MnSO_4 + K_2SO_4 + 2H_2O + Br_2.$$

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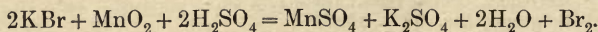
[1] Balard, *Ann. Chim. Phys.*, 1826, [ii.], **36**, 377.

Some bromides, such as those of magnesium, aluminium, and hydrogen, give up their bromine when heated with oxygen, thus :—

$$2MgBr_2 + O_2 = 2MgO + 2Br_2.$$
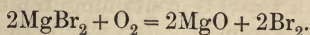
Manufacture.—A modern apparatus for the extraction of bromine is shown in fig. 26. This consists of a tower T, filled with earthenware balls, and connected by means of a wide pipe aa, to a tank W, which is provided with sandstone shelves. The hot mother liquor enters T through the sealed pipe mm, and is evenly distributed over the whole area by means of a sandstone *drum* and perforated plate $h\,h$. In the tower the liquor is subjected to
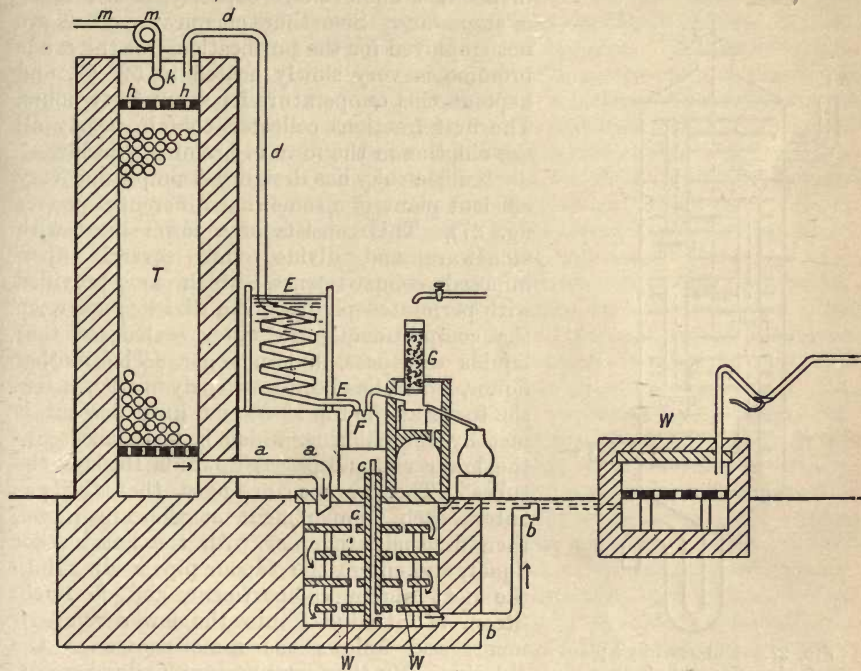
FIG. 26.—Manufacture of bromine.

the action of a stream of chlorine, which passes through the apparatus in the opposite direction, coming from the chlorine still. The bromine is thus liberated according to the equation :—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2,$$
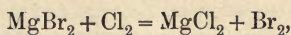
and the liquor passes away through the pipe aa, into the tank W, which is always kept full up to the level of the pipe bb, and hence through the exit pipe. In passing through the tank W the partly spent liquor must flow over the shelves in the direction of the arrows, in doing which it is subjected to the action of a current of steam at high pressure introduced through the pipe cc, and all the bromine and chlorine dissolved in it are thus swept up, together with the fresh chlorine, into the tower T. The bromine vapour and excess of chlorine leave the tower by means of the exit pipe dd, and pass into

a stoneware worm E E, where the bromine is condensed to the liquid form. It is then collected in a tubulated bottle F. The chlorine and uncondensed bromine finally pass into a vessel G, containing iron turnings, which are kept moist by means of a small stream of water, where they combine with the iron to form the corresponding iron compounds.

The bromine thus obtained usually contains from 1 to 4 per cent. of chlorine as bromine chloride, and also small quantities of iodine, cyanogen, bromoform, carbon tetrabromide, and lead bromide. It is partially purified by redistillation, together with ferrous, calcium or potassium bromide, which remove the chlorine. The stills are usually either square sandstone troughs of about 1 cubic metre capacity, or are made of stoneware. Sometimes chemical reagents are not employed for the purification, but the crude bromine is very slowly heated to 59° C., and kept at this temperature for about forty hours. The first fractions collected contain nearly all the chlorine in the form of bromine chloride.

Kubierschky has designed a simple and very efficient plant of a somewhat different type (see fig. 27). This consists of a tower lined with stoneware and divided into several superimposed compartments, which are provided with perforated plates. The divisions between the compartments are water sealed, so that liquids can pass, but not gas. The mother liquor, which has been previously heated, enters the tower at the top at A, and, in its descent, is met by the chlorine, which is introduced into the lower end and passes upwards through the tubes. These are so arranged that the gas enters each compartment at the upper end, then descends, together with the hot mother liquor, and enters the vapour pipe leading into the next higher compartment, and so forth. Steam is introduced into the lower compartment, and follows the same course as the chlorine. By this arrangement undercurrents, which are certain to be formed when a direct upward current is used, are avoided. The bromine leaves the tower at B, and is condensed in an earthenware coil. It is then purified in the refining tower, in which it flows downwards into a vessel containing boiling bromine. Most of the chlorine is driven off through the tower, and the purified bromine is syphoned off.
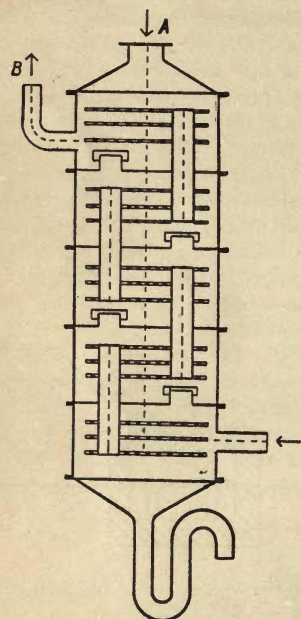
Fig. 27.—Kubierschky's plant for bromine manufacture.

In some American works the mother liquors, after the extraction of sodium chloride, are concentrated and distilled with sulphuric acid and potassium chlorate in stoneware retorts. The liberated bromine is condensed in lead condensers and purified by redistillation.

Electrolytic Processes. — Many electrolytic methods of obtaining bromine from liquors containing bromides have been introduced by Höpfner, Nahnsen, Wünsche, Kossuth, and others, but their use has not become general. The liquors are placed in open vessels furnished with carbon electrodes, and the current passed through at a certain rate. Except in

Kossuth's process, diaphragms are used in order to avoid secondary reactions. The liberated bromine remains in solution in the liquid, and is subsequently separated by distillation and purified.

Purification.—Commercial bromine is not pure. It may contain chlorine, iodine, bromides of chlorine and iodine, and other impurities. There are several methods of getting rid of some or all of these impurities. Piria [1] adds baryta water to the crude bromine until the latter is completely decolorised. The solution thus obtained is evaporated to dryness and calcined, in order to destroy any organic matter and to convert the oxygenated compounds into the corresponding chlorides, bromides, and iodides. The calcined mass is then dissolved in water, treated with sufficient bromine to displace the iodine from the iodides, evaporated to dryness, and again calcined in order to drive off the liberated iodine and excess of bromine. The mass is then treated with alcohol, which dissolves up the barium bromide and leaves the barium chloride behind. The alcoholic solution is filtered, the alcohol evaporated off, and the barium bromide decomposed by distilling with sulphuric acid and manganese dioxide. The liberated bromine is collected in a cool receiver.

In Stas' method [2] for obtaining pure bromine for the determination of the atomic weight of the element, bromine water is added to one-quarter of an aqueous solution of potassium bromide until the iodine which separates out is redissolved and a clear orange-coloured solution is obtained. The remaining three-quarters of the potassium bromide solution is then added, and the mixture repeatedly shaken up with pure carbon bisulphide. The aqueous solution is heated, in order to drive off all traces of carbon bisulphide, and the potassium bromide oxidised to potassium bromate by means of chlorine in presence of an aqueous solution of pure potassium hydroxide. The potassium bromate thus obtained is purified by repeated crystallisation and a portion reconverted to the bromide. A mixture of the two salts in the proportion of 5 molecules of potassium bromide to 1 of bromate is then decomposed by means of pure sulphuric acid, and a part of the bromine thus obtained is digested with milk of lime and aqueous ammonia in order to form an aqueous solution of calcium bromide. This solution is saturated with another portion of the bromine, and water added. The precipitated bromine is separated, treated with pure dry calcium bromide, then left in contact with pure barium oxide for twelve hours and finally poured off and distilled.

Ramsay and Young [3] digest the crude bromine with powdered potassium bromide and distil the mixture. This method only gets rid of the chlorine, which is, however, the principal impurity.

Another method due to Stas [4] and used by van der Plaats is as follows : The bromine is shaken up with distilled water for three hours and then separated by means of a separating funnel. It is then distilled from an aqueous solution of potassium bromide and a little zinc oxide, and collected under water, again distilled, then left standing over phosphorus pentoxide, and finally distilled. This method removes chlorine and iodine, but not organic matter.[5]

[1] Piria, *J. Chim. Méd.*, 1839, [ii.], **4**, 65.

[2] Stas, *Bull. Acad. Roy. Belg.*, 1860, [ii.], **10**, 208 ; *Mem. Acad. Roy. Belg.*, 1865, **35**, 3. See also Richards and Mueller, (*J. Amer. Chem. Soc.*, 1907, **29**, 639) on the preparation of pure bromine from the bromide and bromate of potassium.

[3] Ramsay and Young, *Trans. Chem. Soc.*, 1886, **49**, 453.

[4] Stas, *Mem. Acad. Sci. Bruxelles*, 1881, **42**, 90 ; van der Plaats, *Rec. trav. chim.*, 1886, **5**, 34 ; Brauner, *vide infra*.   [5] Scott, *Trans. Chem. Soc.*, 1913, **103**, 847.

Scott [1] prepares pure bromine by fusing dry, pure potassium bromide with previously fused potassium dichromate, allowing to cool, breaking up the cold fused mass and treating with cold dilute sulphuric acid (450 c.c. of concentrated H_2SO_4 to 700 c.c. of water), to which a little potassium permanganate has been added. The bromine liberated on warming is then dissolved in an aqueous solution of pure potassium bromide and distilled. The pure potassium bromide for this preparation is obtained by boiling a solution of 1500 grams of the salt in an equal weight of water with a few crystals of potassium metabisulphite and about 5 c.c. of concentrated sulphuric acid, adding 100 c.c. of saturated bromine water to the solution and distilling off the bromine. More bromine water is then added and again distilled off, after which the solution is neutralised with potassium carbonate and evaporated to dryness. By this method Scott claims to get rid of iodine either in the form of iodide or iodate.[2]

Properties.—Bromine is the only element, with the exception of mercury, which is liquid at ordinary temperatures. It is a heavy, mobile, volatile liquid, with a very unpleasant, irritating odour. The vapours attack the eyes and mucous membrane, and, when dropped upon the skin, the liquid produces a sore which heals with difficulty. It acts as a violent irritant poison when taken internally. The liquid is so dark in colour that it appears to be nearly black and quite opaque, except in extremely thin layers, when it is seen to be dark reddish-brown by reflected light, and hyacinth-red by transmitted light. The colour of the element becomes markedly paler as the temperature is lowered ; thus, it is nearly black at 0° C., becomes much lighter at − 20°, and is a light reddish-yellow at − 50°.[3] According to Andrews, strongly heated liquid bromine transmits much less light than at ordinary temperatures.

According to Thorpe,[4] the density of the liquid is 3·18828 at 0° C., and 2·98218 at the boiling-point. Ramsay [5] obtained the value 2·9483 at the boiling-point. More recently, Andrews and Carlton [6] have obtained the values 3·11932 at 20°, 3·10227 at 25°, and 3·08479 at 30° C. Pure bromine solidifies at about − 7° to − 7·5°. The earlier investigators found very variable values ranging from − 25° to − 7·5° C., the low values being due to the presence of impurities, chiefly chlorine, in the bromine. According to Philipp,[7] bromine solidifies at − 7·2° to − 7·3° C., but if it contains from 3 to 4 per cent. of chlorine it still remains liquid at − 15°, whilst the presence of 2 per cent. of iodine does not appreciably raise the freezing-point. Solid bromine forms a crystalline mass, which is variously described as steel-grey, reddish-brown, and graphite-like in colour. It becomes colourless at − 252·2° C. Arctowski [8] has obtained it in the form of slender, dark, carmine-red needles, by cooling a concentrated solution of bromine in carbon bisulphide to − 90° C. According to Wahl,[9] crystalline bromine is very similar to

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[1] Scott, *Trans. Chem. Soc.*, 1913, **103**, 847

[2] For further information on the preparation of pure bromine see Baxter, Moore, and Boylston, *J. Amer. Chem. Soc.*, 1912, **34**, 359. Also references cited under the Atomic Weight of Bromine.

[3] Schonbein, *J. prakt. Chem.*, 1852, **55**, 154.

[4] Thorpe, *Trans. Chem. Soc.*, 1880, **37**, 141 and 327.

[5] Ramsay, *Ber.*, 1880, **13**, 2146.

[6] Andrews and Carlton, *J. Amer. Chem. Soc.*, 1907, **29**, 688.

[7] Philipp, *Ber.*, 1879, **12**, 1424.

[8] Arctowski, *Zeitsch. anorg. Chem.*, 1895, **10**, 25.

[9] Wahl, *Proc. Roy. Soc.*, 1913, **A**, **88**, 348.

crystalline chlorine, but all the properties are more pronounced. The crystals, which may be regarded as isomorphous with chlorine and iodine, belong to the orthorhombic system and are strongly pleochroic. The melting-point is $-7.32°$ (Regnault [1]); between $-7.0°$ and $-7.45°$ (Ramsay and Young); $-7.3°$ (van der Plaats [2]), (Meerum Terwogt [3]); -7.2 (Weber).[4] The boiling-point is 63° C. (Pierre [5]); 58° under 760 mm. pressure (Andrews [6]); $58.6°$ under 760 mm. pressure (Landolt [7]); $59.27°$ (Thorpe); $63.05°$ (van der Plaats [2]); 63° (Jahn); $57.65°$ under 749.8 mm. pressure for bromine dried over concentrated sulphuric acid, and $58.85°$ under 755.8 mm. pressure for bromine dried over phosphorus pentoxide (Ramsay and Young); $58.7°$ under 771.2 mm. pressure (Meerum Terwogt [3]); $59.0°$ under a pressure of 773.8 mm. (Eggink [8]); 58.9 under 760 mm. (Perman and Atkinson).[9]

The vapour is orange-red in colour. According to Andrews,[10] if a sealed tube, which is half filled with liquid bromine and half with bromine vapour, be gradually heated to a temperature above the critical point, the whole of the bromine becomes opaque, and the tube appears to be filled with a dark red opaque resin.

Meyer and Züblin [11] found that the density of pure bromine vapour, prepared by the decomposition of platinum bromide, ranged between 3.64 and 3.78 at about 1570° C. The formula Br_2 requires a density of 5.515 (air = 1); and Crafts [12] found that the vapour of bromine was slightly dissociated at 1200° C. Perman and Atkinson find that under a pressure of one atmosphere the dissociation $Br_2 \rightleftharpoons 2Br$ is perceptible at 750° C., and reaches 6.3 per cent. at 1050°. According to Jahn,[13] the vapour density of bromine at about the boiling-point is greater than the value corresponding to the molecule Br_2, and only attains this value at 228° C. The values obtained by this investigator at temperatures between $102.6°$ and $227.92°$ are shown in the accompanying table.

TABLE OF VAPOUR DENSITIES OF BROMINE.

Temperature, ° C.	Vapour Density (Calculated).	Vapour Density (Found). Air = 1.
102·6	5·7122	5·7280
131·92	5·6673	5·6400
175·58	5·6005	5·6040
210·32	5·5473	5·5460
227·92	5·5204	5·5243

[1] Regnault, *Ann. Chim. Phys.*, 1849, [iii.], **26**, 274.
[2] van der Plaats, *Rec. trav. chim.*, 1886, **5**, 34.
[3] Meerum Terwogt, *Zeitsch. anorg. Chem.*, 1905, **47**, 203.
[4] Weber, *J. Amer. Chem. Soc.*, 1912, **34**, 1294.
[5] Pierre, *Ann. Chim. Phys.*, 1847, [iii.], **20**, 5.
[6] Andrews, *Pogg. Annalen*, 1848, **75**, 501.   [7] Landolt, *Annalen*, 1860, **116**, 177.
[8] Eggink, *Zeitsch. physikal. Chem.*, 1908, **64**, 449.
[9] Perman and Atkinson, *Proc. Roy. Soc.*, 1900, **66**, 10 ; Perman, *ibid.*, 1890, **48**, 45.
[10] Andrews, *Chem. News*, 1871, **24**, 75.
[11] Meyer and Züblin, *Ber.*, 1880, **13**, 405.
[12] Crafts, *Compt. rend.*, 1880, **90**, 183 ; 1884, **98**, 1259.
[13] Jahn, *Ber.*, 1882, **15**, 1238.

Langer and V. Meyer[1] found that the vapour density is normal even at ordinary temperatures, if the vapour be diluted with about ten times its volume of air.

Liquid bromine consists essentially of diatomic molecules, but there is a slight association into larger molecules, as has been shown by surface tension methods and by the application of Trouton's Law.[2]

The vapour pressures at temperatures between $-17.12°$ and $56.0°$ C., as found by Ramsay and Young,[3] are as follows :—

TABLE OF VAPOUR PRESSURES OF BROMINE.

Temperature, °C.	Pressure, mm.	Temperature, °C.	Pressure, mm.	Temperature, °C.	Pressure, mm.
Solid Bromine					
-17.12	18·9	$+6.38$	91·7	$+38.61$	375·75
-12.74	28·1	14.30	133·65	41·85	418·6
-12.70	27·65	20.96	181·25	45·5	478·2
-10.36	34·85	22.20	189·75	48·7	540·5
Liquid Bromine					
-6.39	47·05	25.72	220·25	50·2	567·3
-4.79	51·0	28.80	250·55	54·1	636·1
-2.02	59·0	32.70	293·4	56·0	689·0
-0.85	63·2	34.68	321·0		
$+2.78$	75·75	36.98	350·25		

The values at temperatures above $38.61°$ were taken with a different thermometer from the rest and belong to a different series of observations. Cuthbertson and (Mrs) Cuthbertson[4] have measured the vapour pressure of solid bromine down to $-80°$ C. by an optical method, and find irregularities at the melting-point, with slowly rising or falling temperature, which appear to indicate that super-heating and super-cooling take place.

The specific heat of solid bromine between -10 and $-77.75°$ C. is 0·08432, and that of the liquid between $+13°$ and $+45°$ is 0·1071 (Andrews).[5] The specific heat of the vapour at constant pressure is 0·05504, and at constant volume 0·04257 (Strecker[6]). The latent heat of fusion is 16·185 calories (Regnault[7]) and the heat of volatilisation 45·6 calories at the boiling-point.[8] The critical temperature is 302·2° C. (Nadejdin[9]). The viscosity of bromine vapour is 1.869×10^{-4} in absolute C.G.S. units at 98·7° C. (Rankine[10]).

[1] Langer and Meyer, *Ber.*, 1882, **15**, 2769.
[2] Miss Aston and Ramsay, *Trans. Chem. Soc.*, 1894, **65**, 167 ; Walden, *Zeitsch. physikal. Chem.*, 1908, **65**, 129 ; 1909, **66**, 385 ; 1910, **70**, 581. See vol. i. p. 157.
[3] Ramsay and Young, *Trans. Chem. Soc.*, 1886, **49**, 453.
[4] Cuthbertson and (Mrs) Cuthbertson, *Proc. Roy. Soc.*, 1911, **A**, **85**, 306.
[5] Andrews, *Quart. J. Chem. Soc.*, 1848, **1**, 27 ; *Pogg. Annalen*, 1848, **75**, 501. For other measurements see Regnault, *Ann. Chim. Phys.*, 1849, [iii.], **26**, 268.
[6] Strecker, *Wied. Annalen*, 1881, **13**, 20 ; 1882, **17**, 85.
[7] Regnault, *Ann. Chim. Phys.*, 1849, [iii.], **26**, 273.
[8] See Andrews, *loc. cit.* ; Berthelot and Ogier, *Ann. Chim. Phys.*, 1883, [v.], **30**, 410.
[9] Nadejdin, *Wied. Annalen, Beibl.*, 1885, **9**, 721.
[10] Rankine, *Proc. Roy. Soc.*, 1912, **A**, **86**, 162.

Beckmann [1] has made cryoscopic and ebullioscopic determinations of the molecular weights of various substances in bromine. By either method the molecular weight of aluminium bromide corresponds with the formula Al_2Br_6. The molecular weights of stannic bromide, antimony pentabromide, and arsenic tribromide in boiling bromide correspond with the formulæ $SnBr_4$, $SbBr_5$, and $AsBr_3$.

According to Balard, bromine is not a conductor of electricity, and this result has been confirmed by De la Rive and also by Solly. An aqueous solution of the element, however, is an electrolyte (see p. 152). Bruner and Galecki [2] have carried out a series of conductivity experiments with solutions of bromine in nitrobenzene. When the latter is perfectly dry, the solution is a non-conductor, but if the nitrobenzene be moist, conduction takes place. Bruner and Sahbill [3] have investigated the effects of adding various oxides to the solution, and have shown that the addition of water is not entirely responsible for the conductivity of bromine in nitrobenzene. They suggest that the changes in conductivity are due to the formation of conducting additive compounds and the absorption of these by the added oxides. Bruner and Bękier [4] have in a similar manner studied the conductivity of solutions of bromine in liquid sulphur dioxide, and find that when the latter is quite dry the solution does not conduct electricity, but in the presence of moist air it becomes a conductor. The conduction is about a hundred times smaller than that found by Walden. According to Faraday, the vapour of bromine is diamagnetic in air. [5]

The index of refraction of bromine is 1·626 at 12° C. for the line A (Gladstone [6]); 1·571 at 13° for the red (Bleekrode [7]). Rivière [8] has obtained the values shown in the accompanying table.

TABLE OF REFRACTIVE INDICES OF BROMINE.

Line.	Wave Length $\mu\mu$.	Refractive Index.			
		10°	15°	20°	25°
22	790·9	1·6368	1·6327	1·6280	1·6226
23 (Line A)	758·6	1·6394	1·6352	1·6305	1·6250
24	729·0	1·6422	1·6379	1·6330	1·6276
25	701·7	1·6453	1·6408	1·6358	1·6304
26	676·5	1·6486	1·6439	1·6389	1·6335
Lithium line	670·8	1·6495	1·6447	1·6397	1·6343
27	653·2	1·6520	1·6742	1·6422	1·6365
28	631·5	1·6557	...	...	1·6401
29	611·4	1·6598	...	...	1·6438
30	592·5	...	...	...	1·6475
Line D	539·0	...	...	1·6543	1·6483

[1] Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 96; *Zeitsch. physikal. Chem.*, 1903, **46**, 853. [2] Bruner and Galecki, *Zeitsch. physikal. Chem.*, 1913, **84**, 513.
[3] Bruner and Sahbill, *Zeitsch. physikal. Chem.*, 1913, **84**, 558.
[4] Bruner and Bekier, *Zeitsch. physikal. Chem.*, 1913, **84**, 570.
[5] Faraday, *Phil. Mag.*, 1847, [iii.], **31**, 401. [6] Gladstone, *Phil. Trans.*, 1870, **160**, 9.
[7] Bleekrode, *Proc. Roy. Soc.*, 1884, **37**, 339; *Rec. trav. chim.*, 1885, 4, 77.
[8] Rivière, *Compt. rend.*, 1900, **131**, 671. For other measurements see Martens, *Ber. Deut. physikal. Ges.*, 1902, 4, 138; Fricke, *Ann. Physik*, 1905, [iv.], **16**, 865.

The above numbers show that the dispersive power of bromine is very considerable. Thus, at 20° C. it is 0·037 between the lines A and D_2, whilst that of carbon bisulphide is only 0·030. Gladstone[1] has shown that the dispersion equivalent of bromine in solution in the di-iodides of the olefines is 1·22, but that it is less than this in a solution of ethyl bromide. According to Mascart,[2] the refractive index of bromine vapour is 3·85. Cuthbertson and (Mrs) Cuthbertson[3] have shown that the refractivity of bromine vapour for light of wave-length 6438 is 0·001157.

The emission spectrum of bromine has been investigated by Plücker and Hittorf,[4] Salet,[5] and others. That obtained by means of the electric spark presents a large number of lines, not one of which coincides with any of those given by chlorine. Salet also observed that when the vapour of bromine is heated to redness it gives a continuous spectrum, like that produced by an incandescent solid. Chautard[6] has shown that the emission spectrum of bromine obtained by means of the electric spark increases in brightness when submitted to the action of an electro magnet; it also develops a number of fine brilliant lines, particularly in the green part of the spectrum. Wood[7] has shown that bromine vapour may be made to fluoresce when subjected to sunlight, when the containing tube is cooled by means of solid carbon dioxide. The absorption spectrum of the vapour was first described by Miller[8] in 1833. It consists of a large number of bands, which do not correspond with the lines of the emission spectrum. According to Hasselberg,[9] there is a partial extinction of the violet part of the spectrum, and a considerable number of very fine lines in the yellow and orange. Roscoe and Thorpe[10] obtained and compared the absorption spectra of bromine vapour and of iodine monochloride by causing the rays from a lime-light to pass through a long narrow glass tube, containing the vapour, and heated by means of a flame, before falling on the slit. The spectrum of bromine thus obtained consisted of a large number of bands, each of which was made up of a group of fine lines. These bands were more numerous and more intense in the yellow and green part of the spectrum than in the red. They extended from $\lambda = 6801·5$ in the red to $\lambda = 5244·1$ in the green, but beyond these limits the general absorption was too great to allow of any bands being seen. The spectrum obtained differed somewhat according to whether the vapour was at the ordinary temperature or heated; in the former case the bands only extended from $\lambda = 6101·4$ in the red to $\lambda = 5433·2$ in the green. Although the vapour of iodine monochloride has nearly the same molecular weight as that of bromine, and the colour of the vapour is almost identical, the absorption spectrum is not quite the same. Out of sixty-six lines which were mapped out in each spectrum, only two were actually coincident. Liveing and Dewar[11] have shown that the vapour in thin layers absorbs light as far as

[1] Gladstone, *Chem. News*, 1887, **55**, 300.
[2] Mascart, *Compt. rend.*, 1878, **86**, 321.
[3] Cuthbertson and (Mrs) Cuthbertson, *Phil. Trans.*, 1913, **A, 213**, 1.
[4] Plücker and Hittorf, *Proc. Roy. Soc.*, 1864, **13**, 153.
[5] Salet, *Ann. Chim. Phys.*, 1873, [iv.], **28**, 26.
[6] Chautard, *Compt. rend.*, 1874, **79**, 1123.
[7] Wood, *Phil. Mag.*, 1911, [vi.], **21**, 309; *Ber. Deut. physikal. Ges.*, 1911, **13**, 72.
[8] Miller, *Pogg. Annalen*, 1833, **28**, 386.
[9] Hasselberg, *Mem. Acad. Petrograd*, 1878, **26**, 4.
[10] Roscoe and Thorpe, *Phil. Trans.*, 1877, **167**, 207.
[11] Liveing and Dewar, *Chem. News*, 1883, **47**, 121.

$\lambda = 3820$, and is completely transparent above this. As the thickness of the layer increases, the absorption gradually extends to $\lambda = 3350$, and there is a simultaneous gradual increase of general absorption at the more refrangible end of the spectrum, beginning at about $\lambda = 2500$, the vapour remaining transparent to that part of the spectrum between $\lambda = 3350$ and $\lambda = 2500$. According to the same authors, a very thin film of liquid bromine between two quartz plates is transparent to that part of the spectrum between $\lambda = 3650$ and $\lambda = 3400$, and gradually becomes less transparent beyond these points until the absorption becomes complete. The transparency of the liquid film ends on the more refrangible side just where that of the vapour begins. Wood[1] has shown that the absorption spectrum of bromine contains an enormous number of lines, many of which are coincident with lines in the corresponding spectrum of iodine. According to Ribaud,[2] all the absorption rays of bromine exhibit magnetic rotatory polarisation when a suitable vapour pressure is chosen, the appearance of the magnetic rotation spectrum completely changing when the pressure is altered. The same investigator has also measured the coefficient of absorption of bromine vapour under various pressures in ultraviolet light, and finds that the index of extinction is proportional to the pressure. He considers that the kinetic theory of absorption accounts for the facts observed with fine lines, but not for the broad bands. Plotnikoff[3] has investigated the extinction coefficient of solutions of bromine in water, benzene, chloroform, and carbon tetrachloride, for four lines of the mercury spectrum. The absorption follows Beer's law, and the bromine spectrum in the visible region appears to consist of two superposed absorption bands. The same investigator has also shown that bromine, like iodine, is most sensitive to the blue region of the spectrum.

Bromine is less soluble in water than chlorine. Its solubility at different temperatures, as found by Winkler,[4] is shown in the accompanying table.

TABLE OF SOLUBILITY OF BROMINE IN WATER.

Temperature, ° C.	Weight of Water which will dissolve 1 Gram of Bromine.	Weight of Bromine dissolved in 100 Grams of Water.
0·00	24·00	4·167
10·34	26·74	3·740
19·96	27·94	3·578
30·17	29·10	3·437
40·03	29·02	3·446
49·85	28·39	3·522

According to Winkler, liquid bromine itself is insoluble in water, but the vapour dissolves according to Henry's law, as shown in the accompanying table.

[1] Wood, *Phil. Mag.*, 1912, [vi.], **24**, 673.
[2] Ribaud, *Compt. rend.*, 1912, **155**, 900 ; 1913, **157**, 1065.
[3] Plotnikoff, *Zeitsch. physikal. Chem.*, 1912, **78**, 573 ; **79**, 357, 641.
[4] Winkler, *Chem. Zeit.*, 1899, **23**, 687 ; *Zeitsch. physikal. Chem.*, 1906, **55**, 344.

TABLE OF THE COEFFICIENT OF ABSORPTION OF BROMINE VAPOUR IN WATER.

Temperature, ° C.	Pressure, mm.	Coefficient of Absorption.
0·00	56 – 13	60·53
9·94	89 – 16	35·22
20·46	138 – 9	20·87
30·38	179 – 12	13·65
40·31	229 – 26	9·22
50·25	274 – 53	6·50
60·04	314 – 46	4·84
69·98	154 – 54	3·82
80·22	396 – 74	2·94

Bray and Connolly [1] have determined the solubility of bromine in water and the conductivity of the solution at 25° C., and find that 0·21 gram-molecule of bromine is dissolved per litre. Part of the dissolved bromine interacts with the water to form hyprobromous and hydrobromic acids, the hydrolysis constant being :—

$$(H^+)(Br^-)(HBrO)/(Br_2) = 5·2 \times 10^{-9}.$$

A saturated solution of bromine in water at ordinary temperatures has a density of 1·023. According to Berthelot,[2] bromine is more soluble in concentrated hydrochloric acid than in pure water. 100 c.c. of the concentrated acid dissolves 36·4 grammes of the element at 12° C. It is probable that in this case the bromine combines with the hydrochloric acid to form a hydrogen chlorobromide, such as $HCl.Br_2$. Aqueous solutions of the chlorides of barium and strontium also dissolve more bromine than pure water. The element dissolves in all proportions in carbon bisulphide, and is also readily soluble in alcohol, ether, chloroform, acetic acid, liquid sulphur dioxide, etc. The solutions in alcohol and ether are soon decomposed. It is absorbed by wood charcoal, which can take up six or seven times its weight of bromine, the temperature rising more than 30°,[3] and in smaller amounts, by sugar charcoal and soot previously heated to redness.[4] The heat of dissolution of 1 gram atom of bromine in different solvents, as found by Pickering,[5] is shown in the following table.

TABLE OF HEAT OF SOLUTION OF BROMINE IN VARIOUS SOLVENTS.

Solvent.	Calories.
Water	– 754
Chloroform	– 323
Carbon tetrachloride	– 265
Carbon bisulphide	– 7
Aqueous potassium bromide . .	+ 1090

[1] Bray and Connolly, *J. Amer. Chem. Soc.*, 1910, **32**, 932 ; 1911, **33**, 1485.
[2] Berthelot, *Compt. rend.*, 1885, **100**, 761.   [3] Melsens, *Compt. rend.*, 1873, **77**, 781.
[4] Mixter, *Amer. J. Sci.*, 1893, [iii.], **45**, 463.
[5] Pickering, *Trans. Chem. Soc.*, 1888, **53**, 865.

According to Thomsen, the heat of dissolution of 1 gram - molecule of bromine in water is 1080 calories.

The saturated aqueous solution, which is known as *bromine water*, is orange-red in colour. It bleaches organic colouring matters, and loses bromine when in contact with air. The solution is permanent in the dark, but when exposed to sunlight it is decomposed with the formation of hydrogen bromide, which dissolves in the liquid, and the evolution of free oxygen, thus :—

$$2Br_2 + 2H_2O = 4HBr + O_2.$$
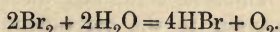
It is used as an oxidising agent in analysis. When a mixture of bromine and a little water is cooled to 0° C., a solid hydrate of bromine of the composition $Br_2 + 10H_2O$ crystallises out in hyacinth - red octahedra.[1] The same hydrate can also be obtained by passing bromine vapour through a tube moistened with water at + 4° C. This hydrate undergoes decomposition into bromine and water at 15°. According to Bakhuis Roozeboom,[2] bromine hydrate has a density of 1·49, and the density of the liquid which can exist in contact with it at 0° is 1·018. The vapour tension of liquid bromine saturated with water at different temperatures is shown in the following table.

TABLE OF VAPOUR TENSION OF LIQUID BROMINE SATURATED WITH WATER.

Temperature.	Vapour Tension.	Temperature.	Vapour Tension.
° C.	mm.	° C.	mm.
2·00	76	6·95	96
3·95	83	7·95	101
4·95	88	12·50	124
5·95	92	15·90	146

The dissociation pressure of the hydrate is shown in the table below.

TABLE OF DISSOCIATION PRESSURE OF BROMINE HYDRATE.

Temperature.	Dissociation Pressure.	Temperature.	Dissociation Pressure.
° C.	mm.	° C.	mm.
0·4	50·5	5·0	81·0
2·0	57·0	5·5	85·0
3·0	63·5	5·9	89·5
4·1	73·0	6·2	93·0

The critical temperature for the dissociation of the hydrate in a closed vessel is 6·2° C., and above this temperature the hydrate cannot exist.[3] At − 0·3° C.,

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[1] Löwig, *Pogg. Annalen*, 1829, **16**, 376.
[2] Bakhuis Roozeboom, *Rec. trav. chim.*, 1884, **3**, 73.
[3] Bakhuis Roozeboom, *Rec. trav. chim.*, 1885, **4**, 65 ; 1886, **5**, 380.

the four phases, ice, hydrate, saturated solution, and vapour, can exist (pressure, 43 mm.).

Bromine readily dissolves in sulphur dioxide, forming an orange-coloured solution, which does not lose its colour when exposed to sunlight.[1] It is also soluble in carbon disulphide, from which it may be crystallised out at $-90°$ C. in reddish-brown crystals.[2]

Bromine strongly resembles chlorine both in its general properties and in those of its compounds. Thus it combines directly with metals to form bromides which are very similar to the corresponding chlorides. The combination, however, takes place with less energy than in the case of chlorine, and the latter element displaces bromine from metallic bromides and hydrogen bromide ; in the case of potassium, for example, according to the equation :—

$$2KBr + Cl_2 = 2KCl + Br_2.$$
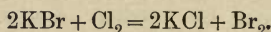
On the other hand, bromine liberates iodine from metallic iodides and hydrogen iodide, thus :—

$$2HI + Br_2 = 2HBr + I_2.$$
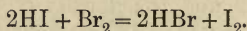
Bromine does not combine directly with oxygen or nitrogen, and apparently not with carbon. It does not combine in the cold with hydrogen, but combination takes place, with the formation of hydrogen bromide, when a mixture of hydrogen and bromine vapour is passed through a tube heated to redness, or when the mixture is ignited. When phosphorus is brought into contact with liquid bromine it detonates, and, when placed in bromine vapour, it takes fire with the formation of bromides of phosphorus. Powdered arsenic and antimony burn when dropped upon liquid bromine, forming the corresponding bromides. Potassium detonates violently when brought into contact with liquid bromine, but no action takes place between perfectly dry bromine and sodium, even when kept in contact for several years, or when the two substances are heated together to $200°$ C.[3] The addition of a drop of water, however, quickly brings about combination, even at ordinary temperatures. Magnesium, iron, and copper are also unattacked at ordinary temperatures by dry bromine, but are converted into the corresponding bromides at a red heat. Gautier and Charpy[4] kept magnesium wire in contact with dry bromine for five years without observing any alteration whatever of the metallic surface. The reaction between aluminium is at first slow, but the metal gradually becomes heated, and the reaction becomes so vigorous that it fuses and takes fire. When magnesium or aluminium is placed in bromine water, hydrogen is evolved and an oxybromide of the metal is obtained. Zinc, iron, and copper do not behave in a similar manner, but slowly dissolve in the solution, without any evolution of gas. Even in the dry state, bromine immediately combines with mercury, forming the bromides.[5] According to Berthelot,[6] bromine partially decomposes water at high temperatures, but the decomposition does not proceed far, as the liberated oxygen reacts in the reverse direction with the hydrogen bromide formed at the same time, thus :—

$$2Br_2 + 2H_2O \rightleftharpoons 4HBr + O_2.$$
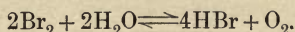
[1] Sestini, *Bull. Soc. chim.*, 1868, **10**, 226.
[2] Arctowski, *Zeitsch. anorg. Chem.*, 1895, **10**, 25.
[3] Merz and Weith, *Ber.*, 1873, **6**, 1518.
[4] Gautier and Charpy, *Compt. rend.*, 1891, **113**, 597.
[5] Shenstone, *Trans. Chem. Soc.*, 1897, **71**, 471.
[6] Berthelot, *Compt. rend.*, 1878, **87**, 667.

Cross and Higgin [1] found that the element decomposed water in the presence of lead acetate, forming lead bromide and lead peroxide. Schönbein [2] has shown that hydrogen peroxide reacts with bromine to form hydrogen bromide and free oxygen, according to the equation :—

$$H_2O_2 + Br_2 = 2HBr + O_2.$$
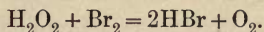
Sulphuretted hydrogen, with or without the presence of water, reacts with the element to form hydrogen bromide and free sulphur, and the latter may combine with the excess of bromine to form sulphur bromide.[3] The reaction is exothermic, thus :—

$$Br_2 + H_2S = 2HBr + S \ . \ . \ . \ . \ . \ . \ +12500 \text{ calories.}$$
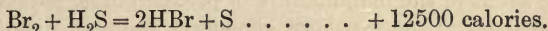
Ammonia reacts with the formation of ammonium and nitrogen bromides. According to Browne and Shetterly,[4] when free bromine is allowed to act upon hydrazine sulphate in alkaline solution, traces of hydrazoic acid are formed, but not in acid solution. Nitric oxide is oxidised to the higher oxides of nitrogen when the gas is passed into liquid bromine cooled to below 0° C. Kretzschmar [5] has shown that when bromine is added to a cold dilute solution of alkali hydroxide the corresponding hypobromite is first formed, and this is afterwards converted into a mixture of bromide and bromate. The change takes place slowly in cold dilute solutions, but rapidly in concentrated solutions, or on heating. Many metallic oxides are decomposed by bromine, yielding the corresponding bromides and free oxygen. This reaction takes place at ordinary temperatures in the case of silver oxide, and at red heat in the case of the oxides of the alkaline earth metals. According to Wilks,[6] when slaked lime is treated with a solution of bromine in carbon tetrachloride a brown product is obtained. With weak solutions of bromine, absorption products are apparently formed, but with concentrated solutions the product appears to be a true compound. The colour of the product increases until constant composition is attained. As in the corresponding case of bleaching powder, the equilibrium concentration of bromine is much lower when dry slaked lime is used. Spiller [7] has shown that on adding bromine water to an excess of an aqueous solution of silver nitrate, silver bromide and hypobromous acid are obtained, and this result has been confirmed by Senderens.[8] Bromine reacts with ethyl alcohol at 25° C., with the formation of ethyl acetate and hydrogen bromide, according to the equation :—

$$2C_2H_5.OH + 2Br_2 = CH_3.COOC_2H_5 + 4HBr.$$
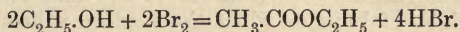
At higher temperatures the reaction becomes very energetic, with the formation of a large number of products. Bromine decomposes oxalic acid and oxalates with the evolution of carbon dioxide. According to Richards and Newsome,[9] the reaction is complete, and takes place in the cold, but more rapidly at high temperatures. The velocity of the reaction increases as the concentration of the oxalic acid rises, until the latter reaches about 3 per cent.,

[1] Cross and Higgin, *Trans. Chem. Soc.*, 1879, **35**, 249.
[2] Schönbein, *Annalen*, 1858, **108**, 169.
[3] Naumann, *Ber.*, 1876, **9**, 1574.
[4] Browne and Shetterly, *J. Amer. Chem. Soc.*, 1908, **30**, 53.
[5] Kretzschmar, *Zeitsch. Elektrochem.*, 1904, **10**, 789.
[6] Wilks, *Proc. Camb. Phil. Soc.*, 1910, **15**, 526.
[7] Spiller, *Chem. News*, 1860, **1**, 38.   [8] Senderens, *Compt. rend.*, 1887, **104**, 175.
[9] Richards and Newsome, *Zeitsch. physikal. Chem.*, 1902, **41**, 544.

after which the velocity decreases. The velocity is decreased by the addition of acids, especially hydrobromic, and increased by neutral salts and alkalies. The main action appears to be :—

$$C_2O_4'' + Br_2 \rightleftharpoons 2CO_2 + 2Br',$$
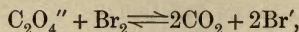
but secondary reactions also take place. Bromine also destroys wood, cork, and other organic substances, staining them yellow, colours starch paste orange-yellow, and destroys the colour of litmus and indigo solutions.

Bromine is largely used either in the free state or as bromides, in medicine, in the coal-tar dye industry, and in photography. It is also used as an oxidising agent in the manufacture of prussian blue, potassium permanganate, etc ; in analytic and synthetic chemistry and as a disinfectant. For the last purpose it is frequently used in the form known as *Bromum solidificatum*, which consists of sticks made of a mixture of kieselguhr, molasses, etc., which are dried, baked, and saturated with liquid bromine. They contain about 75 per cent. of their weight of bromine.

Atomic Weight.—The earlier investigators all obtained values which were too low, chiefly on account of the presence of chlorine in the samples chosen. Thus Balard[1] obtained the value 74·7 by converting potassium bromide into potassium sulphate, and the value 75·3 by reducing silver bromide to metallic silver by means of zinc. Liebig[2] obtained the value 75·2 by the conversion of potassium bromide into silver bromide, and Löwig obtained the value 75·76.

Berzelius,[3] who was the first to obtain an approximately correct value, converted silver bromide into silver chloride by means of chlorine under the influence of heat, and obtained the number 79·36. Marignac[4] obtained the value 79·77 (H = 1) by the conversion of potassium bromate into potassium bromide by means of heat, and 79·75 (H = 1) by adding potassium bromide to a solution of silver nitrate, containing a known weight of silver, until all the latter was precipitated as silver bromide. Dumas,[5] using Berzelius' method, obtained the numbers 80·13, 80·02, and 79·95 in three determinations. Stas obtained the mean value 79·951 (O = 16, Ag = 107·93, Cl = 35·457) by combining the numbers obtained by similar methods to those used by Marignac, with the results of two determinations made by means of the reduction of silver bromate into silver bromide, and four syntheses of silver bromide from its constituent elements. The syntheses of silver bromide by Stas and Marignac correspond to the values 79·914 and 79·919 respectively for the atomic weight of bromine when the modern values Ag = 107·88 and Cl = 35·457 are adopted as the basis of calculation. Baxter[6] has determined the ratio Ag : AgBr by dissolving a known weight of silver in nitric acid and precipitating by means of ammonium bromide, thus obtaining the mean value 79·916 ; and the ratio AgBr : AgCl by converting a known weight of silver bromide into silver chloride by passing chlorine over the heated bromide, thus obtaining the value 79·916 (Cl = 35·473). Goldbaum[7] has determined the atomic weight by means of the electrolysis of a solution of

[1] Balard, *Ann. Chim. Phys.*, 1826, [ii.], **32**, 337.
[2] Liebig, *Schweigger's J. Chem. Phys.*, 1826, **48**, 108.
[3] Berzelius, *Pogg. Annalen*, 1828, **14**, 566.
[4] Marignac, *Bibl. Univ. de Genève*, 1843, **46**, 357.
[5] Dumas, *Ann. Chim. Phys.*, 1859, [iii.], **55**, 162.
[6] Baxter, *J. Amer. Chem. Soc.*, 1906, **28**, 1322 ; *Zeitsch. anorg. Chem.*, 1906, **50**, 382.
[7] Goldbaum, *J. Amer. Chem. Soc.*, 1911, **33**, 35.

sodium bromide, using a rotating silver-plated platinum gauze anode and a mercury cathode, the value found was $79 \cdot 927 \pm 0 \cdot 0014$ (Na = 23·00). By the direct synthesis of hydrogen bromide, Weber[1] has obtained the value 79·911 (H = 1·00762). The International Atomic Weights Commission (1915) have adopted the value 79·92 for the atomic weight of bromine.

Valency.—Bromine usually behaves as a monovalent element, as in the compounds AgBr, KBr, HBr, $CaBr_2$, BrCl, etc., but it is also capable of behaving as a tri-, penta-, or hepta-valent element.

<div align="center">

BROMINE AND HYDROGEN.

HYDROBROMIC ACID.

(Hydrogen Bromide.)

Formula, HBr.   Molecular weight = 80·97.

</div>

Occurrence.—Hydrogen bromide has been found in volcanic gases by Matteucci (see p. 141).

Formation and Preparation.—Bromine resembles chlorine in forming only one definite compound with hydrogen. This contains one atom of each of the constituent elements in the molecule, but the combination cannot be brought about in the cold under the influence of sunlight, as in the case of chlorine. When, however, a mixture of hydrogen and bromine vapour is passed over finely divided metallic platinum, or pieces of charcoal, in a red-hot tube, the elements combine with the formation of gaseous hydrogen bromide.[2] According to Corenwinder,[3] the combination is more readily brought about by passing the gaseous mixture over moderately heated spongy platinum If the mixture be ignited, it burns with a moderately luminous, brassy-yellow flame, and gives off dense fumes of hydrogen bromide. Although sunlight alone will not effect the combination of bromine and hydrogen, it appears to have a considerable influence upon the temperature at which the combination can be brought about. Thus, Kastle and Beatty[4] have shown that although hydrogen and bromine do not combine in the dark at 190° C., the combination is nearly complete at this temperature in the light, the amount of hydrogen bromide formed being proportional to the time of exposure to the light. Even at 100° a small amount of hydrogen bromide is produced in the light. According to Bodenstein and Lind,[5] the reaction between hydrogen and bromine to form hydrogen bromide proceeds to completion at temperatures between 224·7° and 301·3° C., and the rate of change may be expressed by the formula :—

$$dx/dt = k(a - x)(b - x)^{\frac{1}{2}}/[m + x/(b - x)],$$

in which a and b are the initial concentrations of hydrogen and bromine respectively, x is the concentration of the hydrogen bromide at time t, and m is a constant for which these investigators have chosen the value 5·0.

Newth[6] carries out this synthesis in a glass tube about 7 inches in length and $\frac{5}{8}$ of an inch in diameter. The ends of the tube are closed by means of

[1] Weber, *J. Amer. Chem. Soc.*, 1912, **34**, 1294.   See note 7, p. 77.
[2] Merz and Holzmann, *Ber.*, 1889, **22**, 867.
[3] Corenwinder, *Ann. Chim. Phys.*, 1852, [iii.], **34**, 77.
[4] Kastle and Beatty, *Amer. Chem. J.*, 1898, **20**, 159.
[5] Bodenstein and Lind, *Zeitsch. physikal. Chem.*, 1906, **57**, 168.
[6] Newth, *Chem. News*, 1891, **64**, 215.

corks, through each of which pass a small glass tube and a piece of stout wire. The ends of the wires inside the tube are joined together by a short spiral of platinum wire, which is heated to redness by means of an electric current, after hydrogen has been passed through the tube until all the air has been displaced. The hydrogen is then caused to bubble through bromine, contained in a small wash bottle attached to the near end of the tube and kept at a temperature of about 60° by means of a water-bath, before passing into the tube, and the gaseous mixture is caused to unite whilst passing over the platinum spiral. The hydrogen bromide passes out through one or more wash bottles containing water, and is collected by displacement. If the hydrogen be kept in slight excess, the issuing gas will be quite colourless and free from bromine vapour. In order to prevent all chance of an explosion, the narrow tube by which the mixed gases enter the large tube may be plugged with a little wool.

When concentrated sulphuric acid is allowed to react on a metallic bromide, the hydrogen bromide thus formed reduces a part of the sulphuric acid, and bromine is liberated according to the equation :—

$$H_2SO_4 + 2HBr = SO_2 + 2H_2O + Br_2.$$
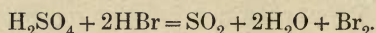
This reaction, therefore, cannot be used for the preparation of hydrogen bromide, as in the formation of hydrogen chloride from a chloride, unless certain precautions are taken. Feit and Kubierschky [1] add dilute sulphuric acid of specific gravity 1·41 to coarsely powdered potassium bromide, and gently warm the mixture until the salt is dissolved. The solution is then distilled until a temperature of 200° C. is attained, when sulphuric acid begins to pass over. The distillation is then stopped, and the distillate redistilled, only that portion which passes over at 126° being collected. The acid thus obtained has a specific gravity of 1·49, and contains 48 per cent. of hydrogen bromide. It is free from sulphuric acid and bromine. Gaseous hydrogen bromide may be obtained from this solution by distillation over anhydrous calcium bromide. Léger [2] prepares the gas by dropping concentrated sulphuric acid on to solid potassium bromide heated in a tubulated retort on the water-bath. The gas is purified from sulphur dioxide and bromine by passing it through a strong solution of bromine in aqueous hydrobromic acid and then through aqueous hydrobromic acid in which amorphous phosphorus is suspended.

Hydrogen bromide is generally prepared by Balard's method, which consists in causing bromine to react with red phosphorus in the presence of water, according to the equation :—

$$2P + 5Br_2 + 8H_2O = 10HBr + 2H_3PO_4.$$
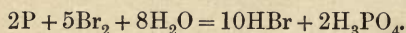
The reaction takes place in two stages. Bromides of phosphorus are first formed, and these are at once decomposed by the water present, thus :—

(1) $PBr_3 + 3H_2O = H_3PO_3 + 3HBr.$
(2) $PBr_5 + 4H_2O = H_3PO_4 + 5HBr.$
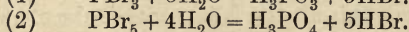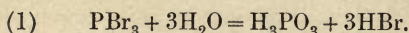
In order to carry out this preparation, a mixture of one part by weight of red phosphorus and two parts of water is placed in the flask A, fig. 28, which is fitted with a rubber bung, through which pass the stem of a stoppered

[1] Feit and Kubierschky, *J. Pharm.*, 1891, [v.], 24, 159 ; *Chem. Zeit.*, 1891, 15, 444.
[2] Léger, *Compt. rend.*, 1892, 115, 946.

dropping funnel and a gas delivery tube. Ten parts of bromine are placed in the funnel, and are then added, drop by drop, to the mixture. Hydrogen bromide is immediately evolved, and each drop is accompanied, in the early part of the operation, by a flash of light. Towards the end of the process it is necessary to heat the flask gently, in order to further the reaction. The evolved gas is passed through the U-tube B, which contains amorphous phosphorus, and serves to prevent any free bromine from passing over, and is collected in the cylinder C, by displacement. Topsoë[1] charges the U-tube B with pieces of yellow phosphorus and broken glass moistened with water, and dries the gas by passing it over fused calcium bromide or phosphorus pentoxide. Linnemann[2] has proposed a modification of this method in which the bromine is dropped upon a mixture of red phosphorus and moist sand covered by a layer of dry sand. Fileti and Crosa[3] have further modified the method by passing the gas into cylinders containing asbestos mixed with red phosphorus and moistened with a concentrated aqueous solution of hydrobromic acid.

Another method of preparing this compound is to pass a current of sulphuretted hydrogen through a layer of bromine contained in a tall cylinder and covered over with a layer of concentrated aqueous hydrobromic acid. The reaction takes place according to the equation :—

$$Br_2 + H_2S = 2HBr + S.$$

FIG. 28.—Preparation of hydrobromic acid.
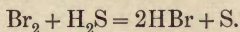
The liberated sulphur is, however, able to combine with the excess of bromine to form sulphur bromide. The evolved gas is purified by passing it through a solution of potassium bromide or hydrogen bromide in which red phosphorus is suspended. According to Recoura,[4] this method of preparation permits the rate of evolution of the gas to be very exactly regulated, and the gas is quite free from bromine vapour and sulphuretted hydrogen. Many other substances containing hydrogen also react with bromine to form hydrogen bromide, among which may be mentioned hydrogen phosphide, ammonia, and hydrazine hydrate.

Hydrogen bromide may also be prepared by heating bromine with sodium sulphite or calcium hypophosphite in the presence of a little water. Gladstone[5] uses a similar method, but replaces the above salts by sodium hyposulphite ; and Léger[6] passes sulphur dioxide into a solution of bromine in concentrated hydrobromic acid, and purifies the evolved gas in the manner described on p. 158. The reaction depends upon the oxidising properties of bromine in the presence of water, thus :—

$$SO_2 + Br_2 + 2H_2O = 2HBr + H_2SO_4.$$
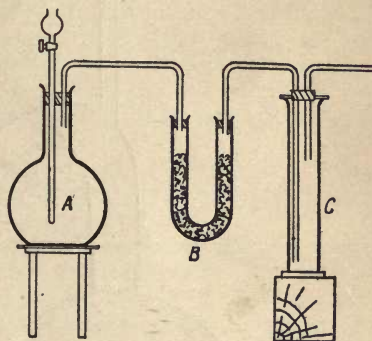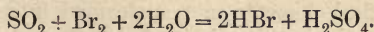
[1] Topsoë, Ber., 1870, 3, 400.
[2] Linnemann, Annalen, 1872, 161, 198.
[3] Fileti and Crosa, Gazzetta, 1891, 21, 64.
[4] Recoura, Compt. rend., 1890, 110, 784.
[5] Gladstone, J. prakt. Chem., 1850, 49, 44.
[6] Léger, Compt. rend., 1892, 115, 946.

According to Scott [1] the employment of sulphur dioxide for the preparation of hydrobromic acid is an improvement on the usual method of obtaining this compound, because phosphorus nearly always contains arsenic, which becomes converted into arsenic bromide during the reaction and passes over with the hydrogen bromide. The preparation is carried out in the apparatus shown in fig. 29. The flask A has a glass tube B sealed into its neck, and the exit tube C is provided with a bulb D, which is just too large to pass into the inner tube E of a Liebig's condenser. The inner tube of the condenser has its end cut off square, and the edges rounded by means of a piece of emery-cloth, so that when the bulb is brought into contact with the end of the tube
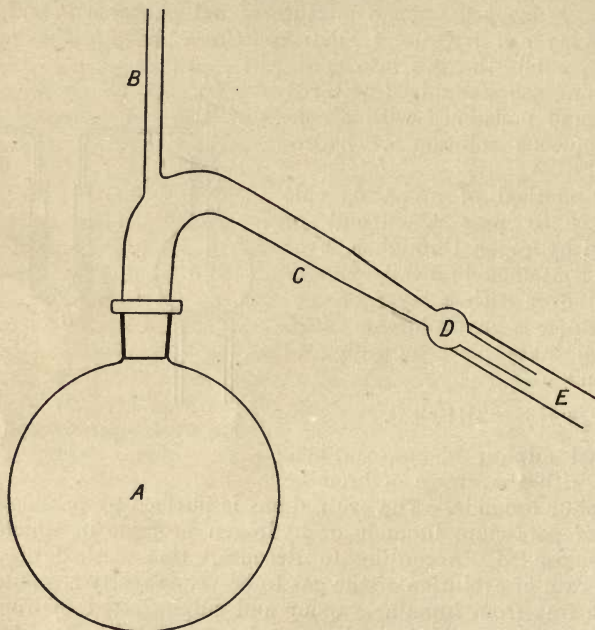
Fig. 29.—Scott's apparatus for preparing hydrobromic acid.

a sufficiently tight joint is obtained to allow of the distillation of the acid without any fuming. A thermometer and a narrow tube through which the sulphur dioxide is passed into the apparatus are passed through B and held in place by a piece of rubber tubing. 350 grams of bromine and 2 litres of water are placed in the flask A, and a rapid current of sulphur dioxide is led into the apparatus, the tube being so arranged that the sulphur dioxide enters the water at about 5 to 10 mm. above the surface of the bromine. When the contents of the flask have been transformed into a pale yellow homogeneous liquid, the solution is distilled, keeping a gentle current of air bubbling through the liquid until the residual acid has a specific gravity of 1·7. The distillate is redistilled ; the first portion which comes over, consisting of water and free halogen, is rejected, and the receiver is changed as soon as

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[1] Scott, *Trans. Chem. Soc.*, 1900, **77**, 648.

the acid begins to distil. The acid is finally redistilled with the addition of a little barium bromide or carbonate, in order to ensure freedom from sulphuric acid.

The action of bromine on organic substances is sometimes made use of for the preparation of hydrogen bromide. Thus, Champion and Pellat[1] allow bromine to fall drop by drop upon paraffin heated to 185° C. and pass the vapour through a U-tube containing phosphorus and broken glass moistened with water in order to free it from all trace of bromine. Willgerodt causes bromine to act upon benzene or toluene, and retains the vapour of the hydrocarbon by means of paraffin. Kastle and Bullock[2] dissolve naphthalene in a small quantity of o-xylene, or kerosene (boiling-point about 150°), in a round-bottomed flask, and then slowly run bromine in by means of a tap funnel, the stem of which dips beneath the surface of the naphthalene solution, when a steady stream of the gas is obtained. This is purified and dried by passing through a Woulff's bottle, which is partially filled with a concentrated solution of hydrobromic acid containing a little red phosphorus in suspension, then through a U-tube containing red phosphorus, and finally through one or more tubes containing phosphorus pentoxide.

Hydrogen bromide is also formed when a stream of hydrogen is passed over certain bromides heated in a glass tube; thus silver bromide in these circumstances yields hydrogen bromide and metallic silver.

An aqueous solution of hydrobromic acid is readily prepared by passing the gas obtained by any of the above methods into cold water. The delivery tube should pass through a cork fitted into the tubulus of a retort arranged as shown in fig. 16, p. 72, with the neck just dipping beneath the surface of the water in the receiver. With this arrangement, should a back rush of water take place, the liquid will not be able to pass into the generating apparatus, but will lodge in the bulb of the retort.

The solution may be obtained directly by passing a current of hydrogen sulphide into water containing an excess of bromine, separating the liberated sulphur by filtration, and distilling the filtrate; also by the action of bromine on sulphur in the presence of water, as in Rother's[3] method, and by the action of bromine on phosphorus in the presence of a considerable amount of water.

It may also be prepared by the decomposition of various bromides by means of sulphuric acid. Thus, when dilute sulphuric acid reacts with barium bromide, double decomposition takes place with the formation of barium sulphate and hydrogen bromide, according to the equation:—

$$H_2SO_4 + BaBr_2 = BaSO_4 + 2HBr.$$
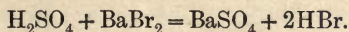
The hydrogen bromide remains in solution in the water with which the sulphuric acid was diluted, and the insoluble barium sulphate is separated by filtration.

Properties. — At ordinary temperatures and atmospheric pressure hydrogen bromide is a colourless gas, with a very irritating odour resembling that of hydrogen chloride, and a sharp acid taste. It has an

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[1] Champion and Pellat, *Compt. rend.*, 1870, **70**, 620.
[2] Kastle and Bullock, *Amer. Chem. J.*, 1896, **18**, 105.
[3] Rother, *Zeitsch. anal. Chem.*, 1883, **22**, 554.

acid reaction, turning blue litmus red, and forms dense white fumes in air. The vapour density at 0° C. under different pressures, as found by Strecker,[1] is shown in the following table, the theoretical value being 2·793 (air = 1) :—

VAPOUR DENSITY OF HYDROGEN BROMIDE.

Pressure.	Vapour Density.	Pressure.	Vapour Density.
mm.		mm.	
690	2·788	216	2·698
622	2·789	211	2·706
512	2·795	204	2·708

According to Biltz,[2] the density is 2·989 at − 15° C., and 2·873 at − 28° C., and normal (2·770) in the neighbourhood of the boiling-point.

Strecker obtained 1·43 for the ratio of the specific heats, from which he calculated the value 0·0820 for the specific heat at constant volume, and the value 0·0573 for the specific heat at constant pressure between 20° and 100° C. According to Müller,[3] the ratio between the two specific heats is 1·364.

The heat of formation, according to Berthelot,[4] is H + Br (solid) = HBr (gas) . . . . + 9400 calories ; H + Br (liquid) = HBr (gas) . . . . + 9500 calories ; H + Br (gas) = HBr (gas) . . . . + 13,500 calories. According to Thomsen,[5] it is H + Br (liquid) = HBr . . . . + 8440 calories.

Cuthbertson and (Mrs) Cuthbertson[6] found the refraction of gaseous hydrogen bromide for the green mercury line (λ = 5461) to be 0·000615.

Faraday[7] liquefied the gas by cooling it to a temperature of − 73° C., obtaining a colourless liquid which solidified to an ice-like mass at − 87°. Melsens[8] has carried out the liquefaction by means of wood charcoal saturated with the gas and placed in a Faraday tube. The melting-point is − 87·9° to − 88·5° C. (Estreicher[9]); − 86·1° (Ladenburg and Krügel[10]); − 86° (M'Intosh and Steele[11]). The boiling-point is − 64·9° (Estreicher) ; − 68·1° (Ladenburg and Krügel); − 68·7° (M'Intosh and Steele). According to Estreicher, and also M'Intosh and Steele,[12] the critical temperature is + 91·3°.

The density of liquid hydrogen bromide, as found by M'Intosh and Steele, is given in the following table :—

[1] Strecker, *Ann. phys. Chem.*, 1882, **17**, 85.
[2] Biltz, *Zeitsch. physikal. Chem.*, 1892, **10**, 354.
[3] Müller, *Ann. phys. Chem.*, 1883, **18**, 104.
[4] Berthelot, *Compt. rend.*, 1877, **84**, 674 ; 1878, **87**, 667.
[5] Thomsen, *Thermochemische Untersuchungen*, 1882, **2**, 28.
[6] Cuthbertson and (Mrs) Cuthbertson, *Phil. Trans.*, 1913, **A, 213**, 1.
[7] Faraday, *Phil. Trans.*, 1845, **135**, 155.
[8] Melsens, *Compt. rend.*, 1875, **77**, 781.
[9] Estreicher, *Zeitsch. physikal. Chem.*, 1896, **20**, 603.
[10] Ladenburg and Krügel, *Ber.*, 1900, **33**, 637.
[11] M'Intosh and Steele, *Proc. Roy. Soc.*, 1904, **73**, 450.
[12] M'Intosh and Steele, *Zeitsch. physikal. Chem.*, 1906, **55**, 129.

DENSITY OF LIQUID HYDROGEN BROMIDE.

Temperature. Absolute. T.	D.	D′.	Temperature. Absolute. T.	D.	D′.
182	2·245	...	195·3	...	2·1932
184	2·237	...	196	2·191	...
184·7	...	2·2337	198	2·183	...
186·0	...	2·2286	198·2	...	2·1823
186	2·229	...	200	2·176	...
188	2·222	...	200·4	...	2·1742
190	2·214	...	202	2·168	...
192	2·206	...	203·8	...	2·1600
193·3	...	2·2047	204	2·160	...
194	2·199	...			

The values under D′ were obtained experimentally, those under D from the formula—

$$D_T = 2·157[1 + 0·0041(204·3 - T)].$$

The vapour pressure of liquid hydrogen bromide, according to the same investigators, is given in the following table :—

VAPOUR PRESSURE OF HYDROGEN BROMIDE.

Temperature, ° C.	Vapour Pressure.		Temperature, ° C.	Vapour Pressure.	
	a mm.	b mm.		a mm.	b mm.
− 65	...	...	− 87	...	283
− 66	...	891	− 87·1	284	...
− 67	...	835	− 88	...	266
− 68	...	785	− 89	...	259
− 68·4	775	...	− 89·3	245	...
− 69	...	743	− 90	...	247
− 70	...	704	− 91	...	239
− 70·7	682	...	− 92	...	222
− 71	...	671	− 92·8	214	...
− 72	...	635	− 93	...	214
− 73	...	609	− 94	...	204
− 74	575	...	− 95	...	195
− 75	...	549	− 96	...	187
− 76	...	519	− 96·3	185	...
− 76·7	501	...	− 97	...	177
− 77	...	483	− 98	...	167
− 78	...	468	− 99	...	157
− 79	...	445	− 100	...	147
− 79·3	431·5	...	− 100·7	142	...
− 80	...	432	− 101	...	136
− 82	...	381	− 102	...	125
− 83	357	...	− 103	...	114
− 84	...	340	− 104	...	102
− 85	...	321	− 104·2	96	...
− 86	...	302	− 105	...	90

The values under a were obtained experimentally, those under b by interpolation.

Whether in the gaseous or liquid state, hydrogen bromide is an extremely bad conductor of electricity. According to M'Intosh and Archibald,[1] the specific conductivity of the liquid is about 0.05×10^{-6}. The aqueous solution is a good electrolyte.

According to Bleekrode,[2] the index of refraction of liquid hydrogen bromide is 1·325 at 10° C. for the D line and 1·330 at 15° C. for white light.

Gaseous hydrogen bromide is readily absorbed by wood charcoal with the evolution of 15,500 calories of heat per gram-molecule.[3] It is also extremely soluble in water, forming a colourless strongly acid solution, which fumes in air when sufficiently concentrated. When the aqueous solution is heated under ordinary pressure it loses mainly hydrogen bromide or water, according as the original solution is concentrated or dilute, until a liquid boiling at 126° under a pressure of 760 mm. is obtained. This acid of constant boiling-point contains from 47 to 48 per cent. of hydrogen bromide, and therefore corresponds to an acid of the composition $HBr.5H_2O$. Roscoe[4] has, however, shown that, as in the case of hydrochloric and hydriodic acids, this liquid is not a definite hydrate, for the composition is a function of the pressure; thus, when the pressure is raised to 1952 mm., an acid boiling at 153° and containing 46·3 per cent. of hydrogen bromide is obtained. According to Berthelot, water dissolves about 600 times its volume of gaseous hydrogen bromide at 10° C. The percentages by weight of the gas in solutions of different densities at 13° to 14° C. were determined by Topsoë,[5] and at 15° C. by Wright[6] and also by Biel.[7]

But the most recent and accurate data are those of Pickering,[8] namely :—

PERCENTAGE OF HYDROGEN BROMIDE IN AQUEOUS SOLUTIONS OF DIFFERENT DENSITIES AT 15° C.

Percentage of HBr.	Density.	Percentage of HBr.	Density.	Percentage of HBr.	Density.
0	0·9991	42·978	1·4233	57·691	1·6514
5·459	1·0387	44·799	1·4491	58·798	1·6694
10·226	1·0757	46·986	1·4792	59·478	1·6814
18·851	1·1228	48·987	1·5095	60·507	1·7004
20·536	1·1653	51·494	1·5481	61·545	1·7200
25·766	1·2167	52·723	1·5679	62·310	1·7334
31·482	1·2784	53·936	1·5875	63·465	1·7524
34·736	1·3164	54·813	1·6015	63·931	1·7630
39·382	1·3745	55·701	1·6167	65·186	1·7845
41·295	1·4002	56·458	1·6285	...	...

[1] M'Intosh and Archibald, *Zeitsch. physikal. Chem.*, 1906, **55**, 150.
[2] Bleekrode, *Proc. Roy. Soc.*, 1884, **37**, 339 ; *Rec. trav. chim.*, 1885, **4**, 77.
[3] Favre, *Ann. Chim. Phys.*, 1874, [v.], **1**, 209.
[4] Roscoe, *Annalen*, 1860, **116**, 214.   [5] Topsoë, *Ber.*, 1870, **3**, 404.
[6] Wright, *Chem. News*, 1871, **23**, 242.   [7] Biel, *Pharm. Journ.*, 1882, [iii.], **12**, 666.
[8] Pickering, *Phil. Mag.*, 1893, [v.], **36**, 111. The density of water at 4° C. is taken as unity.

Bakhuis Roozeboom[1] has determined the weight of hydrogen bromide dissolved in 1 gram of water at various temperatures under a pressure of 760 mm. The values obtained are as follows :—

Temperature, ° C.	Weight of HBr. Grams.	Temperature, ° C.	Weight of HBr. Grams.
− 25	2·550	+ 10	2·103
− 20	2·473	25	1·930
− 15	2·390	50	1·715
− 10	2·335	75	1·505
− 5	2·280	100	1·300
0	2·212		

As in the case of solutions of hydrogen chloride, the solution of hydrogen bromide in water does not take place in accordance with Henry's law. Thus, at 0° C., under a pressure of hydrogen bromide equal to 5 mm. of mercury, 1 gram of water dissolves 1·085 grams of hydrogen bromide, whilst at the same temperature, under a pressure of 760 mm., it dissolves 2·212 grams.[2]

The vapour pressure of aqueous solutions of hydrogen bromide at various temperatures is shown in the following table :—

VAPOUR PRESSURE OF AQUEOUS SOLUTIONS OF HYDROGEN BROMIDE.

(Bakhuis Roozeboom.)

Temperature, ° C.	Solution saturated at 13°.		Solution saturated at 8°.		Solution saturated at − 5°.	
	Tension, mm.	HBr dissolved in 1 Part H_2O.	Tension, mm.	HBr dissolved in 1 Part H_2O.	Tension, mm.	HBr dissolved in 1 Part H_2O.
− 25	100	2·056	140	2·120	300	2·268
− 20	130	2·056	180	2·120	375	2·267
− 15	175	2·056	250	2·119	470	2·266
− 11·3	216	2·055	310	2·118	570	2·265
− 5	298	2·055	430	2·117	730	2·264
− 0	380	2·054	540	2·116		

The solution of the gas in water is accompanied by a greater evolution of heat than in the case of gaseous hydrogen chloride or hydrogen iodide. The heat of solution of 1 gram-molecule of hydrogen bromide in a large quantity of water is 20,000 calories (Berthelot[3]); 19,084 calories (Favre[4]); 19,940 calories (Thomsen[5]). The heat of solution of 1 gram-molecule of hydrogen bromide in n gram-molecules of water, and the heat of dilution of the solutions

[1] Bakhuis Roozeboom, *Rec. trav. chim.*, 1885, **4**, 102.
[2] Bakhuis Roozeboom, *ibid.*, 1886, **5**, 323.   [3] Berthelot, *Compt. rend.*, 1873, **76**, 682.
[4] Favre, *Ann. Chim. Phys.*, 1874, [v.], **1**, 209.
[5] Thomsen, *Thermochemische Untersuchungen*, 1882, **2**, 400.

thus obtained in $(200 - n)$ gram-molecules of water at 15°, as found by Bakhuis Roozeboom,[1] are given below :—

Value of n.	Heat of Solution of 1 Molecule of HBr.	Heat of Dilution in $200 - n$ Molecules of H_2O.
	Calories.	Calories.
0	0	2·0000
1·84	13·260	6·740
2·00	13·920	6·080
2·25	14·650	5·350
2·50	15·200	4·800
2·75	15·700	4·300
3	16·150	3·850
4	17·300	2·700
5	17·900	2·100
6	18·400	1·600
7	18·800	1·200
8	18·900	1·100
10	19·000	1·000

According to Berthelot,[2] the heat of dilution $HBr + nH_2O$ in a large quantity of water can be calculated from the formula :—

$$Q = \frac{12 \cdot 06}{n} - 0 \cdot 29,$$

when n does not exceed 40. For higher values of n it is better to use the formula :—

$$Q = \frac{12 \cdot 06}{n}.$$

The specific and molecular heats of solutions of $HBr.nH_2O$, according to Bakhuis Roozeboom, are shown in the following table :—

Value of n.	Specific Heat.	Molecular Heat.	Value of n.	Specific Heat.	Molecular Heat.
1·84	0·3827	43·6	4·92	0·4711	79·8
2·00	0·3553	41·5	5·69	0·5005	91·7
2·48	0·3524	44·2	7·01	0·5397	111·7
2·72	0·3608	46·8	10	0·6154	160·5
2·92	0·3742	49·9	20·12	0·7641	338·5
4·013	0·4340	66·4	50	0·8876	870
4·65	0·4640	76·3	100	0·9402	1770
4·85	0·4694	78·9	200	0·9688	3566

[1] Bakhuis Roozeboom, *Rec. trav. chim.*, 1886, **5**, 323.
[2] Berthelot, *Compt. rend.*, 1873, **76**, 679.

The molecular conductivity of a solution of 1 gram-molecule of hydrobromic acid in v litres, as found by Ostwald,[1] is as follows :—

Value of v.	Molecular Conductivity.	Value of v.	Molecular Conductivity.
2	364	64	402
4	377	128	405
8	385	256	405
16	391	512	406
32	398	1024	405

The molecular rotation found by Perkin[2] for a saturated solution of hydrogen bromide is shown in the following table :—

Temperature, ° C.	Molecular Magnetic Rotation.
22·0	8·061
21·0	8·415
18·0	8·547
16·5	8·519

Berthelot[3] obtained a solid hydrate of very nearly the composition $HBr.2H_2O$ by passing a current of hydrogen bromide into a saturated solution of the gas at 0° C. and cooling to $-25°$. The melting-point of this hydrate was found to be $-11°$, and the heat of formation in solution was 14,200 calories. Pickering[4] has shown that the strongest aqueous solution of the gas contains 69 per cent. of hydrogen bromide, thus corresponding to the composition of the hydrate $HBr.2H_2O$. The melting-point of this solution is $-11°$. According to Bakhuis Roozeboom,[5] the heat of formation of this hydrate at $-15°$ C. is 16,920 calories, and the density is 2·11 at the same temperature. Berthelot[3] recognised the existence of a second hydrate of the composition $HBr.4·5H_2O$. According to Bakhuis Roozeboom,[5] a monohydrate of the composition $HBr.H_2O$ is formed at low temperatures by the action of gaseous hydrogen bromide on the dihydrate under pressure. A trihydrate and tetrahydrate have been prepared by Pickering,[4] who regards the existence of a pentahydrate as probable.

Gaseous hydrogen bromide is not decomposed when it is passed through a red-hot tube, nor is it decomposed by the action of sunlight.[6] According to Hautefeuille,[7] it is decomposed when heated above 700° C., but, if free from oxygen, it is stable below this temperature. Falckenstein[8] has shown that 0·50 per cent. of the hydrogen bromide is dissociated at 1024° C., 0·73 per cent. at 1108° C., and 1·08 per cent. at 1222°. The liberated bromine is

[1] Ostwald, *J. prakt. Chem.*, 1885, [ii.], **31**, 433.
[2] Perkin, *Trans. Chem. Soc.*, 1889, **55**, 680.
[3] Berthelot, *Ann. Chim. Phys.*, 1878, [v.], **14**, 368 ; *Compt. rend.*, 1878, **86**, 279.
[4] Pickering, *Phil. Mag.*, 1893, [v.], **36**, 111.
[5] Bakhuis Roozeboom, *Rec. trav. chim.*, 1885, **4**, 108 ; 1886, **5**, 363.
[6] Berthelot, *Ann. Chim. Phys.*, 1900, [vii.], **21**, 206.
[7] Hautefeuille, *Compt. rend.*, 1867, **64**, 705.
[8] Falckenstein, *Zeitsch. physikal. Chem.*, 1909, **68**, 270 ; 1910, **72**, 113.

itself partly dissociated at these temperatures according to the reversible equation :—

$$Br_2 \rightleftharpoons 2Br.$$
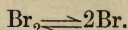
When perfectly dry it does not react with oxygen in the cold, even under the influence of light, but slow decomposition takes place if the gases are moist.[1] When the mixed gases are heated to 500–550° for about 10 hours the reaction is complete :—[2]

$$4HBr + O_2 = 2H_2O + 2Br_2.$$
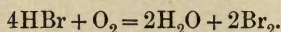
Fluorine and chlorine react with the gas to form hydrogen fluoride and hydrogen chloride, according to the equations :—

(1) $2HBr + F_2 = 2HF + Br_2.$ (2) $2HBr + Cl_2 = 2HCl + Br_2.$
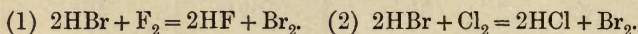
If an excess of chlorine be employed, this combines with the liberated bromine to form bromine chloride :—

$$Cl_2 + Br_2 = 2BrCl.$$
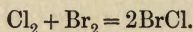
Phosphorus does not act upon a solution of hydrogen bromide in the cold, but reacts vigorously with the gas at a temperature of 100° to 120° in sealed tubes, with the formation of phosphonium bromide, which sublimes over in the cool part of the tube.[3] The gas also reacts with moist red phosphorus under the influence of sunlight, forming phosphonium bromide and phosphoric acid, according to the equation :—

$$2P + 3H_2O + HBr = PH_4Br + H_3PO_3.$$
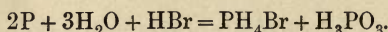
Most metals are converted into bromides when brought into contact with gaseous hydrogen bromide, hydrogen being liberated. This reaction takes place in the cold in the case of iron, zinc, silver, mercury, and the alkali metals, but most of the other metals require a more or less elevated temperature. Gold and platinum remain unattacked even when heated to a temperature of 100° C. in sealed tubes. Aqueous hydrobromic acid dissolves all the metals which are attacked by hydrochloric acid, with the formation of the corresponding bromides and the evolution of hydrogen.

Ammonia and phosphine combine directly with the gas to form ammonium and phosphonium bromide respectively :—

(1) $NH_3 + HBr = NH_4Br.$ (2) $PH_3 + HBr = PH_4Br.$
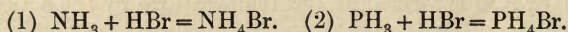
Metallic oxides decompose the gas with the formation of the corresponding bromides and water. In the case of lead monoxide and silver oxide the reaction takes place at ordinary temperatures, thus :—

(1) $PbO + 2HBr = PbBr_2 + H_2O.$ (2) $Ag_2O + 2HBr = 2AgBr + H_2O.$
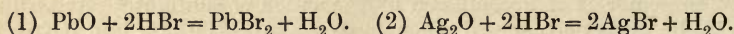
The metallic peroxides and acid oxides react with aqueous hydrobromic acid with the formation of the corresponding bromides and free bromine. Ditte[4] has shown that selenium dioxide and tellurium dioxide combine with hydrogen bromide to form the compounds $SeO_2.2HBr$ and $2TeO_2.3HBr$, and that the latter is decomposed at about 50° C., yielding the compound $TeO_2.HBr$, which is decomposed in its turn at about 400°, yielding the oxybromide TeOBr. Hydrogen bromide is partially decomposed by concentrated sulphuric acid.

[1] Richardson, *Trans. Chem. Soc.*, 1887, **51**, 801.
[2] Berthelot, *Compt. rend.*, 1878, **87**, 667.   [3] Damoiseau, *Compt. rend.*, 1880, **91**, 883
[4] Ditte, *Ann. Chim. Phys.*, 1877, [v.], **10**, 82.

A mixture of nitric acid and aqueous hydrobromic acid dissolves gold and platinum, thus resembling *aqua regia*. The mixture gradually decomposes into nitrogen peroxide, water, and free bromine, the change being hastened by heating. According to Austen,[1] gaseous hydrogen bromide does not react with nitric acid. Smith and Meyer[2] have shown that hydrogen bromide completely decomposes nitrates and arsenates, and partially decomposes vanadates, but has very little action upon phosphates. Haslam[3] has shown that when pure barium sulphate is boiled for a quarter of an hour with a 40 per cent. aqueous solution of hydrogen bromide it is dissolved to the extent of 1 part in 2500. Hydrogen bromide forms additive compounds with many organic substances. Archibald and M'Intosh[4] have prepared the acetone compound $CH_3.CO.CH_3.HBr$ (melting-point, 9° C.), the ether compound $C_2H_5.O.C_2H_5.HBr$ (melting-point, 40° C.), and the alcohol compound $C_2H_5.OH.2HBr$ (melting-point, 85° C.). According to M'Intosh,[5] who has also prepared similar compounds with acetaldehyde, acetic acid, and ethyl acetate, acetic acid does not combine with hydrogen bromide at low temperatures, but Tschitschibabin[6] obtained the compound $2CH_3.CO_2H.HBr$ (melting-point, 7 to 8° C.) by saturating glacial acetic acid with dry hydrogen bromide and keeping the solution in a cool place.

Hydrogen Perbromide.—Bromine is soluble in aqueous hydrobromic acid, forming a dark red liquid from which it is again evolved on exposure to the air, or on heating. The solution appears to contain loose compounds of the type $HBr.Br_2$, which are known as *hydrogen perbromides*. Similar solutions are obtained when bromine is dissolved in aqueous potassium bromide ; in this case with the formation of compounds of the type $KBr.Br_2$, which may be regarded as salts of the hydrogen compounds. Part of the bromine may be precipitated from these concentrated solutions by adding water ; in the case of the solutions in hydrobromic acid, a solution containing 3 molecules of bromine to 1 of hydrogen bromide is finally obtained.[7] The remaining bromine cannot be precipitated by means of water. From the heat of solution of bromine in hydrochloric acid, Berthelot[8] concluded that these substances combined to form the compound $HCl.Br_2$. Richter-Rjewskaja[9] has measured the partial pressure at 30° C. of bromine in hydrobromic acid solutions containing from 3·2 to 10 molecules of water per molecule of hydrogen bromide, and from 9·85 to 96·7 per cent. of bromine. The results obtained lead to the conclusion that solutions containing more than a certain proportion of bromine are not homogeneous, but only emulsions, and that chemical combination appears to take place between the bromine and the acid with the formation of hydrogen perbromides. Büchner and Karsten[10] have investigated the melting-point curve of mixtures of dry bromine and hydrogen bromide in sealed tubes. An eutectic containing about 5 molecules per cent. bromine appears to be formed at about −95° C., but there is no indication of any

[1] Austen, *Amer. Chem. J.*, 1887, **11**, 172.
[2] E. F. Smith and F. L. Meyer, *J. Amer. Chem. Soc.*, 1895, **17**, 735.
[3] Haslam, *Chem. News*, 1886, **53**, 87.
[4] Archibald and M'Intosh, *Trans. Chem. Soc.*, 1904, **85**, 919.
[5] M'Intosh, *Trans. Chem. Soc.*, 1906, **28**, 588.
[6] Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1104.
[7] Bineau, *Ann. Chim. Phys.*, 1843, [iii.], **7**, 264.
[8] Berthelot, *Compt. rend.*, 1885, **100**, 761.
[9] Richter-Rjewskaja, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 441.
[10] Büchner and Karsten, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **11**, 504.

combination of the substances to form a definite chemical compound. These authors conclude that hydrogen bromide and bromine only combine in ionising solvents, the union probably being determined by the bromine ion.

BROMIDES.

The salts of hydrobromic acid are known as bromides. In addition to the normal salts there are acid bromides, double bromides, and perbromides, and also the somewhat doubtful sub-bromides.

The **normal** metallic bromides are formed when the metals are brought into contact with bromine (see p. 154). The combination usually takes place at ordinary temperatures. Thus Kablukoff[1] prepares aluminium bromide by gradually dropping bromine from a tap-funnel on to aluminium chips heated in a glass retort. The bromide which passes over into the receiver is redistilled, when it is obtained as a colourless liquid solidifying to a white mass. Ducelliez and Raynaud[2] prepare anhydrous manganous bromide, $MnBr_2$, by adding dry bromine to finely divided manganese under ether and driving off the ether of crystallisation by means of heat.

Bromides are also formed when bromine vapour is passed over metallic oxides, hydroxides, and carbonates heated to red heat.

$$(1) \quad 4KOH + 2Br_2 = 4KBr + 2H_2O + O_2.$$
$$(2) \quad 2BaO + 2Br_2 = 2BaBr_2 + O_2.$$
$$(3) \quad 2CaCO_3 + 2Br_2 = 2CaBr_2 + 2CO_2 + O_2.$$
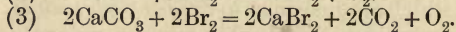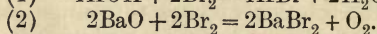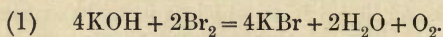
In the case of silver oxide the reaction takes place at ordinary temperatures.

Bromides are also formed by the action of bromine on the corresponding chlorides or iodides, a large excess of bromine being required in the case of the chlorides.

Most metals and metallic oxides yield bromides when gaseous hydrogen bromide is led over them. In many cases, however, the reaction only takes place at a more or less elevated temperature. Bourion[3] prepares anhydrous metallic bromides by acting upon the corresponding oxides at temperatures below red heat with sulphur chloride and hydrogen bromide. Thus, by distilling sulphur chloride at a temperature of 135° in a current of hydrogen bromide on to heated thoria, thorium tetrabromide is obtained. Similarly, chromium sesquioxide gives chromium tribromide. The more readily reduced oxides, such as those of nickel and cobalt, can be converted into anhydrous bromides without the use of sulphur chloride. Barre[4] prepared bromides from the corresponding oxides by means of sulphur bromide at high temperatures. In some cases oxybromides were obtained : thoria gave the oxybromide $ThOBr_2$, and uranoso-uranic acid gave uranyl bromide, UO_2Br_2. There was no reaction with silica even at 900° C.

The bromides are prepared by dissolving metals or metallic oxides in the aqueous acid, by heating the corresponding bromates, either alone or with carbon, when oxygen is given off and the bromide remains behind (see p. 185), and by the liberation of iodine from iodides by means of bromine, thus :—

$$2NaI + Br_2 = 2NaBr + I_2.$$
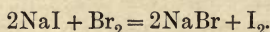
[1] Kablukoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 485.
[2] Ducelliez and Raynaud, *Compt. rend.*, 1914, **158**, 576 ; *Bull. Soc. chim.*, 1914, [iv.], **15**, 273.   [3] Bourion, *Compt. rend.*, 1907, **145**, 243.
[4] Barre, *Bull. Soc. chim.*, 1912, [iv.], **11**, 433.

The normal metallic bromides resemble the chlorides in their properties. They are mostly solid at ordinary temperatures, are readily fusible, and are volatile at high temperatures. They are less fusible and less volatile than the corresponding iodides, but more fusible and more volatile than the corresponding chlorides.[1] Most of the bromides are colourless, but some are more or less highly coloured. Thus, silver bromide is very pale yellow, auric bromide is dark brown, and aurous bromide is greenish yellow, palladium bromide is brown, platinous bromide is brown, and platinic bromide is nearly black, nickel bromide is salmon-yellow, colbalt bromide is green, chromium tribromide is black, bismuth bromide is golden yellow, and copper bromide is black. The hydrated bromide is sometimes different in colour from the anhydrous salt, the colour depending upon the degree of hydration. Thus, Guareschi[2] has obtained the following cobalt bromides:—

$CoBr_2.6H_2O$	red prisms.	$CoBr_2.2H_2O$	reddish violet.
$CoBr_2.5\frac{1}{2}H_2O$	rose colour.	$CoBr_2.H_2O$	blue.
$CoBr_2.5H_2O$	pink.	$CoBr_2.\frac{1}{2}H_2O$	?
$CoBr_2.4H_2O$	reddish violet.	$CoBr_2$(anhydrous)	green.

The bromides of silver, copper, mercury, and palladium are insoluble in water, those of lead and thallium are very sparingly soluble, less so than the corresponding chlorides, and most of the other bromides are readily soluble. Antimony bromide is decomposed by water, with the formation of a basic bromide, bismuth bromide is decomposed with the formation of an insoluble oxybromide. A small amount of water converts arsenic tribromide into an oxybromide, and a larger quantity decomposes it into arsenious oxides and hydrogen bromide. Tin tetrabromide is slowly decomposed by cold water with the formation of the hydroxide, and the same change takes place rapidly on boiling. Nearly all the metallic bromides are stable when heated; those of gold and platinum, however, lose their bromine. According to Guareschi[3] anhydrous lithium bromide evolves bromine when heated to its melting-point, whilst ammonium bromide sublimes and dissociates when heated, but does not evolve free bromine.

When heated in contact with chlorine, bromides lose their bromine and are converted into chlorides, thus:—

$$2KBr + Cl_2 = 2KCl + Br_2.$$
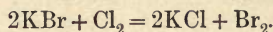
Potilitzin[4] kept sodium bromide in contact with an excess of chlorine in a sealed tube at 20° for thirty-six hours, when 5·48 per cent. of the bromine had been removed. Anhydrous barium bromide was not acted upon by chlorine at temperatures below 100° C. According to Küster,[5] potassium bromide cannot be completely converted into chloride by heating it in a current of dry chlorine, as in the conversion of potassium iodide, unless the operation be carried out at such a high temperature that the potassium begins to volatilise, but in the presence of water the conversion is completed at moderate temperatures. When gaseous chlorine is led into, or chlorine water is added to, a solution of a metallic bromide, the latter immediately becomes coloured yellow by the liberated bromine. Gaseous hydrogen chloride decomposes metallic bromides at red heat, with the formation of the corre-

[1] Bunsen, *Annalen*, 1866, **138**, 263.
[2] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, **48**, 929.
[3] Guareschi, *ibid.*, 1913, **48**, 735.   [4] Potilitzin, *Ber.*, 1879, **12**, 695.
[5] Küster, *Zeitsch. anorg. Chem.*, 1898, **18**, 77.

sponding chlorides and hydrogen bromide. Bromides, with the exception of silver bromide, are decomposed when heated with nitric acid, with the formation of a metallic oxide and the liberation of bromine. By distilling potassium bromide with concentrated nitric acid Landolt[1] obtained a reddish-brown vapour which appeared to consist of a mixture of oxybromides of nitrogen. Concentrated sulphuric acid reacts with the metallic bromides with the formation of the corresponding sulphates or hydrogen sulphates, water, sulphur dioxide, and free bromine. In the case of the alkali metals the first reaction is the formation of the acid sulphate and hydrogen bromide, thus :—

$$KBr + H_2SO_4 = KHSO_4 + HBr.$$
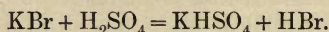
The hydrogen bromide then reacts with the remaining sulphuric acid to form water, sulphur dioxide, and free bromine, according to the equation :—

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$
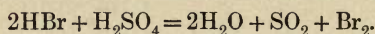
On heating, the acid sulphate is also decomposed by the hydrogen bromide :—

$$2KHSO_4 + 2HBr = K_2SO_4 + SO_2 + 2H_2O + Br_2.$$
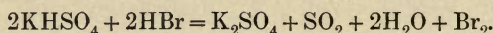
The bromides are decomposed with the liberation of bromine when heated with a mixture of manganese dioxide and sulphuric acid (see p. 142). According to Müller and Kircher,[2] manganese dioxide and acetic acid also decompose the bromides, but lead peroxide and acetic acid have no action upon them. These peroxides also slowly act upon the bromides in neutral solution. De Koninck[3] has shown that when potassium bromide is melted with potassium dichromate it is decomposed with the liberation of bromine, according to the equation :—

$$6KBr + 5K_2Cr_2O_7 = 8K_2CrO_4 + Cr_2O_3 + 3Br_2.$$
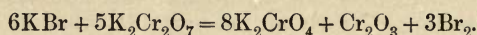
The reaction takes place more rapidly in a stream of oxygen than in carbon dioxide. When a bromide is heated with a chlorate in the presence of a small quantity of acid, it is decomposed with the liberation of bromine.

Acid Bromides.—A few of the normal bromides combine with hydrogen bromide and water to form hydrated acid bromides. Thus, Löwig has prepared the mercury compound $HgBr_2.HBr.4H_2O$. Birnbaum prepared the iridium compound $IrBr_3.3HBr.3H_2O$. Thomsen[4] prepared the compound $AuBr_3.HBr.5H_2O$ by adding bromine to spongy gold, and, as soon as the reaction was over, adding a molecule of hydrobromic acid of sp. gr. 1·38 for each atom of gold, and then more bromine until the gold had completely dissolved. On standing in a cool place a crystalline mass was obtained. The crystals are acicular in form and of a dark cinnabar-red colour. They melt in their own water of crystallisation at a temperature of 25° C. Bromostannic acid, $SnBr_4.2HBr.8H_2O$, was prepared by Rayman and Preis[5] by the action of hydrobromic acid upon tin tetrabromide, and also by the action of tin tetrabromide and bromine upon amyl alcohol. It has also been prepared and investigated by Seubert and Schurmann.[6] The sodium, calcium, strontium, manganese, and iron salts of this acid crystallise with 6 molecules of water,

[1] Landolt, *Annalen*, 1860, **116**, 177.   [2] Müller and Kircher, *Ber.*, 1882, **15**, 812.
[3] De Koninck, *Bull. de l'Association belge des chim.*, 1903, **17**, 15, 157.
[4] Thomsen, *J. prakt. Chem.*, 1876, [ii.], **13**, 337.
[5] Rayman and Preis, *Annalen*, 1884, **223**, 323.
[6] Seubert and Schurmann, *Ber.*, 1887, **20**, 794.

the nickel salts with 8 molecules, and the magnesium and cobalt salts with 10 molecules. Halberstadt [1] obtained the compound $PtBr_4.2HBr.9H_2O$ when preparing platinum bromide by Meyer and Züblin's method. Hydrogen cupric bromide was prepared by Sabatier [2] by passing gaseous hydrogen bromide into a concentrated solution of cupric bromide until the anhydrous cupric bromide which first separated out was redissolved, and cooling the liquid, when black, lustrous, readily decomposed crystals were obtained. Analysis indicated the composition $3CuBr_2.2HBr.6H_2O$, but Sabatier considered the composition $CuBr_2.HBr.2H_2O$ to be more probable. The tellurium compound $TeBr_4.HBr.5H_2O$ was obtained by Metzner [3] by dissolving tellurous anhydride in a cold saturated solution of hydrobromic acid at $-15°$ C., and passing gaseous hydrogen bromide into the liquid. The compound forms slender, red, prismatic needles which melt at $20°$ with liberation of hydrogen bromide, and fume in moist air. Thomas [4] has obtained a solution of the thallium compound $TlBr_3.HBr$ by direct combination of thallium tribromide and hydrobromic acid. The compound has not been isolated.

Double Bromides.—A very large number of double bromides is known. These are usually prepared by dissolving various bromides in an aqueous solution of an alkaline bromide. Thus, lead bromide dissolves in an aqueous solution of potassium bromide, and a double bromide crystallises out on cooling the solution. The composition of this double bromide depends upon the proportions of the lead and potassium salt taken, thus :—

$$(1) \quad PbBr_2 + KBr = PbBr_3K \text{ or } PbBr_2.KBr.$$
$$(2) \quad PbBr_2 + 2KBr = PbBr_4K_2 \text{ or } PbBr_2.2KBr.$$

In a similar manner Sabatier [5] prepared anhydrous cupric potassium bromide, $CuBr_3K$, or $CuBr_2.KBr$, and Rayman and Preis have obtained hydrated double bromides of tin, sodium, calcium, strontium, manganese, etc. (see p. 172). Gutbier and Hüttlinger [6] have prepared double bromides of rhodium and the alkali metals by heating a mixture of finely powdered rhodium and alkali bromide in a stream of bromine. Potassium rhodipentabromide, K_2RhBr_5, forms brilliant dark green plates, ammonium rhodipentabromide, $(NH_4)_2RhBr_5$, is a greenish black, and the corresponding cæsium and rubidium salts are brilliant green in colour. All these rhodium alkali bromides give up the bromine which is attached to the rhodium when heated in a stream of hydrogen. According to Sandonnini and Scarpa,[7] lithium and silver bromides form solid solutions which crystallise at temperatures intermediate between the melting-points of the components, and the bromides of sodium and silver behave similarly.

According to Wells [8] the valency of the metal of the negative haloid has no influence on the type of double bromide formed, and the molecules of the alkali halides have nearly the same combining power as the molecules of the negative halides.

The double bromides have been classified into types by Pfeiffer [9] as shown in the following table :—

[1] Halberstadt, *Ber.*, 1884, **17**, 2962.
[2] Sabatier, *Compt. rend.*, 1894, **118**, 1260.
[3] Metzner, *Compt. rend.*, 1897, **124**, 1448.
[4] Thomas, *Compt. rend.*, 1902, **134**, 545.
[5] Sabatier, *Compt. rend.*, 1894, **118**, 1260.
[6] Gutbier and Hüttlinger, *Ber.*, 1908, **41**, 210.
[7] Sandonnini and Scarpa, *Atti R. Accad. Lincei*, 1913, [**v.**], **22**, ii. 517.
[8] Wells, *Amer. Chem. J.*, 1901, **26**, 389.
[9] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, **31**, 231.

TABLE OF TYPES OF DOUBLE BROMIDES.

I. Cu.	II. Cu.	II. Mg.	II. Zn.	II. Cd.	II. Hg.
$CuBr_2M$ $CuBr_3M_2$ Cu_2Br_3M	$CuBr_3M$ $CuBr_4M_2$	$MgBr_3M$	... $ZnBr_4M_2$ $ZnBr_4M_3$	$CdBr_3M$ $CdBr_4M_2$ $CdBr_5M_3$ $CdBr_6M_4$ $Cd_2Br_7M_3$ $Cd_3Br_8M_2$ Cd_4Br_9M	$HgBr_3M$ $HgBr_4M_2$ $HgBr_5M_3$ ... Hg_2Br_5M $Hg_6Br_{13}M$

II. Sn.	II. Pb.	II. Mn.	II. Co.	II. Ni.	II. Pd.	II. Pt.
$SnBr_3M$ $SnBr_4M_2$	$PbBr_3M$ $PbBr_4M_2$ ... $PbBr_6M_4$ Pb_2Br_5M	... $MnBr_4M_2$	... $CoBr_4M_2$ $CoBr_5M_3$	$NiBr_3M$	... $PdBr_4M_2$	... $PtBr_4M_2$

III. Al.	III. Tl.	III. As.	III. Sb.	III. Bi.	III. Cr.	III. Fe.
$AlBrM$	$TlBr_4M$ ... $TlBr_6M_3$ $Tl_2Br_9M_3$	... ... $As_2Br_9M_3$	... $SbBr_5M_2$ $SbBr_6M_3$ $SbBr_7M_4$ $Sb_2Br_9M_3$ $Sb_3Br_{16}M_7$	$BiBr_4M$ ... ... $Bi_3Br_9M_3$	... $CrBr_5M_2$	$FeBr_4M$ $FeBr_5M_2$

III. Au.	III. Ir.	IV. Ti.	IV. Th.	IV. Sn.	IV. Pb.	IV. Se.
$AuBr_4M$	... ... $IrBr_6M_3$	... $TiBr_6M_2$	... $ThBr_6M_2$	... $SnBr_6M_2$ $SnBr_8M_4$	... $PbBr_6M_2$	... $SeBr_6M_2$

IV. Te.	IV. U.	IV. Os.	IV. Ir.	IV. Pt.	V. Sb.
$TeBr_5M$ $TeBr_6M_2$	... UBr_6M_2	... $OsBr_6M_2$	... $IrBr_6M_2$	... $PtBr_6M_2$	$SbBr_7M_2$

In addition to these double bromides, many similar compounds have been prepared by combining various bromides with different fluorides, chlorides, and iodides. In this manner Defacqz[1] has prepared the fluorobromides of the alkaline earths. Thus, by heating 10 parts of manganese fluoride and 60 parts of barium bromide for one and a half hours at 800 to 1000° C., and then cooling, he obtained a mixture of manganese bromide and barium fluorobromide, $BaF_2.BaBr_2$. The reaction takes place according to the equation :—

$$MnF_2 + 2BaBr_2 = BaF_2.BaBr_2 + MnBr_2.$$
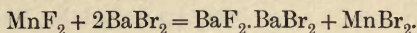
The barium fluorobromide was isolated by treating the cold mass with hot alcohol, in order to dissolve out the manganese bromide, and decanting off the clear liquid. It consists of transparent colourless lamellæ which are slowly decomposed by cold water, and rapidly on boiling. Dilute mineral acids readily decompose it, and so does concentrated sulphuric acid, but it is soluble in concentrated nitric and hydrochloric acids. The strontium and calcium fluorobromides are prepared in the same manner as the barium compound and have nearly the same properties : they are, however, more readily decomposed by water. Two isomeric thallium chlorobromides of the composition $Tl_4Cl_3Br_3$ are known, one form crystallising in orange-coloured plates and the other in blood-red crystals. Thomas[2] has prepared a hydrated thallium chlorobromide, apparently of the composition $TlClBr_2.4H_2O$, by the direct combination of thallous chloride and bromide. On attempting to dehydrate this salt, the compound $Tl_3Cl_2Br_4$ was obtained. By the action of chlorine on thallous bromide the same investigator also obtained the hydrated compound $TlCl_2Br.4H_2O$. Many other similar compounds, such as SbF_5Br, $\left[Tl \begin{smallmatrix} Br_3 \\ Cl_3 \end{smallmatrix} \right] Tl_3$, $\left[Hg \begin{smallmatrix} Cl_2 \\ Br \end{smallmatrix} \right] K_2$, and $\left[Pt \begin{smallmatrix} Cl_4 \\ Br_2 \end{smallmatrix} \right] K_2$, have also been prepared. Many of the bromides also combine with ammonia, and with metallic oxides to form oxybromides. According to Scarpa,[3] silver nitrate and silver bromide form a compound $AgNO_3.AgBr$. Marsh[4] has shown that some double bromides, and also some of the double salts containing bromine and another halogen, absorb ether to form compounds, such as :—

$$LiBr.HgBr_2,4(C_2H_5)_2O.$$
$$LiBr.HgI_2,4(C_2H_5)_2O.$$
$$LiI.HgBr_2,5(C_2H_5)_2O.$$
$$LiBr.HgCl_2,(C_2H_5)_2O.$$
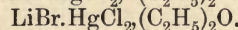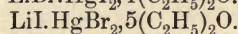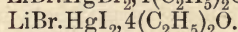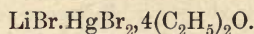
Perbromides or Polybromides.—The perbromides may be regarded as salts of the hydrogen perbromides (see p. 169) or as additive compounds of the normal bromides and bromine. They are unstable bodies, being readily reduced to normal bromides, with the liberation of free bromine. Löwig observed that solutions of alkaline bromides are capable of dissolving a large amount of bromine, producing a dark red liquid which gives up its additional bromine on heating. Berthelot[5] has shown that a cold, nearly saturated, solution of barium chloride, or strontium chloride, absorbs a considerable amount of bromine, apparently with the formation of perbromides,

[1] Defacqz, *Ann. Chim. Phys.*, 1904, [viii.], **1**, 337 ; *Compt. rend.*, 1904, **138**, 197.
[2] Thomas, *Compt. rend.*, 1901, **133**, 735 ; 1902, **134**, 545 ; 1906, **142**, 838.
[3] Scarpa, *Atti R. Accad. Lincei*, 1913, [v.], **22**, ii. 452.
[4] Marsh, *Trans. Chem. Soc.*, 1910, **97**, 2297.
[5] Berthelot, *Compt. rend.*, 1882, **94**, 1619 ; 1885, **100**, 761.

and also that a perbromide of barium of the composition $BaBr_4$ probably exists. Meyer [1] found that the bromides of calcium, strontium, and barium form a deep red pasty mass of crystals which give off bromine at ordinary temperatures until only the colourless bromides are left behind. The perbromides of these metals could not, however, be isolated. Boericke,[2] from the study of the solubility of bromine in aqueous solutions of potassium bromide, concludes that the greater part of the dissolved bromine probably exists as KBr_3, but that compounds of the formula KBr_5 and KBr_7 are also formed in the solution. These results have been confirmed by Worley,[3] who has investigated the solubility of bromine in aqueous potassium bromide solutions over a wide range of concentrations at 18·5° and 26·5° C. For concentrations below 0·1 gram-molecule per litre the curves obtained correspond with the formation of molecules of KBr_3. With higher concentrations the curves indicate the probable formation of small quantities of compounds containing more bromine, such as KBr_5 and KBr_7. Bell and Buckley [4] have made solubility determinations of bromine in aqueous solutions of sodium bromide at 25° C., and have shown that the ratio of bromine to sodium bromide is about Br_2 : $NaBr$ in dilute solutions ; but in more concentrated solutions the ratio is greater, and in nearly saturated solutions it is about $2·5Br_2$: $NaBr$. Tinkler [5] has shown that although neither bromine water nor a dilute aqueous solution of potassium bromide exhibits any absorption in the ultra-violet, on adding the solution of potassium bromide to the bromine water a well-defined absorption band is seen in this part of the spectrum. Solutions of the bromides of sodium, rubidium, calcium, strontium, barium, magnesium, and cadmium, and also of hydrobromic acid, ammonium bromide, and tetra-methyl- and tetra-ethyl-ammonium bromide, were added to bromine water, and in each case exactly the same spectrum as that given when potassium bromide was used was obtained. It therefore appears that all these solutions contain the group Br_3, to the presence of which the absorption band is due. Experiments were also carried out in which solutions of different chlorides were added to the bromine water, and in this case also a spectrum showing one absorption band, which was the same in each case, was obtained. It was therefore concluded that each of these solutions contained the same group $ClBr_2$. The bromine appeared to combine more readily with a bromide than with a chloride. Joseph and Jinendradasa [6] have investigated the constitution of bromine solutions by means of their colour. When a soluble bromide is added to bromine water, the colour of the solution is considerably diminished, the results obtained with the bromides of sodium, potassium, and hydrogen being similar. In each case the decrease in colour depends upon the amount of bromide added until the concentration of the latter has reached normal, when any further addition produces little effect on the colour. It therefore appears that when such bromides are added to bromine water, the colour of the resulting solution is due in part to combined and in part to free bromine, until the concentration of the bromide reaches normal, when the whole of the bromine is in a state of combination. The chief reaction causing the change

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[1] Meyer, *Zeitsch. anorg. Chem.*, 1902, **30**, 113.
[2] Boericke, *Zeitsch. Elektrochem.*, 1905, **11**, 57.
[3] Worley, *Proc. Chem. Soc.*, 1905, **21**, 209.
[4] Bell and Buckley, *J. Amer. Chem. Soc.*, 1912, **34**, 14.
[5] Tinkler, *Trans. Chem. Soc.*, 1907, **91**, 996 ; 1908, **93**, 1611.
[6] Joseph and Jinendradasa, *Proc. Chem. Soc.*, 1910, **26**, 233 ; *Trans. Chem. Soc.*, 1911, **99**, 275.

of colour appears to be the formation of a tribromide. Using a similar method, Joseph [1] has also investigated the existence of polybromides in nitrobenzene solution. From the study of the solubility of bromine in aqueous mercuric bromide, and also of iodine in aqueous mercuric bromide, Herz and Paul [2] conclude that the compounds $HgBr_4$ and $HgBr_2I_2$ exist.

Sub-Bromides.—Compounds of silver with bromine which contain a smaller amount of bromine than the normal bromides are formed by the action of light on the latter, as in the case of photographic plates which have been exposed to light. These products are known as sub-bromides, but there is considerable doubt whether they are true compounds or only mixtures. Carey Lea [3] has produced a series of coloured compounds of silver with bromine (and also with chlorine and iodine) which he calls photosalts, and which appear to be compounds of the normal and sub-bromides, and these salts have since been prepared in various ways by other investigators.[4] Vogel [5] has also prepared a blackish substance which he regards as a sub-bromide of silver, of the composition Ag_4Br_2 or $2Ag.2AgBr$; according to Emszt,[6] however, this substance is only a mixture, and differs in behaviour from the substances produced by light on the photographic plate. Hilpert and Herrmann [7] have shown that metallic silver and copper can be coupled with arsenic tribromide to form the compounds $Ag_3.AsBr_3$ and $7Cu.2AsBr_3$.

COMPOUNDS OF BROMINE WITH THE OTHER HALOGENS.

Bromine combines with fluorine to form bromine trifluoride, BrF_3, and with iodine to form iodine monobromide, IBr (see p. 230). It is also generally considered to combine with chlorine to form bromine monochloride, BrCl, but the existence of this compound has been disproved, as has also the existence of bromine trichloride, $BrCl_3$, which Thomas and Dupuis have described.

Bromine Trifluoride, BrF_3—Moissan [8] found that fluorine combines with bromine vapour in the cold to form a definite compound, and that the same reaction takes place with liquid bromine. The composition of the substance was, however, first established by Lebeau.[9] The reaction is accompanied by a luminous flame when bromine vapour is used, but no flame is produced when the fluorine is caused to combine with dry liquid bromine. The same compound is formed when metallic bromides are decomposed by means of fluorine :—

$$KBr + 2F_2 = KF + BrF_3.$$
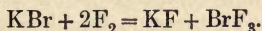
According to Prideaux,[10] liquid fluorine and solid bromine do not react together and no fluoride other than the trifluoride appears to exist.

[1] Joseph, *Trans. Chem. Soc.*, 1913, **103**, 1554.
[2] Herz and Paul, *Zeitsch. anorg. Chem.*, 1914, **85**, 214.
[3] Carey Lea, *Amer. J. Sci.*, 1887, [iii.], **33**, 349, 480, and 489, **34**, 33 ; 1892, [iii.], **44**, 322.
[4] Lüppo-Cramer, *Zeitsch. Chem. Ind. Kolloide*, 1907, **2**, 135 ; 1908, **2**, 360 ; **3**, 33 and 135.   [5] Vogel, *J. Soc. Chem. Ind.*, 1900, **19**, 374.
[6] Emszt, *Zeitsch. anorg. Chem.*, 1901, **28**, 346.
[7] Hilpert and Herrmann, *Ber.*, 1913, **46**, 2218.
[8] Moissan, *Le Fluor et ses Composés*, 1900, 123.
[9] Lebeau, *Compt. rend.*, 1905, **141**, 1018 ; *Bull. Soc. chim.*, 1906, [iii.], **35**, 148 ; *Ann. Chim. Phys.*, 1906, [viii.], **9**, 241.
[10] Prideaux, *Proc. Chem. Soc.*, 1905, **21**, 240 ; 1906, **22**, 19 ; *Trans. Chem. Soc.*, 1906, **89**, 316.

At ordinary temperatures bromine trifluoride is an almost colourless liquid which fumes strongly in contact with air, becoming orange-yellow in colour. The vapour is very irritating, and quickly attacks the skin. On cooling, it solidifies to a crystalline mass consisting of long prisms. According to Lebeau, the melting-point is very nearly 5° C. and the boiling-point appears to lie between 130° and 140° C.: the point could not be exactly determined because the vapour attacked the thermometer. Bromine trifluoride is very reactive, resembling fluorine. The reaction with water is very violent: oxygen is liberated, and a mixture of hypobromous acid, hydrofluoric acid, and traces of bromic acid is obtained. A similar reaction takes place when an aqueous solution of an alkaline carbonate is employed. Iodine displaces the bromine from the trifluoride with a considerable evolution of heat. Even at − 10° the solid compound reacts with this element with incandescence to form iodine pentafluoride and free bromine. Sulphur does not react with solid bromine trifluoride, but burns with a bright flame in the liquid at temperatures just above the melting-point with the formation of fluorides and bromides of sulphur. Red phosphorus and powdered arsenic, antimony, boron, and most metals burn vigorously when thrown in the liquid trifluoride, or into its vapour. Silicon burns with even more vigour than in fluorine. Carbon burns vigorously in the liquid if the temperature be slightly raised. The compound behaves in a similar manner to fluorine towards organic compounds.

Bromine Monochloride, BrCl.—A supposed compound of bromine and chlorine was first obtained in 1826 by Balard,[1] by passing a current of chlorine over bromine and condensing the vapours which were given off by means of a refrigerating agent. According to Bornemann,[2] the combination of these two elements only takes place at temperatures below 10° C. Krutwig [3] has also claimed to prepare the compound by the action of chlorine upon silver bromate at 50° C., silver chloride and oxygen being formed at the same time :—

$$2Cl_2 + 2AgBrO_3 = 2AgCl + 2BrCl + 3O_2.$$
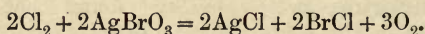
He regarded it as possible that in this reaction an intermediate compound ClO_3Br is first formed, and that this splits up into bromine monochloride and oxygen. Thomas and Dupuis [4] considered that bromine reacts with liquid chlorine to form the monochloride which solidifies at − 39° C. and combines with a further quantity of chlorine to form a red compound which solidifies at − 79°, boils at − 19°, and decomposes below 0°. This mixture was considered by its discoverers to be bromine trichloride. The actual existence of chlorides of bromine has been definitely disproved by Lebeau. From a study of the cooling curves of mixtures of bromine and chlorine, Lebeau [5] considers that these elements form mixed crystals but no definite compounds. Karsten [6] also concludes, from the consideration of the cooling-, solidifying-, and boiling-point curves of mixtures of these two elements, that definite com-

[1] Balard, *Ann. Chim. Phys.*, 1826, [ii.], **32**, 371.
[2] Bornemann, *Annalen*, 1877, **189**, 184.
[3] Krutwig, *Ber.*, 1881, **14**, 304.
[4] Thomas and Dupuis, *Compt. rend.*, 1906, **143**, 282.
[5] Lebeau, *Compt. rend.*, 1906, **143**, 589.
[6] Karsten, *Zeitsch. anorg. Chem.*, 1907, **53**, 365. For other researches on this subject see Andrews and Carlton, *J. Amer. Chem. Soc.*, 1907, **29**, 688 ; Brown, *Phil. Mag.*, 1891, [v.], **31**, 449 ; Berthelot, *Compt. rend.*, 1880, **90**, 841 ; **91**, 951 ; 1882, **94**, 1619 ; Merle, *Monit. Scient.*, 1896, [iv.], **9**, 695, 773 ; and Schönbein, *J. prakt. Chem.*, 1863, **88**, 483.

pounds of bromine and chlorine have no existence. On the other hand, from the contraction of volume observed when bromine and chlorine are mixed, Andrews and Carlton consider that actual chemical combination takes place.

BROMINE AND OXYGEN.

No oxides of bromine have hitherto been obtained with certainty. Gay-Lussac [1] believed he had prepared an oxide, hypobromous anhydride, Br_2O, by the action of bromine on dry mercuric oxide, but Dancer [2] has shown that no such oxide is produced by this reaction. Kämmerer [3] has also described a very unstable oxide, bromine peroxide, BrO_2, which he thought he had prepared by distilling a solution of bromic acid; but the existence of this oxide is not admitted. Richards has also attempted to prepare bromous anhydride, Br_2O_3, but without success. If any oxides of bromine are capable of existence, they must be extremely unstable compounds, on account of the small affinity of bromine for oxygen, as shown by the heat of combination (see p. 205). Two oxy-acids—hypobromous acid, $HOBr$, and bromic acid, $HBrO_3$—are known, though only in dilute solution and in the form of their salts. Perbromic acid was described by Kämmerer, who thought he had prepared it by the action of dry bromine vapour upon perchloric acid, but M'Ivor,[4] Muir,[5] Wolfram,[6] and others have shown that the acid cannot be prepared by this method. Muir has also tried to prepare perbromic acid by the electrolysis of bromic acid, and Robertson [7] has attempted to prepare it by acting upon potassium perchlorate with bromine in the presence of potassium bromide, by acting upon sodium per-iodate with bromine, and by heating potassium bromate with lead peroxide, but both investigators obtained negative results. Richards has described a method by which he believes bromous acid, $HBrO_2$, may be prepared, but the existence of the acid has not been established.

HYPOBROMOUS ACID.

Formula, HOBr.

This acid was discovered in 1826 by Balard.[8]

Preparation.—It is prepared by adding precipitated mercuric oxide, little by little, to bromine water and shaking. An insoluble oxybromide of mercury, Hg_2OBr, is formed, together with mercuric hypobromite and hypobromous acid. A dilute aqueous solution of the acid is obtained from this mixture by distilling the filtered liquid at 40° C. under a pressure of 50 mm. The mercuric oxide used in this reaction can be replaced by mercuric acetate, mercuric nitrate, silver nitrate, or silver oxide.[9, 10]

An aqueous solution of the acid may also be obtained by passing carbon dioxide into a very dilute solution of a hypobromite and then distilling under reduced pressure as described above.[10]

[1] Gay-Lussac, *Compt., rend.*, 1842, **14**, 951.   [2] Dancer, *Annalen*, 1863, **125**, 237.
[3] Kämmerer, *J. prakt. Chem.*, 1863, **90**, 190 ; *Pogg. Annalen*, 1869, **138**, 390, 391.
[4] M'Ivor, *Chem. News*, 1876, **33**, 35.
[5] Muir, *Trans. Chem. Soc.*, 1874, **27**, 324 ; 1876, **30**, 469.
[6] Wolfram, *Annalen*, 1879, **198**, 95.   [7] Robertson, *Chem. News*, 1912, **106**, 50.
[8] Balard, *Ann. Chim. Phys.*, 1826, [ii.], **32**, 337 ; *Pogg. Annalen*, 1835, **34**, 148.
[9] Spiller, *Chem. News*, 1860, **1**, 38 ; 1862, **6**, 249.
[10] Dancer, *Annalen*, 1863, **125**, 237 ; *J. Chem. Soc.*, 1862, **15**, 477.

According to Lebeau,[1] a solution of HBrO is obtained when bromine reacts with fluorine in the presence of water, and also when bromine trifluoride is allowed to slowly react with water.

Properties.—The dilute aqueous solution of hypobromous acid obtained by any of the above methods is a straw-coloured liquid which can be distilled without decomposition at a temperature of 40° C. under a pressure of 50 mm., but is decomposed into bromine and bromic acid at temperatures above about 60° C. The solutions do not contain more than 1 gram of hypobromous acid per 100 c.c. According to Berthelot,[2] the heat of formation of dilute solutions of hypobromous acid is Br_2 (liquid) $+ O +$ water $= 2BrOH$ (dilute) . . . $- 13,400$ calories ; Br_2 (gas) $+ O +$ water $= 2BrOH$ (dilute) . . . $- 6000$ calories. According to Thomsen,[3] the heat of formation of $2BrOH$ in aqueous solution from liquid bromine, oxygen, and water is $- 16,160$ calories.

The solution is immediately decomposed by hydrogen peroxide, with the formation of hydrogen bromide and oxygen :—[4]

$$HOBr + H_2O_2 = HBr + H_2O + O_2,$$
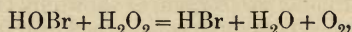
and by urea and other nitrogen compounds, with the liberation of nitrogen and carbon dioxide, thus :—

$$CO(NH_2)_2 + 3HOBr = CO_2 + N_2 + 2H_2O + 3HBr.$$
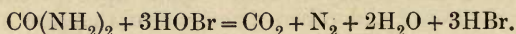
It is also decomposed by silver oxide with the liberation of oxygen :—

$$Ag_2O + 2HOBr = 2AgBr + H_2O + O_2.$$
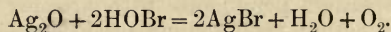
Aqueous solutions of alkaline hypobromites are obtained when bromine is added to dilute solutions of alkaline hydroxides or carbonates (see p. 127). Calcium hypobromite can be prepared by the action of bromine vapour upon solid calcium hydroxide. A red powder is produced which resembles bleaching-powder in odour and properties, and on dissolving this compound in cold water a solution of calcium hypobromite is obtained. Barium hypobromite can be prepared in a similar manner.

Hypobromites can also be obtained by the action of the acid upon metallic hydroxides, thus :—

$$HOBr + NaOH = NaOBr + H_2O,$$
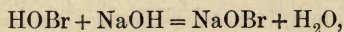
and by the electrolysis of aqueous solutions of alkali bromides, alkali hydroxide is formed at the cathode and alkali hypobromite at the anode.

The solutions of hypobromites are more unstable than those of the hypochlorites ; even when very dilute, they gradually change at ordinary temperatures into a mixture of bromide and bromate, and the change becomes rapid on heating, or in concentrated solution. The presence of an excess of alkali increases the stability of these solutions ; on the other hand, they are decomposed by dilute acids, even carbon dioxide, with the liberation of bromine. The decomposition of hypobromites in alkaline solutions containing a small but constant concentration of hydroxyl ions, and the influence of electrolytes on the hypobromite reaction, have been investigated by

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[1] Lebeau, *Ann. Chim. Phys.*, 1906, [viii.], **9**, 241.
[2] Berthelot, *Compt. rend.*, 1877, **84**, 680 ; *Ann. Chim. Phys.*, 1878, [v.], **13**, 19.
[3] Thomsen, *Thermochemische Untersuchungen*, 1882, **11**, 401.
[4] Tanatar, *Ber.*, 1899, **32**, 1013.

Skrabal.[1] The decomposition is represented at constant temperature by the following kinetic equation :—

$$-d[HBrO]/dt = [H^{\cdot}]\{[Br'] + e[E]\} K[HBrO]^2,$$

where E is the concentration of the electrolyte and e and K are constant factors. An equilibrium

$$HBrO + Br' + H^{\cdot} \rightleftharpoons Br_2 + H_2O,$$

or

$$2HBrO + Br' + H^{\cdot} \rightleftharpoons HBr_3O + H_2O,$$
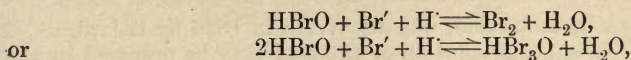
must be quickly set up. Electrolytes accelerate the reaction. Hypobromite solutions react with hydrogen peroxide, evolving oxygen :—

$$H_2O_2 + KOBr = KBr + H_2O + O_2,$$
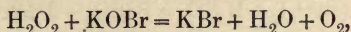
and decompose nitrogenous compounds such as urea in the same manner as hypochlorites, with the liberation of nitrogen. The decomposition is not complete under ordinary circumstances, but may be increased by the addition of dextrose or sucrose. This reaction is used in the estimation of these nitrogen compounds. According to Le Compt,[2] all the nitrogen can be liberated by nascent sodium hypobromite in the presence of an excess of alkali, but Garnier[3] has shown that this method fails with a 2 per cent. solution of urea, though it is quite satisfactory with a 1 per cent. solution. According to Corradi,[4] the amount of nitrogen obtained by the reaction of sodium hypobromite upon carbamide is from 9·8 to 14·6 per cent. too low, but on adding sucrose, lead acetate, and sodium carbonate, and filtering, the results obtained are only about 2·4 per cent. too low.

Constitution.—Hypobromous acid is a very weak acid, and therefore cannot have the constitution HBr : O, as Vorländer[5] has shown that the group H.E : E is characteristic of strong acids. It is therefore considered to have the constitution H.O.Br, in which the bromine is monovalent and the reactive group is missing. The acid may be regarded as water H.O.H, in which one of the hydrogen atoms is replaced with bromine, the arguments in favour of this constitution being the same as those for the constitution of hypochlorous acid (see p. 127).

BROMOUS ACID.

Formula, $HBrO_2$.

By adding an excess of liquid bromine to a concentrated aqueous solution of silver nitrate, Richards[6] obtained an oxy-acid of bromine which contained 2 atoms of oxygen to 1 of bromine. This could either be a mixture of hypobromous and bromic acids or an acid of the composition $HBrO_2$. As, however, it was found that no hypobromous acid was present, it was thought that the acid was bromous acid. The existence of the acid has not yet been confirmed, but Clarens[7] has shown that when hypobromites are converted

[1] Skrabal, *Monatsh.*, 1909, **30**, 51 ; 1911, **32**, 185.
[2] Le Compt, *J. Pharm. Chim.*, 1903, [vi.], **17**, 471.
[3] Garnier, *J. Pharm. Chim.*, 1904, [vi.], **19**, 137.
[4] Corradi, *Boll. chim. farm.*, 1906, **45**, 181.
[5] Vorländer, *Ber.*, 1901, **34**, 1632.
[6] Richards, *J. Soc. Chem. Ind.*, 1906, **25**, 4.
[7] Clarens, *Compt. rend.*, 1913, **156**, 1998 ; **157**, 216.

into bromates they pass through an intermediate stage in which they exist as bromites, and concludes that the bromate is ultimately produced by the oxidation of the bromite by the unchanged hypobromite.

BROMIC ACID.

Formula, $HBrO_3$.

This acid, like hypobromous acid, was discovered in 1826 by Balard.[1]

Preparation.—An aqueous solution of the acid may be prepared by the decomposition of barium bromate by means of sulphuric acid, the reaction taking place according to the equation :—

$$Ba(BrO_3)_2 + H_2SO_4 = BaSO_4 + 2HBrO_3.$$
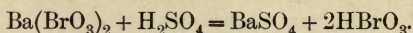
In order to carry out this preparation, 50 parts of sulphuric acid are added to 200 parts of powdered barium bromate in water. When the precipitated barium sulphate has settled, the clear liquid is decanted off, and the excess of sulphuric acid removed by means of baryta water. The liquid is then filtered in order to remove the barium sulphate and concentrated by evaporation. According to Rammelsberg,[2] the acid obtained by this method is not pure, but contains either baryta or sulphuric acid.

A purer solution may be obtained by the action of bromine on silver bromate suspended in hot water ; the reaction takes place according to the equation :—

$$3Br_2 + 5AgBrO_3 + 3H_2O = 5AgBr + 6HBrO_3.$$
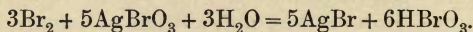
The excess of bromine is driven off by heat and the silver bromide removed by decantation.[3]

When a solution of hypobromous acid (see p. 179) is heated, it is decomposed with the formation of a mixture of bromic and hydrobromic acids. The hydrobromic acid may be removed by adding the correct amount of silver oxide, allowing the silver bromide to settle, and decanting off the clear solution of bromic acid.

A solution of the acid may also be obtained by passing a current of chlorine monoxide into bromine under water :—

$$5Cl_2O + Br_2 + H_2O = 2HBrO_3 + 5Cl_2.$$
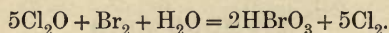
The chlorine which remains in solution is driven off by heat.

According to Riche,[4] the best method of preparing bromic acid is by the electrolysis of bromine water, when the bromine is oxidised by the nascent oxygen.

Properties. — Aqueous solutions of bromic acid are colourless and odourless, and possess a very acid taste but are not corrosive to the skin ; they first redden and then decolorise litmus. These solutions are stable when dilute, but gradually become unstable as the concentration increases. When concentrated by heating on the water-bath, they begin to decompose with evolution of oxygen and bromine when they contain 13·19 per cent. of bromic acid, but by concentration *in vacuo* in the cold a liquid containing

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[1] Balard, *Ann. Chim. Phys.*, 1826, [ii.], **32**, 327.
[2] Rammelsberg, *Annalen*, 1841, **40**, 247.
[3] Kämmerer, *J. prakt. Chem.*, 1862, **85**, 452.
[4] Riche, *Compt. rend.*, 1858, **46**, 348.

50·59 per cent. of the acid can be obtained. On further concentration, however, bromine and oxygen are evolved. The solution containing 50·59 per cent. of bromic acid probably corresponds to the hydrate $HBrO_3.7H_2O$. From the determination of the electric conductivity of solutions of bromic acid, Ostwald[1] concludes that the acid is weaker than hydrobromic acid but stronger than iodic acid. The molecular conductivity of the aqueous solutions is shown in the following table :—

Value of v.	Molecular Conductivity.	Value of v.	Molecular Conductivity.
32	359	256	390
64	370	512	396
128	381	1024	401

According to Berthelot,[2] the heat of formation of bromic acid is Br_2 (liquid) $+ 5O + H_2O +$ water $= Br_2O_5.H_2O$ (dilute) . . . $-49,600$ calories. Thomsen[3] obtained the value $-43,520$ calories.

Iodine decomposes bromic acid with the formation of iodic acid and the liberation of bromine, according to the equation :—

$$I_2 + 2HBrO_3 = 2HIO_3 + Br_2.$$
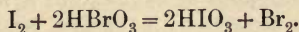
The reaction takes place in the cold, but more quickly on heating. There is no reaction with chlorine. Bromic acid is a powerful oxidising agent. According to Feit and Kubierschky,[4] sulphuretted hydrogen, sulphur dioxide, and thiosulphuric acid are all completely oxidised to sulphuric acid and water by the aqueous solutions of this acid, nitrous acid is oxidised to nitric acid, oxalic acid to carbon dioxide, and water and ferrous salts to ferric salts. The solutions also oxidise the halogen hydrides with the formation of water. In the case of hydrogen iodide the corresponding halogen bromide is also formed, but with hydrogen bromide bromine is liberated. Ostwald[5] has shown that the speed of the reaction between bromic and hydriodic acids is increased by the addition of various acids, and that the accelerating effect is usually proportional to the affinity constant of the acid as determined by its conductivity. There are, however, some exceptions, notably hydrobromic acid, which increases the velocity to a considerably greater extent than would be expected from the value of its affinity constant. Noyes[6] has shown that the reaction is of the second order and that the velocity is proportional to the square of the concentration of the acid. The retarding action of the liberated iodine on the reaction has been investigated by Meyerhoffer[7] and also by

[1] Ostwald, see Kohlrausch-Holborn, *Leitvermögen der Elektrolyte*, 1898, p. 167 ; *J. prakt. Chem.*, 1885, [ii.], **32**, 300.
[2] Berthelot, *Compt. rend.*, 1877, **84**, 674.
[3] Thomsen, *Thermochemische Untersuchungen*, 1882, vol. ii. p. 401 ; *J. prakt. Chem.*, 1875, [ii.], **11**, 133.
[4] Feit and Kubierschky, *Chem. Zeit.*, 1891, **15**, 351.
[5] Ostwald, *Zeitsch. physikal. Chem.*, 1888, **2**, 127.
[6] Noyes, *Zeitsch. physikal. Chem.*, 1896, **19**, 599.
[7] Meyerhoffer, *Zeitsch. physikal. Chem.*, 1888, **2**, 585.

Burchard.[1] The reduction of bromic acid by hydrogen bromide is much slower than by hydrogen iodide. This reaction has been studied by Judson and Walker,[2] who find that it is quadrimolecular and takes place according to the ionic equation :—

$$2H^{.} + Br' + BrO_3' = HBrO + HBrO_2,$$
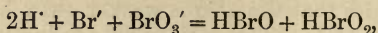
the acids formed being very lightly ionised. When a large excess of sulphuric acid is added, the reaction becomes bimolecular. When pure bromic and hydrobromic acids are employed, the velocity is directly proportional to the concentration of the bromate and bromine ions, and proportional to the square of the concentration of the hydrogen ions. The reactions

$$HBr + HBrO = H_2O + Br_2, \qquad 3HBr + HBrO_2 = 2H_2O + 2Br_2$$
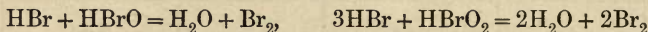
take place with great rapidity. According to Luther and Sammet,[3] the equilibrium constant of the reaction

$$HBrO_3 + 5HBr \rightleftharpoons 3Br_2 + 3H_2O$$
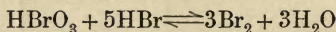
cannot be directly determined by chemical means; but from the E.M.F. of the cell $Pt(H^{.}, BrO_3', Br_2) - (Br_2, Br')Pt$ it was found to be 7.3×10^{-34} at 25° C. According to Tanatar,[4] hydrogen peroxide reduces bromic acid to hydrobromic acid, a little free bromine being produced by the oxidising action of the peroxide on the hydrogen bromide first formed. Vitali[5] has shown that manganous sulphate is oxidised to a manganic salt, forming a violet-red solution, when treated with bromic acid, or with a mixture of sulphuric acid and a bromate ; and that when salts of hydroxylamine or phenylhydrazine are heated with bromic acid, the acid is reduced with the liberation of bromine. Many organic compounds are partly or wholly oxidised by solutions of this acid ; the action with oxalic acid and with the salts of hydroxylamine and phenylhydrazine has already been mentioned ; alcohol and ether are quickly converted into acetic acid and paper is oxidised, bromine being liberated from the acid. There is no reaction with sulphuric and nitric acids.

Bromates —Bromic acid is monobasic and forms only one series of salts, such as $KBrO_3$ and $Ba(BrO_3)_2$, which are known as bromates.

Many bromates may be obtained by dissolving the corresponding oxides, hydroxides, or carbonates in the aqueous solution of the acid.

The alkali bromates may be prepared by the action of bromine on a hot solution of the corresponding alkali hydroxide : only one-sixth of the bromine is oxidised to bromate, the remainder being converted into bromide :—

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$
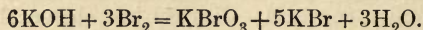
The bromate is then separated from the bromide by crystallisation. According to Feit and Kubierschky,[6] the salt obtained by this method always contains some bromide, but Wagner[7] has shown that it can be obtained pure by repeated recrystallisation.

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[1] Burchard, *Zeitsch. physikal. Chem.*, 1888, **2**, 796 ; see Clarke, *J. Physical Chem.*, 1906, **10**, 679.   [2] Judson and Walker, *Trans. Chem. Soc.*, 1898, **73**, 410.
[3] Luther and Sammet, *Zeitsch. Elektrochem.*, 1905, **11**, 293.
[4] Tanatar, *Ber.*, 1899, **32**, 1013.
[5] Vitali, *Boll. chim. farm.*, 1899, **38**, 201.
[6] Feit and Kubierschky, *Chem. Zeit.*, 1891, **15**, 351.
[7] Wagner, *Zeitsch. anorg. Chem.*, 1899, **19**, 427.

Potassium bromide may be converted into potassium bromate by saturating an alkaline solution of the salt with chlorine, the reaction taking place according to the equation :—

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O,$$
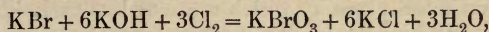
or by fusing it with potassium chlorate :—

$$KBr + KClO_3 = KBrO_3 + KCl.$$
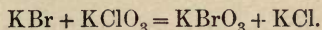
In either case the bromate is separated from the chloride by crystallisation.

The alkali bromates may also be obtained by the electrolysis of solutions of the corresponding bromides.[1] According to Kretzschmar,[2] the velocity coefficient of the formation of bromates is about one hundred times as great as that of the formation of chlorates.

Properties.—The bromates are colourless salts which are nearly all moderately soluble in water ; silver bromate is insoluble in cold, but soluble in hot, water ; mercury and barium bromates are sparingly soluble. Some bromates, such as those of potassium, sodium, silver, and mercury, lose all three atoms of oxygen at red heat, leaving the corresponding bromide behind ; others, such as those of magnesium, aluminium, and zinc, give off five atoms of oxygen and two of bromine, yielding the corresponding metallic oxide. Barium bromate begins to decompose at 260° to 265° C., and the decomposition becomes vigorous at about 300° C., bromine vapour being given off in addition to oxygen. According to Ross,[3] solutions of bromates are decomposed by ultra-violet light with the liberation of bromine. The amount liberated is inversely proportional to the square of the distance of the solution from the source of light. It is very little affected by the concentration, for concentrations between $N/2$ and $N/50$, but is increased by the addition of sugar to the solution. Iodine displaces the bromine from bromates with the formation of the corresponding iodate and free bromine, according to the equation :—

$$2KBrO_3 + I_2 = 2KIO_3 + Br_2.$$
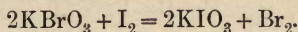
Chlorine has but little action on bromates ; but, according to Potilitzin,[4] if an aqueous solution of sodium bromate be saturated with chlorine and kept for a long time in the dark, bromine is liberated, and the solution contains sodium chloride together with free chloric and bromic acids. Solutions of the salts, like those of the free acid, have powerful oxidising properties and readily oxidise carbon, sulphur, antimony, sulphuretted hydrogen, sulphur dioxide, etc. According to Vitali,[5] bromates are reduced by the same reducing agents as chlorates. Salts of hydrazine and hydroxylamine reduce the alkali bromates, the reactions taking place according to the equations :—

(1) $2NaBrO_3 + 3NH_2.NH_2 = 2NaBr + 6H_2O + 3N_2.$
(2) $4NaBrO_3 + 12NH_2.OH = 4NaBr + 18H_2O + 6N_2 + 3O_2.$
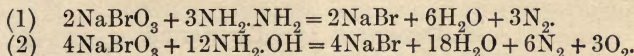
According to Schlötter,[6] in the case of hydroxylamine some nitrous acid is formed together with free nitrogen. The reaction with hydrazine can be

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[1] Vaubel, *Chem. Zeit.*, 1898, **22**, 331.
[2] Kretzschmar, *Zeitsch. Elektrochem.*, 1904, **10**, 789.
[3] Ross, *J. Amer. Chem. Soc.*, 1906, **28**, 786.
[4] Potilitzin, *Ber.*, 1887, **20**, 772.
[5] Vitali, *Giorn. Farm. Chim.*, 1910, **59**, 18.
[6] Schlötter, *Zeitsch. anorg. Chem.*, 1903, **37**, 164 and 172.

used for the estimation of bromates. Browne and Shetterly[1] have shown that hydrazine sulphate is not completely oxidised to nitrogen and water when treated with potassium bromate in the presence of sulphuric acid : a secondary reaction takes place by which more or less azoimide is also formed.

Concentrated sulphuric acid decomposes bromates with the liberation of bromine and oxygen, the reaction apparently taking place according to the equations :—[2]

$$(1) \quad 4KBrO_3 + 4H_2SO_4 = 4KHSO_4 + 4HBrO_3,$$
$$(2) \quad 4HBrO_3 = 2Br_2 + 5O_2 + 2H_2O.$$
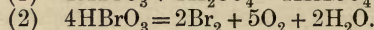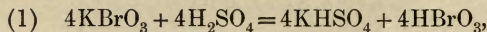
Dilute sulphuric and nitric acids, and also phosphoric, oxalic, and acetic acids decompose the bromates on gently warming, with the evolution of free oxygen and bromine. . .

Randall[3] has shown that when a solution of potassium bromate is added to a solution of potassium iodide containing a considerable quantity of hydrochloric acid, a reaction takes place according to the equation :—

$$3KI + KBrO_3 + 6HCl = 4KCl + 3H_2O + 2ICl + IBr.$$

The reaction may be used for the determination of iodides.

Constitution.—If the bromine in bromic acid be considered as monovalent and the oxygen as divalent, the constitutional formula may be written :—

$$H—O—O—O—Br \, ;$$
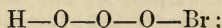
if the bromine be regarded as trivalent, the constitutional formula will be :—

$$H—O—Br\underset{\textstyle O}{\overset{\textstyle O}{\Big\langle}} \; ;$$
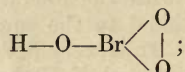
and if it be regarded as pentavalent, the formula becomes :—

$$H—O—Br\underset{\textstyle O}{\overset{\textstyle O}{\Big\langle}} \; .$$
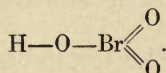
Stanley[4] has suggested that one of the oxygen atoms in chloric acid is tetravalent ; and, if this be so in the case of bromic acid, the constitutional formula may be written :—

$$H—Br\underset{\textstyle O = O.}{\overset{\textstyle O}{\Big\langle}}$$
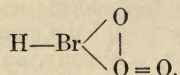
See Constitutional Formula of Chloric Acid (p. 131), where arguments for and against these formulæ are discussed.

DETECTION AND ESTIMATION.

Bromine in the free state may be recognised by the reddish-brown colour of its vapour, by its peculiar, disagreeable odour, and by the orange-yellow colour which it imparts to starch paste. Small quantities of the free element in aqueous solution may be detected by shaking in a test-tube with ether,

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[1] Browne and Shetterly, *J. Amer. Chem. Soc.*, 1908, **30**, 53.
[2] Koninck-Meineke, *Mineralanalyse*, 1904, **2**, 348.
[3] Randall, *J. Amer. Chem. Soc.*, 1910, **32**, 644.
[4] Stanley, *Chem. News*, 1902, **85**, 133.

chloroform, or carbon bisulphide, which dissolve out the bromine, forming a reddish-brown layer above or below the aqueous layer, according to the solvent employed.

Metallic bromides give up a part of their bromine when treated with concentrated sulphuric acid. When heated with a mixture of sulphuric acid and manganese dioxide or potassium dichromate, the whole of the bromine is liberated (see p. 172). When a solution of silver nitrate is added to a solution of a bromide, a very pale yellow, curdy precipitate of silver bromide is obtained. This precipitate is insoluble in dilute nitric acid, soluble with difficulty in ammonium hydroxide, and readily soluble in a solution of potassium cyanide or sodium thiosulphate. Solutions of soluble lead salts, such as lead acetate, give a white crystalline precipitate of lead bromide which is almost insoluble in cold water, but fairly soluble in boiling water. A solution of palladious nitrate gives a reddish-brown precipitate of palladious bromide. Chlorine water liberates bromine from solutions of bromides, imparting a brown colour to the solution. On shaking up with any of the organic solvents mentioned above, the bromine is withdrawn from the aqueous solution by the organic solvent, forming a coloured layer.

When strongly heated, the alkali bromates are converted into bromides with the evolution of oxygen, and the bromides thus obtained will then give the above reactions. Other bromates are decomposed with evolution of bromine and oxygen, leaving an oxide behind (see p. 185). When heated with acids, bromic acid is liberated, but this is soon decomposed, giving off free bromine and oxygen. When a solution of silver nitrate is added to a solution of a bromate, a white crystalline precipitate of silver bromate is obtained, which is sparingly soluble in dilute nitric acid, and soluble in ammonium hydroxide. A solution of mercurous nitrate gives a white precipitate of mercurous bromate. When sulphuretted hydrogen or sulphur dioxide is passed into a solution of a bromate, the latter is reduced to bromide and gives the corresponding reactions.

Determination of Free Bromine.—Free bromine in aqueous solution, or in the gaseous state, is determined by absorption in an excess of potassium iodide solution and estimation of the amount of iodine liberated by the bromine by means of sodium thiosulphate (see p. 206). Each equivalent of bromine liberates one equivalent of iodine.

Determination of Bromine in Bromides.—In the case of free hydrobromic acid or soluble bromides the aqueous solution is acidified with dilute nitric acid and an excess of a solution of silver nitrate added. The precipitated silver bromide is washed, dried, ignited, and weighed, and the percentage of bromine calculated from the weight of silver bromide. The neutral solution may also be titrated with a standard solution of silver nitrate, using a solution of potassium chromate as an indicator. As soon as all the bromide has been converted into silver bromide, the reddish-brown silver chromate begins to be formed. The addition of the silver nitrate is then stopped, and the percentage of bromine calculated from the volume used. Several volumetric methods involving the use of chlorine water are employed for the estimation of bromides. A small quantity of chloroform may be added to the bromide solution, and a standard solution of chlorine water run in from a burette. On shaking, the chloroform becomes first yellow, then orange-coloured, and finally almost colourless, owing to the combination of the chlorine with the liberated bromine to form bromine trichloride. At this point two equivalents of chlorine have been used for each equivalent of

bromine. The process requires considerable care in manipulation. The
bromide solution may also be heated nearly to boiling, and the standard
chlorine water run in without the addition of chloroform. The heating is
continued for about three minutes after the addition of the chlorine water,
when the yellow colour imparted to the solution by the liberated bromine will
have disappeared. The solution is allowed to cool for a few minutes and then
more chlorine water is added, the process being repeated until the solution
no longer becomes yellow in colour on the addition of more chlorine water.
The bromine may also be estimated colorimetrically ; after the addition of
the chlorine water the solution is shaken up with ether and the colour of the
ethereal solution thus obtained compared with a standard ethereal solution
of bromine. All these chlorine methods are only approximate ; they are,
however, well suited for the estimation of small amounts of bromine in
mother liquors.

   Determination of Bromic Acid and Bromates.—Bromic acid and bromates
are determined by heating with an excess of hydrochloric acid and passing
the evolved chlorine into a solution of potassium iodide, when an equivalent
amount of iodine is liberated and dissolved in the excess of potassium iodide.
The quantity of iodine thus liberated is determined by means of a standard
solution of sodium thiosulphate. One equivalent of bromic acid liberates
four equivalents of chlorine, and therefore of iodine, in this reaction. Bromates
may also be determined by means of hydrazine salts and hydroxylamine
(see p. 185).

IODINE AND ITS COMPOUNDS.

IODINE.

Symbol, I.   Atomic weight, 126·92 (O = 16).

Occurrence.—Iodine scarcely ever exists in the free state in nature. It was, however, found by Wanklyn [1] in the waters of Woodhall Spa, near Lincoln, which owe their brown colour to the presence of free iodine. Matteucci [2] has found the element, in combination with hydrogen, as hydriodic acid, in volcanic gases; but it generally occurs combined with metals, as iodides, iodates, and per-iodates. It is very widely distributed throughout the inorganic and organic kingdoms, though always in small quantities and frequently in the merest traces. Minerals containing iodides of mercury, silver, and lead—such as mercuric iodide or coccinite, HgI_2; silver iodide or iodyrite, AgI, etc.—are found in Mexico, South America, and Spain, and Autenrieth [3] has found a basic copper iodide in malachite. Iodine has also been found in zinc ores from Silesia, dolomite from Saxony, limestone from Montpellier, and (probably as iodate) in calcium phosphate from Quercy, in rock salt from Hall, in Austria; in "caliche" or crude sodium nitrate from Chili (mostly as sodium iodate), and in many other minerals. It frequently exists in mineral waters and medicinal springs, among which may be mentioned those of Heilbronn and Karlsbad, in Bavaria; Halle, in Saxony; Marienbad, in Bohemia; Hall, in Austria; Vichy, in France; Bonnington (near Leith), in Scotland; Leamington, Bath, Cheltenham, Harrogate, and Woodhall Spa, in England. Iodine is universally present in sea-water, though always in such minute quantities that the early investigators, Tennant, Davy, Gaultier, and others, were unable to detect it. It was, however, found by Balard in the waters of the Mediterranean, and by Pfaff in those of the Baltic, and Stanford has estimated that the waters of the Atlantic contain 1 part of iodine in 280,000,000. Fresenius [4] has recently found 0·0000247 per cent. of iodine in water from the Dead Sea, the density of the water being 1·555. Chatin [5] carried out a great many investigations during a period of ten years

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[1] Wanklyn, *Chem. News*, 1886, **54**, 300.

[2] Matteucci, *Compt. rend.*, 1899, **129**, 65.

[3] Autenrieth, *Chem. Zeit.*, 1899, **23**, 626.

[4] Fresenius, *Verh. Ges. deut. Naturforch. Aerzte*, 1913, p. 118.

[5] Chatin, *Compt. rend.*, 1850, **31**, 868; 1851, **32**, 669; **33**, 529 and 584; 1852, **34**, 14 and 51; 1853, **37**, 723 and 958; 1854, **38**, 83; **39**, 1083; 1858, **46**, 399; 1860, **50**, 420; **51**, 496.

—from 1850 to 1860—in order to ascertain the amount of iodine present in the atmosphere, rain water, running streams, etc.   He found small amounts were almost universally present in the atmosphere and in rain water, but there was considerably less in mountain air than in that of lower lying lands, especially sea air and that of Paris.   These results were confirmed by the investigations of several chemists, but were strongly disputed by others. Gautier[1] has since shown that iodine does not usually exist in appreciable amount in the atmosphere.   He could not find any in mountain air, and scarcely any in that of forests, but found it in that of Paris and in sea air. He has also shown that the iodine is in these cases due to minute organisms such as spores of algæ, mosses, lichens, etc., suspended in the atmosphere. According to Garrigou,[2] there is neither free iodine, nor gaseous iodides, in the atmosphere of Toulouse.

Nearly all marine animals and plants contain small amounts of iodine, generally as iodides of potassium, sodium, calcium, and magnesium.   Many tropical and subtropical sponges contain considerable quantities of this element; thus, Hundeshagen[3] has found as much as 14 per cent. in one species (*Verongia plicifera*) and from 8 to 10 per cent. in others.   Turkey sponge contains 0·200 per cent.   Iodine also exists in many marine worms, molluscs, and crustaceans, and is present in most fish oils ; cod liver oil is especially rich in the element and contains from about 0·0003 to about 0·0008 per cent. Marine algæ nearly always contain iodine ; there are, however, some exceptions, such as Irish moss (*Chondrus crispus*) and agar-agar (*Euchemia spinosa*).   As a rule, the deep-water algæ contain more iodine than those from comparatively shallow water, as shown by the following table which gives the percentage of iodine in the dried plant :—

Cut weed from shallow water.	*Fucus filum*	0·0894
	,, *vesiculosus* . .	0·001 to 0·0297
	,, *serratus* . . .	0·0856
	Ascophyllum nodosum . .	traces to 0·0572.
Drift weed from deep water.	*Laminaria digitata* (stem) .	0·4535
	,, ,, (frond) .	0·2946
	,, *stenophylla* . .	0·4777
	,, *saccharina* . .	0·23 to 0·2794.

Macrocystis pyrifera, which grows to a length of over 1500 feet, contains 0·0308 per cent. of iodine.

Iodine has also been found in some land and fresh-water plants and animals ; although, strange to say, many plants inhabiting salt marshes or growing near the sea are free from the element.   It has been stated by Justus that iodine is always present in the cell nucleus of animal and vegetable cells ; but Babig[4] has shown this to be incorrect, at least in the case of vegetable cells ; in many plants he not only failed to detect the element, but found that they did not absorb it even when grown in solutions containing potassium iodide.   It exists in various organs in most animals, including man.   The thyroid gland is remarkable for containing a considerable amount of the

[1] Gautier, *Compt. rend.*, 1899, **128**, 643.
[2] Garrigou, *Compt. rend.*, 1899, **128**, 884.
[3] Hundeshagen, *Zeitsch. angew. Chem.*, 1895, **8**, 473.
[4] Babig, *Ber. deut. bot. Ges.*, 1913, **31**, 35.

element. The table below gives the quantity of iodine found by Justus[1] in 100 grams of various human organs :—

Thyroid gland	9·760 mg.
Liver	1·210 ,,
Stomach	0·989 ,,
Spleen	0·560 ,,
Pancreas	0·430 ,,
Lungs	0·320 ,,
Small intestines	0·119 ,,

From the examination of the thyroids of sheep, oxen, and pigs, Aldrich[2] found that the largest thyroids contain the most iodine, and Cameron[3] found an average of 1·16 per cent. of iodine in the thyroids of the ray and dog-fish —an amount far in excess of that found in any mammalian thyroid.

History.—Iodine was discovered in 1812 by Courtois[4] in the mother liquors from the sodium salts obtained from kelp. He had observed the occasional corrosion of the metallic vessels which he used, and, whilst seeking the cause of this trouble, added concentrated sulphuric acid to the liquor. Violet vapours appeared which condensed in brilliant crystalline dark grey scales. The discovery was first announced on 29th November 1813, to the first class of the French Institute by Clément, who had been engaged by Courtois to investigate the new substance. Clément and Desormes studied the compounds of iodine with hydrogen, sulphur, and phosphorus. The element was further investigated by Davy,[5] and more completely by Gay-Lussac,[6] who studied iodic acid and the iodates. These chemists were the first to show that the new substance was an element and allied to chlorine. It was also Gay-Lussac who first proposed the name iodine ($\iota\acute{\omega}\delta\eta\varsigma$, violet) for this element on account of the colour of its vapour. Per-iodic acid was discovered by Magnus and Ammermüller,[7] and hypo-iodous acid by Koene in 1845.

Preparation.—At one time the only source of all the iodine of commerce was seaweed. At first the cut weed alone was used for this purpose, but later on the use of this weed was entirely given up in favour of drift-weed, chiefly *Laminaria digitata* and *L. stenophylla*, on account of their higher iodine content (see p. 190). The chief centres of the industry are the west coast of Scotland, the Hebrides, and the north and west coasts of Ireland and France. It is generally stated in English and German text-books that the ash of the burnt seaweed is known as *kelp* in Scotland, and as *varech*, or *varec*, in Normandy. This statement, however, is not quite correct. In this country the term *kelp* is applied to both the weed and the ash, although the latter is also known as *kelp-ash*. In France, the term *varech* is applied to *all* seaweed (the word being the equivalent to the English word *wrack*), and the burnt ashes are known as *cendres de varech*. During recent years "caliche" or "Chili saltpetre" has become the chief source of

[1] Justus, *Virchow's Arch.*, **170**, 501 ; **176**, 1.
[2] Aldrich, *Amer. J. Physiol.*, 1912, **31**, 31, 125.
[3] Cameron, *Biochem. J.*, 1913, **7**, 466.
[4] Courtois, Clément, and Desormes, *Ann. Chim.*, 1813, **88**, 304.
[5] Davy, *Phil. Trans.*, 1814, Part I., pp. 74, 487.
[6] Gay-Lussac, *Ann. Chim.*, 1813, **88**, 311, 319 ; 1814, **91**, 5.
[7] Magnus and Ammermüller, *Pogg. Annalen*, 1833, **28**, 514 ; *Ann. Chim. Phys.*, 1833, **53**, 92.

the element, the manufacture of iodine from seaweed being practically a dead industry.

Manufacture from Seaweed.—In the earliest method of manufacture the weed was burnt in shallow pits, at a sufficiently high temperature to fuse the ash. The slag thus obtained was then the only source of soda and was also of importance as a source of potash, the iodine obtained being of secondary importance. The value of kelp as a source of soda disappeared with the introduction of the Le Blanc process for the manufacture of this compound. The potash salts were then the most important products obtained, until the discovery of the Stassfurt deposits, when the iodine became the chief product. By this time it was found that about half the iodine was lost when the ash was fused, and more or less care was taken to avoid this. In 1862 Stanford[1] introduced the process of submitting the weed to destructive distillation in retorts. The volatile products, consisting chiefly of tar and ammoniacal liquor, are collected in suitable condensers and the porous residue lixiviated in order to extract the iodides and other salts. The charcoal which remains behind resembles animal charcoal in properties and composition, but is readily distinguished from this by the presence of magnesium salts. This charcoal is a good decoloriser and deodoriser, and has been much used for sewage filtration, and also for the manufacture of " carbon cement," for covering boilers in order to prevent radiation of heat. Although this process was a great improvement on the earlier method, it was not sufficiently economical, and Standford afterwards introduced another process in which the seaweed is boiled with sodium carbonate and filtered through a Taylor filter. The residue consists of a substance called *algulose*; the filtrate is treated with hydrochloric acid, which precipitates a substance known as *alginic acid* or *insoluble algin*, and again filtered. The alginic acid is purified and converted into the sodium salt $C_{76}H_{75}O_{22}N_2Na_5$, when it is known as *algin* or *soluble algin*—a substance resembling gelatin and used for various purposes. Other alginates, such as the aluminium, copper, and iron salts, may also be prepared, and find useful applications. The filtrate is neutralised with sodium hydroxide, evaporated to dryness, and carbonised. It is then known as *kelp substitute*, and contains all the iodine and potash salts originally present. The process has not proved a commercial success.

The kelp or kelp substitute, obtained by one or other of the methods described above is lixiviated in large vats, and the aqueous solution thus obtained concentrated in large open pans. The solution is then allowed to cool, when the alkaline sulphates, chlorides, and carbonates crystallise out, leaving the bromides and iodides in the mother liquor. There are several methods of treating this liquor in order to obtain the iodine, some of which are described below.

(1) In Scotland the mother liquor is treated with sufficient sulphuric acid to decompose the sulphites and sulphides, and allowed to stand. The liberated sulphur, known as *sulphur waste*, is filtered off, and the alkaline sulphates are crystallised out and removed. The mother liquor is then treated with a further quantity of sulphuric acid and transferred to the *iodine stills* (see fig. 30), which consist of iron boilers surrounded by brickwork, and furnished with a leaden hood which can be removed by means of a chain and winch. Each hood is supplied with two leaden pipes (x, x), each of which is connected to a series of glass or earthenware tubulated receivers (y), known

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[1] Stanford, *Pharm. J.*, 1862, **21**, [iii.], 495.

as *aludels* or *udells*, fitting into each other; and also with a hole (*z*) closed by means of a stopper. When the mother liquor has been run into the stills, the hoods are luted on with clay and the exit pipes and aludels connected up. The stills are then gently heated and manganese dioxide added little by little through the hole *z*. A reaction takes place between the sodium iodide, sulphuric acid, and manganese dioxide, according to the equation :—

$$2NaI + 3H_2SO_4 + MnO_2 = MnSO_4 + 2NaHSO_4 + 2H_2O + I_2.$$
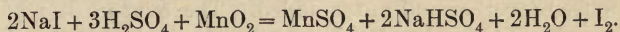
The liberated iodine condenses in the aludels; and the water, which is distilled over with the iodine, drains through the tubuli into the trough beneath. The iodine is collected and resublimed.

(2) In France the mother liquor is usually acidified with sulphuric acid and diluted to 40° (Twaddell). It is then treated with chlorine, care being taken not to add an excess, as this would lead to the formation of iodine
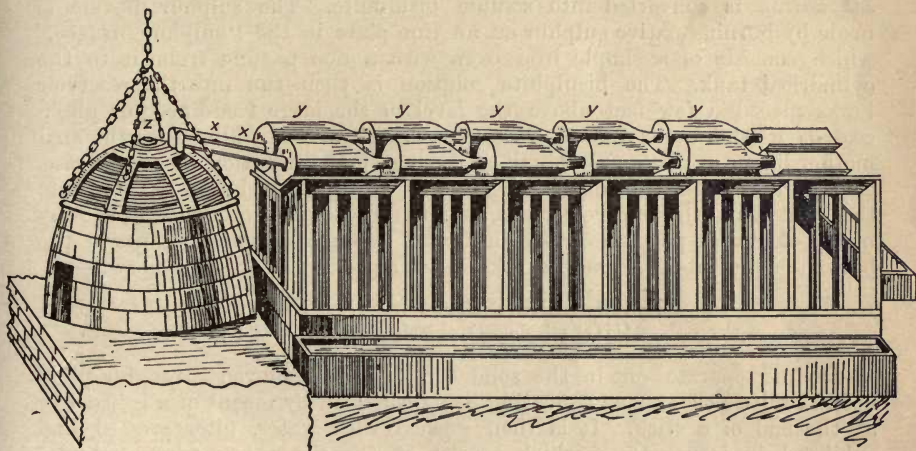
FIG. 30.—Iodine stills.

chloride. The iodine, which separates out in the solid form, is filtered off, dried, and sublimed.

(3) The mother liquor may be acidified with sulphuric acid and heated together with ferric chloride, when the iodine is liberated, according to the equation :—

$$2NaI + 2FeCl_3 = 2FeCl_2 + 2NaCl + I_2,$$
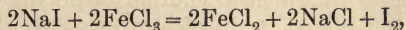
or the ferric chloride may be replaced by potassium chlorate. In either case the liberated iodine is distilled off and purified by resublimation.

(4) The mother liquors may be treated with a mixture of sulphuric and nitric acids, and then agitated with petroleum ether. The liberated iodine dissolves in the latter, and the solution is drawn off from the aqueous portion. It is then agitated with an aqueous solution of sodium hydroxide, by which means the iodine is converted into a mixture of sodium iodide and sodium iodate, both of which remain in solution in the aqueous portion. The petroleum is drawn off and used again, whilst the iodine is liberated by means of hydrochloric acid, according to the equation :—

$$5NaI + NaIO_3 + 6HCl = 6NaCl + 3H_2O + 3I_2.$$
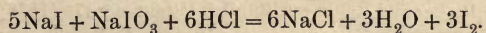
Manufacture from Caliche.—As already stated on p. 189, crude Chili saltpetre or caliche contains a small percentage of iodine, chiefly as sodium iodate. This iodine is extracted in the nitrate districts by means of sodium bisulphite. The first stage in the process is the manufacture of crude sodium carbonate or *sal natron*.[1] In order to prepare this, 85 parts of impure sodium nitrate (from the *aqua vieja* tanks) and 15 parts of fine coal are intimately mixed together and water added. The mixture is made up into a conical mound, which is surrounded by a trench, and ignited. A saturated aqueous solution of the crude sodium carbonate thus obtained is then made and allowed to settle. The clear liquid is run off into another tank, from which it is pumped into a large closed iron cylinder situated at the top of the iodine house. When the cylinder is three-quarters filled with the solution, sulphur dioxide is drawn through perforated pipes passing into the liquid by means of a steam blower fixed to the top of the tank, until the whole of the *sal natron* is converted into sodium bisulphite. The sulphur dioxide is made by burning native sulphur on an iron plate in the "sulphur furnace," which consists of a simple iron oven with a flue passing from it to the cylindrical tank. The bisulphite solution is then run into the reservoir tanks placed a few feet above the level of the large lead-lined (or pitch-coated) wooden tanks or vats, which are about two-thirds filled with the final mother liquor or *aqua vieja* obtained during the purification of the nitrate, containing all the sodium iodate. The bisulphite solution is run into these vats from the reservoir tanks, and the liquid is thoroughly stirred by means of wooden paddles, or by air forced through perforated pipes in the bottom of the vats. A reaction takes place according to the equations:—

$$2NaIO_3 + 2NaHSO_3 = 2Na_2SO_3 + 2HIO_3,$$
$$2HIO_3 + 5Na_2SO_3 = 5Na_2SO_4 + I_2 + H_2O.$$
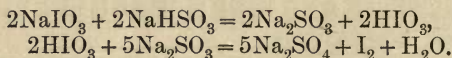
The iodine separates out in the solid form, and is removed through a plug-hole, the little that remains floating being collected by means of a calico bag at the end of a stick. It is then washed with water, filter pressed, and sublimed in iron retorts which consist of a horizontal cast-iron cylinder tapering at the further end in a conical form. The outlet, which is about 6 inches in diameter, is connected to a series of from eight to ten ordinary earthenware drain pipes (or aludels similar to those used in the manufacture of iodine from kelp) luted together with clay. It is then ready for sale.

Electrolytic Methods.—Various electrolytic methods of obtaining iodine have been proposed from time to time. Thus Parker and Robinson[2] have patented a process by which a solution of alkaline iodides is acidified with sulphuric acid and placed in an electrolytic cell which is divided into two compartments by means of a diaphragm, and provided with a carbon or platinum anode and an iron cathode. A current is sent through the liquid, and the iodine, which is liberated at the anode, is collected, washed with cold water, and dried in a current of hot air.

Extraction of Iodine from Phosphates.—Several methods for the extraction of iodine from phosphates containing the element have been proposed from time to time. Thiercelin[3] places a mixture of equal quantities of the phosphate, sulphuric acid, and water in a vat. The mass is kept stirred by

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[1] Newton, *J. Soc. Chem. Ind.*, 1903, **22**, 469.
[2] Parker and Robinson, English Patent, 11,479 (1888).
[3] Thiercelin, *Bull. Soc. chim.*, 1874, [ii.], **22**, 435.

means of paddles, and the reaction proceeds under the influence of its own heat. The liberated iodine passes over into a crystallising chamber.

Laboratory Methods of Preparation.—Iodine is readily prepared in the laboratory by gently heating a mixture of sodium or potassium iodide, manganese dioxide, and sulphuric acid in a retort. The reaction takes place according to the following equation :—

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$
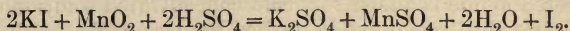
The liberated iodine distils over, and condenses in the form of dark grey crystals. A second method of preparation is by the action of chlorine or bromine on an iodide, thus :—

$$2NaI + Cl_2 = 2NaCl + I_2.$$
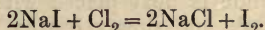
Iodine may also be prepared by the decomposition of an iodide by means of concentrated nitric acid, thus :—
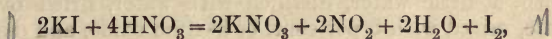
$$2KI + 4HNO_3 = 2KNO_3 + 2NO_2 + 2H_2O + I_2,$$

or by the decomposition of an iodide by means of concentrated sulphuric acid, thus :—

$$2KI + 3H_2SO_4 = 2KHSO_4 + 2H_2O + SO_2 + I_2.$$
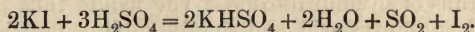
Recovery of Iodine from Laboratory Residues.—There are several methods in use for the recovery of iodine from laboratory residues. Beilstein's method is to evaporate the solution down to dryness with excess of sodium carbonate, heat the residue until it becomes white, add an excess of sulphuric acid, and pass oxides of nitrogen (obtained by heating starch with nitric acid) through the solution until all the iodine has evaporated. The iodine is then washed in cold water, dried over sulphuric acid, and gently sublimed. In Gladstone and Tribe's [1] method the residues (from organic compounds) are poured on to an excess of copper-zinc couple moistened with water or alcohol in a flask fitted with a reflux condenser. The residue is digested with hot water in order to dissolve out the zinc iodide, and the iodine liberated by means of bleaching powder, or by any of the usual means. Gill [2] uses sodium iodide instead of the usual potassium salt in iodometric analysis, and recovers the iodine by evaporating down the residues, heating in an air oven until quite dry, and extracting the coarsely powdered residue with absolute alcohol in a Soxhlet apparatus. The sodium iodide is recovered from the alcohol by crystallisation, and the crystals, which may be submitted to recrystallisation from alcohol if required, are dried in an air oven and then under reduced pressure in order to expel all traces of alcohol.

Purification of Iodine.—The chief impurities found in commercial iodine are chlorides, bromides, and cyanides of iodine, traces of various salts and water. Stas [3] prepared pure iodine from the commercial product by two processes :—

(1) A solution of potassium iodide in its own weight of water is saturated with iodine, water is then added until a slight permanent precipitate is obtained. This is allowed to settle and the clear liquid decanted off, and shaken with three-quarters of the amount of water required to precipitate all

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[1] Gladstone and Tribe, *Trans. Chem. Soc.*, 1883, **43**, 345.
[2] Gill, *Analyst*, 1913, **38**, 409.
[3] Stas, *Mém. Acad. Roy. Belg.*, 1865, **35**, 3 ; *Chemical Proportions*, 1867, p. 137.

the iodine which can be precipitated by this method (determined by a separate test with a little of the solution). The separated iodine is washed by decantation until the washings are free from potassium iodide and then distilled with water. The crystals thus obtained are allowed to drain, dried *in vacuo* over anhydrous calcium nitrate, and finally mixed with 5 per cent. of barium oxide and distilled twice.

(2) Powdered iodine is added to a cold concentrated solution of ammonia, and the precipitated nitrogen iodide washed by decantation with more of the ammonia solution, in order to remove the ammonium iodide. It is then washed with a little cold water, on a funnel with a neck drawn to a fine point, until the nitrogen iodide becomes brownish and the wash-water yellowish brown in colour. The iodide is next placed with ten times its weight of water in a large glass flask and slowly heated to 60°–65° C. When the decomposition of the iodide is completed, the mixture is heated to 100° C. for a few minutes and allowed to cool. The solid matter which separates out is washed with a little water, distilled with water, dried over anhydrous calcium nitrate, mixed with 5 per cent. of barium oxide, and distilled twice.

Meineke[1] purifies iodine by repeated sublimation with potassium iodide ; also by precipitation from a mixture of previously purified potassium iodide and iodate, by means of sulphur dioxide. The iodine thus obtained is dried over concentrated sulphuric acid and finally sublimed with a little barium oxide. He also purifies this element by fusing it with a concentrated solution of calcium chloride containing a little potassium iodide and a few drops of hydrochloric acid. The cake of iodine thus obtained is washed, dried, and sublimed with a little barium oxide. It is finally sublimed alone.

Lean and Whatmough[2] prepare cuprous iodide by adding a solution of copper sulphate saturated with sulphur dioxide to a solution of potassium iodide. The reaction takes place according to the equation :—

$$2CuSO_4 + 2KI + SO_2 + 2H_2O = Cu_2I_2 + K_2SO_4 + 2H_2SO_4.$$
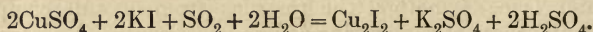
The precipitated cuprous iodide is washed with sulphurous acid, boiled with water, filtered, and dried by heating in a current of carbon dioxide. The dry compound is then decomposed by passing a current of dry air over it at a temperature of 240° C., yielding a very pure iodine.

Ladenburg[3] precipitates silver iodide by adding a solution of silver nitrate to a solution of potassium iodide, shakes the precipitate with ammonium hydroxide for twenty-four hours, in order to dissolve out the silver chloride, and reduces the silver iodide by means of zinc and sulphuric acid. He then adds nitrous acid to the solution of zinc iodide, submits the precipitated iodine to steam distillation, and finally dries over anhydrous calcium chloride.

Baubigny and Rivals[4] add sodium carbonate to an iodide solution, and then oxidise the latter to iodate with potassium permanganate. They then reduce five-sixths of the oxidised solution by means of neutral sodium sulphite and add the remaining one-sixth of unreduced iodate solution, when all the iodine is liberated according to the equation :—

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

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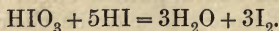
[1] Meineke, *Chem. Zeit.*, 1892, **16**, 1126.
[2] Lean and Whatmough, *Trans. Chem. Soc.*, 1898, **73**, 148.
[3] Ladenburg, *Ber.*, 1902, **35**, 1256.
[4] Baubigny and Rivals, *Compt. rend.*, 1903, **137**, 927.

The separated iodine is filtered, washed, and sublimed in the usual manner. It is then free from chlorine and bromine.

Baxter [1] distils a mixture of iodine and potassium iodide, converts the distilled iodine into hydriodic acid by means of pure hydrogen sulphide, separates the sulphur by filtration, boils for several hours in order to expel the hydrocyanic acid, and distils with potassium permanganate. The whole process is then repeated three more times, by which time the iodine is quite free from halogens and iodine cyanide.

Baxter also prepares pure iodine by oxidising to iodic acid, which latter is purified by fractional crystallisation from concentrated nitric acid. The iodic acid is heated in a current of dry air at 100° C. until water ceases to be evolved, and the temperature is then raised to 220°–240° C. The iodine pentoxide thus obtained is decomposed by heating in a current of air at 350° C., the iodine condensed and finally remelted to remove any possible traces of water. [2]

A convenient method of obtaining pure iodine consists in heating together fused, powdered potassium bichromate and iodide :— [3]

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 3I_2.$$
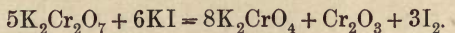
Physical Properties.—Iodine is a soft, friable, blackish-grey, crystalline solid with a semi-metallic lustre somewhat resembling that of graphite ; the colour of the pure substance is darker than that of the ordinary commercial product. It is opaque except in very thin plates, when it transmits light of a red colour. Dewar [4] has obtained transparent films of iodine by condensation on a glass surface at a temperature of $-180°$ to $-190°$ C. It has a sharp, astringent taste, and acts as a powerful poison. When sublimed, it crystallises in orthorhombic bipyramids. Larger crystals may be obtained from a solution of iodine in ether, or from an aqueous solution of hydriodic acid. Kurbatoff [5] has shown that when solutions of iodine in various solvents are evaporated, the iodine separates out in dendritic monoclinic crystals below about 46°–47° C. Above this temperature the ordinary rhombic plates are obtained. The crystals polarise light. [6]

Stas found the specific gravity of iodine to be 4·948 at 17° C. ; Ladenburg [7] obtained the value 4·933 at 4° ; and Billet found the value 4·825 for solid iodine at 107° C., and 4·004 for the liquid at the same temperature ; Drugman and Ramsay [8] obtained the value 3·706 at 184·5° C. (the boiling-point) ; and Dewar [9] obtained the value 4·8943 at $-38·85°$ C.

Iodine melts at about 114° C. to a brown liquid. According to Ramsay and Young, the melting-point lies between 113·8° and 114·3° C. ; Ladenburg found the melting-point of pure iodine obtained by his method of purification (see p. 196) to be 116·1° C., and Regnault [10] found the freezing-point to be 113·6° C. According to Ramsay and Young, iodine boils at 184·35° C. under a pressure of 760 mm. ; Ladenburg obtained the value 183·05° C. (corr.).

[1] Baxter, *J. Amer. Chem. Soc.*, 1904, **26**, 1577.
[2] Baxter, *ibid.*, 1910, **32**, 1591.
[3] L. L. de Koninck, *Bull. Acad. Roy. Belg.*, 1903, **17**, 15 ; L. W. Andrews, *Amer. Chem. J.*, 1903, **30**, 428.
[4] Dewar, *Proc. Chem. Soc.*, 1898, **14**, 241 ; *Chem. News*, 1898, **78**, 325.
[5] Kurbatoff, *Zeitsch. anorg. Chem.*, 1907, **56**, 230.
[6] Conroy, *Proc. Roy. Soc.*, 1876, **25**, 51.   [7] Ladenburg, *Ber.*, 1902, **35**, 1256.
[8] Drugman and Ramsay, *Trans. Chem. Soc.*, 1900, **77**, 1228.
[9] Dewar, *Chem. News*, 1905, **91**, 216.
[10] Regnault, *Ann. Chim. Phys.*, 1856, [iii.], **46**, 257.

Iodine volatilises spontaneously in the air at ordinary temperatures, giving off an odour somewhat resembling that of chlorine, but less unpleasant and irritating. Thus, if a little iodine be placed in the bottom of a flask, minute crystals of the element will soon be deposited on the sides of the latter.

The vapour pressure of iodine has been carefully investigated by Ramsay and Young.[1] Two series of results were obtained by these investigators, the first of which is given below.

VAPOUR PRESSURE OF IODINE.

Solid Iodine.		Liquid Iodine.	
Temperature, ° C.	Pressure, mm.	Temperature, ° C.	Pressure, mm.
58·1	4·9	114·1	89·8
64·5	6·05	114·9	93·55
66·3	6·25	117·8	103·0
75·2	11·5	120·4	113·4
80·4	15·15	123·15	124·5
86·0	21·25	125·5	135·8
91·8	28·95	127·1	142·9
91·9	29·6	166·6	475·0
96·8	37·8	169·4	505·5
102·7	50·65	171·7	535·6
105·7	59·85	174·5	575·3
113·8	87·0	177·6	630·3
		177·7	633·9
		180·75	680·5
		186·4	764·2

The intersection of the vapour pressure curves for solid and liquid iodine was found to be at 114·3° C., the vapour pressure then being 90 mm. Hence, when the pressure is reduced below 90 mm., iodine cannot be melted, but passes directly from the solid to the gaseous state.

Baxter, Hickey and Holmes[2] have found the following values for the vapour pressure at temperatures between 0° and 55° C. :—

Temperature, ° C.	Vapour Pressure in mm.	Temperature, ° C.	Vapour Pressure in mm.
0	0·030	40	1·025
15	0·131	45	1·498
25	0·305	50	2·154
30	0·469	55	3·084
35	0·699		

[1] Ramsay and Young, *Trans. Chem. Soc.*, 1886, **49**, 453.
[2] Baxter, Hickey, and Holmes, *J. Amer. Chem Soc.*, 1907, **29**, 127.

The earlier determinations of the vapour density of iodine were made by Gay-Lussac, Dumas, Bineau, and Deville and Troost. At comparatively low temperatures it is about $8 \cdot 72$ (air $= 1$) or $125 \cdot 9$ (H $= 1$); the molecular weight at these temperatures is therefore $251 \cdot 8$, and the iodine molecule is diatomic. V. Meyer[1] has found the following values for the vapour density at temperatures between 253° and about 1570° C. :—

Temperature, ° C.		Vapour Density.	Temperature, ° C.		Vapour Density.
	253	8·86	about	842	6·76
about	450	8·85	,,	1027	5·75
,,	586	8·72	,,	1570	5·70

Crafts and Meier[2] obtained similar results, and found the vapour density began to be abnormal between 600° and 700° C. According to Biltz and Meyer,[3] the vapour density decreases in value until a temperature of 1700° C. is attained, when the value obtained corresponds to a monatomic molecule; above this temperature the value remains constant. These results point to a gradual dissociation of the diatomic molecule, the iodine molecule being more easily dissociated than the bromine or chlorine molecule. The percentage of dissociated molecules at various temperatures has been calculated by Naumann.[4] According to Starck and Bodenstein,[5] the mean values of the equilibrium constant $K' = {}^p I^2 /_p I_2$ (the pressure being expressed in atmospheres) are :—

$$0 \cdot 0114 \text{ at } 800° \text{ C.}$$
$$0 \cdot 0474 \text{ ,, } 900 \text{ ,,}$$
$$0 \cdot 165 \text{ ,, } 1000 \text{ ,,}$$
$$0 \cdot 492 \text{ ,, } 1100 \text{ ,,}$$
$$1 \cdot 23 \text{ ,, } 1200 \text{ ,,}$$

and the heat of the reaction $2I = I_2$ is 36,860 gram-calories at constant pressure. Bjerrum[6] found the heat of formation of the molecule I_2 from its atoms to be 35,700 calories at temperatures in the region of 3000° C., and the atomic heat of iodine vapour to be $3 \cdot 1 \pm 0 \cdot 3$ between 0° and 3000° C. The specific heat of solid iodine between 9° and 98° C. is $0 \cdot 05412$ (Regnault), that of liquid iodine is $0 \cdot 0630$,[7] and that of iodine vapour is $0 \cdot 03489$ at constant pressure, and $0 \cdot 02697$ at constant volume.[8] The latent heat of fusion is $12 \cdot 9$ calories, and the latent heat of vaporisation is $44 \cdot 8$ calories

[1] V. Meyer, *Ber.*, 1880, **13**, 394, 401; 1881, **14**, 1453.
[2] Crafts and Meier, *Compt. rend.*, 1880, **90**, 690; 1881, **92**, 39; *Ber.*, 1880, **13**, 851, 870.
[3] Biltz and Meyer, *Ber.*, 1889, **22**, 725.
[4] Naumann, *Ber.*, 1880, **13**, 1050.
[5] Starck and Bodenstein, *Zeitsch. Elektrochem.*, 1910, **16**, 961.
[6] Bjerrum, *Zeitsch. physikal. Chem.*, 1912, **81**, 281.
[7] These constants are calculated from thermodynamical data. The figures given by Favre and Silbermann (*Ann. Chim. Phys.*, 1853, [iii.], **37**, 469), etc., are incorrect. See Abegg and Auerbach, *Handbuch der anorganischen Chemie*, 1913, **4**, [ii.], 355.
[8] Strecker, *Wied. Annalen*, 1881, **13**, 20.

at the melting-point and 41·6 at the boiling-point per gram. According to Gay-Lussac, solid iodine does not conduct electricity, and this result was confirmed by Solly. Inglis and Knox found that the fused element conducted the current from a battery of from 60 to 90 cells. Bruner and Galecki[1] have shown that a solution of iodine in perfectly dry nitrobenzene does not conduct electricity, but in a moist solution conduction takes place.

When seen by transmitted white light, the saturated vapour possesses a beautiful deep blue colour which is so intense that a layer, 10 cms. thick, appears opaque, except at the edges. By reflected light it appears to be quite black. The unsaturated vapour is violet-coloured. According to Dewar,[2] the colour of the saturated vapour is less intense *in vacuo* than in air at the same temperature. Lommel[3] found that the vapour of iodine exhibited an orange-yellow fluorescence, especially when exposed to the green rays of the spectrum. The violet and ultra-violet rays did not cause any fluorescence and were not markedly absorbed. The intensity of the fluorescence of iodine vapour when subjected to sunlight is influenced by the presence of other gases. Thus, Wood[4] found the fluorescence was diminished when carbon dioxide, air, hydrogen, or the vapour of ethyl alcohol was admixed with the iodine vapour; and Franck and Wood[5] have shown that for a given pressure of the admixed gas the diminution of the intensity of the fluorescence increases with the electronegative character of the gas, argon and helium being the least and chlorine the most active of the gases investigated. According to Franck and Hertz,[6] when the fluorescence of iodine vapour is excited by polarised light, the direction of vibration of the light-emitting particles is mainly at right angles to the plane of polarisation. By subjecting iodine vapour to intense illumination by light of wave-length extending from beyond $\lambda = 700\mu\mu$ to $\lambda = 185\mu\mu$, M'Lennan[7] obtained a fluorescence spectrum containing a large number of narrow bands extending from about $\lambda = 460\mu\mu$ to $\lambda = 210\mu\mu$. The spectra did not show any of the lines found in the fluorescence spectrum of iodine by Wood in 1911. Wood[8] has investigated the resonance spectrum of iodine. That obtained when iodine vapour is subjected to the influence of the green and yellow rays from a mercury lamp, consists of a series of isolated lines separated from one another by intervals of about 65 to 70 Ångström units. The spectrum excited by the green line consists of a series of 25 doublets with a constant difference between the frequencies of the two components. As the frequency increases, the frequency difference between the first members of the successive doublets shows a slight increase. The spectrum excited by the two yellow lines consists of a series of 15 equidistant doublets, the series excited by the line of wave-length $\lambda = 5790\cdot5$ being much more intense than that due to the line of wave-length $\lambda = 5769\cdot5$. The frequency of the doublets excited by the yellow lines shows no such

[1] Bruner and Galecki, *Zeitsch. physikal. Chem.*, 1913, **84**, 513.

[2] Dewar, *Chem. News*, 1898, **78**, 325.

[3] Lommel, *Ann. Phys. Chem.*, 1883, **19**, 356.

[4] Wood, *Phil. Mag.*, 1911, [vi.], **21**, 309 ; *Ber. deut. physikal. Ges.*, 1911, **13**, 72.

[5] Franck and Wood, *Phil. Mag.*, 1911, [vi.], **21**, 314 ; *Ber. deut. physikal. Ges.*, 1911, **13**, 78.

[6] Franck and Hertz, *Ber. deut. physikal. Ges.*, 1912, **14**, 423.

[7] M'Lennan, *Proc. Roy. Soc.*, 1913, **A**, **88**, 289.

[8] Wood, *Physikal. Zeitsch.*, 1910, **11**, 1195 ; *Phil. Mag.*, 1911, [vi.], **21**, 261 ; **22**, 469 ; 1912, [vi.], **24**, 673 ; 1913, [vi.], **26**, 828.

regularity as that found in the case of the green line. The excitation is evidently multiplex, a number of adjacent frequencies being excited, and the spectrum obtained when an ordinary Cooper-Hewitt mercury lamp is used is quite different from that given with the same lines when the mercury arc in quartz is used as the exciting agent. The lines of the resonance spectrum do not necessarily coincide with those of the absorption spectrum, but the iodine vapour always emits a line, the resonance radiation line, of identical wave-length with that of the exciting line, and this line is accompanied by a group of companion lines similar to the other groups which are seen at intervals along the spectrum. On reducing the density of the iodine vapour in the resonance tube, a band spectrum is obtained, which is more readily absorbed by the iodine vapour than are the lines of the resonance spectrum. When the spectrum is excited by means of polarised light, the resonance lines are also polarised. Franck and Wood [1] have shown that the presence of gases of the helium group tends to transform the resonance spectrum into the usual banded spectrum obtained when white light is used as the exciting agent, helium being the most active in bringing about the change. When the helium is replaced by chlorine, a banded spectrum is not obtained ; but Franck [2] has shown that other gases, such as hydrogen, nitrogen, and oxygen, behave similarly to the inert gases except that whilst the total light emission is not diminished by the presence of the gases of the helium group it is decreased when other gases are employed, the diminution increasing with the electro-affinity of the added gas. The absorption spectrum of iodine vapour was first studied in 1833 by Miller and Daniell,[3] who observed a number of fine lines extending from the red to the violet. These bands were afterwards carefully mapped out by Thalén [4] in 1869. According to Wood,[5] the absorption spectrum of iodine contains a vast number of lines (estimated at over 50,000), a great many of which are coincident with lines in the corresponding bromine spectrum. Plücker and Hittorf [6] passed an electric discharge through a heated Geissler's tube containing a trace of iodine vapour and obtained an emission spectrum containing many bright lines which, however, did not correspond to the absorption spectrum of Thalén. Salét [7] afterwards obtained the same spectrum as Plücker and Hittorf, and also an emission spectrum in which the lines were identical with the dark bands obtained by Thalén. On heating to redness, a continuous spectrum was obtained. According to Gladstone,[8] the spectrum given by iodine, whether in the state of vapour or dissolved in carbon bisulphide, is abnormal.

The effect of a magnetic field on the vapour of iodine between crossed nicols has been investigated by Heurung [9] and also by Wood.[10] On applying the magnetic field, a considerable illumination in the green part of the spectrum is obtained and several new lines appear. Only a small portion

[1] Franck and Wood, *Phil. Mag.*, 1911, [vi.], **21**, 265 ; *Ber. deut. physikal. Ges.*, 1911, **13**, 84.
[2] Franck, *Ber. deut. physikal. Ges.*, 1912, **14**, 419.
[3] Miller and Daniell, *Phil. Mag.*, 1833, [iii.], **2**, 381.
[4] Thalén, *K. Svenska Vet.-Akad. Handl.*, 1869.
[5] Wood, *Phil. Mag.*, 1912, [vi.], **24**, 673.
[6] Plücker and Hittorf, *Phil. Trans.*, 1865, **155**, 1.
[7] Salét, *Phil. Mag.*, 1872, [iv.], **44**, 156 ; *Compt. rend.*, 1872, **74**, 1249, **75**, 76.
[8] Gladstone, *Chem. News*, 1887, **55**, 300.
[9] Heurung, *Ann. Physik*, 1911, [iv.], **36**, 153 ; 1912, [iv.], **37**, 1046.
[10] Wood, *Ann. Physik*, 1912, [iv.], **37**, 594.

of the light appears to be polarised, as the magneto-optical effect is not eliminated either by rotating the analyser or by inserting a quarter wave plate.

The dispersion equivalent in methylene di-iodide is 3·65. According to Cuthbertson and (Mrs) Cuthbertson,[1] the refractivity of iodine vapour for light of wave-length $\lambda = 6438$ is 0·00210.

Owen and Pealing[2] have shown that condensation nuclei are produced in large numbers when moist air or oxygen containing iodine vapour is acted upon by light. The nuclei are very unstable and soon disappear in the dark. When the air or oxygen is replaced by hydrogen, carbon dioxide, or coal gas, or when the water vapour is replaced by that of ethyl alcohol, the nuclei are not obtained, and iodine vapour alone does not contain nuclei which serve for the condensation of supersaturated water vapour.

Cryoscopic and ebullioscopic determinations have been made in iodine. Beckmann[3] has determined the molecular weights of stannic iodide, antimony iodide, arsenic iodide, mercuric iodide, and aluminium iodide by the cryoscopic method, and has shown that potassium iodide has a normal molecular weight in dilute solutions but polymerises in more concentrated solutions, whilst the iodides of cæsium, sodium, and lithium polymerise at all concentrations. The mean molecular depression of the freezing-point is 210. The same investigator has also made ebullioscopic determinations with liquid iodine, using a jacket of boiling aniline. The iodides of the alkali metals show a tendency to give high values, especially in the case of sodium iodide and lithium iodide, but the values obtained are much more nearly normal than in the cryoscopic method. Tin, antimony, and bismuth dissolve in the monatomic form. The mean ebullioscopic constant is 110. Olivari[4] has determined the molecular weights of a number of hydrocarbons and other organic compounds in iodine by the cryoscopic method and has also determined the molecular weights of stannic iodide, antimony iodide, arsenic iodide, and mercuric iodide in dilute solutions in iodine. The mean value found for the depression of the freezing-point was 213. In very dilute solutions the molecular weights of the alkali iodides KI, RbI, and NH_4I are almost normal; they increase with the concentration until a certain point is reached, when they again decrease, until with very high concentration they are less than the theoretical values. Some alkyl ammonium iodides behave similarly.

Iodine is less soluble in water than either chlorine or bromine; according to Hartley and Campbell,[5] it dissolves in the following proportions :—

Temperature, ° C.	Grammes of Iodine per 1000 grammes of Water.
18	0·2765
25	0·3395
35	0·4661
45	0·6474
55	0·9222

[1] Cuthbertson and (Mrs) Cuthbertson, *Phil. Trans.*, 1913, **A**, **213**, 1.
[2] Owen and Pealing, *Phil. Mag.*, 1911, [vi.], **21**, 465.
[3] Beckmann, *Zeitsch. anorg. Chem.*, 1909, **63**, 63 ; 1912, **77**, 200 and 275.
[4] Olivari, *Atti R. Accad. Lincei*, 1909, [v.], **18**, ii. 384 ; 1913, [v.], **22**, ii. 697 ; 1914, [v.], **23**, i. 41.
[5] Hartley and Campbell, *Proc. Chem. Soc.*, 1908, **24**, 58 ; *Trans. Chem. Soc.*, 1908, **93**, 741.

Bray and Connolly[1] have determined the solubility of iodine in water and the conductivity of the solution at 25° C. 1 litre of water dissolves 1·32 millimolecules of I, and the hydrolysis constant is found to be

$$(H^+)(I^-)(HIO)/(I_2) = 0·3 \times 10^{-12}.$$

The solution is pale brownish-yellow in colour, and smells of iodine. It becomes discoloured when exposed to direct sunlight, owing to the formation of hydriodic acid, which dissolves in the water. The discoloured solution is capable of dissolving more iodine, producing an orange-yellow solution. Hypo-iodous acid is formed in the solution to a very slight extent in addition to the hydriodic acid, thus :—

$$I_2 + H_2O \rightleftharpoons H^{\cdot} + I' + HIO.[2]$$
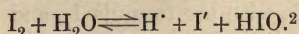
Iodine is readily soluble in an aqueous solution of potassium iodide, aqueous hydriodic acid, methyl, ethyl, and amyl alcohols, glycerol, ether, organic acids and esters, pyridine, etc., forming reddish-brown solutions. It also dissolves in chloroform, bromoform, carbon bisulphide, liquid hydrocarbons, etc., forming violet-coloured solutions, which become black and opaque when concentrated. The solution in carbon bisulphide is diathermanous. The cause of the difference in colour of the various solutions has not been satisfactorily explained. According to Loeb,[3] who determined the vapour pressure of iodine in carbon bisulphide and ether, the iodine exists in different molecular states in different coloured solutions. It appears from his results that in brown solutions the iodine has the molecular weight I_4, whilst in violet solutions it has a molecular weight between I_2 and I_3. Wiedemann[4] found that a solution of iodine in carbon bisulphide became brown when cooled in a mixture of solid carbon dioxide and ether, and Liebreich found that solutions of iodine in fatty esters became violet-coloured when heated to 80° C. It thus appears that the molecule I_4 in the brown solution is split up on heating, yielding the molecule I_2 which gives a violet-coloured solution. Gautier and Charpy[5] obtained solutions of iodine in different solvents which gradually varied from violet to brown and distinguished four sets of colours : violet, red, red-brown, and brown. Lachmann,[6] however, found these different colours were due to the use of impure solvents and showed that with pure solvents the solutions only have two colours, violet and brown. The first colour is obtained with saturated solvents such as chloroform, and the second with unsaturated solvents such as alcohol, etc. On adding alcohol to a solution of iodine in chloroform, the colour gradually changes from violet through shades of red-violet, red, and red-brown to brown. It had already been shown that in some of the brown solutions, e.g. that in aqueous potassium iodide, the iodine forms unstable per-iodides such as $KI.I_2$; and Lachmann, reviving a former suggestion of Beckmann, assumes the existence of additive products which are probably unstable, in all brown solutions, and supposes that the

[1] Bray and Connolly, J. Amer. Chem. Soc., 1910, 32, 932 ; 1911, 33, 1485. See also G. Jones and Hartmann, ibid., 1915, 37, 241.
[2] Casanova and Carcano, Boll. chim. farm., 1912, 51, 289.
[3] Loeb, Zeitsch. physikal. Chem., 1888, 2, 606.
[4] Wiedemann, Wied. Annalen, 1890, 41, 299.
[5] Gautier and Charpy, Compt. rend., 1890, 110, 189 ; 111, 645.
[6] Lachmann, J. Amer. Chem. Soc., 1903, 25, 50.

iodine in these solutions is probably in a condition of equilibrium between simple solution and the additive product.

$$\text{Solvent} + I_2 \rightleftharpoons (\text{solvent} + I_2).$$
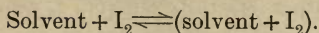
In the case of the violet solutions he assumes the iodine to exist as molecules of I_2. With reference to the above-mentioned work of Wiedemann and Liebreich, Lachmann says : "This view is supported by the fact that brown solutions tend to become violet when heated, and conversely, violet solutions become brown on being cooled sufficiently. As heat produces dissociation and cold induces association, the facts are in excellent agreement with expectation." A similar explanation has also been put forward by Strömholm.[1] Beckmann[2] has shown that the molecular weight of iodine in many solvents corresponds with the formula I_2, and therefore concludes that the colour of the brown solutions is connected with combination between the iodine and the solvent. From the determination of the freezing-point depression produced by iodine and certain solvents, first separately and then together, in bromoform and also ethylene dibromide, Hildebrand and Glascock[3] conclude that combination does take place in brown solutions, but not in the violet, because only in the former is the total depression less than the sum of the separate depressions. According to Waentig,[4] the iodine is partly combined with the solvent in all solutions, according to the reversible equation :—

$$\text{Solvent } I_2 \rightleftharpoons \text{Solvent} + I_2.$$
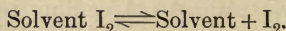
The amount of combination being much less in the violet solutions than in the brown. The spectrum of the violet solutions approximates to that of iodine vapour. From the investigation of the absorption spectra of iodine solutions in various solvents Ley and Engelhardt[5] conclude that brown solutions of iodine contain additive compounds, but the constitution of the violet solutions is still uncertain. As the result of an extensive ultra-microscopic examination of solutions in different solvents, Amann[6] concludes that iodine can exist in solution in seven different forms, and that alterations of colour of such solutions are not only due to the formation of compounds with the solvent, but also to the occurrence of free colloidal iodine. The colour changes due to light probably consist mainly in the reduction of the additive compounds, free iodine acting as a catalyst.

The heats of solution of iodine in different solvents, as found by Pickering,[7] are shown in the table below.

Benzene	.	.	.	.	− 3057 calories.
Chloroform	.	.	.	.	− 3007 ,,
Carbon tetrachloride	.	.	.	− 2891 ,,
Carbon bisulphide	.	.	.	− 2504 ,,
Alcohol	.	.	.	.	− 857 ,,
Ether	.	.	.	.	− 768 ,,
Ammonium chloride solution	.	.	− 1538 ,,
Potassium iodide solution	.	.	− 546 ,,

[1] Strömholm, *Zeitsch. physikal. Chem.*, 1903, **44**, 721.
[2] Beckmann, *Zeitsch. physikal. Chem.*, 1907, **58**, 543.
[3] Hildebrand and Glascock, *J. Amer. Chem Soc.*, 1909, **31**, 26.
[4] Waentig, *Zeitsch. physikal. Chem.*, 1909, **68**, 513.
[5] Ley and Engelhardt, *Zeitsch. anorg. Chem.*, 1911, **72**, 55.
[6] Amann, *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 235 ; **7**, 67 ; *Kolloid. Chem. Beihefte*, 1912, **3**, 337.   [7] Pickering, *Trans. Chem. Soc.*, 1885, **53**, 865.

According to Guichard,[1] carbon previously heated to 600° C. absorbs 34·2 per cent. of iodine at ordinary temperatures, and various oxides—*e.g.* iodic anhydride, silica, alumina, magnesia, etc.—also absorb iodine. Corridi has shown that animal charcoal absorbs iodine when placed in a solution of this element, and that the iodine is retained by the charcoal even when the latter is heated at 120° C. for many hours. The amount thus absorbed varies from 4·87 to 7·50 per cent., according to the solvent used.[2]

Chemical Properties.—Iodine resembles chlorine and bromine in chemical properties. It is, however, less stable in combination with electropositive elements and is therefore liberated from such compounds by either chlorine or bromine, thus :—

$$2KI + Cl_2 = 2KCl + I_2.$$
$$2NaI + Br_2 = 2NaBr + I_2.$$
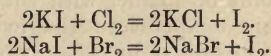
On the other hand, it is more stable in combination with electronegative elements and displaces both chlorine and bromine from such compounds, thus :—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$
$$2KBrO_3 + I_2 = 2KIO_3 + Br_2.$$
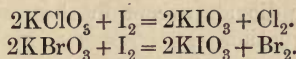
The heats of formation of the hydrogen compounds of these three elements are shown below.

$$(Cl) + (H) = \quad 22,001 \text{ calories.}$$
$$Br + (H) = \quad 8,337 \quad \text{,,}$$
$$[I] + (H) = \quad -6,036 \quad \text{,,}$$
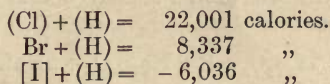
The heats of formation of the oxy-acids of these elements are :—

$$(Cl) + 3(O) + (H) = 23,761 \text{ calories.}$$
$$Br + 3(O) + (H) = \quad 5,344 \quad \text{,,}$$
$$[I] + 3(O) + (H) = 43,211 \quad \text{,,}$$
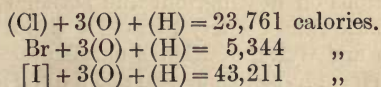
It is evident from the above figures that the affinity of chlorine for hydrogen is greater than that of bromine and that the affinity of bromine is greater than that of iodine. On the other hand, the affinity of chlorine for oxygen is greater than that of bromine but less than that of iodine.

Iodine combines directly with most of the elements, either in the cold or when heated with them. Ordinary oxygen has no action upon it,[3] but ozone converts it into a mixture of oxides ; thus, Ogier[4] caused the two elements to unite by submitting them to the silent electric discharge. Sulphur, selenium, and tellurium all unite with the element, forming mixtures of iodides. When a solution, of equal molecular proportions of sulphur and iodine in carbon bisulphide, is allowed to evaporate, dark grey crystals of sulphur mono-iodide, S_2I_2, are obtained (see Vol. VII.). When solid phosphorus is brought into contact with iodine, combination takes place with such vigour that the phosphorus first melts and then bursts into flame. Phosphorus di-iodide, P_2I_4, and phosphorus tri-iodide, PI_3, are both obtained by dissolving phosphorus and iodine in carbon bisulphide, and either allowing the solvent to evaporate or cooling it down (see Vol. VI.). Powdered arsenic, antimony, and bismuth, all

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[1] Guichard, *Compt. rend.*, 1910, **151**, 236.
[2] For particulars of the absorptive power of carbon see this series, Vol. V.
[3] Guichard, *Bull. Soc. chim.*, 1912 [iv.], **11**, 431.
[4] Ogier, *Compt. rend.*, 1878, **86**, 722.

take fire when thrown into iodine vapour with the formation of the corre-
sponding iodides. Pure boron does not combine with iodine even when
heated to 1200° C., but impure boron gives a small quantity of boron tri-
iodide, BI_3, when heated to a red heat. Carbon does not combine with the
element, but silicon unites with it at a red heat, forming silicon tetra-iodide,
SiI_4. The iodides of the non-metals are very volatile and are usually de-
composed by water. When potassium and iodine are melted together,
combination takes place with explosion. If sodium, however, be used in the
place of the potassium, combination does not take place.[1] According to
Shenstone,[2] pure dry iodine rapidly attacks pure dry mercury even in the cold,
and Meyer[3] found that pure dry iodine attacked gold when heated to between
50° C. and the melting-point of iodine, with the formation of amorphous
iodide of gold; above this temperature the iodide was obtained in the
crystalline form. Iodine is oxidised by the oxygen compounds of chlorine
and by fuming nitric acid; fuming sulphuric acid also partially oxidises it,
forming at the same time a crystalline oxy-iodide of sulphur. It dissolves in
liquid sulphur dioxide, forming a violet-coloured solution, but is not acted
upon by gaseous sulphur dioxide except in the presence of water, when it
reacts according to the equation :—

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI.$$
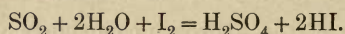
Neutral and acid sulphites behave in a similar manner, but thiosulphates are
converted into tetrathionates :—

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$
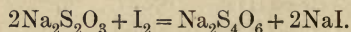
According to Müller,[4] sodium dithionate and sodium trithionate both
decolorise iodine solutions on heating, but the action is so slow in the cold
that sodium thiosulphate can be safely titrated with iodine in their presence.
According to Foerster and Gyr, a solution of an alkaline hydroxide reacts with
a solution of iodine to form hypo-iodous acid and a hypo-iodite, but the reaction
is not complete and the final solution contains free iodine and alkali.[5]

When a solution of iodine is added to starch paste, or when iodine vapour
is brought into contact with starch granulose, a deep blue colour is produced.
This colour disappears on heating to about 80° C., but reappears on cooling.
It is permanently destroyed by continued boiling and also by chlorine or
bromine water, and by a solution of mercuric chloride. The production of
this colour forms an extremely sensitive test for free iodine and also for
starch. A glucoside known as "saponarin" which occurs in the epidermal
cells of various plants is also coloured blue by iodine, and, as in the case of
starch, the colour disappears on warming and reappears on cooling.[6] *Lichenin*,
or moss starch, is coloured a dirty blue by iodine, and *inulin* is coloured
yellow. The nature of this blue colour has been much disputed. At one
time it was generally regarded as a loose additive compound, but is now
usually considered to be a solid solution of iodine in starch. Andrews and
Goettsch,[7] however, disagree with this view, and as a result of their investiga-

[1] Merz and Weith, *Ber.*, 1873, **6**, 1518.
[2] Shenstone, *Trans. Chem. Soc.*, 1897, **71**, 471.
[3] Meyer, *Compt. rend.*, 1905, **139**, 733.
[4] Müller, *Bull. Soc. chim.*, 1909, [iv.], **5**, 1119.
[5] Foerster and Gyr, *Zeitsch. Elektrochem.*, 1903, **9**, 1.
[6] Barger, *Proc. Chem. Soc.*, 1906, **22**, 194 ; *Trans. Chem. Soc.*, 1906, **89**, 1210.
[7] Andrews and Goettsch, *J. Amer. Chem. Soc.*, 1902, **24**, 865.

tions conclude that iodine starch is a chemical compound. According to Barger and Field,[1] when the blue substances obtained with iodine and starch, saponarin or chololic acid are crystalline, they may be additive products of iodine in atomic proportions, but there is also a considerable adsorption of iodine when they are colloidal, and separate in the amorphous state. The presence of an electrolyte is necessary to bring about this adsorption. Barger and Starling[2] regard the blue crystals as solid solutions of iodine in the organic substance, and state that colourless crystals of the organic substances, once they are formed, cannot be made to take up iodine. All the blue crystals obtained are more or less pleochroic.

Uses of Iodine.—By far the largest portion of the iodine of commerce is used in medicine, both in the free state and in combination. Tincture of iodine consists of a solution of iodine and potassium iodide in rectified spirits of wine. Hydriodic acid, iodides of potassium, arsenic, lead, mercury, iron, etc., and organic compounds such as iodoform (CHI_3), ethyl iodide (C_2H_5I) and iodole ($C_4I_4.NH$), are all used either internally or externally or as antiseptics. A considerable quantity of iodine is also used in the manufacture of aniline dyes, as in the preparation of Hoffmann violet and aniline green, and also in making erythrosin and the blue-shade eosins from fluorescine. A smaller amount is used in photography and chemical analysis.

Atomic Weight.—The atomic weight of iodine[3] has been very frequently determined by means of a number of methods. Gay-Lussac,[4] from the synthesis of zinc iodide, obtained the value 125. Berzelius,[5] by changing silver iodide into silver chloride, obtained the value 126·23 ; and Dumas,[6] using the same method, obtained the number 126·8. Marignac[7] obtained the mean value 126·80 by means of the synthesis of silver iodide, and the mean value 126·847 by determining the quantity of potassium iodide required to precipitate a known amount of silver dissolved in nitric acid. Stas,[8] using Marignac's first method, obtained the value 126·80 from five concordant experiments ; by means of the analysis of silver iodate he obtained the value 126·89. More recently, slightly higher results have been obtained. Thus, by heating silver iodide in a current of chlorine until all the iodine was displaced, and reducing the silver chloride thus obtained to metallic silver, Ladenburg[9] obtained the number 126·94 ($O = 16$). Köthner and Aeuer,[10] using the same method, found the value 126·92 ($O = 16$), and, by heating silver in a stream of iodine vapour, they obtained the value 126·91. By the synthesis of silver iodide from a weighed amount of silver, and also by the conversion of silver iodide into silver bromide and silver chloride, Baxter[11] obtained the mean values

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[1] Barger and Field, *Trans. Chem. Soc.*, 1912, **101**, 1394.

[2] Barger and Starling, *Proc. Chem. Soc.*, 1914, **30**, 2.

[3] In calculating the atomic weight of iodine the following modern values for the atomic weights of the other elements concerned have been adopted : $O = 16\cdot000$, $Ag = 107\cdot880$, $Cl = 35\cdot457$, $Br = 79\cdot916$, $K = 39\cdot100$.

[4] Gay-Lussac, *Ann. Chim.*, 1814, **91**, 5.

[5] Berzelius. *Pogg. Annalen*, 1828, **14**, 558.

[6] Dumas, *Ann. Chim. Phys.*, 1859, [iii.], **55**, 163.

[7] Marignac, *Bibl. Univ. de Genève*, 1843, **46**, 363.

[8] Stas, *Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels*, 1865.

[9] Ladenburg, *Ber.*, 1902, **35**, 2275 ; *Liebig's Annalen*, 1905, **338**, 259.

[10] Köthner and Aeuer, *Ber.*, 1904, **37**, 2536 ; *Liebig's Annalen*, 1904, **337**, 123, 367 ; 1905, **338**, 262.

[11] Baxter, *J. Amer. Chem. Soc.*, 1904, **26**, 1577 ; 1905, **27**, 876.

126·922, 126·928, and 126·925 respectively.   By the reduction of iodic acid by means of hydrazine, or other suitable reducing agent, and the titration of the hydriodic acid formed with a weighed amount of silver, Baxter and Tilley [1] obtained the value 126·938 (O = 16).   Baxter [2] has redetermined the ratio Ag : I, and obtained the value 126·932 for iodine.   In 1914 Guichard [3] decomposed iodine pentoxide by heat, condensed the iodine, and absorbed the oxygen with red-hot copper.   The results yielded a value of 126·915 for the atomic weight of iodine.

The value adopted by the International Atomic Weights Commission (1915) is 126·92.

Iodine usually behaves as a monovalent element, but in some compounds it appears to be tri-, penta-, or hepta-valent.

IODINE AND HYDROGEN.

HYDRIODIC ACID.

(*Hydrogen Iodide.*)

Formula, HI.

Occurrence.—Hydrogen iodide is found in volcanic gases (see p. 189).

Preparation.—When a mixture of iodine vapour and hydrogen is passed over red-hot finely divided platinum or charcoal at a bright red heat, partial combination takes place with the formation of hydriodic acid, or hydrogen iodide.[4]   The action is, however, markedly reversible, thus :—

$$H_2 + I_2 \rightleftharpoons 2HI.$$
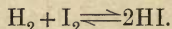
If a solution of iodine in water be exposed to sunlight, partial decomposition of the water takes place, with the formation of hydrogen iodide, which remains in solution ; and the liberation of oxygen, according to the equation :—

$$2H_2O + 2I_2 = 4HI + O_2.$$
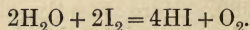
A dilute solution of hydrogen peroxide is also decomposed by iodine with the formation of hydriodic acid and oxygen, thus :—

$$H_2O_2 + I_2 = 2HI + O_2.$$
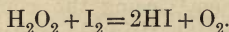
On the other hand, a concentrated solution of hydriodic acid is decomposed by hydrogen peroxide with the liberation of free iodine.[5]

Iodine reacts with various compounds of hydrogen, *e.g.* phosphoretted hydrogen, PH_3, ammonia, NH_3, and many organic compounds, with the formation of hydriodic acid.   Thus, Kastle and Bullock [6] prepare this compound by placing a mixture of iodine, finely divided resin, and white sand in a small glass retort and gently warming.   The gas is purified by successively passing it through a Woulff's bottle, a tube containing red phosphorus, and a calcium chloride cylinder filled with alternate layers of

[1] Baxter and Tilley, *J. Amer. Chem. Soc.*, 1909, **31**, 201.
[2] Baxter, *J. Amer. Chem. Soc.*, 1910, **32**, 1591.
[3] Guichard, *Compt. rend.*, 1914, **159**, 185.
[4] Merz and Holzmann, *Ber.*, 1889, **22**, 867.
[5] Schönbein, *J. prakt. Chem.*, 1861, **84**, 385.
[6] Kastle and Bullock, *Amer. Chem. J.*, 1896, **18**, 105.

glass wool and phosphorus pentoxide. According to Casanova and Carcano,[1] when iodine is allowed to act upon tannin in the presence of water it is completely converted into hydriodic acid.

Hydriodic acid cannot be prepared by the action of sulphuric acid on potassium or sodium iodides, because sulphur dioxide and free iodine are simultaneously formed, thus :—

$$3H_2SO_4 + 2KI = 2KHSO_4 + I_2 + SO_2 + 2H_2O.$$
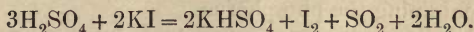
In this reaction therefore the iodides resemble the bromides and differ from the chlorides. As in the formation of hydrogen bromide from alkaline bromides, hydrogen iodide may be obtained by the action of phosphoric acid on these iodides.[2] It was formerly prepared by heating a mixture of finely powdered sodium iodide and concentrated phosphoric acid ; the reaction takes place according to the equation :—

$$NaI + H_3PO_4 = HI + NaH_2PO_4.$$
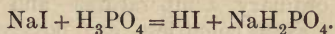
A dilute aqueous solution of hydriodic acid can also be obtained by the action of hydrogen sulphide upon iodine suspended in water, thus :—

$$H_2S + I_2 = 2HI + S.$$
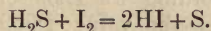
The action ceases when the solution attains a specific gravity of 1·56, because the heat produced by the solution of the product is not sufficient to carry on the process beyond this point.[3]

Hydriodic acid is most conveniently prepared by the action of phosphorus upon iodine in the presence of water, thus :—

$$P + 5I + 4H_2O = 5HI + H_3PO_4.$$
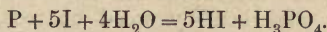
In order to carry out this preparation, place 1 part by weight of red phosphorus and 20 parts of iodine in a flask A (see fig. 28, p. 159), provided with a rubber bung, through which passes the stem of a dropping funnel, and a delivery tube. Gradually drop water from the dropping funnel on to the mixture, keeping the flask and its contents cool by immersion in cold water, until no further evolution of gas can be seen, when the flask may be gently warmed. The hydrogen iodide, which is rapidly evolved, is passed through a U-tube B, containing red phosphorus in order to arrest any iodine vapour with which it may be contaminated. The gas may be collected over mercury or by downward displacement ; or, if an aqueous solution be desired, the gas may be passed through a retort, the bottom of which dips just below the surface of the water contained in a beaker as shown in fig. 16, p. 72. By using this arrangement, any back rush of water into the generating flask is avoided. In Lothar Meyer's[4] modification of this method 100 parts of iodine are mixed with 10 parts of water in a tubulated retort, and a mixture of 5 parts of red phosphorus in 10 parts of water is gradually added from a dropping funnel. Any iodine which may be carried over with the hydriodic acid may be removed by washing with a little water. In this method, as the phosphorus is never in excess, there

[1] Casanova and Carcano, *Boll. chim. farm.*, 1912, **51**, 289.
[2] Lepsius, *Ber.*, 1890, **23**, 1642.
[3] See Vol. VII. for further details.
[4] L. Meyer, *Ber.*, 1887, **20**, 3381.

is no risk of the hydrogen iodide being contaminated with phosphoretted hydrogen, as it may be in the more usual method of preparation.

Gaseous hydrogen iodide may also be prepared by adding a solution of 2 parts of iodine in 1 part of an aqueous solution of hydriodic acid of specific gravity 1·7, drop by drop, to red phosphorus which is just covered over with water. Towards the end of the process it is necessary gently to warm the flask containing the phosphorus.

Aqueous hydriodic acid may be prepared by mixing finely powdered iodine with the calculated quantity of barium peroxide which has been ground up with water.[1] Oxygen is evolved, and the solution, which contains barium iodide, is filtered. More iodine is added to the filtrate and sulphur dioxide passed into the solution, when barium sulphate is precipitated and the solution becomes colourless. On distilling the clear solution, an acid containing 55 per cent. hydrogen iodide passes over at 127° C.

Properties.—At ordinary temperatures and atmospheric pressure, hydrogen iodide exists as a colourless gas possessing a pungent odour somewhat resembling that of hydrogen chloride. It has a strongly acid reaction, and forms dense white fumes in air. The specific gravity of the gas is 4·3757 (air = 1) according to Thomsen, and 4·4429 according to Gay-Lussac. Biltz[2] obtained the value 4·569 at − 17° C. and 4·619 at − 24·9° C. The specific heats at constant volume and pressure respectively are 0·0394 and 0·0550 between 20° and 120°.[3] According to Berthelot,[4] the heat of formation of gaseous hydrogen iodide is H + I (solid) = HI (gas) . . . − 6400 calories; H + I (liquid) = HI (gas) . . . − 4500 calories; H + I (gas) = HI (gas) . . . − 800 calories. Thomsen obtained the value − 6036 calories with solid iodine at 17°, and the value − 436 at 180° C.

The gas is readily absorbed by wood charcoal with the evolution of 22,000 calories of heat per gram-molecule.[5] It is also extremely soluble in water, forming a colourless acid solution which rapidly becomes brown when exposed to the air owing to oxidation and the solution of the liberated iodine. The heat evolved by the solution of 1 gram-molecule of hydrogen iodide in 700 c.c. of water is 19,570 calories (Longuinine); 18,900 calories (Favre and Silbermann); 19,210 calories (Thomsen). According to Berthelot,[6] the heat of dilution of hydrogen iodide in a large quantity of water is given by the equation $Q = \dfrac{11·74}{n} - 500$ when n does not exceed 20. For higher values of n it is better to use the equation $Q = \dfrac{19·57}{10n}$. The heat of solution of 1 molecule of hydrogen iodide in n molecules of water, and the heat of dilution of the solution thus obtained in $(300 - n)$ molecules of water, according to Thomsen,[7] is shown in the following table :—

[1] Bodroux, *Compt. rend.*, 1906, **142**, 279 ; Kassner, *Apoth. Zeit.*, 1909, **24**, 562.
[2] Biltz, *Zeitsch. physikal. Chem.*, 1892, **10**, 354.
[3] Strecker, *Wied. Annalen*, 1882, **17**, 93.
[4] Berthelot, *Compt. rend.*, 1877, **84**, 674 ; *Ann. Chim. Phys.*, 1878, [v.], **15**, 185 ; **16**, 442.
[5] Favre, *Ann. Chim. Phys.*, 1874, [v.], **1**, 209.
[6] Berthelot, *Compt. rend.*, 1873, **76**, 679.
[7] Thomsen, *Thermochemische Untersuchungen*, 1883, vol. iii. p. 76.

Value of n.	Heat of Solution of 1 Molecule of HI in n Molecules of H_2O.	Heat of Dilution in $(300 - n)$ Molecules of H_2O.
	calories.	calories.
2	12,540	6670
3	14,810	4400
5	17,380	1830
10	18,580	630
20	18,990	220
50	19,140	70
100	19,180	30
500	19,210	...

The molecular conductivity of solutions of 1 gram-molecule of hydrogen iodide in v litres, according to Ostwald,[1] at 25°, is shown as follows:—

v.	Molecular Conductivity.	v	Molecular Conductivity.
2	364	64	402
4	376	128	405
8	384	256	406
16	391	512	406
32	397	1024	404

The molecular magnetic rotation of a saturated aqueous solution of hydrogen iodide at different temperatures as found by Perkin[2] is given in the following table:—

Temperature, °C.	Molecular Rotation.	Temperature, °C.	Molecular Rotation.
21·1	17·769	15·2	18·403
16·5	17·868	15·9	18·451
17·6	18·117	20·4	18·428
21·5	18·308	...	...

A saturated solution of the gas at 0° C. has a specific gravity of 1·99. When an aqueous solution of hydrogen iodide is distilled in an atmosphere of hydrogen (in order to prevent oxidation), it behaves in a similar manner to the corresponding chlorine and bromine compounds. The solution, whether concentrated or dilute, yields an acid of constant composition. This acid

[1] Ostwald, *J. prakt. Chem.*, 1885, [ii.], **31**, 433.
[2] Perkin, *Trans. Chem. Soc.*, 1889, **55**, 680.

was regarded as a definite hydrate until Roscoe [1] proved that the strength of the acid obtained depends upon the pressure. Thus at 774 mm. pressure the solution boils at 127° C., has a specific gravity of 1·67, and contains 57 per cent. of hydrogen iodide. Again, when a stream of dry hydrogen is passed through an aqueous solution of hydriodic acid the latter will attain a constant composition independent of the original concentration and depending upon the temperature at which the liquid is kept. Thus at 16° to 19° C. the constant acid contains 60·3 to 60·7 per cent. of hydrogen iodide, and at 100° C. it contains 58·2 to 58·5 per cent. Topsöe [2] found the solution boiling at 127° C. had a specific gravity of 1·708 and contained 57·74 per cent. of hydrogen iodide. The following table gives the specific gravity and percentage of hydrogen iodide contained in an aqueous solution of the gas at temperatures between 12° and 14° C., as found by this investigator :—

Temperature, °C.	Specific Gravity.	Percentage of HI	Temperature, °C.	Specific Gravity.	Percentage of HI.
12	1·708	57·74	13	1·347	36·07
13·7	1·706	57·64	13	1·309	33·07
12·5	1·703	57·42	13·5	1·274	30·20
13	1·692	57·28	13·5	1·2535	28·41
13·7	1·674	56·15	13·8	1·225	25·86
14	1·630	53·93	13·8	1·191	22·63
12·5	1·603	52·43	13·5	1·164	19·97
13	1·5727	50·75	13·5	1·126	15·73
13·5	1·542	49·13	13·5	1·102	13·09
13	1·528	48·22	13	1·095	12·21
13	1·4865	45·71	13·5	1·077	10·15
13	1·451	43·39	13·5	1·0524	7·019
13	1·413	40·45	13·5	1·017	2·286
13	1·382	38·68			

The specific gravity is given in terms of that of water at the same temperature.

The percentage by weight of hydrogen iodide in aqueous solutions of different densities at 15° C., as found by Wright,[3] is shown in the table below :—

Density of Solution.	Percentage of HI.	Density of Solution.	Percentage of HI.
1·708	51·9	1·297	30·3
1·551	47·2	1·175	18·5
1·442	39·2	1·053	5·9

According to Berthelot,[4] 1 volume of water dissolves about 425 volumes of hydrogen iodide.

[1] Roscoe, *J. Chem. Soc.*, 1861, **13**, 146.
[2] Topsöe, *Ber.*, 1870, **3**, 402.
[3] Wright, *Chem. News*, 1871, **23**, 253.
[4] Berthelot, *Compt. rend.*, 1873, **76**, 679.

Water saturated with hydrogen iodide has very nearly the composition $HI + 3H_2O$. Berthelot[1] cooled this liquid to $- 30°$ C., but could not obtain any crystals. He concluded that there is nothing to indicate that this liquid is a definite chemical compound, but considered that the hydrate $HI + 4.5H_2O$ exists and perhaps also a hydrate of the composition $HI + 6.5H_2O$. According to Pickering,[2] at least three crystalline hydrates exist: the dihydrate $HI.2H_2O$, melting at $- 43°$ C.; the trihydrate $HI.3H_2O$, melting at $- 48°$ C.; and the tetrahydrate $HI.4H_2O$, melting at $- 36.5°$ C. There is also a possible hydrate of the composition $HI.17H_2O$.

Hydrogen iodide is one of the most readily liquefiable gases known. Liquid hydrogen iodide was first obtained in 1835 by Kemp[3] as a yellow liquid and was afterwards obtained by Faraday[4] at $0°$ C. under a pressure of four atmospheres, and at ordinary atmospheric pressure by cooling in a bath of ether and solid carbon dioxide. On further cooling to $- 55°$ C. it solidified to a colourless ice-like mass of greater density than the liquid. The melting-point is $- 50.8°$ C. Liquid hydrogen iodide boils at $- 34.1°$ C. according to Estreicher,[5] at $- 36.7$ °C. according to Ladenburg and Krügel,[6] and at $- 35.7°$ C. according to M'Intosh and Steele.[7] The critical temperature is $150.7°$ C., and the viscosity temperature coefficient is 0.70. The liquid is a very bad conductor of electricity, the specific conductivity being about 0.2×10^{-6}.

According to Bleekrode,[8] the index of refraction of liquid hydrogen iodide is 1.466 at $16.5°$ C. for the D line, and according to Cuthbertson and (Mrs) Cuthbertson,[9] the refractivity of gaseous hydrogen iodide is 0.000615 for the green mercury line ($\lambda = 5461$).

The following tables give the density and vapour pressure of liquid hydrogen iodides at different temperatures according to M'Intosh and Steele:—[10]

DENSITY OF LIQUID HYDROGEN IODIDE.

T. (abs.).	D.	D′.	T. (abs.).	D.	D′.
222	2·863	...	232	2·822	...
223·3	...	2·8600	232·9	...	2·819
224	2·855	...	234	2·813	...
224·9	...	2·8496	236	2·805	...
226	2·847	...	236·3	...	2·8034
227·0	...	2·8412	238	2·796	...
228	2·838	...	240	2·787	...
229·3	...	2·8330	240·4	...	2·7862
230	2·830	...	242	2·779	...

The values under D′ were obtained experimentally, those under D were obtained by interpolation.

[1] Berthelot, *Compt. rend.*, 1878, **86**, 279.
[2] Pickering, *Ber.*, 1893, **26**, 2307.
[3] Kemp, *Phil. Mag.*, 1835, [iii.], **7**, 444.
[4] Faraday, *Phil. Trans.*, 1845, **I**, 170.
[5] Estreicher, *Zeitsch. physikal. Chem.*, 1897, **20**, 603.
[6] Ladenburg and Krügel, *Ber.*, 1900, **33**, 637.
[7] M'Intosh and Steele, *Proc. Roy. Soc.*, 1904, **73**, 450.
[8] Bleekrode, *Proc. Roy. Soc.*, 1884, **37**, 339.
[9] Cuthbertson and (Mrs) Cuthbertson, *Phil. Trans.*, 1913, **A, 213**, 1.
[10] M'Intosh and Steele, *Zeitsch. physikal. Chem.*, 1906, **55**, 130.

VAPOUR PRESSURE OF LIQUID HYDROGEN IODIDE.

Temperature, °C.	Vapour Pressure.		Temperature, °C.	Vapour Pressure.	
	a mm.	b mm.		a mm.	b mm.
− 35	...	783	− 56	...	274
− 35·9	769	...	− 57	...	258
− 36	...	750	− 58	...	244
− 36·9	713	...	− 59	...	230
− 37	...	718	− 59·5	224	...
− 38	...	686	− 60	...	218
− 39	...	657	− 61	...	206
− 39·4	644	...	− 62	...	194
− 40	...	628	− 63	...	183
− 41	...	600	− 63·5	185	...
− 41·7	518	...	− 64	...	173
− 42	...	573	− 65	...	162
− 43	...	547	− 66	...	152
− 43·5	530	...	− 67	...	143
− 44	...	519	− 68	...	134
− 45	...	494	− 68·4	126	...
− 46	...	471	− 69	...	126
− 47	...	448	− 70	...	118
− 47·7	438	...	− 71	...	111
− 48	...	425	− 72	...	103
− 49	...	404	− 73	...	97
− 50·6	376	...	− 73·5	92	...
− 51	...	364	− 74	...	90
− 52	...	343	− 75	...	84
− 53	...	325	− 76	...	79
− 54	...	307	− 77	...	73
− 54·8	303	...	− 77·9	74	..
− 55	...	289	− 78	...	70

The values under *a* were obtained experimentally, those under *b* by interpolation.

Gaseous hydrogen iodide is readily decomposed by heat into its constituent elements (see p. 208). Thus, when a heated wire is plunged into the gas, or when the latter is passed through a hot tube, the violet-coloured vapour of iodine at once appears. The amount of decomposition increases with the temperature, but is independent of the pressure.[1] Falckenstein[2] has shown that 32·9 per cent. of the compound is dissociated at 1022° C., and 37·55 per cent. at 1217°. The liberated iodine is itself partially dissociated at these temperatures, according to the reversible equation :—

$$I_2 \rightleftharpoons 2I.$$

According to Lemoine,[3] the gas, when pure, remains absolutely unchanged in the dark and is only very slowly decomposed by sunlight, the decomposi-

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[1] For a short discussion of Bodenstein's work on this subject, see this series, Vol. I. p. 172 ; also *Zeitsch. physikal. Chem.*, 1897, **22**, 1, 23.
[2] Falckenstein, *Zeitsch. physikal. Chem.*, 1909, **68**, 270 ; 1910, **72**, 113.
[3] Lemoine, *Compt. rend.*, 1877, **85**, 144.

tion being brought about by the blue and violet rays. The aqueous solution is not decomposed by sunlight, but when in contact with air, decomposition takes place even in the dark.[1] Creighton and Mackenzie[2] have investigated the effects of the β and γ rays from radium bromide upon solutions of hydrogen iodide. In the absence of oxygen the hydrogen iodide is not decomposed ; but when oxygen is present, the rate of decomposition is increased by the radium rays, the effect becoming relatively less as the temperature is raised. At 24° C. the β and γ rays together cause the liberation of a smaller amount of iodine than do the γ rays alone. Hydrogen iodide is also decomposed by chlorine and bromine with the formation of hydrochloric and hydrobromic acid, and the liberation of iodine according to the equations :—

$$2HI + Cl_2 = 2HCl + I_2.$$
$$2HI + Br_2 = 2HBr + I_2.$$
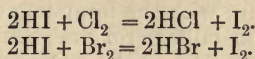
If an excess of the halogen be used, iodine chloride or bromide is also formed. When a mixture of oxygen and hydrogen iodide is passed through a heated porcelain tube, a reaction takes place between the gases with the formation of water and free iodine according to the equation :—

$$4HI + O_2 = 2H_2O + 2I_2.$$
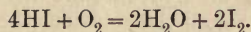
According to Austen,[3] when nitrous oxide and gaseous hydrogen iodide are brought together, a cloud of fine white needles is formed which gradually becomes reddish in colour, and drops of a solution of iodine in hydriodic acid collect on the bottom of the containing vessel. Finally, the bottom and sides of the latter become covered with crystals of iodine. The reaction appears to be :—

$$N_2O + 10HI = 2NH_4I + H_2O + 4I_2.$$
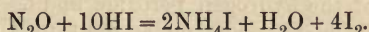
Gaseous nitric acid takes fire in the same circumstances and burns with a red flame surrounded by a halo of iodine vapour, and a cloud of minute crystals of iodine. When fuming nitric acid is dropped into the gas, a red flame is obtained and iodine is liberated. Sulphur and selenium readily decompose the gas at ordinary temperatures, and sulphur dioxide decomposes it with a deep red flash, and immediately covers the sides of the containing vessel with crystals of iodine. The reaction takes place according to the equation :—

$$SO_2 + 4HI = 2H_2O + S + 2I_2.$$
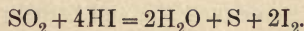
Working with concentrations between 0·005 and 0·1 normal at a temperature of 30° C., Golblum and Lew[4] have shown that the reaction between hydriodic and chromic acids is quadrimolecular, but that it becomes termolecular when a large excess of chromic acid is used. They have also shown that the oxidation of the hydriodic acid is greatly accelerated in the presence of hydrochloric acid, which appears to act as a catalyst, the reaction proceeding two hundred times as fast in N/10HCl solution. A large excess of hydrochloric acid, like an excess of chromic acid, converts the action into a termolecular one.

[1] Berthelot, *Compt. rend.*, 1898, **127**, 143, 795.
[2] Creighton and Mackenzie, *Amer. Chem. J.*, 1908, **39**, 474.
[3] Austen, *Amer. Chem. J.*, 1889, **11**, 172 and 270.
[4] Golblum and Lew, *J. Chim. phys.*, 1912, **10**, 310,

According to Damoiseau,[1] when a current of hydrogen iodide is passed over white phosphorus, the latter melts and a mixture of 'phosphonium and phosphorus iodides is obtained, according to the equation :—

$$5P + 8HI = 2PH_4I + 3PI_2.$$
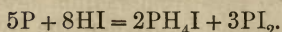
The same reaction takes place, but more slowly, when a piece of white phosphorus is introduced into a concentrated solution of hydrogen iodide. Red phosphorus has but little action upon hydrogen iodide even at 100° C., the small amount of phosphonium iodide formed, apparently, being produced from the white phosphorus with which the red is contaminated.

If ignited magnesium or sodium be brought into gaseous hydrogen iodide, it continues to burn for an instant and then becomes extinguished. The gas readily acts upon mercury with the formation of mercurous and mercuric iodides. It also acts upon metallic peroxides such as manganese dioxide and lead peroxide, with the formation of the corresponding iodides, water, and free iodine, thus :—

$$PbO_2 + 4HI = PbI_2 + 2H_2O + I_2.$$
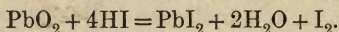
The aqueous solution is a strong monobasic acid which is, however, weaker than aqueous hydrochloric or hydrobromic acids. When a fairly strong electric current is passed through the solution, the hydriodic acid is oxidised to iodic acid and hydrogen is evolved. The solution is decomposed by hydrogen peroxide with the formation of water and the liberation of free iodine according to the equation :—

$$H_2O_2 + 2HI = 2H_2O + I_2.$$
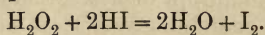
According to Brode,[2] the velocity of the reaction is directly proportional to the concentration of the hydrogen peroxide and of the iodine ions. It is increased by the addition of acids, on account of the catalytic influence exerted by the hydrogen ions thus introduced. Ferrous sulphate, copper sulphate, molybdic acid, and tungstic acid also considerably increase the velocity, probably on account of intermediate reactions.

Norris and Cottrell[3] have carefully studied the properties of liquid hydrogen iodide. This substance is rapidly decomposed by sunlight with the liberation of iodine, which dissolves in the liquid, forming a reddish-purple solution. It readily attacks silver, mercury, iron, aluminium, sodium, and potassium, forming the iodides of these metals and evolving hydrogen. It has much less action on copper and tin, and little or none on lead, cadmium, arsenic, antimony, bismuth, zinc, and magnesium. Cupric oxide and manganese dioxide are rapidly dissolved in the liquid with the liberation of iodine. Calcium carbonate and anhydrous sodium carbonate are not acted upon. Sulphur gradually dissolves in the liquid with the formation of hydrogen sulphide and liberation of iodine. Sulphur dioxide reacts with the formation of water and hydrogen sulphide and the liberation of iodine and plastic sulphur. Chlorine reacts with explosive violence, forming hydrogen chloride and liberating iodine. Gaseous ammonia also reacts with considerable violence with the formation of ammonium iodide. Water does not mix with liquid hydrogen iodide even when the two liquids are shaken together. Hydrogen iodide combines with a number of organic substances to form

[1] Damoiseau, *Compt. rend.*, 1880, **91**, 883.
[2] Brode, *Zeitsch. physikal. Chem.*, 1901, **37**, 257.
[3] Norris and Cottrell, *Amer. Chem. J.*, 1896, **18**, 96.

additive compounds. Archibald and McIntosh [1] have prepared the acetone compound $CH_3.CO.CH_3.HI$, the ether compound $C_2H_5.O.C_2H_5.HI$, and the alcohol compound $C_2H_5.OH.HI$. McIntosh [2] has also prepared the aldehyde compound $3CH_3.CHO.2HI$ and the ethyl acetate compound $CH_3.CO_2.C_2H_5.HI$. According to the last chemist, acetic acid does not combine with hydrogen iodide at low temperatures.

Hydrogen Per-Iodide.—The dark brown solution obtained when iodine is dissolved in aqueous hydriodic acid is usually considered to contain unstable compounds of iodine with hydrogen iodide, such as $HI.I_2$. These compounds are known as per-iodides of hydrogen, and the corresponding salts obtained by dissolving iodine in aqueous solutions of iodides are · called per-iodides or poly-iodides (see p. 221). According to Osaka,[3] the rise of the freezing-point produced when iodine is added to an aqueous solution of hydrogen iodide (or potassium iodide) is proportional to the amount of iodine added, and is greater for the acid than for the potassium salt. The total concentration of ions and undissociated molecules is therefore decreased by the addition of iodine, and the affinity constant of the iodides must be greater than that of the tri-iodides.

THE IODIDES.

The salts of hydriodic acid are known as iodides ; acid and double salts, and also the somewhat doubtful sub-iodides, are known in addition to the normal salts.

Normal Iodides.—The normal iodides may be obtained by the direct combination of the metal and iodine, frequently at ordinary temperatures (see p. 206). Guichard [4] has experimented with sealed evacuated tubes containing a metal at one end and iodine at the other, with an asbestos plug between. In the case of iron, if the metal be kept at 500° C. and the iodine at 180°, a sublimation of deep red crystals of ferrous iodide is obtained. Nickel and uranium also yield iodides under the same conditions, but a different arrangement is required for metals such as aluminium, which yield very volatile iodides. In this case the tube is bent, the metal is placed in the bend, the iodine at one end, and the other end is left to receive the iodide. The metal is kept at 500° and the iodine at 180° as before, but the end intended to receive the iodide is kept at 15°C. Ducelliez [5] prepares anhydrous manganese iodide by adding iodine to finely divided manganese under anhydrous ether. The iodides may be also obtained by passing iodine vapour over the heated oxides and hydroxides of those metals, such as potassium, sodium, lead, and bismuth, which have a greater affinity for iodine than for oxygen, and by passing hydrogen iodide over certain metals and metallic oxides. They are prepared by dissolving such metals as zinc and magnesium, or metallic oxides, in the aqueous acid, and also by the decomposition of those iodates which split up when heated into the corresponding iodides and free oxygen (see p. 244). According to Muntz,[6] the iodates may be decomposed by means of micro-organisms with the production of iodides. Insoluble iodides are prepared by adding a solution of a soluble iodide to a solution of a soluble salt of the metal required. Thus, if a solution of potassium iodide be added

[1] Archibald and McIntosh, *Trans. Chem. Soc.*, 1904, **85**, 919.
[2] McIntosh, *J. Amer. Chem. Soc.*, 1906, **28**, 588.
[3] Osaka, *Zeitsch. physikal. Chem.*, 1900, **38**, 743.
[4] Guichard, *Compt. rend.*, 1907, **145**, 807.
[5] Ducelliez, *Bull. Soc. chim.*, 1913, [iv.], **13**, 815.
[6] Muntz, *Compt. rend.*, 1885, **101**, 248.

to a solution of mercuric chloride, a salmon-coloured precipitate of mercuric iodide, which rapidly becomes bright scarlet in colour, is obtained, thus :—

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$
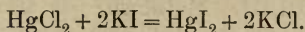
The normal metallic iodides closely resemble the corresponding chlorides and bromides, but they are less fusible and less volatile. They are nearly all very readily soluble in water; some, however, such as the iodides of silver and mercury, are insoluble, and lead iodide is only very sparingly soluble in the cold. Some iodides, such as those of arsenic, antimony, and tin, are decomposed by water. Arsenious iodide yields a mixture of arsenic iodide and arsenic, but in most cases oxy-iodides are formed. These iodides are soluble without decomposition in certain solvents such as chloroform, carbon bisulphide, etc.

Some of the metallic iodides are more or less highly coloured. Thus, mercurous iodide is green and mercuric iodide is bright scarlet when prepared at ordinary temperatures. The latter becomes lemon-yellow in colour when heated above $116 \cdot 5°$ C., and retains this colour on cooling, unless disturbed by touching with a glass rod or other means, when it immediately becomes scarlet again. Silver iodide is light yellow, and lead iodide is a rich deep yellow when precipitated from solution; the latter precipitate is, however, fairly soluble in hot water, and crystallises out in beautiful golden-yellow scales on cooling. Gold iodide is yellow, bismuth iodide is brownish grey, and the iodides of arsenic and antimony are red.

Most of the iodides remain unchanged when heated, but those of gold, platinum, and palladium are decomposed. According to Merz and Weith,[1] potassium iodide remains quite unaltered when fused in an atmosphere of carbon dioxide. Schulze[2] found that the iodides of silver and mercury remain completely unchanged when heated in contact with oxygen; the alkaline iodides are partly decomposed, and all the other iodides are completely decomposed, under the same circumstances. When heated in an atmosphere of hydrogen, the iodides are partially decomposed, with the formation of hydriodic acid. According to Leeds,[3] aqueous solutions of iodides, to which hydrochloric or sulphuric acid has been added, are only decomposed by light when free oxygen is present, the amount of decomposition being proportional to the concentration and to the time of exposure. Ross[4] has shown that the amount of iodine liberated from an aqueous solution of an iodide in a given time is inversely proportional to the square of the distance of the solution from the source of light, and directly proportional to the concentration for concentrations between 3N and N/1000.

All the iodides are decomposed by chlorine and bromine with the liberation of iodine and the formation of the corresponding chlorides and bromides (see p. 205); by many acids, such as concentrated nitric acid and sulphuric acid (see p. 195), and hydrochloric acid, which decomposes them at red heat with the formation of hydriodic acid and a chloride, thus :—

$$KI + HCl = KCl + HI.$$
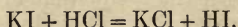
Schwezoff[5] has investigated the oxidising action of sulphuric acid, hydrochloric acid, and nitric acid on the iodides of sodium, potassium, and cadmium in

[1] Merz and Weith, *Ber.*, 1880, **13**, 1475
[2] Schulze, *J. prakt. Chem.*, 1880, **21**, 407.
[3] Leeds, *Pharm. J.*, 1879, [iii.], **9**, 1117 ; *J. Amer. Chem. Soc.*, 1880, **2**, 249.
[4] Ross, *J. Amer. Chem. Soc.*, 1906, **28**, 786.
[5] Schwezoff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 219.

diffused sunlight, a constant current of air being passed through the mixture in order to keep the concentration of oxygen constant. Nitric acid reacts rapidly (even in the dark), but the reaction with sulphuric or hydrochloric acid is much slower. Equivalent quantities of sodium, potassium, and cadmium iodides evolve equal amounts of iodine under similar conditions. According to Kernot and Pietrafesa,[1] the rate of reaction between potassium dichromate and potassium iodide in the presence of hydrochloric acid is proportional to the concentration of each of the reacting substances. Under corresponding conditions the speed is affected most by the acid and least by the iodide. The speed of the reaction is also accelerated by colloidal platinum or ferrous sulphate, which acts as a catalyst.

The iodides are also decomposed by hydrogen peroxide in acid solution, with liberation of iodine and the ultimate oxidation of part of the iodine to iodic acid,[2] according to the equations :—

$$(1) \quad 2HCl + H_2O_2 = 2H_2O + Cl_2.$$
$$(2) \quad I + 3Cl = ICl_3.$$
$$(3) \quad 5ICl_3 + 9H_2O \rightleftharpoons HIO_3 + 15HCl + I_2.$$
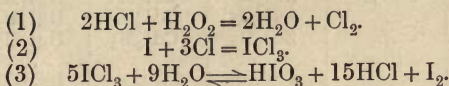
Acid Iodides.—These are combinations of normal iodides and hydrogen iodide, and are often combined with water. A hydrated acid iodide of bismuth of the composition $BiI_3.HI.4H_2O$ was obtained in 1845 by Arppe, and similar compounds of platinum of the composition $PtI_4.2HI.9H_2O$ by Topsöe in 1870. More recently Berthelot[3] has obtained the lead compound $PbI_2.HI.10H_2O$ by saturating a mixture of lead iodide and water with hydrogen iodide. The lead iodide dissolves, and the liquid becomes brown in colour. On cooling, the salt is deposited in pale yellow crystals which are decomposed by heat and also by an excess of water, leaving a residue of lead iodide. The crystals lose hydrogen iodide when exposed to air and light. The same author obtained a silver compound of the composition $3AgI.HI.14H_2O$ by dissolving silver iodide in hydriodic acid and exposing the solution to the air, when the salt crystallises out in transparent lamellæ, which become yellow when exposed to light and air, and are decomposed by heat and also by water. Young[4] has obtained an acid iodide of tin by cooling a saturated solution of stannous iodide in hydriodic acid by means of ice-water, when the substance crystallises out in pale yellow needles. These could not be dried without decomposition, and therefore could not be directly analysed; an indirect method of analysis, however, led to the conclusion that the composition of the substance was $SnI_2.HI$. A hydrated acid iodide of tellurium of the composition $TeI_4.HI.8H_2O$ has been obtained by Metzner[5] by treating telluric acid with a cold concentrated solution of hydriodic acid and passing a current of hydrogen iodide through the liquid. Black quadratic needles were formed, and, on cooling the solution, a thick mass of these crystals was obtained. The salt is deliquescent, and, when exposed to the air, is transformed into a viscous brown liquid. It melts at 55° C., and, if heated above this point, first gives off water and then hydrogen iodide, finally leaving a grey residue of tellurium iodide.

Double Iodides.—A large number of double iodides are known. They

[1] Kernot and Pietrafesa, *Rend. Accad. Sci. Fis. Met. Napoli*, 1911, [iii.] A, **16**, 275.
[2] Auger, *Compt. rend.*, 1911, **152**, 712.
[3] Berthelot, *Compt. rend.*, 1880, **91**, 1024.
[4] Young, *J. Amer. Chem. Soc.*, 1897, **19**, 851.
[5] Metzner, *Compt. rend.*, 1897, **124**, 1448.

are prepared by dissolving the required iodide in a solution of an alkali iodide. Thus, silver iodide dissolves in an aqueous solution of potassium iodide, and the double salt AgI_2K crystallises out on cooling :—

$$AgI + KI = AgI_2K.$$
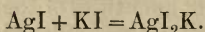
The double iodides have been classified into types by Pfeiffer,[1] as shown in the table below.

TYPES OF IODO-SALTS.

I. Cu.	I. Ag.	II. Mg.	II. Zn.	II. Cd.	II. Hg.	II. Sn.
CuI_2M	AgI_2M AgI_3M_2 Ag_2I_3M	MgI_3M	ZnI_3M ZnI_4M_2 ZnI_5M_3	CdI_3M CdI_4M_2 CdI_5M_3	HgI_3M HgI_4M_2 HgI_5M_3 ... Hg_2I_5M $Hg_3I_8M_2$ $Hg_3I_{10}M_4$	SnI_3M ... ...

II. Pb.	II. Co.	II. Ir.	II. Pt.	III. Al.	III. Tl.	III. As.
PbI_3M PbI_4M_2 ... ... $Pb_3I_{10}M_4$	... CoI_4M_2	... IrI_4M_2	PtI_3M	AlI_4M	TlI_4M ... ... TlI_8M_5 TlI_9M_3	AsI_4M ... ... $As_2I_9M_3$

III. Sb.	III. Bi.	III. Au.	III. Ir.	IV. Pb.	IV. Te.	IV. Ir.	IV. Pt.
SbI_4M ... ... SbI_7M_4 Sb_2I_7M $Sb_2I_9M_3$ $Sb_4I_{15}M_3$	BiI_4M BiI_5M_2 BiI_6M_3 BiI_7M_4 $Bi_2I_9M_3$ $Bi_3I_{11}M_2$ $Bi_3I_{13}M_4$ $Bi_3I_{14}M_5$ $Bi_5I_{21}M_6$	AuI_5M	... ... IrI_6M_3	... PbI_6M_2	TeI_5M TeI_6M_2	... IrI_6M_2	... PtI_6M_2

According to Wells,[2] the valency of negative halides appears to have little, if any, influence upon the types of double halides formed, and whatever the valency of these negative halides may be, their combining power is nearly the same as that of the alkali halides.

[1] Pfeiffer, *Zeitsch. anorg. Chem.*, 1902, **31**, 191.
[2] Wells, *Amer. Chem. J.*, 1901, **26**, 389.

Dam and Donk [1] have determined the solubility isothermals for 0°, 30°, and 50° C. in the system AgI.KI, and H_2O. The only double salts are AgI.KI at 0°, AgI.2KI at 30°, and AgI.KI at 50° C. Sandonnini and Scarpa [2] have investigated the system LiI—AgI and NaI—AgI by means of thermal analysis. The iodides of lithium and sodium form solid solutions within very wide limits.

Besides these double iodides similar compounds have been obtained in which part of the iodine is replaced by one of the other halogens. Thus Defacqz [3] has prepared and described the fluor-iodides of the alkaline earths. Barium fluor-iodide has the composition $BaF_2.BaI_2$. It is prepared by heating 10 parts of manganese fluoride and 80 parts of barium iodide to about 800° C. for about an hour. The reaction takes place according to the equation :—

$$MnF_2 + 2BaI_2 = BaF_2.BaI_2 + MnI_2.$$
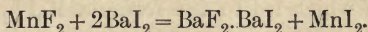
Barium fluoriodide consists of very deliquescent, transparent colourless lamellæ which readily turn yellow in contact with air owing to the liberation of iodine. It is decomposed by water and also by dilute mineral acids. The corresponding strontium and calcium compounds $SrF_2.SrI_2$ and $CaF_2.CaI_2$ are prepared in the same manner, and have similar properties. Two antimony fluor-iodides $(SbFl_5)_2I$ and $(SbFl_5)I$ are also known.

The iodides also form compounds with other elements and groups. Thus, many combine with ammonia. Antimony and tellurium combine with iodine and oxygen to form oxy-iodides, and bismuth and tin form similar compounds with iodine and sulphur. According to Scarpa,[4] silver nitrate forms a compound with silver iodide of the composition $3AgNO_3.2AgI$. Péchard [5] found that dry solid potassium iodide absorbs large quantities of sulphur dioxide, becoming yellow in colour although no iodine is liberated. The sulphur dioxide is given off again on heating. When the gas is passed through an aqueous solution of potassium iodide, a similar change takes place, the liquid becoming yellow in colour. The iodides of sodium, ammonium, barium, and calcium give rise to similar compounds when treated in the same manner. Marsh [6] has shown that many double iodides and the allied double halogen compounds absorb ether, forming such compounds as :—

$$KI.HgI_2.4(C_2H_5)_2O, \qquad LiI.AgI.3(C_2H_5)_2O,$$
$$NaI.HgI_2.6(C_2H_5)_2O, \qquad LiBr.HgI_2.4(C_2H_5)_2O.$$
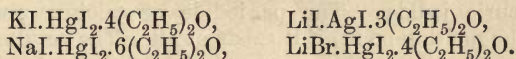
Per-iodides.—The per-iodides, or poly-iodides may be regarded as salts of the per-hydriodic acids (see p. 217) or as additive compounds of the normal iodides and iodine. They are readily reduced to normal iodides, possess a well-defined crystalline form, and have distinct physical constants. Most of the known per-iodides are tri-iodides, but penta- and hepta-iodides have also been obtained. Ammonium per-iodide was known to Berzelius under the name of ammonium bin-iodide, and a number of per-iodides of organic bases have been described by Pelletier, Herepath, Jörgensen, and others. The iodine, in a solution of iodine in aqueous potassium iodide, was considered to be loosely combined with the potassium iodide, to form a compound such as

[1] Van Dam and Donk, *Chem. Weekblad.*, 1911, **8**, 846.
[2] Sandonnini and Scarpa, *Atti R. Accad. Lincei*, 1913, [v.], **22**, ii. 517.
[3] Defacqz, *Compt. rend.*, 1904, **138**, 197 ; *Ann. Chim. Phys.*, 1904, [viii.], **1**, 337.
[4] Scarpa, *Atti R. Accad. Lincei*, 1913, [v.], **22**, ii. 452.
[5] Péchard, *Compt. rend.*, 1900, **130**, 1188.
[6] Marsh, *Trans. Chem. Soc.*, 1910, **97**, 2297.

$KI.I_2$, and in 1877 Johnson [1] succeeded in preparing crystals of potassium tri-iodide by slowly evaporating a saturated solution of iodine in aqueous potassium iodide over sulphuric acid. Dark blue prismatic crystals were obtained which were very deliquescent, and, when placed in water, were decomposed into potassium iodide and free iodine. Analysis gave the composition KI_3. Cæsium tri-iodide, CsI_3, and penta-iodide, CsI_5, rubidium tri-iodide, RbI_3, and potassium hepta-iodide, KI_7, have also been obtained by Wells and Wheeler, Dawson, and others. Meldrum [2] has prepared a hydrated potassium lead per-iodide by slowly heating a mixture of 150 grams of potassium iodide, 4 grams of lead iodide, 70 grams of iodine, and 90 c.c. of water to the boiling-point and filtering. After a time crystals were formed which were collected and drained on a porous tile. They were shining, violet-coloured prisms, the analysis of which led to the formula $K_9Pb_{14}I_{19}.10H_2O$. The salt is not hygroscopic. The formation of per-iodides in solution may be investigated by various indirect means. Thus Tinkler [3] has studied the state of iodine in different solvents by means of ultra-violet absorption spectra of its solutions. Whilst neither a N/1000 solution of iodine in water, chloroform, or alcohol, nor a dilute aqueous solution of potassium iodide show any absorption bands, and very little general absorption, on adding an iodide of potassium, sodium, magnesium, barium, cadmium, aluminium, hydrogen, ammonium, or tetramethyl ammonium to N/1000 aqueous iodine, the spectrum shows two absorption bands and considerable general absorption. In every case the colour of the solution changes from reddish brown to yellow, and the spectra obtained were identical. All these solutions therefore appear to contain the same ion, probably I_3, and the tri-iodides of all the above bases exist in aqueous solution. Dawson [4] has investigated the formation of per-iodides in nitrobenzene solution by the determination of the composition of the aqueous solutions which are in equilibrium with the nitrobenzene solutions of iodine and iodides.

Olivari [5] has determined the freezing-point curves for mixtures of metallic iodides with iodine, by means of an ordinary cryoscopic apparatus. The curves obtained show that mercuric iodide does not form a per-iodide; there is, however, an eutectic point in the curve at about 101·4° and 12·5 molecules per cent. mercuric iodide. The per-iodide of calcium must be greatly dissociated at the melting-point, if it exists at all. The results obtained with the per-iodides of tetramethyl ammonium iodide and phenyltrimethyl ammonium iodide confirm Abegg and Hamburger's [6] conclusion that the stability of the per-iodides increases with the electropositive character of the cation.

The existence of potassium tri-iodide has been denied by several investigators. Parsons and Corliss [7] have shown that there is no evidence of the formation of solid per-iodides in aqueous-alcoholic solutions of iodine with potassium iodide, and also that in aqueous solutions the iodine can be partially separated from the potassium iodide by diffusion. They conclude from their results that per-iodides are not formed to any appreciable extent, and attribute

[1] Johnson, *Trans. Chem. Soc.*, 1877, **1**, 249.
[2] Meldrum, *Proc. Chem. Soc.*, 1908, **24**, 97.
[3] Tinkler, *Trans. Chem. Soc.*, 1907, **91**, 996 ; 1908, **93**, 1611.
[4] Dawson, *Trans. Chem. Soc.*, 1902, **81**, 524 ; 1904, **85**, 791 ; 1908, **93**, 1308
[5] Olivari, *Atti R. Accad. Lincei*, 1908, [v.], **17**, ii. 717.
[6] Abegg and Hamburger, *Zeitsch. anorg. Chem.*, 1906, **50**, 403.
[7] Parsons and Corliss, *J. Amer. Chem. Soc.*, 1910, **32**, 1367.

the increased solubility of iodine in a solution of an iodide, compared to the solubility in pure water, to the high solvent power of the dissolved solid.   As a result of an investigation of the system KI, I and H_2O, Parsons and Whittemore[1] conclude that potassium poly-iodides do not exist at 25° C., and Bell and Buckley[2] have shown that when iodine is dissolved in an aqueous solution of sodium or potassium bromide at 25° C., double compounds are only formed in very minute quantities, if at all.   Kremann and Schoulz[3] have made a thermal investigation of the system KI—I_2, from the results of which they conclude that the compound KI_4 or $2KI.3I_2$ exists, though in a highly dissociated state in the fused mixture, but that there is no evidence of the existence of any poly-iodide poorer in iodine.   They have also investigated the electrolysis of solutions of the alkali iodides, and conclude that the tendency of the alkali iodides to form per-iodides decreases in the order cæsium, rubidium, ammonium, potassium, lithium, or sodium.   Herz and Paul[4] have studied the solutions of iodine in mercuric chloride and bromide, and conclude that the mercury polyhaloids $HgBr_2I_2$ and $HgCl_2I_2$ exist.

Sub-Iodides.—When silver iodide is exposed to the action of light, a change takes place and silver compounds containing less iodine than the normal iodide are formed.   These products are known as sub-iodides, but it is not known with certainty whether they are true chemical compounds or only mixtures.   Carey Lea[5] has obtained a series of coloured compounds of silver and iodine (and also chlorine and bromine) which he calls photosalts, and which appear to be compounds of the normal and sub-iodides.   Similar substances have also been prepared by other methods by various chemists.[6] Vogel[7] has also prepared a compound which he regards as a sub-iodide of silver of the composition 2Ag.2AgI ; but, according to Emszt,[8] this substance is different from the sub-iodides obtained by the action of light on the normal salt, and is in reality only a mixture of silver and silver iodide.   A bismuth sub-iodide has been supposed to exist, but Marino and Becarelli[9] have investigated the system Bi – I by thermal analysis and can find no indication of the existence of any compound of these two elements other than the tri-iodide BiI_3.

COMPOUNDS OF IODINE WITH THE OTHER HALOGENS.

Iodine combines with all the other halogens, forming readily decomposable compounds.   Only one compound of iodine and fluorine, the pentafluoride IF_5, is known.   Two chlorides, the monochloride ICl and the trichloride ICl_3, certainly exist, and two others, the tetrachloride ICl_4 and the pentachloride ICl_5, have been described.   Iodine tribromide is unknown, but the monobromide IBr certainly exists, and perhaps also the pentabromide IBr_5.   In addition to these compounds, a hydrated oxyfluoride and an oxychloride of iodine have been described, also a double compound of iodine monochloride

[1] Parsons and Whittemore, *J. Amer. Chem. Soc.*, 1911, **33**, 1933.
[2] Bell and Buckley, *J. Amer. Chem. Soc.*, 1912, **34**, 10.
[3] Kremann and Schoulz, *Monatsh.*, 1912, **33**, 1391.
[4] Herz and Paul, *Zeitsch. anorg. Chem.*, 1914, **85**, 214.
[5] Carey Lea, *Amer. J. Sci.*, 1887, [iii.], **33**, 349, 480, and 489 ; **34**, 33 ; 1892, [iii.], **44**, 322.
[6] Lüppo-Cramer, *Zeitsch. Chem. Ind. Kolloide*, 1907, **2**, 135 ; 1908, **2**, 360 ; **3**, 33 and 135.
[7] Vogel, *J. Soc. Chem. Ind.*, 1900, **19**, 374.
[8] Emszt, *Zeitsch. anorg. Chem.*, 1901, **28**, 346.
[9] Marino and Becarelli, *Atti R. Accad. Lincei*, 1912, [v.], **21**, ii. 695.

and hydrogen chloride $ICl.HCl$, and a hydrated pentabromide of doubtful existence.

Iodine Pentafluoride, IF_5, was discovered in 1871 by Gore,[1] who obtained it by heating iodine with pure dry silver fluoride in a platinum tube. It was afterwards prepared by Moissan[2] by the direct action of fluorine on iodine. According to Prideaux,[3] liquid fluorine does not dissolve iodine and does not react with it. Iodine pentafluoride is a colourless liquid which solidifies to a camphor-like mass at 8° C., and boils at 97° C. It fumes in air and has a very irritating action on the respiratory organs. When heated to 400°–500° C., it is decomposed, with the liberation of iodine. It is very reactive, being readily decomposed by sulphur, phosphorus, arsenic, antimony, and carbon in the cold; and by silicon, chlorine, and bromine on heating. It is also decomposed by water with the formation of hydrofluoric acid and iodine pentoxide, according to the equation :—

$$2IF_5 + 5H_2O = I_2O_5 + 10HF.$$
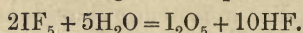
Concentrated sulphuric acid slowly decomposes it with the formation of hydrofluoric acid. Aqueous solutions of potash or soda rapidly decompose it, forming the corresponding fluorides and iodates.

Iodine Oxyfluoride Hydrate, $IOF_3.5H_2O$, or $IF_3(OH)_2.4H_2O$, has been obtained by Weinland and Reischle[4] by dissolving iodic acid in a solution of hydrofluoric acid in glacial acetic acid. On evaporating the solution, the oxyfluoride crystallised out in the form of colourless needles which fumed in air, evolving hydrogen fluoride. When alcohol was used in the place of acetic acid, the product was contaminated with iodine. Colourless prismatic needles of pyridine trifluoro-iodate, $IF_3(OH)_2.C_5NH_5$, were obtained by dissolving a mixture of pyridine and iodic acid in the acetic acid solution of hydrogen fluoride, and evaporating over concentrated sulphuric acid. When a concentrated aqueous solution of this salt was allowed to crystallise slowly, *pyridine difluoro-iodate*, $IF_2O(OH)C_5NH_5$, was obtained. The *penta-* and *hepta-fluoro-iodates* were also prepared. The same investigators obtained colourless crystals of *phenyl iodoxyfluoride hydrofluoride*, $C_6H_5.IOF_2.HF$, by dissolving iodobenzene in a concentrated alcoholic solution of hydrogen fluoride and crystallising out. In a similar manner, by using the iodotoluenes, the *o-*, *m-*, and *p-tolyl iodoxyfluoride hydrofluorides* $C_6H_4.CH_3.IOF_2.HF$ were obtained, and by using a mixture of iodobenzene and iodic acid they prepared the compound $IOF_3.C_6H_5.IOF_2$.

Iodine Monochloride, ICl, was first described by Gay-Lussac. It is prepared by passing dry chlorine over dry iodine, when the two elements unite according to the equation :—

$$I_2 + Cl_2 = 2ICl.$$
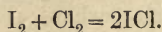
It may also be obtained by distilling 1 part of iodine with 4 parts of potassium chlorate. The iodine displaces the chlorine in the chlorate, thus :—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2,$$
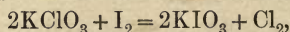
and the liberated chlorine then combines with the remaining iodine, forming the mono- and tri-chlorides of iodine.[5]

[1] Gore, *Chem. News*, 1871, **24**, 291.
[2] Moissan, *Compt. rend.*, 1902, **135**, 563.
[3] Prideaux, *Proc. Chem. Soc.*, 1905, **21**, 19 ; *Trans. Chem. Soc.*, 1906, **89**, 316.
[4] Weinland and Reischle, *Zeitsch. anorg. Chem.*, 1908, **60**, 163.
[5] Thorpe and Perry, *Trans. Chem. Soc.*, 1892, **61**, 925.

A third method, due to Bunsen, is to boil iodine with an excess of concentrated aqua regia, and, when the reaction is over, dilute with water and shake up with ether in order to dissolve out the chloride. The ethereal solution is then separated and the ether evaporated off, when the iodine monochloride remains behind.

Bigot [1] causes chlorine to act upon iodine in presence of a little water and thus prepares impure iodine monochloride, which he uses in organic reactions.

Iodine monochloride is a reddish-brown oily liquid which solidifies on cooling in long, well-defined, ruby-red crystals. It possesses an odour between that of chlorine and iodine, and has a very strong action upon the skin. The melting-point is variously given as 24·7° C. (Hannay [2]); 25° C. (Trapp [3]); 30° C. (Schützenberger [4]); but the most probable value is 27·2° C. [5] The boiling-point is between 100·5° C. and 101·5° C. (Hannay); 101·3° C. (Thorpe [6]); 101° C. (Oddo and Serra [7]). Gernez [8] found that a layer 30 cms. thick of the vapour gave an absorption spectrum showing twenty lines in the red and two in the yellow. The density is 3·18223 at 0° C. and 2·88196 at 101·3° C. (Thorpe); the following table shows the density at different temperatures between 0° and 98° C. as found by Hannay :—

Temperature, ° C.	Density.	Temperature, ° C.	Density.
0	3·263	60	3·084
16·5	3·222	72	3·032
18·2	3·206	75	3·036
30	3·180	86	2·988
32	3·176	90	2·984
45	3·132	95	2·964
48	3·127	98	2·958

The vapour density (H = 1) is 80·29 at 120° C., and 83·2 at 512° C. (Hannay). According to Berthelot,[9] the heat of formation is I (solid) + Cl (gas) = ICl (solid) . . . + 6700 calories; I (gas) + Cl (gas) = ICl (solid) . . . + 12,100 calories. According to Thomsen,[10] the heat of formation of liquid iodine monochloride from solid iodine and gaseous chlorine is + 11,650 calories.

According to Bruner and Bekier,[11] fused iodine monochloride between silver electrodes undergoes continuous electrolysis, chlorine being evolved at the anode. A solution of the monochloride in liquid sulphur dioxide is a conductor.

[1] Bigot, *Ann. Chim. Phys.*, 1891, [vi.], **22**, 464.
[2] Hannay, *Trans. Chem. Soc.*, 1873, **26**, 815.
[3] Trapp, *J. prakt. Chem.*, 1854, **63**, 108.
[4] Schützenberger, *Chem. Zeit.*, 1862, **5**, 1.
[5] Stortenbeker, *Rec. trav. chim.*, 1888, **7**, 152 ; Oddo, *Gazzetta*, 1901, **31**, ii. 146.
[6] Thorpe, *Trans. Chem. Soc.*, 1880, **37**, 141 and 327.
[7] Oddo and Serra, *Gazzetta*, 1899, **29**, ii. 343.
[8] Gernez, *Compt. rend.*, 1872, **74**, 465.
[9] Berthelot, *Compt. rend.*, 1880, **90**, 841.
[10] Thomsen, *Ber.*, 1882, **15**, 3021.
[11] Bruner and Bekier, *Zeitsch. Elektrochem.*, 1912, **18**, 368 ; *Zeitsch. physikal. Chem.*, 1913, **84**, 570.

Trapp [1] and Stortenbecker [2] have shown that there are two isomeric modifications of this compound, which are known as α- and β-iodine monochloride. The α- modification is obtained by suddenly cooling the liquid distillate. It forms long ruby-coloured needles which melt at 27·2° C. The specific heat is 0·083. The β-modification is obtained by keeping the freshly distilled liquid for a considerable time at − 10° C., when it crystallises out in brownish-red leaves, the temperature meanwhile rising to between 13° and 14° C. According to Tanatar, [3] β-iodine monochloride may also be obtained by sowing a crystal of this modification in the fused α-modification. The melting-point of β-iodine monochloride is 13·9° C., and the specific heat is 0·102. The α-modification is the stable form, and the β-modification the labile. The two modifications appear to be identical when fused.

Iodine monochloride is dissociated when heated, yielding iodine trichloride and free iodine :—

$$3ICl \rightleftharpoons ICl_3 + I_2.$$
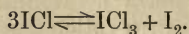
It is also decomposed by water with the liberation of iodine and iodic and hydrochloric acids and an odorous yellow volatile compound which may be extracted with ether. [4] The composition of this compound appears to be $ICl.HCl$.

Aqueous solutions of potassium or sodium hydroxide behave in a somewhat similar manner to water, yielding the corresponding alkali iodates and chlorides and free iodine, thus :—

$$5ICl + 6KOH = KIO_3 + 5KCl + 2I_2 + 3H_2O.$$
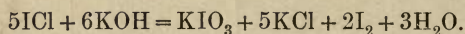
If an excess of alkali be used, the liberated iodine is converted into a mixture of iodate and iodide, and Grünelberg [5] has shown that if a small quantity only of alkali be taken, potassium chlorate and free iodine are obtained. Aqueous ammonia behaves differently, yielding a mixture of nitrogen iodide and ammonium chloride.

Solutions of hypochlorous acid or of hypochlorites are decomposed by this substance, yielding chlorine and iodic acid or an iodate. Solutions of chloric acid or of chlorates behave in a similar manner. [6]

Sulphuretted hydrogen and sulphur dioxide both decompose iodine monochloride, liberating iodine.

There is only a slight reaction when sulphur is brought into contact with iodine monochloride, the products being free iodine and sulphur chloride. The action with selenium is more vigorous, and it is still more vigorous with tellurium. Phosphorus pentachloride reacts with the formation of a double chloride of the composition $PCl.ICl$ and phosphorus trichloride.

Iodine monochloride has a more or less energetic action on most metals. Thus, it unites with powdered antimony with great energy, yielding a mixture of antimony chloride and iodide. It unites with still more energy with arsenic and with less energy with bismuth. It readily combines with tin-foil, evolving white fumes of stannic chloride and iodide. With aluminium-foil there is little or no action at first, but after a little while the metal burns

[1] Trapp, *loc. cit.*
[2] Stortenbecker, *Rec. trav. chim.*, 1888, **7**, 152 ; *Zeitsch. physikal. Chem.*, 1892, **10**, 183.
[3] Tanatar, *J. Russ. Phys. Ges.*, 1893, **25**, 97.
[4] Schützenberger, *Compt. rend.*, 1877, **84**, 389.
[5] Grünelberg, *J. prakt. Chem.*, 1853, **60**, 172.
[6] Henry, *Ber.*, 1870, **3**, 892.

with a bluish-white flame.   The action on copper-foil is very slow ; but finely divided copper reacts with considerable energy, forming a mixture of cuprous chloride and iodide, together with a little cupric chloride and free iodine.   Potassium at once explodes when brought into contact with this compound, but sodium has no action upon it unless the mixture be rubbed in a mortar, when combination takes place with the formation of sodium chloride and iodide.   Iodine monochloride combines with lead peroxide, cupric oxide, and mercuric oxide with the formation of the corresponding chlorides and iodides, the liberation of iodine, and the evolution of oxygen.   It unites with galena, PbS, to form chlorides of sulphur and lead iodide.

Iodine monochloride dissolves in carbon tetrachloride, producing a red solution.   When dissolved in carbon bisulphide to form a saturated solution, white fumes are evolved, and, on adding water to the solution, a heavy oily substance consisting of a mixture of carbon bisulphide, carbon tetrachloride, and carbon sulphochloride is thrown down.   It bleaches indigo and litmus solutions.

Iodine monochloride is used in organic chemistry for the purpose of introducing iodine into different compounds.   It sometimes gives chloro-iodo derivatives.

Iodine Trichloride, ICl_3.—This compound, like the monochloride, was discovered in 1814 by Gay-Lussac.[1]   It is prepared by passing a large excess of chlorine over gently heated iodine, or iodine monochloride :—

$$(1) \quad I_2 + 3Cl_2 = 2ICl_3,$$
$$(2) \quad ICl + Cl_2 = ICl_3.$$
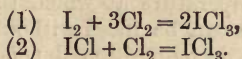
The trichloride is deposited as a crystalline sublimate on the cooler parts of the apparatus.   According to Thomas and Dupuis,[2] the most practicable method of obtaining considerable quantities of this chloride in a pure state is by the action of liquid chlorine on iodine.   A brown mass is obtained, which is transformed in presence of an excess of chlorine into a yellow powder. This powder is the iodine trichloride, which is only very slightly soluble in liquid chlorine.   The same investigators also obtained this chloride by acting upon certain metallic iodides, e.g. lead iodide, with liquid chlorine, when a mixture of iodine trichloride and a metallic chloride is obtained, thus :—

$$PbI_2 + 4Cl_2 = PbCl_2 + 2ICl_3.$$
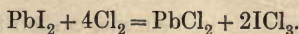
It may also be obtained by acting upon hydriodic acid with a large excess of chlorine, thus :—

$$HI + 2Cl_2 = HCl + ICl_3,$$
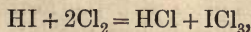
by the action of gaseous hydrogen chloride, or of a concentrated aqueous solution of hydrochloric acid, upon iodic acid ; and by heating iodine pentoxide with phosphorus pentachloride,[3] or iodine pentabromide with phosphorus trichloride :—

$$IBr_5 + PCl_3 = ICl_3 + PBr_5.$$
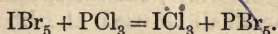
According to Krutwig,[4] chlorine reacts with silver iodate at a high temperature with the formation of silver chloride and iodine trichloride.

[1] Gay-Lussac, *Ann. Chim. Phys.*, 1814, **91**, 5.
[2] Thomas and Dupuis, *Compt. rend.*, 1906, **143**, 282.
[3] Brenken, *Ber.*, 1875, **8**, 487.
[4] Krutwig, *Ber.*, 1881, **14**, 304.

The first products of the reaction appear to be silver chloride and an oxychloride of iodine, thus :—

$$AgIO_3 + Cl_2 = AgCl + IClO_3.$$
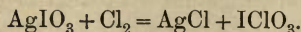
The oxychloride then splits off oxygen, forming the monochloride, which then combines with more chlorine to form the trichloride :—

$$(1) \quad 2IClO_3 = 2ICl + 3O_2,$$
$$(2) \quad ICl + Cl_2 = ICl_3.$$
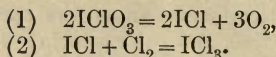
Iodine trichloride crystallises in long yellow hygroscopic needles, or sometimes in lamellæ, which sublime at ordinary temperatures, giving off irritating vapours. It melts at 25° C. (Trapp, Brenken); 33° C. (Christomanos,[1] V. Meyer). The density is 3·1107 at 15° C.[1] According to Berthelot,[2] the heat of formation is I (solid) + Cl_3 (gas) = ICl_3 (solid) . . . + 16,300 calories ; I (gas) + Cl_3 (gas) = ICl (solid) . . . + 21,700 calories ; ICl (solid) + Cl_2 (gas) = ICl_3 (solid) . . . + 9600 calories. According to Thomsen,[3] the heat of formation of solid iodine trichloride from solid iodine and gaseous chlorine is + 21,490 calories, and that of solid iodine trichloride from liquid iodine monochloride and gaseous chlorine is + 15,660 calories.

Iodine trichloride is readily dissociated by heat into iodine monochloride and free chlorine, but there is considerable disagreement among different investigators as to the temperature at which this takes place. According to L. Meyer, the substance can be fused without alteration but is then decomposed, the amount of decomposition depending upon the temperature and pressure. According to Melikoff,[4] the vapour of iodine trichloride is completely converted into iodine monochloride and free chlorine at a temperature of 77° C. under a pressure of one atmosphere. Christomanos[1] says it changes markedly in air, oxygen, or carbon dioxide even at − 12° C., and the decomposition is complete at 47·5° C. It can only be kept for any length of time at ordinary temperatures in dry chlorine.

According to Bruner and Galecki,[5] a solution of iodine trichloride in nitrobenzene, whether perfectly dry or moist, possesses considerable conductivity ; and, according to Bruner and Bekier,[6] a solution in liquid sulphur dioxide is also a conductor.

Iodine trichloride is soluble in benzene, carbon tetrachloride, phosphorus oxychloride, etc. It is less readily soluble in water than the monochloride, forming a yellow, fuming, strongly acid liquid. More or less decomposition of the aqueous solution takes place with the formation of the same products, as in the case of the monochloride (see p. 226), 10 to 20 parts of water to 1 of trichloride are required before the reaction is complete. When less water is used, part of the chloride remains in solution.

Aqueous alkali hydroxides decompose iodine trichloride with the formation of the corresponding chlorides, chlorates, and iodates, water and free iodine ; if an excess of the alkali be used, the liberated iodine is converted into a mixture of iodide and iodate. An alcoholic solution of the trichloride

[1] Christomanos, *Ber.*, 1877, 10, 434.
[2] Berthelot, *Compt. rend.*, 1880, 90, 841 ; 91, 191.
[3] Thomsen, *Ber.*, 1882, 15, 3021.
[4] Melikoff, *Ber.*, 1875, 8, 490.
[5] Bruner and Galecki, *Zeitsch. physikal. Chem.*, 1913, 84, 513.
[6] Bruner and Bekier, *Zeitsch. physikal. Chem.*, 1913, 84, 570.

reacts with alcoholic potash to form potassium iodide, iodate, and chloride, and iodoform. Ammonia combines with the chloride to form ammonium chloride and nitrogen iodide.

The trichloride behaves in a similar manner to the monochloride, towards hypochlorous and chloric acids and their salts. Gaseous chlorine monoxide reacts with it to form iodine pentoxide and free chlorine according to the equation :—

$$2ICl_3 + 5Cl_2O = I_2O_5 + 8Cl_2.$$
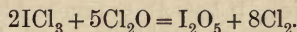
The same reaction takes place if the chlorine monoxide be dissolved in carbon tetrachloride.

Solid potassium does not immediately take fire when brought into contact with iodine trichloride, but the mixture decrepitates violently when rubbed with a glass rod. Silver-foil is converted into the iodide and chloride of silver when placed in an aqueous solution of the trichloride. A small amount of silver oxide, in the presence of water, gives silver chloride and iodic acid ; but larger quantities of the oxide yield silver iodate, and, on boiling with an excess of silver oxide, silver per-iodate is obtained. Mercuric oxide reacts slowly with the formation of mercuric chloride and iodide and the evolution of free chlorine and oxygen.

Iodine trichloride reacts with carbon bisulphide according to the equation :—

$$4CS_2 + 6ICl_3 = 2CCl_4 + 2CSCl_2 + 3S_2Cl_2 + 3I_2.$$
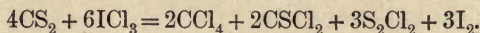
It decomposes alcohol and ether.

Iodine trichloride forms well-crystallised double salts with the chlorides of the alkali metals, ammonium, and magnesium. Weinland and Schlegelmilch [1] have prepared a hydrated double salt of iodine trichloride and cobalt chloride, iodine trichloride—cobalt chloride, $2ICl_3.CoCl_2.8H_2O$, by adding iodine to a solution of cobalt chloride in water, passing in chlorine at ordinary temperatures until all the iodine had dissolved, and cooling the solution, when the double salt crystallised out in deep orange-red hygroscopic needles. Iodine trichloride—nickel iodide, $2ICl_3.NiCl_2.8H_2O$, was obtained in a similar manner, and also the corresponding manganese, zinc, calcium, strontium, and beryllium salts. Double compounds of the trichloride and chlorides of non-metals, such as the sulphur compounds $SCl_2.2ICl_3$ and $SCl_4.ICl_3$, have also been obtained.

Iodine trichloride is a powerful antiseptic : it is employed in medicine and surgery and also as a chlorinating compound in organic chemistry.

According to Schützenberger,[2] iodine trichloride may be regarded as a combination of ICl_5 and ICl; on the other hand, Philip regards it as a compound of iodine monochloride and chlorine, $ICl + Cl_2$, whilst Oddo considers it to be a salt similar in constitution to the organic compounds $(C_6H_5)_2ICl$ and C_6H_5\ICl. According to Stanley,[3] it has the constitution $I—Cl\begin{smallmatrix}Cl\\ \|\\ N\\ Cl\end{smallmatrix}$ on account of its analogy to hydrazoic acid, $H—N\begin{smallmatrix}\\ \|\\ N\end{smallmatrix}$.

Iodine Tetrachloride, ICl_4.—By keeping liquid iodine monochloride for some time Kämmerer [4] obtained small, well-formed, hygroscopic, red

[1] Weinland and Schlegelmilch, *Zeitsch. anorg. Chem.*, 1902, **30**, 134.
[2] Schützenberger, *Compt. rend.*, 1877, **84**, 389.
[3] Stanley, *Chem. News*, 1902, **85**, 133.   [4] Kämmerer, *J. prakt. Chem.*, 1859, **83**, 83.

octahedral crystals together with free iodine. He considered these crystals to be iodine tetrachloride and supposed the monochloride to be dissociated according to the equation :—

$$8ICl = 2ICl_4 + 3I_2.$$
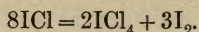
Hannay,[1] however, could not obtain this compound, and its existence is considered to be very doubtful.

Iodine Pentachloride, ICl_5.—According to Liebig, dry iodine combines with chlorine to form iodine pentachloride, and Hannay has shown that solid iodine trichloride dissolves in liquid chlorine to form a red liquid of approximately the composition ICl_5. On changing the pressure, however, chlorine is evolved, and iodine trichloride remains behind. Brenken[2] could not obtain any higher chloride than the trichloride, and the existence of the pentachloride, like that of the tetrachloride, is considered doubtful.

Iodine Oxychloride.—An oxychloride of iodine is obtained when chlorine monoxide is absorbed by iodine. It forms orange-red needles which are very unstable. The composition appears to be $IOCl_3$.[3]

Iodine Monobromide, IBr.—This compound was discovered in 1826 by Balard.[4] It is prepared by the action of bromine upon iodine in a current of carbon dioxide. The excess of bromine is carried off in the current, and the iodine monobromide remains behind as a crystalline mass. The reaction takes place according to the equation :—

$$I_2 + Br_2 = 2IBr.$$
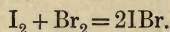
It may also be prepared by the action of iodine monochloride on disulphur dichloride, and also by passing alkyl iodides into a flask filled with bromine vapour.[5]

Iodine monobromide is an iodine-coloured, crystalline substance which smells strongly of bromine and attacks the eyes and skin, colouring the latter a yellow-brown. It is soluble in alcohol, ether, chloroform, and carbon bisulphide, forming reddish-brown solutions. It melts at 36° C., and may be sublimed, yielding a mass of arborescent crystals. The vapour is copper-red in colour, when in thin layers ; a layer 80 cms. thick is deep red in colour and gives an absorption spectrum of very fine lines situated in the red, yellow, and orange. This spectrum is not the same as that obtained by passing light through successive layers of iodine and bromine vapour.[6] The density at different temperatures, as found by Meerum Terwogt,[7] is given in the accompanying table :—

Temperature, ° C.	Density.
0	4·4157
10	4·4135
42	3·7616
50	3·7343

The heat of formation is I (solid) + Br (liquid) = IBr (solid) . . . + 2470 calories ; I (solid) + Br (solid) = IBr (solid) . . . + 2340 calories ; I (gas)

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[1] Hannay, *Trans. Chem. Soc.*, 1879, **35**, 169.
[2] Brenken, *Ber.*, 1875, **8**, 487 ; Stortenbeker, *Zeitsch. physikal. Chem.*, 1889, **3**, 11.
[3] Schützenberger, *Ber.*, 1869, **2**, 218.
[4] Balard, *Pogg. Annalen*, 1826, **8**, 114, 319, 461.
[5] Hannay, *Trans. Chem. Soc.*, 1873, **26**, 815.
[6] Gernez, *Compt. rend.*, 1872, **74**, 1190.
[7] Meerum Terwogt, *Zeitsch. anorg. Chem.*, 1905, **47**, 203.

$+$ Br (gas) $=$ IBr (solid) . . . $+11,900$ calories.[1]   The specific heat of the vapour at constant volume is $0 \cdot 029$, and at constant pressure [2] $0 \cdot 039$.

According to Bruner and Bekier,[3] the specific conductivity of fused iodine monobromide at $40°$ C. is $3 \cdot 078 \times 10^{-4}$, and its solution in liquid sulphur dioxide is a conductor.   Bruner and Galecki [4] have also shown that a solution of iodine monobromide in nitrobenzene, whether dry or moist, possesses considerable conductivity.

Iodine monobromide may be distilled with partial decomposition.   It decolorises indigo solution and turns starch paste a reddish brown.

Iodine Pentabromide, IBr_5.—When an excess of bromine is heated with iodine, a dark brown liquid is obtained, which may have the composition IBr_5.   This liquid is soluble in water, and the solution thus obtained bleaches litmus, and reacts with aqueous solutions of potassium or sodium hydroxide, to form the corresponding bromides and iodates.   When exposed to sunlight, it is decomposed, yielding a mixture of hydrobromic and iodic acids.   The same compound can be obtained by means of the action of iodine on phosphorus bromide.   By allowing this liquid, mixed with a little water, to stand in the cold, Löwig obtained brownish-yellow crystals which he believed to be iodine pentabromide hydrate.   The crystals dissociated at $4°$ C. into iodine bromide and water.   Bornemann does not, however, consider that this hydrate has any existence, and supposes the crystals obtained by Löwig's method to consist of a mixture of iodine bromide and ice.   The existence of both the pentabromide and its hydrate is doubtful.

IODINE AND OXYGEN.

The affinity of iodine for oxygen is very feeble, although it is superior to that of chlorine or bromine.   The only oxides that have been isolated with certainty are the pentoxide I_2O_5 and the tetroxide I_2O_4, but iodine trioxide, I_2O_3, probably exists, and several other oxides of more or less doubtful composition and existence have been described.   Two well-defined oxy-acids are known—iodic acid, HIO_3, and per-iodic acid, H_5IO_6,—in addition to which hypo-iodous acid and hypo-iodites are known in dilute solution, although neither the acid nor its salts have been isolated.

HYPO-IODOUS ACID.
Formula, HOI.

A dilute solution of this acid may be prepared by shaking up a solution of iodine with freshly prepared mercuric oxide and filtering the solution :—

$$HgO + 2I_2 + H_2O = HgI_2 + 2HOI ;$$
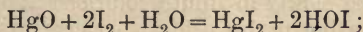
by using finely divided iodine in suspension in water, a stronger solution may be obtained.   According to Taylor,[5] the proportion of hypo-iodous acid formed increases with the fineness of division of the iodine, and decreases as the proportion of iodine to water increases and also with the time occupied in

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[1] Berthelot, *Compt. rend.*, 1880, **90**, 841 ; **91**, 951.
[2] Strecker, *Wied. Annalen*, 1882, **17**, 85.
[3] Bruner and Bekier, *Zeitsch. Elektrochem.*, 1912, **18**, 368 ; *Zeitsch. physikal. Chem.*, 1913, **84**, 570.
[4] Bruner and Galecki, *Zeitsch. physikal. Chem.*, 1913, **84**, 513.
[5] Taylor, *Chem. News*, 1897, **75**, 97 ; **76**, 27 ; *Proc. Chem. Soc.*, 1902, **18**, 72.

shaking and filtering. By using 2 parts of precipitated iodine to 1000 parts of water, and shaking with mercuric iodide for a little over a minute, about 44 to 52 per cent. of the possible amount of iodine was converted into hypo-iodous acid, and from 90 to 95 per cent. of the total iodine in the filtered solution existed as hypo-iodous acid.

A mixture of hypo-iodous and iodic acids is formed when an oxidising agent such as chlorine, bromine, ozone, potassium iodate, or potassium permanganate is allowed to act upon hydrogen iodide in dilute aqueous solution. Apparently hypo-iodous acid is the first product of the oxidation of hydrogen iodide.

Iodine reacts with silver salts, yielding a mixture of silver iodide, hypo-iodous acid, and another acid. According to Taylor,[1] the reaction may be represented by the equation : —

$$AgX + I_2 + H_2O = AgI + HOI + HX;$$
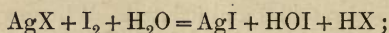
but owing to the unstable nature of the hypo-iodous acid, a second reaction occurs in which the hypo-iodous acid is converted into iodide and iodate, according to the equation :—

$$3HOI + 3AgX = 2AgI + AgIO_3 + 3HX,$$
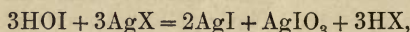
the second reaction being accelerated by rise of temperature or an increase in concentration.

Hypo-iodous acid is a weaker acid than hypochlorous acid ; it is very unstable and is quickly converted into a mixture of hydriodic and iodic acids, which then react together, yielding free iodine and water. According to Casanova and Carcano,[2] the reaction between iodine and water to produce hydriodic and hypo-iodous acids cannot be demonstrated directly because of this reverse action regenerating water and free iodine, but the acid may be fixed by means of an alkali. The fresh solution of the acid varies in colour from greenish yellow to brown, according to the concentration. The dilute solution has an odour resembling that of iodoform, whilst the odour of a concentrated solution resembles that of iodine.

Hypo-iodites.—When an aqueous solution of an alkaline hydroxide is added to water in which iodine is suspended, a mixture of hypo-iodite and iodide is obtained, the action being reversible :—

$$2KOH + I_2 \rightleftharpoons KI + KOI + H_2O.$$
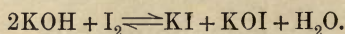
The hypo-iodite is, however, gradually converted into iodide and iodate,[3] thus :—

$$3KOI = 2KI + KIO_3.$$
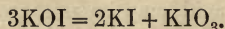
The change takes place slowly in dilute solutions at ordinary temperatures, but is hastened by heating or by using a concentrated solution. Skrabal[4] has shown that electrolytes accelerate the decomposition of hypo-iodites, but their influence is much less than in the analogous hypobromite reaction.

Alkali hypo-iodites are also formed when iodine monochloride is allowed to act upon an aqueous solution of an alkali hydroxide, the reaction taking place according to the equation :—

$$2MOH + ICl = MOI + MCl + H_2O.$$
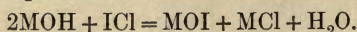
[1] Taylor, *Trans. Chem. Soc.*, 1913, **103**, 31.
[2] Casanova and Carcano, *Boll. chim. farm.*, 1912, **51**, 289.
[3] Skrabal, *Chem. Zeit.*, 1905, **29**, 550.
[4] Skrabal, *Monatsh.*, 1911, **32**, 167.

When potassium or sodium hydroxide is used, the hypo-iodite formed gradually changes into a mixture of iodide and iodate ; but when ammonium hydroxide is employed, the resulting ammonium hypo-iodite is decomposed in a different manner, so that nitrogen iodide is formed.[1] Iodine reacts with slaked lime and, water at ordinary temperatures, forming a substance which resembles bleaching-powder in general properties, and which is probably the corresponding iodine compound.[2]

Solutions of hypo-iodites are gradually converted into iodates and iodides, the change being hastened by heating. They have a peculiar odour and possess bleaching properties.

According to Auger,[3] hypo-iodites react with iodides and hydrogen carbonates to form the corresponding normal carbonate, water, and free iodine, according to the equation :—

$$MOI + MI + 2MHCO_3 = 2M_2CO_3 + H_2O + I_2 ;$$
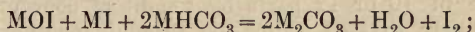
but as the liberated iodine is reconverted into hypo-iodite by the normal carbonate, it is necessary to saturate the hydrogen salt with carbon dioxide in order that the reaction shall be complete in the sense of the above equation.

Constitution.—The same arguments which are used for the constitution of hypochlorous and hypobromous acids (see p. 181) apply to hypo-iodous acid, and the formula is usually written H.O.I, the acid being regarded as water, H.O.H, in which one of the hydrogen atoms is replaced with iodine. On account of the anomalous behaviour of iodine when oxidised by chlorine in aqueous solution, Skrabal and Buchta[4] do not regard this compound as an acid, but as a base, iodine hydroxide.

Iodine Trioxide, I_2O_3.—An oxide of iodine was obtained by Ogier[5] by passing ozonised oxygen over iodine at the bottom of a glass flask at a temperature of 40° to 50° C., and collecting the solid oxide thus formed in a series of glass tubes containing platinum spirals. He supposed this substance to be iodine trioxide. It is a pale yellow, extremely light powder which deliquesces in moist air, forming a syrupy liquid of much smaller bulk than the original powder. On the addition of more water, it is converted into iodic acid and free iodine. When heated to 125° C., it is decomposed into its constituent elements and a small amount of iodine pentoxide, which is destroyed on heating to a higher temperature.

Iodine Tetroxide, I_2O_4.—According to Millon,[6] when a solution of iodic acid in sulphuric acid is heated for some time at nearly its boiling-point, the iodic acid is decomposed, oxygen is given off, the solution becomes yellow in colour, and, on cooling, yellow lamellæ are obtained. These are of variable composition, but appear to be a mixture of $I_2O_4 + H_2SO_4$ and I_2O_4. When the heating is continued until iodine vapours are evolved, the liquid becomes green in colour and deposits a substance of the composition $I_2O_4.2H_2SO_4$. If this is separated from the mother liquor and left for some days in moist air, it is decomposed into sulphuric acid and an oxide of iodine, apparently of the composition I_2O_4, which is partially converted into iodine

[1] Orton and Blackmann, *Trans. Chem. Soc.*, 1900, **77**, 830.
[2] Lunge and Schloch, *Ber.*, 1882, **15**, 1883.
[3] Auger, *Compt. rend.*, 1912, **154**, 1806.
[4] Skrabal and Buchta, *Chem. Zeit.*, 1909, **33**, 1184 and 1193.
[5] Ogier, *Compt. rend.*, 1877, **85**, 957.
[6] Millon, *Ann. Chim. Phys.*, 1844, [iii.], **12**, 330.

pentoxide and free iodine. On washing with water and then with alcohol and drying, the oxide is obtained approximately pure.

If the heating of the solution of iodic acid in sulphuric acid described above be continued until a considerable amount of iodine has been driven off, an orange - yellow crystalline substance is deposited. This appears, according to Millon, to have the composition $I_{10}O_{19}.10H_2SO_4$, and when this is exposed to moist air, it leaves a residue of the composition $I_{10}O_{19}$. More recently Kappeler [1] has prepared this oxide by Millon's method, and also Kämmerer's oxide, I_6O_{13}, but found them to be identical with the tetroxide I_2O_4. By treating a saturated solution of iodine in chloroform with ozone, Fichter and Rohner [2] obtained a yellowish-white precipitate which appeared to have the composition I_4O_9, and which they regarded as an iodine iodate, $I(IO_3)_3$.

If a mixture of 10 or 12 parts by weight of concentrated nitric acid and 1 part of finely divided iodine be ground together in a mortar, a voluminous yellow powder is obtained, which, according to Kämmerer, [3] has the composition $I_2O_4(NO_3)_2$. On leaving this substance under a cover in presence of quicklime, iodine tetroxide remains behind. Kappeler has also prepared this compound, which he regards as an iodine nitrate of the composition $I(NO_3)_3$ or $IO(NO_3)$. It rapidly decomposes when exposed to light or moisture.

Iodine tetroxide is an amorphous pale yellow powder. It is not hygroscopic and is unchanged by light, or by dry or moist air. According to Muir, [4] this oxide begins to decompose when heated to about 130° C., iodine and oxygen being liberated. It reacts slowly with cold water with the production of iodine and iodic acid, the same change taking place much more rapidly with hot water. The reaction takes place according to the equation :—

$$5I_2O_4 + 4H_2O = 8HIO_3 + I_2.$$
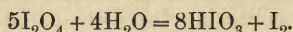
Dilute sulphuric acid also converts iodine tetroxide into free iodine and iodic acid, the change taking place slowly in the cold and rapidly on boiling. Cold concentrated sulphuric acid slowly dissolves it with partial oxidation to iodine pentoxide, and on heating a little iodine is evolved, whilst fuming sulphuric acid dissolves it with partial oxidation to the pentoxide. Nitric acid, whether concentrated or dilute, behaves in the same manner as dilute sulphuric acid, and cold concentrated hydrochloric acid reacts with the evolution of chlorine and the formation of a yellow liquid which contains iodic acid, and probably iodine chloride. On heating this solution for some time with an excess of hydrochloric acid, the iodic acid is entirely decomposed. Aqueous alkali solutions yield a mixture of iodate and iodide, thus :—

$$3I_2O_4 + 6KOH = 5KIO_3 + KI + 3H_2O.$$
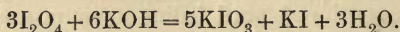
Iodine tetroxide is insoluble in dry ether or glacial acetic acid, and these liquids have no action upon it. It reacts with absolute alcohol with extreme slowness, being decomposed into iodine, which passes into solution, and iodine pentoxide. A similar change takes place with phenol, aniline, or pyridine. The oxide combines with sulphur trioxide to form a very hygro-

[1] Kappeler, *Ber.*, 1911, 44, 3496.
[2] Fichter and Rohner, *Ber.*, 1909, 42, 4093.
[3] Kämmerer, *J. prakt. Chem.*, 1861, 83, 65.
[4] Muir, *Proc. Chem. Soc.*, 1909, 25, 88 ; *Trans. Chem. Soc.*, 1909, 95, 656.

scopic, pale yellow compound of the composition $I_2O_4.3SO_3$, which begins to decompose into iodine, oxygen, and sulphur trioxide at about 120° C.

IODINE PENTOXIDE.

Formula, I_2O_5.

Iodine pentoxide was discovered almost simultaneously in 1813 by Davy and Gay-Lussac.

Formation.—It may be prepared by the action of concentrated sulphuric acid on iodic acid at 170° C. According to Chrétien,[1] sulphuric acid dissolves about one-fifth of its weight of iodic acid at 200° C., but the solution is always accompanied by the evolution of oxygen, thus showing that partial decomposition has taken place. If the solution be poured into a porcelain crucible containing a little fuming nitric acid, colourless crystals of iodine pentoxide are obtained. These contain about 2 or 3 per cent. of sulphuric acid, but the latter may be eliminated by finely powdering the crystals and redrying.

This oxide may also be prepared by acting upon iodic acid with concentrated nitric acid.[2]

The most general method of preparing the oxide is to heat iodic acid[3] alone to a temperature not exceeding 240° C., when water is split off according to the equation :—

$$2HIO_3 = I_2O_5 + H_2O.$$
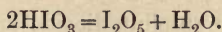
In a similar manner per-iodic acid may be heated alone when it is decomposed into iodine pentoxide, water, and oxygen :—

$$2H_5IO_6 = I_2O_5 + 5H_2O + O_2.$$
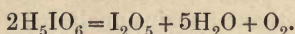
According to Basset and Fielding,[4] iodine pentoxide is formed by the action of chlorine monoxide upon iodine trichloride, chlorine being liberated, thus :—

$$5Cl_2O + 2ICl_3 = I_2O_5 + 8Cl_2.$$
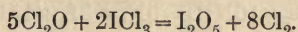
Chlorine heptoxide reacts with iodine, forming a white powder which is decomposed when heated to 100° C. into perchloric acid and iodine pentoxide.

Guichard[5] prepares pure iodine pentoxide by the action of the vapours of nitrogen pentoxide upon iodine moistened with fuming nitric acid.

The direct synthesis of iodine pentoxide from its elements can only be carried out by submitting a mixture of dry oxygen and iodine to the silent electric discharge, or by allowing ozonised oxygen to act upon iodine (see p. 205).

Properties.—Iodine pentoxide, as usually prepared, is a white amorphous powder, but it can also be obtained in the form of small crystalline scales. It has a faint odour, resembling that of iodine, and a sharp acid taste.

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[1] Chrétien, *Compt. rend.*, 1896, **123**, 814.
[2] Le Scœur, *Bull. Soc. chim.*, 1889, [iii.], **1**, 563.
[3] Baxter and Tilley (*J. Amer. Chem. Soc.*, 1909, **31**, 201) show that HIO_3 may be completely dehydrated to I_2O_5 at 110° C. by heating a sufficiently long time, but if heated quickly to this temperature it may melt with separation of $I_2O_5.HIO_3$. The temperature of dehydration may be safely raised to 240°, but not beyond.
[4] Basset and Fielding, *Chem. News*, 1886, **54**, 205.
[5] Guichard, *Compt. rend.*, 1909, **148**, 923.

Its density is 4·7987 at 9° (Kämmerer[1]); and 5·037 at 0° (Ditte[2]).   The coefficient of dilatation between 0° and 51° C. is 0·000066.   The heat of formation is I_2 (solid) $+ O_5$ (gas) $= I_2O_5$ (solid) . . . $+ 48,000$ calories (Berthelot[3]); I_2 (solid) $+ O_5$ (gas) $= I_2O_5$ (solid) . . . $+ 45,020$ calories (Thomsen[4]).   The oxide is extremely soluble in water, forming a solution of iodic acid ; sparingly soluble in alcohol ; and insoluble in ether, carbon bisulphide, chloroform, and liquid hydrocarbons.   According to Berthelot,[5] it can be kept unchanged in diffused light at ordinary temperatures, but is slowly decomposed into oxygen and iodine by direct sunlight.   When heated above 300° C., iodine pentoxide is decomposed into its constituent elements, and the undecomposed portion becomes brown in colour.   According to Guichard,[6] when the oxide is heated at 259° C. *in vacuo*, the evolution of gas is proportional to the duration of heating, but very little decomposition takes place below this temperature.   The brown colour of the residue is due to traces of iodine which are retained by the solid. The colour is not altered by heating for some hours at 270° C., nor by treating with solvents for iodine, and it can only be removed by treatment with a solvent for the oxide.

Iodine pentoxide is a powerful oxidising agent.   Under ordinary pressure it does not react with hydrogen below 300° C., but in presence of spongy platinum, or in a sealed tube under a pressure of two atmospheres, it reacts at 250° C. with the formation of water and hydrogen iodide :—

$$6H_2 + I_2O_5 = 5H_2O + 2HI.$$
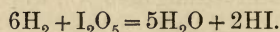
It readily oxidises sulphur to sulphur dioxide and trioxide, powdered carbon to carbon dioxide, finely divided organic matter to carbon dioxide and water, and powdered oxidisable metals to their oxides.   The action is very vigorous, and explosion may take place if the mixture be heated.   Acetylene is oxidised at 35° C., but methane remains unaltered even when heated to 80° C. It has no action upon nitric oxide, and none upon gaseous ammonia at ordinary temperatures ; but, on gently warming, a vigorous reaction takes place with the formation of water and the liberation of nitrogen and iodine :—

$$3I_2O_5 + 10NH_3 = 5N_2 + 3I_2 + 15H_2O.$$
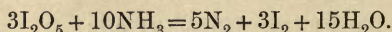
Sulphuretted hydrogen reacts in the cold with iodine pentoxide to form water, hydrogen iodide, iodine, and sulphur.   Sulphur dioxide has no action in the cold, but when heated yields sulphur trioxide and free iodine.   According to Weber,[7] when heated to 100° C. sulphur trioxide combines with iodine pentoxide to form a crystalline compound of the composition $I_2O_5.3SO_3$. Gaseous hydrogen iodide reacts energetically at ordinary temperatures with the formation of water and iodine trichloride, and the liberation of chlorine. Carbon monoxide has no action in the cold, but if the iodine pentoxide be heated at one point by means of a hot wire, the reaction thus started proceeds without further heating, carbon dioxide is formed, and iodine is liberated, thus :—

$$5CO + I_2O_5 = 5CO_2 + I_2.$$
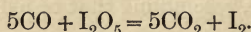
[1] Kämmerer, *Pogg. Annalen*, 1867, **138**, 390.
[2] Ditte, *Compt. rend.*, 1870, **70**, 621.
[3] Berthelot, *Ann. Chim. Phys.*, 1878, [v.], **13**, 20.
[4] Thomsen, *Thermochemische Untersuchungen*, 1883, vol. ii. p. 164.
[5] Berthelot, *Compt. rend.*, 1898, **127**, 143 and 795.
[6] Guichard, *Compt. rend.*, 1908, **147**, 1306 ; 1911, **153**, 1226 ; *Bull. Soc. chim.*, 1909, [iv.], **5**, 86.
[7] Weber, *Ber.*, 1887, **20**, 86.

This reaction takes place even when the carbon monoxide is diluted with 30,000 times its volume of air, and is made use of in the estimation of this gas in the atmosphere.[1]

IODIC ACID.

Formula, HIO_3.

Iodic acid, like its anhydride, was simultaneously discovered by Gay-Lussac and Davy in 1813. It occurs in sodium iodate in Chili saltpetre and in certain phosphates, and, as calcium iodate, in sea-water.

Formation.—Iodic acid is usually prepared by heating 1 part of finely powdered iodine with 10 parts of concentrated nitric acid of specific gravity 1·5 in a retort. The solution is evaporated to dryness and the yellowish residue redissolved in water, and again evaporated to dryness at 100° to 130° C. in order to get rid of the nitric acid still retained by the powder. The solution in water and evaporation to dryness are repeated several times, more nitric acid being eliminated each time. The method is tedious, and the yield is not very satisfactory. Scott and Arbuckle,[2] have therefore introduced a modification of the process in which they use a round-bottomed flask with a ground-in neck carrying two tubes, similar to that employed by them in the preparation of hydrobromic acid (see p. 160), but with a reflux condenser sealed into the tube C. A tube reaching almost to the bottom of the flask is fitted through B by means of a piece of rubber tubing, in order that a current of oxygen may be passed through the boiling acid. Finely powdered iodine boiled in this apparatus with ten or twelve times its weight of nitric acid of specific gravity 1·5 is completely converted into iodic acid in about twenty-five minutes. A modification of the nitric acid method is also used by Nicloux [3] for the preparation of pure iodic acid for the estimation of carbon monoxide. A mixture of chromic and sulphuric acids may be used instead of nitric acid for the oxidation of iodine to iodic acid; but if chromic acid alone be used, a basic chromium iodate is obtained.[4]

The acid may also be prepared by passing an excess of chlorine through water in which finely divided iodine is suspended, thus :—

$$I_2 + 5Cl_2 + 6H_2O = 10HCl + 2HIO_3.$$
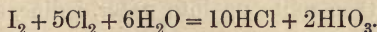
The hydrochloric acid is eliminated by means of silver oxide. At least 20 parts of water to 1 of iodine must be used in order that the reaction may be completed, as if less water be taken, the hydrochloric acid formed during the reaction becomes sufficiently concentrated to react on the iodic acid with the formation of the compound $ICl.HCl$.[5]

By boiling an iodate with dilute sulphuric acid the corresponding sulphate and free iodic acid are obtained. Barium iodate is usually employed for this purpose. The precipitated barium sulphate is filtered off, the filtrate is evaporated to a syrupy consistency and left for several days at the ordinary temperature, when iodic acid crystallises out. The crystals thus obtained are always contaminated with sulphuric acid, which is eliminated by repeatedly

[1] See Lévy and Pécoul, *Compt. rend.*, 1906, **142**, 162 ; Lévy, *J. Soc. Chem. Ind.*, 1912, **30**, 1437 ; Morgan and MacWhorter, *J. Amer. Chem. Soc.*, 1907, **29**, 1589.

[2] Scott and Arbuckle, *Proc. Chem. Soc.*, 1901, **17**, 2 ; *Trans. Chem. Soc.*, 1901, **79**, 302.

[3] Nicloux, *Compt. rend.*, 1912, **154**, 1166.

[4] Walz, *Chem. News*, 1872, **9**, 1126.

[5] Sodini, *Ber.*, 1876, **9**, 1126.

dissolving in water, adding a little barium iodate, boiling, filtering off the precipitated barium sulphate, and crystallising out. According to Stas, the acid prepared by this method always contains traces of either sulphuric acid or barium. Guichard[1] has, however, shown that it may be purified by adding the aqueous solution of impure acid to an equal volume of nitric acid of specific gravity 1·33, and concentrating until the iodic acid (which is insoluble in nitric acid of specific gravity 1·4) separates out. The process is repeated, if necessary, until the acid is pure.

Kämmerer[2] prepares the acid by means of the action of silver iodate on iodine suspended in water :—

$$5AgIO_3 + 6I + 3H_2O = 6HIO_3 + 5AgI.$$
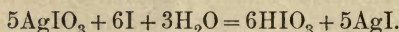
The silver iodide is separated by decantation and the liquor evaporated to a syrupy consistency, when iodic acid crystallises out. The silver iodate for this reaction is obtained by converting barium iodate into ammonium iodate by means of ammonium carbonate, and treating the ammonium iodate thus obtained with silver nitrate.

Iodic acid is also obtained by the action of iodine on an aqueous solution of bromic or chloric acid :—

(1) $2HBrO_3 + I_2 = 2HIO_3 + Br_2,$
(2) $2HClO_3 + I_2 = 2HIO_3 + Cl_2.$
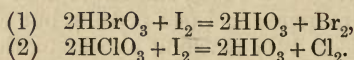
If perchloric be used instead of chloric acid, the result of the reaction is still iodic acid, and not per-iodic acid as might be expected.

When an electric current is passed through an aqueous solution of hydriodic acid, or through water in which iodine is suspended, the iodine is oxidised by the nascent oxygen, and a solution of iodic acid is obtained. According to Riche,[3] this is the best method of preparing this acid.

Hantzsch[4] has obtained iodic acid by means of the action of water on triazo-iodide ; the immediate products of the reaction are hypo-iodous acid and azoic acid :—

$$H_2O + N_3I = HIO + N_3H.$$
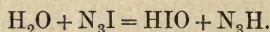
The hypo-iodous acid then splits up into water, iodine, and iodic acid in the usual manner :—

$$5HIO = 2H_2O + 2I_2 + HIO_3.$$
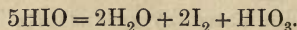
According to Auger,[5] the acid is produced in theoretical amount when iodine is oxidised by hydrogen peroxide in the presence of hydrochloric or hydrobromic acid, provided the iodine is kept in solution by the addition of hydriodic acid (or by some other means). The reaction may be represented by the equations :—

(1) $2HCl + H_2O_2 = 2H_2O + Cl_2.$
(2) $I + 3Cl = ICl_3.$
(3) $5ICl_3 + 9H_2O \rightleftharpoons 3HIO_3 + 15HCl + I_2.$
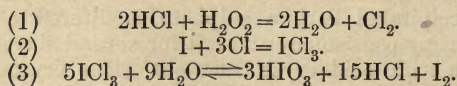
Properties.—Iodic acid crystallises from its solution by slow evaporation in transparent, colourless crystals which are said to be dimorphous. It may

[1] Guichard, *Compt. rend.*, 1909, **148**, 928.
[2] Kämmerer, *Pogg. Annalen*, 1871, **138**, 227.
[3] Riche, *Compt. rend.*, 1858, **46**, 348.   [4] Hantzsch, *Ber.*, 1900, **33**, 522.
[5] Auger, *Compt. rend.*, 1911, **152**, 712.

also be obtained as a white powder by the rapid cooling of a concentrated solution. According to Ditte,[1] the specific gravity is 4·869 at 0° C., and 4·816 at 50·8° C. The coefficient of dilatation between 0° and 50·8° C. is 0·0002242, and the specific heat is 0·1625. According to Berthelot,[2] the heat of formation is iodine (solid) $+ O_3 + H = HIO_3$ . . . $+ 59,800$ calories; I_2O_5(solid)$+ H_2O = 2HIO$ . . . $+ 2180$ calories; Thomsen[3] obtained the value $(I.O^3H)$ . . . $+ 57,963$ calories.

Iodic acid is extremely soluble in water without sensible variation of temperature, forming an acid solution which first reddens and then bleaches litmus. It is very sparingly soluble in absolute alcohol and insoluble in ether, chloroform, carbon bisulphide, liquid hydrocarbons, and acetic acid. The solubility in a mixture of alcohol and water increases with the proportion of water present. These aqueous-alcoholic solutions cannot be preserved, as the alcohol is oxidised by the acid. According to Ditte, a saturated aqueous solution has a specific gravity of 2·842 at 12·5° C., and boils at 104° under 760 mm. pressure. On the other hand, according to Kämmerer, the most concentrated solution, obtained by dissolving 1·874 parts of iodine pentoxide in 1 part of water, has a specific gravity of 2·1629 at 13° C. and boils at 100°. At $-17°$ C. it completely solidifies to a crystalline mass. The specific gravity of aqueous solutions of iodic acid of different concentrations at 17° C., as found by Thomsen[4] is as follows :—

Concentration.	Specific Gravity.
$HIO_3 + 10H_2O$	1·6609
$HIO_3 + 20H_2O$	1·3660
$HIO_3 + 40H_2O$	1·1945
$HIO_3 + 80H_2O$	1·1004
$HIO_3 + 160H_2O$	1·0512
$HIO_3 + 320H_2O$	1·0258

The amount of iodic acid in saturated solutions at various temperatures, according to Groschuff,[5] is shown in the following table :—

Temperature, ° C.	Percentage of HIO_3.
0	74·1
60	80·0
85	83·0
101	85·2

The addition of sulphuric acid or nitric acid decreases the solubility of iodic acid in water, and in concentrated solutions causes a crystalline deposit.

By cooling the most concentrated solution of iodic acid obtainable to $-17°$, Kämmerer[6] obtained crystals which melted at $-15°$. He found these to contain 49·58 per cent. of iodine, and concluded they were a hydrate of the composition $2HIO_3.9H_2O$. The existence of this hydrate has not, however, been confirmed, and Groschuff could not obtain it, though he was able to demonstrate the existence of a crystalline compound of the formula

[1] Ditte, *Ann. Chim. Phys.*, 1870, [4], 21, 5 ; *Compt. rend.*, 1870, 70, 621.
[2] Berthelot, *Compt. rend.*, 1877, 84, 734.
[3] Thomsen, *Thermochemische Untersuchungen*, 1883, 2, 164.
[4] Thomsen, *Ber.*, 1874, 7, 71.
[5] Groschuff, *Zeitsch. anorg. Chem.*, 1905, 47, 331.
[6] Kämmerer, *Pogg. Annalen*, 1869, 138, 400.

$I_2O_5.\frac{1}{3}H_2O$ or HI_3O_8. This compound has also been prepared by Baxter and Tilley,[1] who regard it as having the composition $I_2O_5.HIO_3$.

Solutions of iodic acid are decomposed by the electric current, yielding oxygen at the positive pole and iodine at the negative pole. According to Ostwald,[2] the electric conductivity of iodic acid is less than that of hydriodic acid. The molecular conductivity of solutions containing 1 gram-molecule of the acid in v litres is given in the accompanying table.

Value of v.	Molecular Conductivity.	Value of v.	Molecular Conductivity.
2	193	64	349
4	229	128	364
8	268	256	371
16	301	512	376
32	327	1024	377

Iodic acid loses water when heated : the dehydration is practically [3] complete at 180° C., and only iodine pentoxide remains ; at 300° it is decomposed into its constituent elements. It is also decomposed into its elements by sunlight.[4] At ordinary temperatures it remains unchanged over concentrated sulphuric acid, but becomes completely dehydrated at 170° C. Sulphuric acid heated to 200° dissolves about one-fifth of its weight of iodic acid ; bubbles of oxygen are given off, thus showing that partial decomposition is taking place, and on continued heating the liquid becomes yellow in colour, and several compounds, including two lower oxides of iodine combined with sulphuric acid, are obtained (see p. 233).

Iodic acid is a powerful oxidising agent, as it readily yields its oxygen with liberation of iodine. Thus, when a little sulphur dioxide is passed into an aqueous solution of the acid, sulphuric acid and free iodine are produced according to the equation :—

$$5SO_2 + 2HIO_3 + 4H_2O = 5H_2SO_4 + I_2.$$
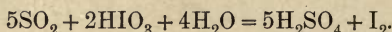
If a larger quantity of sulphur dioxide be taken, the products of the reaction are sulphuric and hydriodic acids :—

$$3SO_2 + HIO_3 + 3H_2O = 3H_2SO_4 + HI.$$
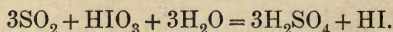
Patterson and Forsyth [5] have shown that the velocity of the reaction between iodic and sulphurous acids is considerably accelerated when methyl, ethyl, or n-propyl alcohol is added to the solution, the increase in velocity being practically proportional to the quantity of alcohol added. When acetone is added to the aqueous solution, the velocity of the reaction is accelerated until about 50 per cent. of acetone has been added, when any further addition rapidly diminishes the velocity. When sulphuretted hydrogen is

[1] Baxter and Tilley, *J. Amer. Chem. Soc.*, 1909, **31**, 201.
[2] Ostwald, *J. prakt. Chem.*, 1885, [ii.], **31**, 433 ; **32**, 300 ; Rothmund and Drucker, *Zeitsch. physikal. Chem.*, 1903, **46**, 849.
[3] A trace of water remains even at 240° (Baxter and Tilley, *loc. cit.*).
[4] Berthelot, *Compt. rend.*, 1898, **127**, 795.
[5] Patterson and Forsyth, *Trans. Chem. Soc.*, 1912, **101**, 40.

passed into an aqueous solution of the acid, the gas is oxidised to water and sulphur and iodine are liberated :—

$$2H_2S + 2HIO_3 = 3H_2O + 2S + I_2.$$
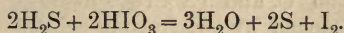
Raffo and Rossi [1] have shown that when colloidal sulphur is added to iodic acid a deep red colour due to the liberation of iodine is at once obtained, and afterwards a voluminous dark red precipitate, consisting of a mixture of iodine and sulphur, separates out. The sulphur appears to be oxidised by the iodic acid to SO_2, which is further oxidised to H_2SO_4, whilst the hydriodic acid first formed is oxidised to free iodine and water.

According to Auger,[2] hydrogen peroxide slowly decomposes dilute solutions of iodic acid in the cold. When the solutions contain less than 0·6 per cent. of acid, iodine is liberated according to the equation :—

$$2HIO_3 + 5H_2O_2 = I_2 + 6H_2O + 5O_2,$$
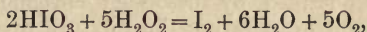
but when they contain over 0·8 per cent., the solution remains colourless, because the oxidation of the iodine according to the equation

$$I_2 + 5H_2O_2 = 2HIO_3 + 4H_2O$$
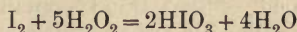
proceeds more rapidly than the decomposition of the iodic acid.

The oxides of nitrogen, NO, N_2O_3, and N_2O_4, and also nitrous acid, are oxidised to nitric acid by aqueous solutions of iodic acid, and carbon monoxide is oxidised to the dioxide. The different varieties of carbon are converted into carbon dioxide when heated with the acid in sealed tubes ; wood carbon at 160° C., sugar carbon at 175° to 180°, horn carbon, coke, and coal at 180°, anthracite at 210°, and graphite with difficulty at 240° ; the diamond still remains unchanged even at 260°. Sulphur is converted to sulphuric acid when heated with iodic acid to 150° in a sealed tube ; selenium is similarly changed into selenic acid at 200°. Phosphorus (yellow or red) is converted into phosphoric acid, and powdered arsenic into arsenic acid. Amorphous boron is oxidised to boric acid at 40° C., and crystallised silicon to silica at 250°.[3] Many organic compounds are also oxidised by this acid.

Chlorine and bromine have no action upon iodic acid ; hydrochloric acid gives water, iodine trichloride, and free chlorine, whilst hydriodic acid gives water and free iodine. The speed of the reaction between hydriodic and iodic acids is much greater than that between hydriodic acid and bromic or chloric acids.[4] It is increased by the addition of hydrobromic, hydrochloric, nitric, and sulphuric acids, and, to a greater extent, by hydriodic and iodic acids. From the empirically obtained velocity equation the reaction appears, according to Dushman,[5] to be

$$2HI + IO'_3 = 2HOI + IO'$$
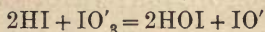
in the absence of an excess of iodine, and to be

$$HI + HI_3 + IO'_3 = HOI + HOI_3 + IO'$$
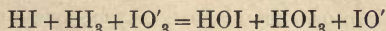
in the presence of an excess of iodine. The compound HOI_3 is not known and only has a hypothetical existence. The reaction is reversible, but Luther

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[1] Raffo and Rossi, *Zeitsch. Chem. Ind. Kolloide*, 1912, **10**, 278.
[2] Auger, *Compt. rend.*, 1911, **153**, 1005.
[3] Ditte, *Compt. rend.*, 1870, **70**, 621.
[4] Burchard, *Zeitsch. physikal. Chem.*, 1888, **2**, 796.
[5] Dushman, *J. Physical Chem.*, 1904, **8**, 453.

and Sammet[1] have shown that the decomposition is almost complete in acid solution. The equilibrium constant of the reaction, according to these investigators, is $2\cdot8 \times 10^{-47}$ at 25° C. and $5\cdot2 \times 10^{-42}$ at 60°.

Many metals are attacked by an aqueous solution of iodic acid with the production of well-defined salts. Thus, sodium, potassium and magnesium are readily attacked even in the cold ; aluminium rather less readily ; zinc and cadmium slowly in the cold, but rapidly on heating. Mercury, when heated with the acid, gives a mixture of iodate and iodide ; silver is only slowly acted upon even when heated, yielding silver iodate and iodide ; and tin, lead, gold, platinum, and palladium are not attacked either in the cold or when heated.

Iodic acid forms complex acids with a number of anhydrides and acids. According to Berg,[2] chrom-iodic acid, $IO_2.O.CrO_2.OH + 2H_2O$, or $HIO_3.CrO_3 + 2H_2O$, is obtained by dissolving chromic anhydride and iodic acid in a little water and evaporating the mixture over sulphuric acid. It forms small, red, deliquescent crystals, which, when heated, first melt and then evolve oxygen. The acid acts as an oxidising agent, but with less energy than chromic acid. Blomstrand[3] obtained molybdo-iodic acid, $I_2O_5.2MoO_3.2H_2O$, as a yellowish transparent mass, by acting upon a mixture of barium iodate and molybdate with dilute sulphuric acid, and evaporating down the solution. The same acid was afterwards obtained by Chrétien[4] by acting upon a solution of the potassium salt in nitric acid with sulphuric acid and concentrating the solution *in vacuo*. The same investigator also prepared an iodotungstic acid and an iodophosphoric acid of the composition $P_2O_5.18I_2O_5.4H_2O$.

When a mixture of a solution of ferrous sulphate and sulphuric acid is treated with iodic acid, a brown coloration is obtained similar to that given when nitric acid is added to the same mixture.

The Iodates.—The salts of iodic acid are known as iodates. Unlike chloric and bromic acids, it forms acid and double salts in addition to the normal salts.

Most of the normal iodates may be obtained by dissolving the corresponding metals in an aqueous solution of the acid, or by dissolving the oxides, hydroxides, or carbonates of the metals in the acid solution.

They may also be obtained by heating the per-iodates (see p. 249).

The iodates of the alkali and alkaline earth metals may be prepared by the action of iodine upon an aqueous solution of the corresponding hydroxide. Only one-sixth of the iodine is oxidised to iodate in this reaction, the remainder being converted into iodide, thus :—

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O.$$
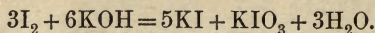
The solution of the hydroxide is poured on to the iodine until a colourless solution is obtained. The sparingly soluble iodate is separated from the iodide by fractional crystallisation, or the mixture may be evaporated to dryness and extracted with alcohol in order to dissolve out the iodide. The iodate which remains behind is then dissolved in water, neutralised with acetic acid, and again evaporated to dryness. The residue is then washed with alcohol in

[1] Luther and Sammet, *Zeitsch. Elektrochem.*, 1905, **11**, 293.
[2] Berg, *Compt. rend.*, 1887, **104**, 1514.
[3] Blomstrand, *J. prakt. Chem.*, 1889, [ii.], **40**, 305.
[4] Chrétien, *Compt. rend.*, 1896, **123**, 178.

order to remove the acetate formed, and the iodate is obtained in a pure state.

Potassium iodate is also prepared by heating a mixture of iodine, potassium chlorate, and water in a large flask, adding a little nitric acid, in order to start the reaction.[1] Chlorine is liberated, and the solution contains a mixture of potassium iodate, potassium chloride, and some iodine monochloride. According to Basset,[2] the reaction takes place according to the equation :—

$$6I_2 + 10KClO_3 + 6H_2O = 6KHI_2O_6 + 4KCl + 6HCl,$$
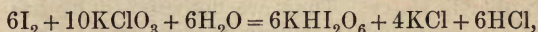
and on further evaporation the solution gives off chlorine together with iodine monochloride, thus :—

$$12KHI_2O_6 + 8KCl + 12HCl = 11KHI_2O_6 + 9KCl + 6H_2O + ICl + ICl.HCl + 4Cl_2.$$
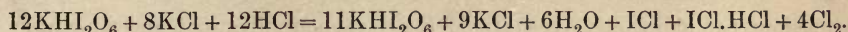
According to Thorpe and Perry,[3] however, the primary and main reaction is a simple metathesis :—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2 ;$$
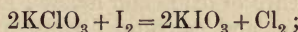
the liberated chlorine then attacks any iodine that is not within the sphere of action of the heated chlorate, with the formation of chlorides of iodine. Potassium chloride and per-iodates are only formed when the mixture is heated to too high a temperature. Schlötter[4] has shown that the reaction is dependent upon the concentration of the nitric acid, and also upon the proportion of iodine to chlorate. With dilute nitric acid the reaction is :—

$$10KClO_3 + 6I_2 + 6H_2O = 10KIO_3 + 2HIO_3 + 10HCl ;$$
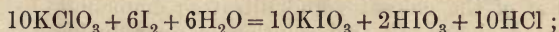
but with more concentrated acid it is

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$
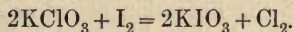
When the proportion of iodine to chlorate is 1 : 2, the reaction is

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2,$$
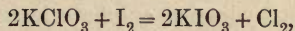
but when the proportion is 1 : 1, the reaction is

$$KClO_3 + I_2 = KIO_3 + ICl.$$
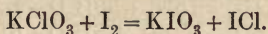
Iodates of the alkali and alkaline earth metals may also be prepared by heating the corresponding iodide together with potassium chlorate on the sand-bath at the temperature at which the chlorate gives off a regular stream of oxygen. The nascent oxygen oxidises the iodide to iodate, thus :—

$$BaI_2 + 2KClO_3 = Ba(IO_3)_2 + 2KCl.$$
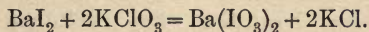
Barium iodate may be prepared by passing a stream of chlorine into a solution of barium chloride in which iodine is suspended ; by adding barium chloride to a solution of potassium iodate, when barium iodate is formed by double decomposition, and separates out as a white precipitate ; or by adding iodine to a hot solution of barium hydroxide, when the very sparingly soluble barium iodate is precipitated.[5] In the latter method of preparation only one-sixth of the iodine is converted into the iodate, the remaining five-sixths existing as barium iodide.

[1] Millon, *Ann. Chim. Phys.*, 1843, [iii.], **9**, 401.
[2] Basset, *Trans. Chem. Soc.*, 1890, **57**, 761.
[3] Thorpe and Perry, *Trans. Chem. Soc.*, 1892, **61**, 925.
[4] Schlötter, *Zeitsch. anorg. Chem.*, 1905, **45**, 270.
[5] Stevenson, *Chem. News*, 1877, **36**, 201.

When an electric current is passed through a neutral solution of potassium iodide in the presence of potassium chromate, a solution of potassium iodate is obtained.[1]

The iodides may also be oxidised to iodates by means of oxidising agents such as ozone and potassium permanganate.

Most of the iodates are well-defined crystalline salts. With the exception of those of the alkali metals and ammonium, they are either very sparingly soluble, or insoluble in water. They are decomposed by heat ; sometimes, as in the case of potassium iodate, oxygen is given off, and the corresponding iodide remains behind :—

$$2KIO_3 = 2KI + 3O_2,$$
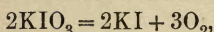
sometimes the iodine and five-sixths of the oxygen are liberated, and a metallic oxide, which may be further decomposed into oxygen and the metal, remains behind ; in some cases, such as sodium iodate, a part of the iodine and oxygen is liberated, leaving a mixture of oxide and iodide ; and some iodates, such as those of barium, strontium, and calcium, liberate part of their iodine and oxygen, yielding the corresponding per-iodate :—

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$
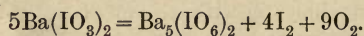
Like the free acid, iodates act as oxidising agents. Thus, when they are heated with readily oxidisable substances, such as carbon and sulphur, they are decomposed with explosive violence, though the action is less vigorous than in the case of the chlorates and nitrates ; ammonium iodate explodes even when heated alone. In acid solution many reducing agents, such as nascent hydrogen, sulphuretted hydrogen, sulphur dioxide, and ferrous salts, decompose the iodates with the liberation of iodine. Vitali[2] has shown that the salts of hydroxylamine and phenyl-hydrazine decompose iodates even in the cold. This reaction may be used for the estimation of hydrazine salts ; according to Rimini,[3] when hydrazine sulphate is used the reaction may be represented by the equations :—

$$(1)\quad 15N_2H_4,H_2SO_4 + 10KIO_3 = 15N_2 + 30H_2O + K_2SO_4 + 10H_2SO_4 + 10HI,$$
$$(2)\quad 10HI + 2KIO_3 + H_2SO_4 = K_2SO_4 + 6H_2O + 6I_2.$$
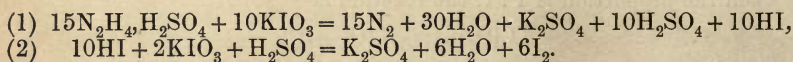
The estimation is simplified by carrying out in alkaline solution, when the reaction takes place according to the equation :—

$$3N_2H_4,H_2SO_4 + 2KIO_3 + 6KOH = 3N_2 + 2KI + 3K_2SO_4 + 12H_2O.$$
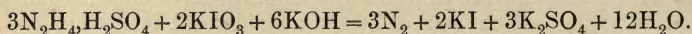
Brown and Shetterly[4] has shown that when a solution of hydrazine sulphate is treated with potassium iodate in the presence of sulphuric acid, no azoimide or ammonia is produced. The reaction therefore differs from that which takes place when hydrazine sulphate is treated with potassium bromate and sulphuric acid (see p. 186).

Hydriodic acid decomposes iodates with the formation of the corresponding iodide and water and the liberation of iodine. Hydrochloric acid acts in a similar manner, forming a metallic chloride, water, iodine trichloride, and free chlorine. No iodine is liberated when an iodate is heated with sulphuric acid unless a reducing agent, such as ferrous sulphate, is also present.

[1] Müller, *Zeitsch. Elektrochem.*, 1899, **5**, 469.
[2] Vitali, *Boll. chim. farm.*, 1899, **38**, 201.
[3] Rimini, *Gazzetta*, 1899, **29** (i.), 265 ; *Atti R. Accad. Lincei*, 1906, [v.], **15** (2), 320.
[4] Brown and Shetterly, *J. Amer. Chem. Soc.*, 1908, **30**, 53.

On boiling an iodate with dilute sulphuric, or nitric, acid, a mixture of free iodic acid and the corresponding sulphate or nitrate is obtained. Iodates form a number of complex compounds with phosphoric, molybdic, and tungstic acids,[1] and also with the selenates.[2]

Solutions of potassium iodate and iodide readily react in the presence of a small amount of an acid, the quantity of iodine liberated being directly proportional to the amount of acid present.[3] The reaction does not take place so readily when the potassium iodide is replaced by potassium bromide, and when potassium chloride is used the reaction takes place even more slowly, and a considerable quantity of acid is required.[4] Even carbon dioxide is able to bring about the liberation of iodine when led into the mixed solution of potassium iodate and iodide, but not when passed into a mixed solution of potassium iodate and bromide or chloride.[5] Andrews[6] has shown that when a solution of potassium iodate is added to a solution of potassium iodide containing a considerable excess of hydrochloric acid, a reaction takes place according to the equation :—

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O,$$
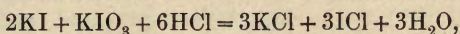
and that similarly, when the potassium iodate is added to a solution of iodine containing a considerable excess of hydrochloric acid the iodine is gradually converted into iodine monochloride. Stock[7] has shown that when a solution of potassium iodide and iodate is added to a slightly acid solution of an aluminium salt, aluminium hydroxide and free iodine are precipitated. In the case of aluminium sulphate the reaction takes place according to the equation :—

$$Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2.$$
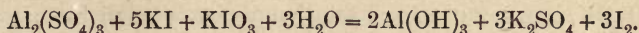
The reaction is rapid at first, but is only partial in the cold; if, however, the mixture be heated on the water-bath and the liberated iodine be removed by means of sodium thiosulphate, the reaction becomes complete and serves for the estimation of aluminium. A similar reaction may be used for the estimation of iron and chromium ;[8] in both cases the precipitated hydroxide is granular and can be readily filtered and washed, thus presenting an advantage over the ammonium hydroxide method of obtaining these hydroxides. Moody[9] carries out the estimation of aluminium, iron, and chromium by Stock's method of heating the mixed solution in a Voit flask in a current of hydrogen or steam, and titrating the solution of the liberated iodine in potassium iodide with sodium thiosulphate. According to this investigator, the reaction takes place with solutions of the salts of many other metals. It is quantitative with cobalt, nickel, and stannic salts ; in the case of zinc salts, although the amount of iodine liberated is very constant, it is only 80·1 per cent. of the theoretical quantity, the reaction taking place according to the equation :—

$$15ZnSO_4 + 20KI + 4KIO_3 + 12H_2O = 3Zn_5(OH)_8SO_4 + 12K_2SO_4 + 12I_2.$$
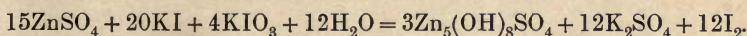
[1] Chrétien, *Compt. rend.*, 1896, **123**, 178.
[2] Weinland and Barttlingck, *Ber.*, 1903, **36**, 1397.
[3] Fessel, *Zeitsch. anorg. Chem.*, 1900, **23**, 60.
[4] Bugarszky, *Zeitsch. anorg. Chem.*, 1896, **10**, 387.
[5] Ditz and Margoshes, *Zeitsch. angew. Chem.*, 1901, **14**, 1082.
[6] Andrews, *J. Amer. Chem. Soc.*, 1903, **25**, 756.
[7] Stock, *Compt. rend.*, 1900, **130**, 175 ; *Ber.*, 1900, **33**, 548.
[8] Stock and Massaciu, *Ber.*, 1901, **34**, 467.
[9] Moody, *Amer. J. Sci.*, 1905, [iv.], **20**, 181 ; 1906, [iv.], **22**, 176 and 379 ; 1908, [iv.], **25**, 76.

Ammonium salts are almost completely hydrolised. In the case of ammonium molybdate the reaction takes place according to the equations :—

(1)　　　$3(NH_4)_6Mo_7O_{24},4H_2O = 18NH_3 + 21H_2MoO_4.$
(2)　$21H_2MoO_4 + 35KI + 7KIO_3 = 21K_2MoO_4 + 21I_2 + 21H_2O.$
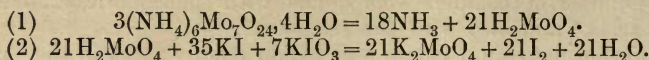
The free ammonia acts upon three-sevenths of the iodine on distilling, unless the mixture is acidified.

Acid Iodates.—The acid iodates may be considered either as molecular compounds of the normal iodates with iodic acid, or, more probably, as salts of other iodine oxy-acids. Taking the former view, the compounds formed by the combination of 1 molecule of iodic acid with 1 molecule of a normal iodate are known as di-iodates or acid iodates, such as potassium di-iodate, $KIO_3.HIO_3$, and those formed by the combination of 2 molecules of the acid with 1 of the normal salt are known as tri-iodates or di-acid iodates. If, however, they are regarded as salts of other acids, the di-iodates must be represented by the formula $R'HI_2O_6$, and the tri-iodates by the formula $R'H_2I_3O_9$ (see p. 247). Meerburg[1] has prepared potassium di-iodate, $KIO_3.HIO_3$, and potassium tri-iodate, $KIO_3.2HIO_3$, also ammonium and sodium tri-iodates, but could not obtain sodium di-iodate, as when this salt should have been obtained the pyro-compound $Na_2O.2I_2O_5$ was isolated instead.

Double Iodates.—Just as the normal iodates can combine with iodic acid to form acid iodates, so they can also combine with one another to form double iodates. The alkali iodates also combine with iodides, bromides, chlorides, and other salts. Thus Berg[2] has prepared potassium chrom-iodate, $IO_2.O.CrO_2.OK$, by concentrating a solution of potassium dichromate and iodic acid in a slight excess of chromic acid, and has also obtained similar chrom-iodates of ammonium, sodium, manganese, cobalt, and other metals. Blomstrand[3] has prepared potassium sulphato-iodate, $KO.IO(OH).O.SO_2.OK$, by mixing potassium pyrosulphate and potassium iodate in concentrated solution, and has also obtained a number of molybdo-iodates and tungsto-iodates. Chrétien[4] has prepared sodium molybdo-iodate, $I_2O_5.2MoO_3.Na_2O.H_2O$, by boiling a mixture of 100 grammes of sodium iodate and 70 grammes of molybdic anhydride in 3–4 litres of water, and has also obtained potassium iodotungstate, $2I_2O_5.4WO_3.2K_2O.8H_2O$. Weinland and Prause[5] have prepared several alkali tellur-iodates such as potassium tellur-iodate, $K_2O.I_2O_5.2TeO_3.6H_2O$; and Weinland and Barttlingck[6] have obtained two series of selenate-iodates of the types $2SeO_3.I_2O_5.2M_2O.H_2O$ (or $MHSeO_4.MIO_3$) and $2SeO_3.I_2O_5.2M_2O.5H_2O$ (or $MHSe_4.2HIO_3.MIO_3.H_2O$).

Constitution.—The constitution of iodic acid is not known with certainty. If it be considered as a monobasic acid analogous to chloric or bromic acid, it should be represented by the constitutional formula :—

$$I—O—O—OH, \quad or \quad O{\Big\rangle}I—OH,$$
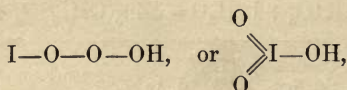
[1] Meerburg, *Zeitsch. anorg. Chem.*, 1905, **45**, 324.
[2] Berg, *Compt. rend.*, 1887, **104**, 1514 ; 1890, **111**, 42.
[3] Blomstrand, *J. prakt. Chem.*, 1889, [ii.], **40**, 305.
[4] Chrétien, *Compt. rend.*, 1896, **123**, 178.
[5] Weinland and Prause, *Ber.*, 1900, **33**, 1015.
[6] Weinland and Barttlingck, *Ber.*, 1903, **36**, 1397.

according to whether the iodine be regarded as monovalent or pentavalent. This constitution, however, is very improbable because the acid does not appear to have any real analogy to chloric and bromic acids. The salts of these acids are very soluble, whilst, with the exception of the alkali salts, the iodates are insoluble or very sparingly soluble. The heat of formation of iodic acid is much greater than that of chloric and bromic acids, and the latter acids do not yield any anhydride corresponding to iodine pentoxide when heated. The acid is also distinguished from chloric and bromic acids by its power of forming acid and double salts (see p. 246). Solutions of the acid salts give the ions $\overset{+}{K}$ and $\overset{-}{H}I_2O_6$, and Thomsen [1] considers the acid to be dibasic and represents it by the formula $H_2I_2O_6$, or $I.IO_6H_2$, which agrees with the formula for per-iodic acid, $H_3IO_6H_2$. Blomstrand,[2] from the consideration of the acid iodates, concludes that the acid is analogous to metaphosphoric acid and that it should have the constitutional formula $IO.(O.OH)$, in which the iodine is pentavalent. If this view be accepted, the di-iodides will be represented by the formula $R'O.IO : O_2 : IO.OH$, or $R'O.IO(OH).O.IO_2$, and the tri-iodates by the formula $KO.IO(OH).O.IO(OH).O.IO_2$. Potassium sulphatiodate will have the formula $KO.IO(OH).O.SO_2.OK$, and potassium molybdo-iodate the formula $KO.IO(OH).O.MoO_2.OK.H_2O$. Rosenheim and Liebknecht [3] agree with Thomsen in doubling the formula for iodic acid, and thus representing it as dibasic. According to these chemists, the di-iodates are atomic compounds of the formula $HR'I_2O_6$, and potassium molybdo-iodate has the constitution $KIO_3.MoO_3$. According to Oddo,[4] iodic acid has a mesocyclic structure.

PER-IODIC ACID.

Formula, H_5IO_6.

This acid was discovered in 1833 by Magnus and Ammermüller.[5] It occurs as sodium per-iodate in Chili saltpetre.

Preparation.—Magnus and Ammermüller's method of preparing ortho-per-iodic acid is to dissolve sodium iodate in a cold dilute solution of nitric acid, and add a solution of silver nitrate, when an orange-yellow precipitate of the silver compound $Ag_2H_3IO_6$ is obtained. This precipitate is dissolved in hot dilute nitric acid, and the solution evaporated on the water-bath until orange-coloured crystals of silver meta-per-iodate, $AgIO_4$, are obtained :—

$$2Ag_2H_3IO_6 + 2HNO_3 = 2AgIO_4 + 2AgNO_3 + 2H_2O.$$
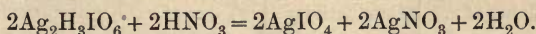
The crystals are separated from the mother liquor and decomposed by means of cold water into per-iodic acid and silver per-iodate according to the equation :—

$$2AgIO_4 + 4H_2O = H_5IO_6 + Ag_2H_3IO_6.$$
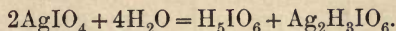
The insoluble salt is filtered off and the solution of per-iodic acid evaporated, at first on the water-bath, and then to dryness *in vacuo* over sulphuric acid.

In Kämmerer's method the acid is prepared by the decomposition of silver iodate by means of chlorine or bromine. The precipitated silver chloride or bromide is separated by decantation or filtration and the liquor evaporated as described above.

[1] Thomsen, *Ber.*, 1874, **7**, 112.   [2] Blomstrand, *loc. cit.*
[3] Rosenheim and Liebknecht, *Annalen*, 1899, **308**, 40.
[4] Oddo, *Atti R. Accad. Lincei*, 1907, [v.], **15**, ii. 500.
[5] Magnus and Ammermüller, *Pogg. Annalen*, 1833, **28**, 514.

The ortho-acid may also be obtained by the decomposition of barium periodate by means of sulphuric acid. The precipitated barium sulphate is separated by decantation or filtration and the clear liquid evaporated.

When iodine is oxidised by means of a concentrated solution of perchloric acid, per-iodic acid and free chlorine are formed, according to the equation :—

$$2HClO_4 + I_2 + 4H_2O = 2H_5IO_6 + Cl_2.$$
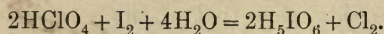
The chlorine may be driven off by heating on the water-bath.

Philip [1] has obtained the acid by the action of iodine trichloride upon silver oxide in suspension in boiling water. The precipitated silver chloride is separated in the usual manner.

Müller and Friedberger [2] prepare the acid by the electrolysis of a 50 per cent. aqueous solution of iodic acid contained in a porous cell immersed in dilute sulphuric acid. The anode, which dips in the iodic acid solution, is of lead coated with lead peroxide, and the cathode is of platinum.

Properties. — Ortho-per-iodic acid forms colourless, transparent, deliquescent prisms. The melting-point is 133° (Rammelsberg); 130° (Bengieser); $134 \pm 4.5°$ (Carnelly).[3] According to Thomsen,[4] the heat of formation of the solid hydrate is $I \text{ (solid)} + O_6 + H_5 = H_5IO_6 \text{ (solid)} \ldots + 185,780$ calories. The acid is very soluble in water and rapidly deliquesces in moist air. It is less soluble in absolute alcohol and only sparingly soluble in ether. The alcoholic and ethereal solutions gradually become brown in colour, owing to oxidation, the dissolved per-iodic acid being reduced to iodic acid. The density of aqueous solutions of the acid at 17° C., as found by Thomsen,[5] is shown in the following table :—

Number of Molecules of Water.	Density.
$H_5IO_6 + \quad 20H_2O$	1·4008
$40H_2O$	1·2165
$80H_2O$	1·1121
$160H_2O$	1·0570
$320H_2O$	1·0288

The heat of solution of 1 gram-molecule of per-iodic acid in water is -1380 calories (Thomsen). The molecular conductivity of 1 gram-molecule of the acid in v litres of water is given in the table below :— [6]

Value of v.	Conductivity.	Value of v.	Conductivity.
4	108	128	312
8	139	256	348
16	179	512	374
32	223	1024	387
64	270		

[1] Philip, *Ber.*, 1870, **3**, 4.
[2] Müller and Friedberger, *Ber.*, 1902, **35**, 2652.
[3] Carnelly, *Trans. Chem. Soc.*, 1878, **33**, 273.
[4] Thomsen, *Thermochemische Untersuchungen*, 1883, vol. ii. p. 166.
[5] Thomsen, *Ber.*, 1874, **7**, 71.
[6] Ostwald, *J. prakt. Chem.*, 1885, [ii.], **32**, 311 ; Rothmund and Drucker, *Zeitsch. physikal. Chem.*, 1903, **46**, 849.

According to Astruc and Murco,[1] methyl orange is the only indicator which should be used with per-iodic acid. The reaction is progressive and uncertain, and varies with the nature of the alkaline solution when phenolphthalein is employed, and the same results are obtained in a more marked degree with litmus, rosolic acid or Poirrier's blue. Crystals of per-iodic acid are unaltered when heated to 100° C., but partial decomposition takes place at about the melting-point of the acid, and at 138°–140° they are completely decomposed into iodic acid, oxygen, and water vapour. According to Lamb,[2] the decomposition begins at 110° under ordinary pressure ; and on keeping the acid for 20–25 hours at 100° under a pressure of 12 mm., it is transformed into **meta-per-iodic acid,** HIO_4 ; at 138° a large amount of iodine pentoxide is formed. The anhydride I_2O_7 could not be obtained. **Meso-per-iodic acid,** H_3IO_5, has not yet been isolated.

Per-iodic acid is a powerful oxidising agent ; thus it immediately oxidises sulphuretted hydrogen and sulphur dioxide to sulphuric acid with the liberation of iodine, phosphorus is converted into phosphoric acid, cuprous and ferrous salts into cupric and ferric salts, zinc into zinc oxide, iron into ferric oxide, and copper into copper iodate. It differs from iodic acid, however, in precipitating tannin from solutions. According to Tanatar,[3] hydrogen peroxide reduces per-iodic acid in alkaline solution, and Auger[4] has shown that in dilute solution it rapidly and completely reduces the acid to iodic acid, only a trace of free iodine being formed, whilst in concentrated solution the reaction is incomplete and much iodine is liberated. Hydriodic acid decomposes per-iodic acid with the liberation of iodine, and hydrochloric acid decomposes it with the formation of iodic acid, water, and free chlorine, according to the equation :—

$$H_5IO_6 + 2HCl = HIO_3 + 3H_2O + Cl_2.$$
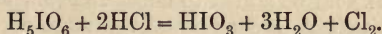
The acid is also decomposed by sulphuric acid.

The Per-iodates.—The salts of per-iodic acid are known as per-iodates. In addition to the normal or meta-per-iodates of the composition $M'IO_4$, there is a number of complex salts of the types

$$M_4I_2O_9, \ M_3IO_5, \ M_8I_2O_{11}, \ M_5IO_6, \ M_{12}I_2O_{13},$$
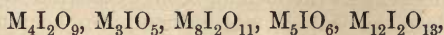
where M represents a monovalent metal.

Many of the per-iodates may be obtained by dissolving the corresponding oxides, hydroxides, or carbonates in the aqueous solution of the acid. In this manner Wells[5] has prepared cæsium per-iodate, $CsIO_4$, and cæsium hydrogen iodate-per-iodate $HCsIO_3, IO_4.2H_2O$.

The alkali per-iodates may be prepared by the electrolysis of a cold alkaline solution of the corresponding iodide in presence of potassium chromate, preferably using an anode of lead peroxide.[6]

They may also be obtained by adding a solution of a hypochlorite to an alkaline solution of the corresponding iodide.

When a current of chlorine is passed into a concentrated solution of sodium iodate and sodium hydroxide heated on the water-bath, a mixture of

[1] Astruc and Murco, *Bull. Soc. chim.*, 1902, [iii.], **27**, 927.
[2] Lamb, *Amer. Chem. J.*, 1902, **27**, 134.
[3] Tanatar, *Ber.*, 1899, **32**, 1013.
[4] Auger, *Compt. rend.*, 1911, **153**, 1005.
[5] Wells, *Amer. Chem. J.*, 1901, **26**, 278.
[6] Müller, *Zeitsch. Elektrochem.*, 1904, **10**, 49.

two sodium per-iodates, $Na_2H_3IO_6$ and $Na_3H_2IO_6$, and sodium chloride is obtained. When this method is used for the preparation of potassium per-iodate, it is necessary to concentrate the solution of potassium hydroxide and iodate before passing in the chlorine, on account of the greater solubility of the potassium meta-per-iodate. Barker[1] has prepared cæsium and rubidium per-iodates by this method; the salts are isomorphous with the potassium salt.

When barium iodate is heated to redness, it is converted into barium per-iodate, with the liberation of iodine and oxygen, according to the equation : —

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$
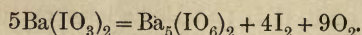
The same reaction may be used for the preparation of the per-iodates of calcium and strontium. A mixture of barium iodide and barium peroxide may be calcined instead of the iodate.

Per-iodates may also be obtained by the action of iodine on peroxides; thus, when barium peroxide is calcined with iodine it yields barium per-iodate, and if a red-hot point is brought into contact with a mixture of iodine and sodium peroxide, the whole mass becomes incandescent, and sodium per-iodate is formed together with some sodium iodate. The mass is extracted with water in order to separate the sodium iodate and uncombined iodine.

Many per-iodates may be prepared by precipitation from a solution of an alkali per-iodate. According to Kimmins,[2] this is the best method of preparing the silver salts. Sodium per-iodate is dissolved in water containing nitric acid, and the silver salt precipitated by means of silver nitrate. The composition of the salt obtained depends upon the concentration of the nitric acid; if just sufficient acid be added to effect the solution of the sodium salt, a dark brown precipitate of secondary silver meso-per-iodate, Ag_2HIO_5 (see p. 252), is formed; with a slight excess of acid a dark red precipitate of secondary silver ortho- (or para-) per-iodate, $Ag_2H_3IO_6$ (see p. 252), is thrown down; with still more nitric acid a slate-coloured precipitate, apparently of tertiary silver ortho- (or para-) per-iodate, is obtained; and if the sodium salt be dissolved in concentrated nitric acid, orange-coloured crystals of hydrated silver meta-per-iodate, $AgIO_4.H_2O$, are formed. On keeping these crystals at a temperature of 130° C. for six hours, the water of crystallisation is driven off and the anhydrous silver meta-per-iodate, $AgIO_4$, is obtained. The same author has also obtained light yellow crystals of the composition $Ag_4I_2O_9.3H_2O$, claret-coloured crystals of the composition $Ag_4I_2O_9.H_2O$, and a chocolate-coloured powder of the composition $Ag_4I_2O_9$. In a similar manner, by adding a solution of lead acetate acidified with acetic acid to a cold solution of dipotassium hydrogen per-iodate, a per-iodate of lead is produced which, according to Giolitti,[3] has the composition $PbHIO_5$. On heating this salt a per-iodate of the composition $Pb_2I_2O_9$ is obtained. The same investigator has also prepared lead per-iodates of the composition $PbHIO_5.H_2O$ and Pb_2HIO_6, and the three copper per-iodates $Cu_4I_2O_{11}$, $Cu_5I_2O_{12}.7H_2O$ and $Cu_5I_2O_{12}.3H_2O$.

Most per-iodates are very slightly soluble, or insoluble, in water, but readily soluble in dilute nitric acid. They are, in most cases, decomposed below 300° C. into the corresponding iodate and free oxygen. This is especially

[1] Barker, *Trans. Chem. Soc.*, 1908, **93**, 15.
[2] Kimmins, *Trans. Chem. Soc.*, 1887, **51**, 367.
[3] Giolitti, *Gazzetta*, 1902, **32**, ii., 340.

the case with the per-iodates of the type MIO_4; those of the type M_5IO_6 are more stable : some, such as those of the alkali and alkaline earth metals, not being decomposed even at red heat, whilst others yield a mixture of iodide and oxide. The per-iodates are powerful oxidising agents, behaving towards sulphuretted hydrogen, sulphur dioxide, and ferrous salts in a similar manner to the free acid. According to Péchard,[1] the reaction is markedly different from that of the iodates. In some cases they behave like a compound of an iodate and active oxygen. Thus, a neutral solution of the monosodium salt decomposes hydrogen peroxide according to the equation :—

$$NaIO_4 + H_2O_2 = NaIO_3 + H_2O + O_2,$$
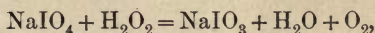
one-half of the oxygen being derived from the per-iodate, and the other from the peroxide. Auger[2] has shown that the sodium salt $Na_2H_3IO_6$ is very slowly decomposed by hydrogen peroxide, with the formation of sodium iodate, $NaIO_3$, and a larger amount of free oxygen than corresponds with the equation, owing to the catalytic decomposition of the peroxide. Per-iodates oxidise oxalic acid with extreme slowness ; but on adding manganous sulphate to the solution, the per-iodate oxidises the manganese salt to manganese dioxide, and the latter, together with the iodic acid which is simultaneously produced, is at once reduced by the oxalic acid. Vitali[3] has examined the behaviour of iodates and per-iodates towards a large number of reducing agents, and found that (unlike chlorates and perchlorates) both kinds of salt are reduced by the same agents, whilst in some cases neither salt underwent any change. Aqueous solutions of per-iodates liberate iodine from solutions of iodides. According to Péchard,[4] the reaction, in the case of sodium meta-per-iodate and sodium iodide, takes place according to the equation :—

$$3NaIO_4 + 2NaI + 3H_2O = NaIO_3 + 2Na_2H_3IO_6 + I_2.$$
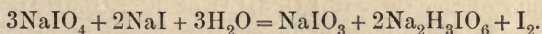
The reaction, however, is not complete, and on long standing the alkaline mixture gradually becomes neutral owing to the reaction

$$2Na_2H_3IO_6 + I_2 = 3NaIO_3 + NaI + 3H_2O.$$
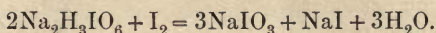
The per-iodates, like the iodates, form double compounds with molybdenum trioxide and tungsten trioxide. Rosenheim and Liebknecht[5] have obtained penta-sodium hexa-tungsto-per-iodate, $5Na_2O.I_2O_7.12WO_3 + 16H_2O$, and the corresponding potassium, strontium, and barium salts, which contain 8, 28, and 12 molecules of water of crystallisation respectively ; trisodium mono-tungsto-per-iodate, $3Na_2O.I_2O_7.2WO_3 + 4H_2O$; and diammonium sodium mono-tungsto-per-iodate, $2(NH_4)_2O.Na_2O.I_2O_7.2WO_3 + 16H_2O$.

Constitution.—From the study of the heat of neutralisation of per-iodic acid Thomsen[6] found that it behaved as a dibasic acid of the formula $H_3IO_4(OH)_2$; but as there are still three atoms of hydrogen in this formula which are not normally basic, and which can readily be expelled from many of the salts in the form of water, he concluded that the acid was tetrabasic

[1] Péchard, *Compt. rend.*, 1899, **128**, 1101.
[2] Auger, *Compt. rend.*, 1911, **153**, 1005.
[3] Vitali, *Giorn. Farm. Chim.*, 1910, **59**, 18.
[4] Péchard, *Compt. rend.*, 1900, **130**, 1705.
[5] Rosenheim and Liebknecht, *Annalen*, 1899, **308**, 40.
[6] Thomsen, *Ber.*, 1873, **6**, 2.

and decatomic, and proposed to double the formula, which thus becomes $H_6I_2O_8(OH)_4$, and adopted the constitutional formula :—

$$
\begin{array}{cccc}
H & H & H & H \\
| & | & | & | \\
O\text{————}O\text{————}O\text{————}O
\end{array}
$$

$$IO\diagup \quad \diagdown O\diagup \quad \diagdown O\diagup \quad \diagdown O\diagup \quad \diagdown OI$$

$$\| \qquad \| \qquad \|$$

$$H_2O \quad H_2O \quad H_2O$$
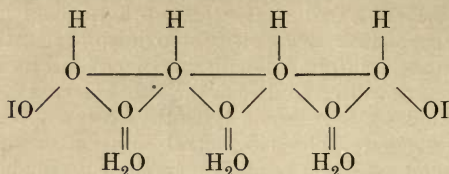
in which the iodine is monovalent and the oxygen di- and tetra-valent. Basarow,[1] however, does not agree with this view, but considers per-iodic acid to be dibasic and pent-atomic, and represents it by the formula $(HO)_2.IO.(OH)_3$, in which two of the hydroxyl groups behave as acid hydroxyl, and the other three behave as alcoholic hydroxyl, and the iodine is heptavalent. Blomstrand[2] also represents the constitution of the acid, which he calls ortho-per-iodic acid, by the formula $OI(OH)_5$, and derives the following acids from the ortho acid by the elimination of water :—

Di-ortho-per-iodic acid . . . $O\diagdown\diagup \begin{array}{l} IO(OH)_4 \\ IO(OH)_4. \end{array}$

Meso-per-iodic acid . . . $IO_2(OH)_3$.

Di-meso-per-iodic acid . . . $O\diagdown\diagup \begin{array}{l} IO_2(OH)_2 \\ IO_2(OH)_2. \end{array}$

Meta-per-iodic acid . . . $IO_3(OH)$.
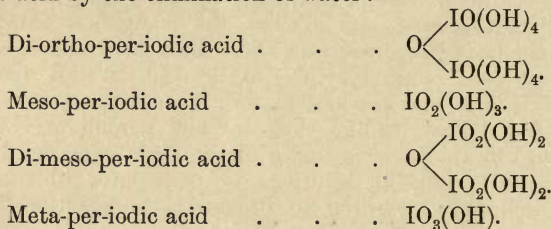
Only the last of these acids has been isolated by direct dehydration. Thomsen regards the salts of the type $R'_4I_2O_9.3H_2O$ or $R''_2I_2O_9.3H_2O$, as normal periodates and those in which more hydrogen is replaced by metal as mono-, di-, or tri-basic, according to the number of hydrogen atoms replaced, thus :—

Monobasic lead per-iodate . . . $Pb_3I_2O_{10}.2H_2O$.
Dibasic zinc per-iodate . . . $Zn_4I_2O_{11}.H_2O$.
Tribasic silver per-iodate . . . $Ag_{10}I_2O_{12}$.
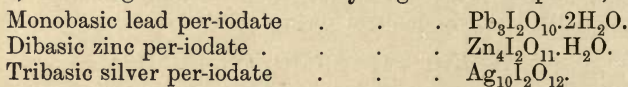
The salts of the type $R'IO_4$, which he represents as $R'_2I_2O_8$, he regards as acid salts, but considers the constitution of these salts to be distinct from that of the normal and basic salts, because they are isomorphous with the perchlorates. Basarow considers the salts of the type $R'IO_4$ to be salts of meta-per-iodic acid, bearing the same relation to the per-iodates $R_2H_3IO_6$ that the metaphosphates do to the phosphates, and also recognises pyro-per-iodates of the type $\begin{array}{l} (R'O)_2.IO_2 \\ (R'O)_2.IO_2 \end{array}\diagdown\diagup O$. Kimmins,[3] who calls the salts of the type $R'_2H_3IO_6$ para-per-iodates, has also shown that there are four distinct series of salts, which may be represented as derived from the following acids :—

Meta-per-iodic acid . . . HIO_4.
Meso-per-iodic acid . . . H_3IO_5.
Para-per-iodic acid . . . H_5IO_6.
Di-per-iodic acid . . . . $H_4I_2O_9$.

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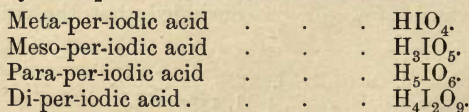
[1] Basarow, *Ber.*, 1873, **6**, 92.
[2] Blomstrand, *J. prakt. Chem.*, 1886, [ii.], **32**, 433 ; *Zeitsch. anorg. Chem.*, 1892, **1**, 10.
[3] Kimmins, *Trans. Chem. Soc.*, 1889, **55**, 148.

The ortho-, or para-, per-iodates are classified into normal, quaternary, tertiary, secondary, and primary salts according to the number of hydrogen atoms replaced by metal :—

$$Normal \qquad OI(OM)_5.$$

$$Quaternary \qquad OI\langle {}^{(OM)_4}_{(OH).}$$

$$Tertiary \qquad OI\langle {}^{(OM)_3}_{(OH)_2.}$$

$$Secondary \qquad OI\langle {}^{(OM)_2}_{(OH)_3.}$$

$$Primary \qquad OI\langle {}^{(OM)}_{(OH)_4.}$$
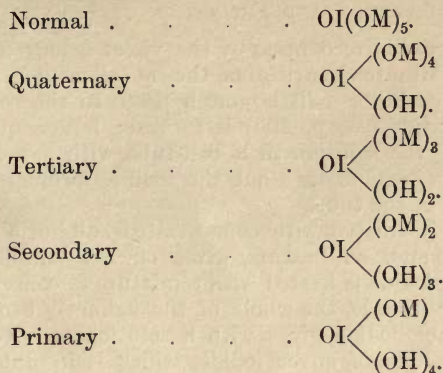
In a similar manner the meso-per-iodates are classified into normal, secondary, and primary salts,

$$Normal \qquad O_2I(OH)_3.$$

$$Secondary \qquad O_2I\langle {}^{(OM)_2}_{(OH).}$$

$$Primary \qquad O_2I\langle {}^{(OM)}_{(OH)_2.}$$
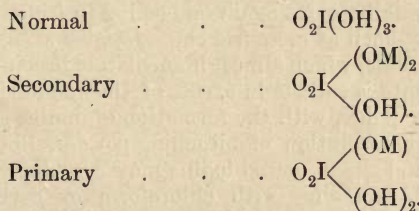
From the determination of the electrical conductivity of solutions of per-iodic acid, Ostwald[1] arrives at the conclusion that the acid is polybasic ; on the other hand, Walden[2] has shown, from the conductivity of a solution of monosodium per-iodate, that this is a salt of a monobasic acid. According to the latter chemist, those salts in which there are 2 atoms of sodium to 1 of iodine, do not behave as dibasic salts, and must be considered as of an unstable pyro-per-iodic acid, $H_4I_2O_9$, whilst those salts in which there are 5 monovalent atoms to 1 of the hydrate H_5IO_6 are basic salts. On account of the stability and ease of formation of penta-argentic per-iodate, Rosenheim and Liebknecht[3] regard per-iodic acid as being normally a pentabasic acid, which is converted by strong bases into normal salts of the monobasic meta-per-iodic acid, and Giolitti[4] has shown that this view is supported by the behaviour of the copper per-iodates (see p. 250). The latter chemist has also shown that per-iodic acid is monobasic towards sodium hydroxide when helianthin is employed as indicator, but is found to be dibasic by Bottger's electrometric method.[5] According to Oddo,[6] per-iodic acid has a mesocyclic

[1] Ostwald, *J. prakt. Chem.*, 1885, [ii.], **32**, 300.
[2] Walden, *Zeitsch. physikal. Chem.*, 1888, **2**, 65.
[3] Rosenheim and Liebknecht, *Annalen*, 1899, **308**, 40.
[4] Giolitti, *Gazzetta*, 1902, **32**, ii. 340.
[5] Giolitti, *Atti R. Accad. Lincei*, 1905, [v.], **14**, i. 217.
[6] Oddo, *Atti R. Accad. Lincei*, 1907, [v.], **15**, ii. 500.

structure.   From the investigation of the neutralisation of per-iodic acid Dubrisay[1] concludes that in solution per-iodic acid behaves as a tribasic acid.

DETECTION AND ESTIMATION OF IODINE.

Free iodine is readily recognised by the violet colour of its vapour, and also by its odour.   Minute quantities of the free element in aqueous solution may be detected by adding a little starch paste to the solution, when the dark blue starch iodide (see p. 206) is formed ; larger quantities may be detected by shaking the solution in a test-tube with a little chloroform or carbon bisulphide, which dissolve out the iodine, forming a violet-coloured layer at the bottom of the tube.

When an iodide is treated with concentrated sulphuric acid, part of the iodine is liberated, and, on heating, gives off the familiar violet-coloured vapour.   When the iodide is heated with a mixture of concentrated sulphuric acid and manganese dioxide, the whole of the iodine is evolved (see p. 195). A solution of a soluble iodide gives with a solution of silver nitrate a pale yellow curdy precipitate of silver iodide, which is insoluble in ammonium hydroxide and also in nitric acid, but soluble in a solution of sodium thiosulphate or potassium cyanide.   With a solution of a soluble lead salt, such as lead acetate, a yellow precipitate of lead iodide is obtained, which is soluble in boiling water and crystallises out again on cooling in iridescent golden scales. Soluble mercury salts, such as mercuric chloride, give a salmon-coloured precipitate of mercuric iodide, which almost immediately becomes bright scarlet in colour.   The precipitate is soluble in excess of the mercuric chloride solution and also of potassium iodide, with the formation of double salts.

Chlorine water, or a solution of bleaching-powder, liberates iodine from solutions of iodides, and the liberated iodine may be detected either by means of starch paste or by shaking with chloroform or carbon bisulphide, as described above.

Iodates are converted into iodides by heating (see p. 244), when they give the above reactions.   They do not yield free iodine when treated with concentrated sulphuric acid unless a reducing agent, such as ferrous sulphate, is also present.   A solution of a soluble iodate gives with silver nitrate solution a white curdy precipitate of silver iodate which is sparingly soluble in nitric acid and readily soluble in ammonium hydroxide.   Sulphur dioxide precipitates the pale yellow silver iodide from this ammoniacal solution. Soluble barium salts give a white precipitate of barium iodate, soluble with difficulty in nitric acid, when added to solutions of iodates.   A solution of mercurous nitrate gives a curdy pale yellow precipitate of mercurous iodate. Solutions of iodates are reduced by sulphuretted hydrogen and sulphur dioxide with the formation of iodides (see p. 244).

Determination of Free Iodine.—Free iodine is estimated by titrating a solution of the element in an aqueous solution of potassium iodide with a standard solution of sodium thiosulphate.   The determination is of great importance in analytical chemistry, because it is employed in the estimation of all those substances, such as chlorine and bromine, which liberate a definite amount of iodine from solutions of potassium iodide ; and of those substances, such as chromic acid, manganese dioxide, and potassium permanganate, which liberate chlorine from hydrochloric acid ; the chlorine thus

[1] Dubrisay, *Compt. rend.*, 1913, **157**, 1150.

produced is passed into a solution of potassium iodide, and the liberated iodine is titrated with sodium thiosulphate. It is also used in the estimation of readily oxidisable substances such as arsenic trioxide, which in the presence of water are oxidised by free iodine, with the simultaneous formation of hydrogen iodide. An excess of a standard solution of iodine in potassium iodide is added to the substance and the excess determined by means of sodium thiosulphate.

Determination of Iodine in Iodides.—In the case of soluble iodides about 0·5 to 1·0 gramme of the salt is dissolved in water ; the solution is acidified with dilute nitric acid, and an excess of a solution of silver nitrate added. The precipitated silver iodide is washed, dried, ignited and weighed. The percentage of iodine is calculated from the weight of silver iodide obtained. The salt may also be estimated volumetrically by adding a standard solution of silver nitrate to the iodide solution and using a solution of potassium chromate as an indicator. The process is stopped as soon as the brown silver chromate begins to be formed, and the volume of silver nitrate solution used is then read off. The percentage of iodine in the solution is calculated from the amount of silver nitrate used. Another method of estimation is to distil a mixture of the iodide and a pure ferric salt (most conveniently iron alum or ferric chloride) in a retort. The liberated iodine, which passes over with the aqueous vapour, is received in a solution of potassium iodide and then titrated with N/10 sodium thiosulphate in the usual manner. Other volumetric methods for the determination of iodine in iodides are by means of silver nitrate and starch iodide, by nitrous acid and carbon disulphide, and by potassium permanganate. All these methods may also be used for the determination of iodine in free hydriodic acid. Insoluble iodides are treated with sodium thiosulphate, in which they dissolve, and the metal precipitated as sulphide by means of ammonium sulphide. The filtrate is evaporated with soda and the residue heated to incipient redness in a platinum dish in order to destroy the sodium thiosulphate and tetrathionate ; the fused mass is then dissolved in hot water and distilled with an excess of ferric chloride, or ferric sulphate, as described above. Some insoluble iodides may be decomposed by boiling with potassium hydroxide or sodium carbonate : the solution is freed from the metal by means of ammonium sulphide and filtered. The filtrate is evaporated to dryness and ignited. The ignited mass is then dissolved in water and the iodine determined by distillation with ferric oxide or chloride. Silver iodide may also be decomposed by fusion with sodium carbonate ; the fused mass is extracted with water, and the iodine in the extract determined as before.

Determination of Iodic Acid and Iodates.—Iodic acid and iodates are determined by heating with an excess of pure fuming hydrochloric acid. The chlorine evolved by the reaction is received in a solution of potassium iodide, and the amount of iodine thus liberated is determined by means of a standard solution of sodium thiosulphate : one equivalent of iodic acid sets free four equivalents of chlorine, and therefore four equivalents of iodine, in this reaction. They may also be determined by mixing with dilute sulphuric acid, adding an excess of potassium iodide, and ascertaining the amount of liberated iodine by means of sodium thiosulphate. One-sixth of the iodine thus found is derived from the iodic acid or iodate.

CHAPTER VI.

MANGANESE AND ITS COMPOUNDS.

MANGANESE.

Symbol, Mn. Atomic weight, $54 \cdot 93$ (O = 16).

Occurrence. — Manganese is very widely distributed in nature, though it is never found in the free state. The principal sources of its ores are Russia, Germany, the Caucasus, India, Brazil, and the United States. The most common ores are the oxides : *Pyrolusite*, MnO_2; *Braunite*, Mn_2O_3; *Hausmannite*, Mn_3O_4; and the hydrated oxide *Manganite*, $Mn_2O_3.H_2O$. It is also found as sulphide in *Alabandite* or *Manganese blende*, MnS; and *Haurerite*, MnS_2; as carbonate in *Rhodochrosite* or *Manganese spar*, $MnCO_3$; as sulphate in *Szmikite*, $MnSO_4.H_2O$; as phosphate in *Hureaulite*, $H_2Mn_5(PO_4)_4.4H_2O$; as silicate in *Rhodonite*, $MnSiO_3$; as tungstate in *Hübnerite*, $MnWO_4$; and as mixed oxides and salts in *Manganese calcite*, $(Mn,Fe)CO_3$; *Chalkophanite*, $Mn_2O_7(Zn,Mn)H_4$; *Psilomelane*, $(Mn,Ba)O.MnO_2$; *Wolframite*, $(Mn,Fe)WO_4$; *Franklinite*, $(Fe.Mn,Zn)(FeO_2)_2$; *Jacobsite* or *Manganese spinel* $(Mn,Mg)(Fe,Mn)_2O_4$; *Sussexite*, $(Mn,Mg,Zn)(BO_2).OH$; and many other compounds. *Wad* is an impure, earthy, hydrated oxide of manganese which is produced by the decomposition of other manganiferous minerals. It generally occurs in low-lying districts. In small amounts, often causing the peculiar colour of the mineral, manganese is found in many silicates, iron ores, lime-stones, and marbles,[1] in most volcanic and metamorphic rocks,[2] in some kinds of coal, and in meteorites. Riccardi[3] has found the element in the volcanic ashes from Etna, and Cornu[4] has shown that it exists in the atmosphere of the sun. Manganese occurs in small amounts in sea-water.[5] According to Dieulafait,[6] who has examined a large number of samples of sea-water from the Atlantic and Indian Oceans, the Red Sea, and the Mediterranean Sea, the manganese exists in sea-water in the form of carbonate. This becomes oxidised near the surface of the water and is slowly precipitated, thus gradually forming manganiferous deposits. It is also found in many mineral waters, especially chalybeate waters.[7] Jadin and Astruc[8] found from 0·09 to 0·20 mg. of manganese per litre in the

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[1] Dieulafait, *Compt. rend.*, 1884, 98, 589 and 643 ; 1885, 100, 662.
[2] Wells, *Amer. J. Sci.*, 1852, [ii.], 13, 9.
[3] Riccardi, *Compt. rend.*, 1882, 94, 586 and 1657.
[4] Cornu, *Compt. rend.*, 1878, 86, 315.
[5] Forschammer, *Proc. Roy. Soc. Edin.*, 1850, 2, 303.
[6] Dieulafait, *Compt. rend.*, 1883, 96, 125.   [7] Becchi, *Ber.*, 1872, 5, 292.
[8] Jadin and Astruc, *Compt. rend.*, 1913, 157, 338.

mineral waters from Vichy and Boulou, but could find no traces of the element in most of the samples of drinking water which they examined. A deposit from the city water pipes of Hutchinson, in the Arkansas valley, was found by Bailey[1] to contain 45·92 per cent. of manganese sesquioxide when dried at 100° C. From the many rocks and minerals in which it occurs, manganese passes into the soil. Contino[2] has examined a number of Italian soils of different natures, and always found manganese present in amounts varying from traces to 0·48 per cent. of Mn_3O_4. De Sornay[3] found that the soils of Mauritius contained from 0·027 to 0·409 per cent. of manganese.

The element is liable to pass from the soil into the bodies of plants. Thus, De Vry[4] has found manganese in the ashes of beech nuts; Kachler[5] has found it combined with magnesium and oxalic acid in the cambium sap of pine trees; Guérin[6] has found it in the woody tissues of a very large number of plants; Hamlin[7] found 0·0076 per cent. of manganese in the ash of the castor bean; and the ashes of the tobacco, tea, coffee, and some other plants are so rich in the element that Maumené[8] attributes the success or otherwise of the culture of these plants to its presence or absence in the soil in which they are grown. According to Guthrie and Cohen,[9] the presence of manganese in the soil has a detrimental effect upon grass, and although it may be originally present in an innocuous form, it ultimately becomes toxic through oxidation. Leidreiter[10] has shown that small amounts of manganese in the soil have a beneficial effect upon many plants, including oats, beans, mangolds, and potatoes, but that larger amounts are injurious, and this conclusion has been to some extent confirmed by Pfeiffer and Blanck.[11] On the other hand, Varvaro[12] states that manganese dioxide hinders the germination of beans, and, even in small amounts, acts as a poison to horse-beans. Sannino and Tosatti[13] have tried the effect of manuring grape vines with manganese sulphate and found the yield was considerably increased the first year (probably on account of adding a sulphate), but the amount of dextrose was less and that of acid greater than in the case of the un-manured vines. In the second year the amount of dextrose and acid are about normal, but the increase in the yield was much less marked. According to Bernardini,[14] the chief function of manganese in manure is to produce soluble compounds of calcium and magnesium from insoluble forms, whilst Bertrand[15] regards it as a catalyst. As might be expected, the manganese in grapes passes into the various wines. Prandi and Civetta,[16]

[1] Bailey, *J. Amer. Chem. Soc.*, 1904, **26**, 714.
[2] Contino, *Staz. Sperim. agrar. ital.*, 1911, **44**, 51.
[3] De Sornay, *Bull. Assoc. Chim. Sucr. Dist.*, 1912, **30**, 96.
[4] De Vry, *Chem. News*, 1871, **23**, 155.
[5] Kachler, *Monatsh.*, 1886, **7**, 410.
[6] Guérin, *Compt. rend.*, 1897, **125**, 311.
[7] Hamlin, *Biochem. Bull.*, 1913, **2**, 410.
[8] Maumené, *Compt. rend.*, 1884, **98**, 845, 1056, and 1416.
[9] Guthrie and Cohen, *Agric. Gaz. N.S. Wales*, 1910, **21**, 219.
[10] Leidreiter, *Bied. Zentr.*, 1911, **40**, 531.
[11] Pfeiffer and Blanck, *Landw. Versuchs-Stat.*, 1912, **77**, 33.
[12] Varvaro, *Chem. Zentr.*, 1913, **1**, 546; *Staz. Sperim. agrar. ital.*, 1912, **45**, 917.
[13] Sannino and Tosatti, *Atti R. Accad Lincei*, 1913, [v.], **22**, ii. 237.
[14] Bernardini, *Chem. Zentr.*, 1910, **2**, 406; *Staz. Sperim. agrar. ital.*, 1910, **43**, 217.
[15] Bertrand, *Bied. Zentr.*, 1913, **42**, 214; *Proceedings of the Eighth International Congress of Applied Chemistry*, 1912.
[16] Prandi and Civetta, *Staz. Sperim. agrar. ital.*, 1911, **44**, 66.

who have examined a number of wines, found from 0·53 to 1·65 parts of manganese per million, the better qualities of wine containing the most manganese. The presence of manganese is of importance to certain lower forms of vegetable life ; thus, Bertrand [1] has shown that small amounts of the element have a favourable influence upon the growth of the mould *Aspergillus niger*, and is absolutely necessary to its sporulation ; Bertrand and Sazerac [2] have also found that the addition of minute quantities of manganese considerably increases the conversion of alcohol into acetic acid by the ferment *Mycoderma aceti*. Just as the manganese in the soil passes into land plants, so that in sea-water passes into marine plants. According to Forschammer, [3] the ash of *Zostera marina* contains about 4 per cent. of Mn_3O_4, and *Padina pavonia* contains 8·19 per cent. of manganese in the dried plant.

Manganese also occurs in small amounts in the bodies of animals and in animal products. According to Campani, [4] it is found in the corpuscles, and also in the clear serum, from the blood of oxen ; and according to Cottereau [5] and others, it exists in human blood, whilst Béchamp [6] has found it in the liver, and Horsford [7] in normal urine. Maumené, however, could find no manganese in human blood, and very little in urine. According to Carles, [8] traces of manganese are found in human blood, but not in that of oxen, rabbits, fowls, or ducks. It is also present in larger amount in the liver and kidneys, and in still larger quantities in the hair and nails. Bradley [9] found manganese in most of the organs of fresh-water mussels, especially in the gills and mantles. The element appears to play a rôle in the respiration of these molluscs, as they cannot live in lakes which are poor in manganese. According to Bertrand and Medigreceanu, [10] manganese is present in small amounts in most of the organs and tissues of mammals, birds, and fishes, and also in those of the invertebrata ; they failed, however, to find it in the white of birds' eggs. The gastropods and lamellibranchia contain the most manganese of the invertebrata. The animal kingdom appears to be on the whole much poorer in this element than does the vegetable kingdom.

History.—Pyrolusite was known under the name of *Magnesia nigra* to the ancients, who, however, confounded it with magnetic oxide of iron, or loadstone ; although Pliny distinguished two varieties of loadstone, one of which was black and non-magnetic in properties. It was used for a variety of purposes, including the decolorisation of glass. In the Middle Ages the magnetic oxide of iron was called *Magnes* or *Magnesius lapis*, whilst pyrolusite was known as *magnesia*. Pyrolusite was generally regarded as an ore of iron until Pott, in 1740, proved that it contained no iron and that a series of well-defined salts could be obtained from it. Scheele, [11] in 1774, proved that the ore contained a new element, but Gahn was the first to isolate the metal, although Bergmann appears to have obtained it in an impure state.

[1] Bertrand, *Compt. rend.*, 1911, **152**, 225 ; 1912, **154**, 381 and 616.
[2] Bertrand and Sazerac, *Compt. rend.*, 1913, **157**, 149.
[3] Forschammer, *Pogg. Annalen*, 1855, **95**, 60.
[4] Campani, *Gazzetta*, 1872, 469 ; *Ber.*, 1872, **5**, 287.
[5] Cottereau, *J. Chim. Méd.*, 1849, [iii.], **5**, 179.
[6] Béchamp, *Compt. rend.*, 1859, **49**, 895.
[7] Horsford, *Amer. J. Sci.*, 1851, [ii.], **11**, 259.
[8] Carles, *Ann. Chim. anal.*, 1912, **17**, 411.
[9] Bradley, *J. Biol. Chem.*, 1910, **7**, 36 ; **8**, 237.
[10] Bertrand and Medigreceanu, *Compt. rend.*, 1912, **154**, 1450 ; **155**, 82.
[11] Scheele, *Opuscula*, 1785.

Preparation.—A considerable number of methods are in use, or have been proposed, for the preparation of metallic manganese. These may all, however, be classified under five heads : (1) Reduction of an oxide by means of carbon ; (2) Reduction of an oxide by means of aluminium ; (3) Reduction of the halogen salts by means of sodium or magnesium ; (4) Reduction of a solution of a salt of manganese by means of various metals ; (5) Reduction of a solution of a salt of manganese by means of electrolysis.

(1) *Reduction of an Oxide by means of Carbon.*—When an oxide of manganese is heated together with carbon (or in a current of hydrogen), it is not reduced to the metallic state until a white heat has been attained. According to Greenwood,[1] the temperature of reduction is 1105° C. John [2] mixed the finely powdered oxide with oil and heated the mixture to redness. This was repeated seven times, and the mass was then made into a thick paste with a little oil, placed in a charcoal-lined crucible, and completely covered over with powdered charcoal. The crucible was then heated to the highest temperature attainable in a powerful blast-furnace. The crude metal thus obtained contained carbon and silicon, but by heating a second time in a charcoal crucible it was obtained in a fairly pure state. The method was modified by Deville,[3] who heated to white heat artificially prepared manganese dioxide, with an insufficient amount of sugar charcoal to bring about complete reduction. In Tamm's [4] method manganese dioxide is mixed with lamp-black and a flux consisting of powdered soda-lime, glass, and fluorspar. The mixture is placed in a plumbago crucible and strongly heated in a blast-furnace. The impure product is again fused with half its own weight of manganese carbonate. A metal containing 99·91 per cent. manganese was obtained by this method. Moissan [5] heats an intimate mixture of the oxide with carbon in an electric furnace, using an arc obtained with a current of 300 ampères at 60 volts. The reduction is complete in five or six minutes. With a current of 100 ampères at 50 volts the reduction takes from ten to fifteen minutes. Manganese thus prepared usually contains from 4 to 5 per cent. of carbon, but it may be obtained practically free from this element by using a slight excess of the oxide. As the metal volatilises in the electric furnace, it is necessary to avoid prolonged heating. The method is used commercially, but is not so economical as Goldschmidt's aluminium reduction process.

(2) *Reduction of the Oxide by means of Aluminium.*—Tissier [6] was the first to show that powdered aluminium decomposes many metallic oxides, sometimes with explosive violence, but he failed to obtain any action with the oxides of zinc or manganese. Green and Wahl [7] afterwards obtained metallic manganese by heating the monoxide together with metallic aluminium and a flux of fluorspar or cryolite, in a crucible lined with lime or magnesia ; but the modern method of preparing the metal by reduction of the oxide with aluminium is due to Goldschmidt.[8] The oxide is mixed with coarsely powdered aluminium and the mixture placed in a large crucible of refractory

[1] Greenwood, *Trans. Chem. Soc.*, 1908, **93**, 1491.
[2] John, *Gehlen's J. Chem. Phys.*, **3**, 452.
[3] Deville, *Ann. Chim. Phys.*, 1856, [iii.], **46**, 182.
[4] Tamm, *Chem. News*, 1872, **26**, 111.
[5] Moissan, *Compt. rend.*, 1893, **116**, 349 ; *Ann. Chim. Phys.*, 1896, [vii.], **9**, 286.
[6] Tissier, *Compt. rend.*, 1856, **43**, 1187.
[7] Green and Wahl, *J. Soc. Chem. Ind.*, 1893, **12**, 361.
[8] Goldschmidt, *Zeitsch. Elektrochem.*, 1898, **4**, 494 ; *J. Soc. Chem. Ind.*, 1898, **17**, 543.

earth. The reaction is started by means of a piece of magnesium ribbon surrounded with barium peroxide, or by means of a little aluminium mixed with an easily reducible oxide or peroxide, and, once started, proceeds rapidly to completion, so much heat being evolved that the manganese is fused. The method is very rapid and convenient, and is much used as an industrial process. The metal thus prepared is free from carbon, and only contains small quantities of silicon, iron, and other elements. In order to avoid contamination with aluminium, it is necessary to keep the oxide in slight excess.

(3) *Reduction of the Halogen Salts of Manganese.*—The halogen salts of manganese may be reduced by means of metallic sodium or magnesium. In Brünner's[1] process 2 parts of anhydrous manganese fluoride are mixed with 1 part of sodium. The mixture is placed in a crucible and covered with a layer of sodium chloride and fluorspar. The crucible is strongly heated, and the metal is obtained in a more or less impure condition. It may be purified by remelting under a layer of sodium chloride to which a little potassium nitrate or chlorate has been added. The manganese fluoride may be replaced with manganese chloride. Fremy[2] has obtained crystals of manganese by allowing the vapour of sodium to react with that of manganese chloride. Glatzel[3] prepares the metal by fusing a mixture of 1 part powered manganese chloride and 2 parts potassium chloride in a blast-furnace, and gradually adding (in four or five portions) small pieces of metallic magnesium until an amount equal to one-sixth of the weight of manganese chloride has been introduced. The mixture is heated until a light white cloud appears on the surface of the molten mass, when it is allowed to cool. The methods of Brünner and Glatzel have been of some industrial importance, but are now largely superseded.

(4) *Reduction of Solutions of Manganese Salts by means of Various Metals.*—According to Manck, manganese can be precipitated from a neutral solution of manganous chloride or nitrate by means of magnesium, and this statement is supported by Phipson.[4] On the other hand, Commaille[5] could only obtain manganese hydroxide by this method, and Kern[6] has shown that when magnesium is added to a saturated solution of manganous chloride, mangano-manganic oxide is obtained, after about six to eight hours, hydrogen being freely evolved. The reaction takes place in two stages, in the first of which manganese oxide is formed, as follows:—

$$3MnCl_2 + 3Mg + 3H_2O = 3MnO + 3MgCl_2 + 3H_2.$$
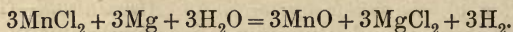
The manganous oxide is then oxidised by the water according to the equation:—

$$3MnO + H_2O = Mn_3O_4 + H_2.$$
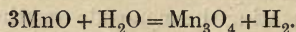
Hibbs and Smith[7] have attempted to effect the reduction in the presence of alcohol and ether, in order to reduce the liability of the manganese to oxidise. The results obtained confirm those of Commaille and Kern, a hydrated oxide being apparently the result of the reaction. Other metals, such as

[1] Brünner, *Pogg. Annalen*, 1857, **101**, 264; 1858, **103**, 139.
[2] Fremy, *Compt. rend.*, 1857, **44**, 632.
[3] Glatzel, *Ber.*, 1889, **22**, 2857.
[4] Phipson, *Jahresberichte*, 1864, 192.
[5] Commaille, *Compt. rend.*, 1866, **63**, 556.
[6] Kern, *Chem. News*, 1876, **33**, 236.
[7] Hibbs and Smith, *J. Amer. Chem. Soc.*, 1894, **16**, 822.

zinc, aluminium, and silver, may be used in the place of magnesium for the reduction, but the manganese oxidises so rapidly in the presence of water that it is necessary to amalgamate it at the moment of formation.   Giles [1] obtains the metal by simply treating a solution of manganous chloride with sodium amalgam ; hydrogen is evolved, and an amalgam of manganese is formed.   This is quickly washed, dried, and placed in a glass tube closed at one end and the mercury driven off, leaving the manganese behind as a brownish-black powder.

(5) *Reduction of Solutions of Manganese Salts by Electrolysis.*—By passing an electric current of great intensity through a solution of manganous chloride, using platinum electrodes, Bunsen [2] obtained metallic manganese, and Moissan [3] has also employed this method, using a mercury cathode.   Chlorine is evolved, and the amalgam obtained, which contains about 4 per cent. of manganese, is washed, dried, and the mercury driven off.   The method has also been employed by Diehl [4] and by Guntz, [5] but it is only of interest from the theoretical point of view.

Properties.—The physical properties of manganese vary considerably, according to the method of preparation and the degree of purity.   Pure manganese, obtained by Goldschmidt's method, has a brilliant lustre, resembling that of iron, but with a reddish tinge.   It is hard and brittle, but it will not scratch glass.   The presence of the silicon considerably increases the hardness.   According to Bullock, [6] when manganese is prepared by Brünner's method (see p. 260), the metal is very brittle and so hard that a file will scarcely touch it.   The fractured surface, which is steel-grey in colour, will scratch glass, and remains bright for a long time when exposed to the atmosphere.   The metal obtained by distilling off the mercury from manganese amalgam is a very porous, blackish-grey mass which is readily reduced to powder by slight pressure.   The density of the metal varies between 6·85 (Bergmann) and 8·01 (John), according to the method of production and the degree of purity.   According to Glatzel, [7] pure manganese has a specific gravity of 7·3921 at 22° C. ; and according to Prelinger, [8] manganese obtained from the amalgam has a density of $7·4712 \pm 0·003$ at 4° C.   The melting-point is 1260° C. ; [9] 1245° C. (Heräus). [10]   Manganese volatilises when strongly heated, even at temperatures just above its melting-point. [11]   It boils at 1900° C. [12]   Moissan [13] volatilised nearly 400 grams of the metal in ten minutes by heating in the electric furnace with a current of 380 ampères at 60 volts.   It is more readily volatile than nickel, iron, chromium, molybdenum, tungsten, or uranium.   Regnault [14] found the specific heat to be 0·1332 between 13° and 97° C.   The specific

[1] Giles, *Phil. Mag.*, 1862, [iv.], **24**, 328.
[2] Bunsen, *Ann. Chim. Phys.*, 1854, [iii.], **41**, 354.
[3] Moissan, *Ann. Chim. Phys.*, 1880, [v.], **21**, 231 ; *Compt. rend.*, 1879, **88**, 180.
[4] Diehl, *Chem. Zeit.*, 1885, **9**, 1894.
[5] Guntz, *Bull. Soc. chim.*, 1892, [viii.], **7**, 275.
[6] Bullock, *Chem. News*, 1899, **60**, 20.
[7] Glatzel, *Ber.*, 1889, **22**, 2859.
[8] Prelinger, *Monatsh. Chem.*, 1893, **14**, 367.
[9] Burgess and Waltenberg, *J. Washington Acad. Sci.*, 1913, **3**, 371.
[10] Heräus, *Zeitsch. Elektrochem.*, 1902, **8**, 185 ; Von de Weyde, *Ber.*, 1879, **12**, 441, gives 1900° C.
[11] Jordan, *Compt. rend.*, 1878, **86**, 1374 ; 1893, **116**, 752.
[12] Greenwood, *Proc. Roy. Soc.*, 1909, **A**, **82**, 396 ; 1910, **A**, **83**, 483.
[13] Moissan, *Ann. Chim. Phys.*, 1896, [vii.], **9**, 133 ; *Compt. rend.*, 1906, **142**, 425.
[14] Regnault, *Ann. Chim. Phys.*, 1861, [iii.], **63**, 18.

and atomic heats at different temperatures as found by Lämmel[1] are shown in the following table:—

SPECIFIC AND ATOMIC HEATS OF MANGANESE.

Temperature, °C.	Specific Heat.	Atomic Heat.
-100	0·0979	5·38
0	0·1072	5·9
100	0·1143	6·29
190–200	0·1214	6·68
300	0·1309	7·20
500	0·1652	9·09

According to Gladstone,[2] the molecular refraction of manganese is 0·222 in its salts and 0·476 in the permanganates. The vapour of the metal gives a characteristic spectrum, with a continuous absorption in the blue and red; this is the spectrum given by the gas issuing from the Bessemer furnace.[3] Fritsch[4] has measured about 1300 lines in this spectrum, and Casaretto[5] has examined the band spectrum obtained by introducing manganese chloride into the flame of the oxygen-coal gas blowpipe. Measurements were made between $\lambda = 4402\cdot4$ and $\lambda = 6707\cdot6$. There are ten similarly constituted groups of bands in this region: the frequencies of the constituent bands of the respective groups are related to one another, and the differences between the frequencies of corresponding bands of the different groups are very nearly constant. Other manganese salts give the same band spectrum, so that it appears to be due to the metal itself. According to Lambert,[6] the absorption spectrum of manganous chloride shows bands at $\lambda = 557\cdot50$–$513\cdot0$, $\lambda = 442\cdot50$–$420\cdot0$, $\lambda = 412\cdot25$–$410\cdot25$, $\lambda = 401\cdot00$–$400\cdot0$, $\lambda = 397\cdot75$–$396\cdot25$, and $\lambda = 395\cdot95$–$394\cdot50$. Jaeschke and Meyer[7] have examined the absorption spectrum of solutions of manganese salts in different states of oxidation; and although there is a great similarity in the spectra of all the compounds, they find the violet end of the spectrum to be sensitive to change in valency and the central band is moved towards the red end of the spectrum as the valency increases. The absorption spectrum given by the salts of manganese in solution is composed of a number of bands in the orange, blue, and violet.

According to Weiss and Onnes,[8] pure manganese is paramagnetic, but becomes ferromagnetic on heating. As the magnetic properties are not intensified by cooling in solid hydrogen, these investigators conclude that manganese exhibits a new type of paramagnetism, because, according to Curie's law, the magnetism should increase on cooling. Müller[9] has shown that when used as an anode in electrolysis, manganese becomes passive in alkaline sodium sulphate or phosphate solutions, but behaves normally in

[1] Lämmel, *Ann. Physik*, 1905, [iv.], 16, 551.
[2] Gladstone, *Phil. Mag.*, 1868, [iv.], 36, 311 ; *Proc. Roy. Soc.*, 1870, 18, 49.
[3] Thálen, *Ann. Chim. Phys.*, 1865, [iv.], 18, 202.
[4] Fritsch, *Wied. Annalen*, 1905, [iv.], 16, 793.
[5] Casaretto, *Zeitsch. wiss. Photochem.*, 1910, 8, 381.
[6] Lambert, *Compt. rend.*, 1905, 141, 357.
[7] Jaeschke and Meyer, *Zeitsch. physikal. Chem.*, 1913, 83, 281.
[8] Weiss and Onnes, *Compt. rend.*, 1910, 150, 687.
[9] Müller, *Zeitsch. Elektrochem.*, 1905, 11, 755.

acid and neutral electrolytes. According to Ostwald,[1] the heat of ionisation for one valence is 240.

Manganese is rapidly oxidised in air at ordinary temperatures, so that it must be kept under rock-oil, or in air-tight vessels. It decomposes water with the evolution of hydrogen. The reaction takes place even in the cold, but more readily on heating. The metal obtained electrolytically by Bunsen's method oxidises in moist air as readily as does potassium.[2] According to Moissan,[3] when the mercury is distilled off from the manganese amalgam at temperatures below about 360° the resulting metal is pyrophoric. The metal is very soluble in dilute acids. Concentrated sulphuric acid slowly attacks it in the cold, and readily on heating, sulphur dioxide being evolved. Concentrated nitric acid reacts vigorously with powdered manganese, a slight explosion taking place. Montemartini[4] has shown that ammonia, together with hydrogen, nitrogen, and nitrous oxide, is produced by the action of nitric acid on manganese. According to Santi,[5] the metal is also attacked by a solution of ammonium chloride. When finely powdered the metal readily reduces aqueous solutions of the salts of arsenic, antimony, bismuth, tin, lead, copper, iron, nickel, cobalt, chromium, cadmium, and zinc, yielding the corresponding metals. It is insoluble in liquid ammonia.[6]

Manganese combines directly with most of the non-metallic elements. When heated it is attacked by phosphorus, boron, carbon, and silicon, forming phosphides, borides, carbides, and silicides of manganese. The carbide of the composition Mn_3C is hard and brittle; it is rapidly oxidised in air, and is decomposed by water with the formation of manganese hydroxide, methane, and hydrogen, according to the equation:—

$$Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2.$$
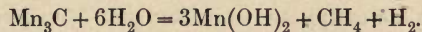
Hilpert and Paunescu[7] have prepared a series of manganese carbides, containing up to more than 20 per cent. of carbon, by treating finely powdered manganese with methane, or a mixture of methane and hydrogen. The carbides containing less than 7 per cent. of carbon were ferromagnetic Hilpert and Dieckmann[8] have obtained the two manganese phosphides $MnP + MnP_2$ by heating a mixture of manganese and red phosphorus in an exhausted sealed tube.

In the form of powder, manganese absorbs bromine with the formation of manganous bromide, and burns in chlorine to form manganous chloride. Moissan[9] has shown that massive manganese is only superficially attacked by fluorine at ordinary temperatures, but the finely powdered metal yields a mixture of MnF_2 and MnF_3, the temperature rising so much during the reaction that a platinum boat containing the manganese was melted. According to Lorenz and Heusler,[10] the metal forms no compound with hydrogen when heated in this gas. Lidoff[11] has shown that nitrogen is absorbed by manganese

[1] Ostwald, *Zeitsch. physikal. Chem.*, 1893, **11**, 501.
[2] Bunsen, *Ann. Chim. Phys.*, 1854, [iii.], **41**, 355.
[3] Moissan, *Ann. Chim. Phys.*, 1880, [v.], **21**, 231.
[4] Montemartini, *Gazz.*, 1892, **22**, 426.
[5] Santi, *Boll. chim. farm.*, 1904, **43**, 673.
[6] Gore, *Proc. Roy. Soc.*, 1873, **21**, 140.
[7] Hilpert and Paunescu, *Ber.*, 1913, **46**, 3479.
[8] Hilpert and Dieckmann, *Ber.*, 1914, **47**, 780.
[9] Moissan, *Compt. rend.*, 1900, **130**, 622.
[1] Lorenz and Heusler, *Zeitsch. anorg. Chem.*, 1893, **3**, 225.
[11] Lidoff, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1238.

at red heat even more readily than by magnesium, and Wedekind and Weit [1] have shown that nitrides of the composition Mn_3N_2, Mn_5N_2, and Mn_7N_5 exist. According to Guntz,[2] the pyrophoric manganese obtained by distilling the mercury from manganese amalgam at 200°–250° under reduced pressure is very reactive. When heated to about 250° at one point in a current of carbon monoxide, the metal becomes red hot; and if the external heating be then stopped and the current of carbon monoxide increased, the manganese is oxidised with so much energy that it becomes quite hot, and the gas is absorbed so rapidly that a partial vacuum is formed. The reaction takes place according to the equation :—

$$Mn + CO = MnO + C \text{ (amorphous)} \ldots 33\cdot3 \text{ Calories.}$$
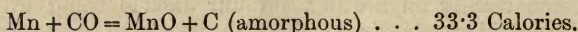
With carbon dioxide the reaction is even more energetic,

$$2Mn + CO_2 = 2MnO + C \ldots 46\cdot3 \text{ Calories.}$$
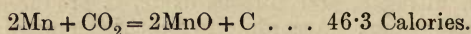
In a similar manner the pyrophoric metal burns in sulphur dioxide, combining with both the sulphur and the oxygen to form manganous sulphide and oxide, according to the equation :—

$$3Mn + SO_2 = MnS + 2MnO \ldots 82\cdot4 \text{ Calories.}$$
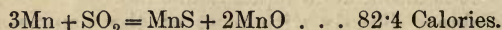
It spontaneously inflames in a current of nitrogen tetroxide, with the formation of oxides of manganese and a little nitrate, but the non-pyrophoric metal must be gently heated before the reaction can take place. It reacts vigorously with boron trichloride; if the current of the chloride be very rapid, nearly all the boron combines with the manganese to form manganese boride, but with a gentle current free boron appears to be formed. The pyrophoric metal also burns when gently heated in a stream of phosphorus pentachloride vapour. The presence of manganese causes zinc sulphide to show a reddish-yellow phosphorescence, and to emit light when scratched or rubbed.[3]

According to Levin and Tammann,[4] manganese destroys porcelain at high temperatures.

Atomic Weight.—The atomic weight of manganese has been frequently determined, and the values obtained by different investigators are, with a few exceptions, fairly consistent. Turner [5] determined the amount of chlorine in manganous chloride by means of silver, and found the value 54·87 ($Ag = 107·88$, $Cl = 35·457$); and Berzelius,[6] using the same method, and taking the same values for the atomic weights of silver and chlorine, obtained the value 55·07. By the reduction of a known amount of manganous sulphate to manganous sulphide, and weighing the sulphide thus obtained, Von Hauer [7] found $Mn = 54·92$ ($O = 16$, $S = 32·065$). Dumas,[8] by treating a weighed amount of manganese chloride in solution with a known weight of silver dissolved in nitric acid, obtained the value 54·916. Schneider [9] determined the amount of carbon and hydrogen in dry manganese oxalate, $MnC_2O_4, 2H_2O$, and

[1] Wedekind and Weit, *Ber.*, 1908, **41**, 3769.
[2] Guntz, *Bull. Soc. chim.*, 1892, [iii.], **7**, 275.
[3] Grüne, *Ber.*, 1904, **37**, 3076.
[4] Levin and Tammann, *Zeitsch. anorg. Chem.*, 1905, **47**, 136.
[5] Turner, *Pogg. Annalen*, 1829, **14**, 211 ; *Trans. Roy. Soc. Edin.*, 1831, **11**, 143.
[6] Berzelius, *Pogg. Annalen*, 1830, **18**, 74.
[7] Von Hauer, *J. prakt. Chem.*, 1857, **72**, 360.
[8] Dumas, *Ann. Chim. Phys.*, 1859, [iii.], **55**, 151 ; *Ann. Chim. Pharm.*, 1860, **113**, 25.
[9] Schneider, *Pogg. Annalen*, 1859, **107**, 605.

obtained the value 54·03. Rawack,[1] by the determination of the weight of water formed during the reduction of a known amount of mangano-manganic oxide, found the number 54·08 ($O = 16$, $H = 1·00762$). Dewar and Scott[2] made two sets of analyses of silver permanganate, and from the results, Clarke calculates the mean values 55·01 and 54·95 ($O = 16$, $Ag = 107·880$). By converting manganese oxalate into the monoxide and then into the sulphate, Marignac[3] obtained the value 55·022 as the mean of seven experiments. Weeren,[4] by converting manganous oxide, and also manganous sulphide, into manganous sulphate, obtained the value 55·00 ($O = 16$). By the analysis of manganous bromide and chloride Baxter and Hines[5] obtained the mean value 54·928 ($O = 16$, $Ag = 107·880$); and Hinrichs, using the data obtained by Baxter and Hines, concludes that the value adopted should be 55. From the recalculation of the values obtained by the above chemists, Clarke[6] considered the most probable value to be 54·947. The International Atomic Weights Commission for the year 1915 have adopted the value 54·93 ($O = 16$).

Valency.—Manganese functions towards oxygen as a di-, tri-, tetra-, hexa-, hepta-, and perhaps octa-, valent element.

Uses.—Metallic manganese is largely used in the form of alloys with other metals such as ferro-manganese, spiegeleisen, and manganese bronze (see below). Pyrolusite is employed in the manufacture of chlorine and iodine, in the manufacture of a black enamel for pottery, as a drier for oils, and as a depolariser in Le Clanché batteries. Other naturally occurring oxides, such as wad, are used as pigments. Several of the salts of manganese have a technical application: manganese chloride is used for dyeing cotton, manganous sulphate is employed in calico printing, and the sulphate, borate, and resinate are used in driers. Potassium permanganate and sodium permanganate are used as disinfectants, the latter often being mixed with sodium manganate.[7] Aluminium permanganate has also been used for this purpose.

Alloys.—Manganese readily alloys with a number of metals to form alloys, the most important of which are ferro-manganese, spiegeleisen, ferro-silicon manganese or silicon spiegel, manganese bronze, manganese brass, cupro-manganese, and manganese German silver.

The iron alloys of manganese, ferro-manganese, spiegeleisen, and silicon spiegel will be described under Iron in Volume IX.

Manganese Bronze.—Most so-called manganese bronzes do not contain any tin, and are really manganese brass. In many cases also no manganese is present, the manganese which had been added to the alloy having acted as a deoxidiser and passed away as slag. Most of the bronzes contain iron. True manganese bronze is prepared by adding small pieces of hot cupro-manganese, or ferro-manganese, to ordinary bronze melted in a crucible under a layer of charcoal, or by first melting the copper and cupro-manganese and then adding the required amount of tin. Manganese bronzes containing from 4 to 6 per

[1] Rawack, *Pogg. Annalen*, 1859, **107**, 605.
[2] Dewar and Scott, *Ann. Phys. Beibl.*, 1881, **5**, 817 ; *Proc. Roy. Soc.*, 1883, **35**, 44.
[3] Marignac, *Ann. Chim. Phys.*, 1884, [vi.], **1**, 289.
[4] Weeren, *Dissertation* (Halle, 1890) ; *Chem. Zentralblatt*, 1893, **11**, 470.
[5] Baxter and Hines, *J. Amer. Chem. Soc.*, 1906, **28**, 1560.
[6] Clarke, *A Recalculation, etc.*, 1910, p. 415. Compare *Phil. Mag.*, 1881, [v.], **12**, 101 ; *Amer. Chem. J.*, 1881, **3**, 263.
[7] Condy, Eng. Patent, 1884, 10,015.

cent. of manganese are used for fire-box stays, as they retain their strength at high temperatures. Some so-called manganese bronzes are used for ships' propellers, on account of their resistance to corrosion by sea-water.

Manganese Brass.—Alloys of manganese, copper, and zinc are white or yellow in colour according to the proportion of each element in the alloy. According to Parks, an alloy containing 70 parts copper, 30 parts manganese, and 20 to 30 parts zinc is silver-like in appearance, and can be rolled or forged at red heat. An alloy of 7 parts copper, 3 parts manganese, and 1 to 2 parts silver may be used for soldering manganese brass. The addition of aluminium (up to 5 per cent.) is said to increase the strength and elasticity of manganese brass, to make it more easy to cast, and to render the alloy more resistant to the action of corrosive liquors. These aluminium-manganese brasses have been introduced under the name of "immadium" alloys. An alloy of the following composition

Copper	.	.	.	.	67·5 parts.
Manganese	.	.	.	18	,,
Zinc	.	.	.	.	13	,,
Silicon	.	.	.	.	5	,,
Aluminium	.	.	.	1·2	,,

is said to be superior to German silver for the manufacture of rheostats.

Cupro-Manganese.—This alloy can be prepared by exposing a mixture of powdered manganese oxide, coal dust, and granulated copper, all covered with a layer of fluorspar, to a white heat for several hours. Cupro-manganese, when containing up to 4 per cent. of manganese, is copper-red in colour, while with 10 to 15 per cent. of manganese, it is yellowish grey, becoming grey with more manganese than this (up to 30 per cent. of manganese).[1] When the alloy contains about 8 per cent. of manganese, it can be readily rolled, but becomes very brittle when the percentage is increased to 12 or 15 per cent. Cupro-manganese reduces the oxides produced by melting bronze, etc.; and when small quantities of the alloy are added for this purpose, very little of the manganese remains in the finished bronze.

Manganese German Silver.—Several alloys of copper, zinc, and ferro-manganese resemble German silver in colour and properties, and can be used as a substitute for this alloy. An alloy containing

Copper	.	.	.	.	.	.	60
Ferro-manganese (60 per cent. Mn)	.	.	40
Zinc	.	.	.	.	.	.	10

is suitable for bearings, valves, etc.

Other Manganese Alloys.—Some manganese alloys containing nickel are employed for electrical resistances and similar purposes. *Manganin*, one of the best known of these alloys, contains 84 per cent. of copper, 12 per cent. of nickel, and 4 per cent. of manganese.

A number of alloys of manganese with aluminium, arsenic, antimony, tin, bismuth, and boron are of interest because of their magnetic properties. Heussler's alloy contains aluminium, copper, and manganese, and is distinctly magnetic. The magnetic properties of a series of ternary alloys of copper, manganese, and tin have been investigated by Ross and Gray,[2] those of a

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[1] Valencienne, *Compt. rend.*, 1870, **70**, 607.
[2] Ross and Gray, *Proc. Roy. Soc. Edin.*, 1910, **31**, 85.

series of nickel-manganese alloys by Gray,[1] and those of a series of cobalt-manganese alloys by Hiege.[2] Schoen[3] has shown that whilst the manganese-arsenic alloys corresponding with the composition MnAs and Mn_2As are not magnetic, those alloys containing about 47·5 per cent. of arsenic become magnetic on quenching from 850° C., and those containing from 52·8 to 55 per cent. of arsenic are magnetic even when slowly cooled. Martin[4] has studied the magneto-optical properties of the alloys of tin, antimony, and bismuth with manganese corresponding with the compounds Mn_4Sn, MnSb, and MnBi. A thermal investigation of the system manganese-silver has been made by Arrivault,[5] who has shown that a definite compound MnAg probably exists.

Detection of Manganese.—Manganese forms a pink or flesh-coloured precipitate of manganese sulphide, MnS, which is soluble in dilute acids. Consequently, manganese is not precipitated with hydrogen sulphide in *acid solution* in Group 2, but comes down in Group 4, along with the sulphides of zinc, cobalt, and nickel, which are thrown down in alkaline solution by ammonium sulphide. To separate the manganese from these sulphides we proceed as follows:—[6]

ZINC GROUP.

The precipitate with Am_2S may contain MnS, ZnS, CoS, NiS, together with finely divided sulphur. Wash thoroughly. Digest with *cold, very dilute* HCl. FILTER.

· FILTRATE. Contains manganese and zinc chlorides. Boil off H_2S. If liquid is turbid, add a little $KClO_3$ and boil until clear. Cool. Add NaOH in moderate excess, and *filter cold.*	RESIDUE. Consists of cobalt and nickel sulphides (Black).

FILTRATE. Contains zinc (which gives a white precipitate with H_2S).	RESIDUE. Contains manganese. This should turn brown on filter. To confirm : (1) Boil a little of the precipitate with PbO_2 and concentrated HNO_3 ; dilute, and allow to stand. *Crimson colour* of permanganate proves **Mn.** (2) Fuse precipitate in borax bead. Amethyst bead in outer flame proves **Mn.**

Manganese gives a characteristic spectrum. When a non-luminous flame acts on manganese chloride, a green flame is produced which, through the spectroscope, gives the following lines in the green and yellow : 5587 (a), 5392 (β), and 5195 (γ). The spark spectrum of manganese gives a number of bright lines, such as 6022, 6017, and 6014 in the orange ; 4824 and 4784 in the green ; 4766, 4762, and 4754 in the blue ; 4235 and 4228 in the indigo (Lecoq de Boisbaudran).

Estimation.—(1) *As Phosphate.*—To the solution of manganese salt, containing ammonium chloride and some free ammonia, a soluble phosphate

[1] Gray, *Phil. Mag.*, 1912, [vi.], **24**, 1. [2] Hiege, *Zeitsch. anorg. Chem.*, 1913, **83**, 253.
[3] Schoen, *Metallurgie*, 1911, **8**, 739.
[4] Martin, *Ann. Physik*, 1912, [iv.], **39**, 625 ; *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 318.
[5] Arrivault, *Compt. rend.*, 1913, **156**, 1539.
[6] R. M. Caven, *Systematic Qualitative Analysis*, 1909, p. 125.

is added, and the resulting buff-coloured precipitate of manganese phosphate is filtered off, ignited, and weighed as $Mn_2P_2O_7$.

(2) *As Carbonate.*—To the solution of manganese salt a soluble carbonate is added, and the precipitate of $MnCO_3$ is filtered off, ignited to bright red heat, and weighed as Mn_3O_4.

(3) *As Sulphide.*—The manganese is precipitated in alkaline solution with hydrogen sulphide, filtered, washed with H_2S-water, and ignited in a Rose crucible with excess of sulphur in a stream of hydrogen; or the sulphide may be simply ignited in air, when it passes into Mn_3O_4. Very often the manganese is thrown down from solution as MnO_2 by treating with bromine water and ammonia, sulphuric acid, and ammonium persulphate, or with nitric acid and a chlorate. The precipitate is then ignited and weighed as Mn_3O_4.

In nature manganese always occurs associated with iron; and in order to separate the two, the solution, after heating with ammonium chloride, is neutralised with ammonia, and the iron precipitated with ammonium acetate. The manganese is then estimated in the filtrate as above described.

Volumetrically.—Manganese may be estimated: (1) by titrating with potassium permanganate in the presence of zinc sulphate;[1] (2) by converting small quantities into permanganate by boiling the manganese salt with concentrated nitric acid, solid lead peroxide, and a little sulphuric acid, and filtering through asbestos. Another method is to warm with nitric acid and sodium bismuthate,[2] or with silver nitrate, sulphuric acid, and sodium persulphate. The amount of permanganate thus produced is then estimated by titrating with oxalic acid or hydrogen peroxide. If, however, only very small quantities of manganese are to be estimated, the manganese is turned into permanganate by adding glycerol and caustic soda, and passing air or oxygen through the solution, and the amount of manganese present is then estimated colorimetrically by comparing the red colour produced with that of standard solutions of potassium permanganate.[3]

Sometimes manganese is estimated by precipitating hydrated MnO_2 by boiling with dilute sulphuric acid and ammonium persulphate, and then the MnO_2 is estimated volumetrically by the methods described below under the heading "Evaluation of Manganese Ores." Sometimes, however, the MnO_2 is filtered off, ignited, and weighed as Mn_3O_4.

Evaluation of Manganese Ores.—For technical purposes (*e.g.* if the manganese ore is required for the manufacture of chlorine for bleaching-powder) the most important component of manganese ores is the manganese dioxide in it, which is usually determined by estimating the amount of "available oxygen" (*i.e.* the amount of oxygen which will oxidise hydrochloric acid liberating chlorine) in the ore. Two principal methods are in use:—

(1) *Bunsen's Method.*[4]—By this method the amount of chlorine evolved when the ore is treated directly with hydrochloric acid in a distilling-flask is measured by distilling the chlorine directly into a solution of potassium iodide, when the following change takes place:—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O,$$
$$Cl_2 + 2KI = 2KCl + I_2.$$
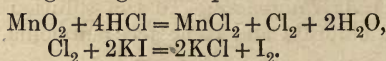
The liberated iodine is then directly estimated by titrating with sodium thiosulphate, using starch as indicator in the ordinary way. Thus it will be

[1] Volhard's method, see p. 285; Cahen and Little, *Analyst*, 1911, **36**, 52.
[2] Little, *Analyst*, 1912, **37**, 554.   [3] Tarugi, *Gazzetta*, 1906, **36**, i. 332.
[4] Bunsen, *J. Chem. Soc.*, 1856, **8**, 219.

seen that to every molecule of MnO_2 (87 parts) present, two atoms of iodine are liberated.

(2) *Fresenius and Will's gravimetric method* [1] consists in treating the ore with oxalic acid and sulphuric acid, when the following change occurs :—

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

So that every 2 molecules (*i.e.* 88 parts) of CO_2 evolved correspond to 1 molecule (87 parts) of MnO_2 present. The determination is carried out in a weighed apparatus provided with a drying tube, and the loss of weight gives the quantity of carbon dioxide evolved.

MANGANESE AND THE HALOGENS.

Manganese and Fluorine.

Manganous fluoride, [2] MnF_2, may be prepared by dissolving metallic manganese or manganous carbonate, $MnCO_3$, in aqueous hydrofluoric acid, being deposited when the solution is boiled as an amethyst-coloured, or white, crystalline powder. The substance is insoluble in water, but is soluble in aqueous hydrogen fluoride, and it is also soluble in manganous chloride, so that it may be crystallised from this latter medium by melting together 160 grams MnF_2 with 220 grams $MnCl_2$, slowly cooling the melt, and then extracting in succession with water, dilute acetic acid, and finally with water again. It is thus obtained in rose-coloured prisms of sp. gr. 3·98 melting at 856° C. The substance is also soluble in concentrated hydrochloric and nitric acids. When heated in oxygen, it is partially oxidised to Mn_3O_4 at 400° C. and completely at 1000°; it is completely reduced by hydrogen at 1000° C., but is not attacked by carbon at 1200° C. When boiled with water it is hydrolysed into an oxyfluoride; while when subjected to the action of steam at 1000° C., it is transformed into MnO; sulphuretted hydrogen at the same temperature yields green crystalline MnS. When boiled with aqueous solutions of caustic soda or potash, manganous fluoride yields an oxide of manganese; when fused with potash in the presence of an oxidising agent such as potassium chlorate, potassium manganate, K_2MnO_4 is produced.

The substance dissolves in liquid ammonia, producing addition compounds $3MnF_2.2NH_3$. The heat of formation [3] is given as :—

$$(Mn, 2F, H_2O) = 156,800 \text{ calories,}$$
$$Mn(OH)_2, 2HF, Aq. = 28,100 \text{ calories.}$$
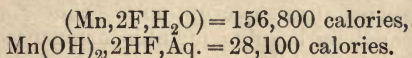
Berthelot gives the heat of formation 155,500 calories.

Manganic fluoride, [4] MnF_3, may be obtained in the anhydrous form by allowing fluorine gas to act on MnF_2, $MnCl_2$ or, still better, MnI_2.

It is thus obtained as a purple substance of sp. gr. 3·54. It decomposes when heated into the di-fluoride MnF_2 and free fluorine. It dissolves in strong acids, forming unstable dark brown solutions; it is decomposed by water, producing with a little water a dark precipitate and a red solution, gradually turning pink, the products of decomposition being a mixture of $MnF_2.HF$ and hydrated manganese oxide.

[1] *Annalen*, 1843, **47**, 87.
[2] See Moissan and Venturi, *Compt. rend.*, 1900, **130**, 1158.
[3] E. Petersen, *Zeitsch. physikal. Chem.*, 1889, **4**, 384.
[4] See Moissan, *Compt. rend.*, 1900, **130**, 622.

The hydrated salt $MnF_3.3H_2O$ [1] was obtained by Berzelius by evaporating manganese sesquioxide, Mn_2O_3, with excess of aqueous hydrogen fluoride, when it formed dark brown columns, which, viewed by transmitted light, appeared of a transparent ruby-red colour. This hydrated form is decomposed by excess of water. Ammonia gives $Mn_2O_3.H_2O$.

When metallic fluorides are added to a solution of manganese tri-fluoride, and the whole is allowed to evaporate, it is possible to obtain [2] such double fluorides as $MnF_3.2KF + H_2O$, $MnF_3.2KF + 2H_2O$, $MnF_3.2NaF$, $MnF_3.AgF + 4H_2O$, etc.

Manganese tetrafluoride, MnF_4, has not yet been isolated; Christensen [3] states that the product of dissolving manganese di-oxide in hydrogen fluoride is not MnF_4, but MnF_3; definite salts, however, are known, for example :—

Potassium manganifluoride, K_2MnF_6, $(2KF.MnF_4)$, is obtained by producing potassium manganite by boiling potassium manganate, K_2MnO_4, with water, and treating the substance with a mixture of KF and HF. It is thus obtained as golden-yellow, hexagonal tablets, which are decomposed by water. The salt dissolves in hydrochloric acid to form a dark solution, which evolves chlorine on warming. The solution decolorises indigo, decomposes hydrogen peroxide, and oxidises oxalic acid to carbon di-oxide— being a strong oxidising agent.

Rubidium manganifluoride, Rb_2MnF_6, is similarly prepared, [4] and has very similar properties.

Similar compounds with sodium and ammonium fluoride were isolated by Christensen. [3]

Permanganic oxyfluoride, MnO_3F, appears to have been isolated by Wöhler, [5] by allowing concentrated sulphuric acid to act on a mixture of 2 parts of $KMnO_4$ and 1 part of CaF_2 in a platinum retort. A yellow gas was evolved, which turned violet in the air, attacked glass, and was decomposed with water, yielding permanganic acid, $HMnO_4$, and hydrogen fluoride. Wöhler thought the substance was manganese heptafluoride, MnF_7. See "Permanganic Oxychloride," p. 274.

Manganese and Chlorine.

Manganous chloride, $MnCl_2$.—This chloride was found in saline deposits left on Vesuvius after the eruption of 1855.

It may be prepared by burning metallic manganese in chlorine gas, or by passing hydrogen chloride over hot manganous carbonate, $MnCO_3$. As thus obtained it forms a rose-coloured crystalline mass. Heated to redness it fuses and decomposes in moist air at this temperature, yielding hydrogen chloride and oxides of manganese. At a high temperature in an atmosphere of hydrogen chloride it is volatile without decomposition, [6] yielding

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[1] Berzelius, *Pogg. Annalen*, 1824, **I**, 24. See also Christensen, *J. prakt. Chem.*, 1887, [ii.], **35**, 68. According to the latter, Nicklès gave this compound, erroneously, the formula $Mn_2F_8.10H_2O$. Müller and Koppe, *Zeitsch. anorg. Chem.*, 1910, **68**, 160–64.

[2] Christensen, *J. prakt. Chem.*, 1887, [ii.], **35**, 57, 161, 541 ; Müller and Koppe, *Zeitsch. anorg. Chem.*, 1910, **68**, 160–64.

[3] Christensen, *J. prakt. Chem.*, 1887, [ii.], **35**, 165.

[4] Weinland and Lauenstein, *Zeitsch. anorg. Chem.*, 1899, **20**, 40.

[5] Wöhler, *Pogg. Annalen*, 1826, **9**, 619. See also Dumas, *Ann. Chim. Phys.*, 1827, **36**, 82.

[6] See Wright and Menke, *Trans. Chem. Soc.*, 1880, **37**, 22.

a vapour whose density was determined as 1·35 against 1·26 calculated for $MnCl_2$.[1] The chloride may be ignited in hydrogen without reduction.

Manganous chloride may be obtained in aqueous solution by dissolving metallic manganese in aqueous hydrogen chloride, hydrogen being evolved, or by treating manganous carbonate with hydrogen chloride, or by dissolving the oxides in hydrochloric acid.

The cheapest source of manganese is the dioxide, MnO_2, which is always impure, being contaminated as a rule with iron. Manganous chloride may be obtained from this as a by-product by working up the residues obtained in the preparation of chlorine : $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$. These residues[2] are evaporated to drive off the free hydrogen chloride, diluted with water, and about one-tenth of the solution is precipitated with sodium carbonate. This precipitate, which consists of $MnCO_3 + Fe(OH)_3$, is washed with hot water and then boiled with the rest of the solution. The whole of the iron is thus precipitated as ferric hydroxide, the manganous carbonate going into solution in its place. The liquid should then be free from iron which can be easily ascertained by testing with a little potassium ferrocyanide solution—the presence of iron revealing itself as a blue precipitate, whereas in the absence of iron only a white precipitate is obtained.

The filtrate is usually contaminated with calcium, barium, and copper. The copper may be removed by passing hydrogen sulphide into the acid solution, while if calcium and barium are present the manganese is precipitated as sulphide with ammonium sulphide, the precipitate being then well washed with hot water and redissolved in hydrogen chloride, when a solution of pure $MnCl_2$ is obtained. For the preparation of pure $MnCl_2$, see also Richards and Wrede.[3]

When the solution is evaporated,[4] there crystallises out between 15° and 20° pink monoclinic crystals of the formula $MnCl_2.4H_2O$, isomorphous with $NaCl.2H_2O$. At 58·089° C. this hydrate[3] splits off water and becomes $MnCl_2.2H_2O$, which at 198°, in an atmosphere of steam, again loses water, yielding the anhydrous salt $MnCl_2$.

If the concentrated solution of manganous chloride be cooled, there separates out below $-2°$ C. the hexahydrate $MnCl_2.6H_2O$.

In addition to the tetrahydrate $MnCl_2.4H_2O$ above mentioned, Marignac[5] showed that an isomeric tetrahydrate may be obtained by slowly evaporating the mother liquors from which the first modification has separated out. This second modification forms monoclinic crystals which are isomorphous with the crystals of hydrated ferrous chloride $FeCl_2.4H_2O$. The second modification is somewhat more soluble than the first modification.

Brandes[6] gives the following data as regards the solubility of the second modification :—

1 part by weight of the crystals dissolves in 0·66 part water at 10° C., 0·37 at 31·25°, 0·16 at 87·5°, 0·16 at 106°.

[1] Dewar and Scott, *Ann. Phys. Beibl.*, **7**, 149 ; Brit. Assoc. Report, York, 1881, p. 597.
[2] See Everitt, *J. prakt. Chem.*, 1835, **5**, 35 ; Kolbe, *ibid.*, 1872, [ii.], **5**, 445 ; Bayer, *ibid.*, 1872, [ii.], **5**, 443 ; Kappers, *Ber.*, 1872, **5**, 582.
[3] Richards and Wrede, *Zeitsch. physikal. Chem.*, 1907, **61**, 313–20.
[4] See Kusnetzoff, *J. Russ. Chem. Soc.*, 1898, **30**, 741 ; Dawson and Williams, *Zeitsch. physikal. Chem.*, 1899, **31**, 59 ; Richards and Churchill, *Zeitsch. physikal. Chem.*, 1898, **28**, 313 ; J. Süss, *Zeitsch. Kryst. Min.*, 1912, **51**, 248–68.
[5] Marignac, *Compt. rend.*, 1857, **45**, 650.
[6] Brandes, *Pogg. Annalen*, 1830, **20**, 556.

The following numbers refer to the solubility of $MnCl_2$ in water; 100 parts of water dissolve:—

Temperature, ° C.	8°	25°	30°	57·85°	80°	100°
Grams of $MnCl_2$	6·2	77·2	80·7	105·7	112·7	116.

Dawson and Williams[1] give the following data for the saturated solution:—

Temperature, °C. .	25°	30°	40°	50°	57·65°	60°	70°	80°
Specific gravity	1·4991	1·5049	1·5348	1·5744	1·6097	1·6108	1·6134	..
Grams $MnCl_2$ in 100 grams H_2O .	77·18	80·71·	88·59	98·15	105·4	108·6	110·6	112·7
Mols. $MnCl_2$ to 100 mols. H_2O .	11·05	11·55	12·69	14·05	15·10	15·55	15·84	16·14

The absorption spectrum of manganous chloride is given by Jaeschke and Meyer.[2]

Manganous chloride is also soluble in alcohol, forming a green solution which burns with a red flame; it is insoluble in ether or turpentine oil. The heat of formation of $MnCl_2$ is given by Thomsen[3] as follows:—

$$(Mn,Cl_2) = 111,990 \text{ calories}, \quad (Mn,Cl_2,Aq.) \quad = 128,000 \text{ calories}.$$
$$(Mn,Cl_2,4H_2O) = 126,460 \text{ calories}, \quad (MnCl_2,4H_2O) = \quad 14,470 \text{ calories}.$$
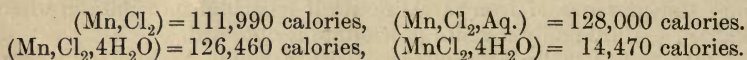
Berthelot gives $(Mn,Cl_2) = 112,600$ calories.

The heat of solution of $MnCl_2$ is 16,010 calories; the heat of solution of $MnCl_2.4H_2O$ is 1540 calories.

Manganous chloride forms double salts with the chlorides of the alkali metals and some other chlorides; the following are well-known examples:—[4]

$MnCl_2.2KCl + 2H_2O$, triclinic deliquescent crystals, obtained by cooling concentrated solutions of $MnCl_2$ and KCl.

$MnCl_2.2RbCl + 2H_2O$, $MnCl_2.CsCl + 2H_2O$, $MnCl_2.2CsCl_2 + 2H_2O$,
$MnCl_2.2NH_4Cl + 2H_2O$, $2MnCl_2.2NH_4Cl + H_2O$, $2MnCl_2.MgCl_2 + 11H_2O$,
$MnCl_2.2CdCl_2 + 12H_2O$, are other examples of double salts obtained by similar methods.

Manganese trichloride, $MnCl_3$, and **Manganese tetrachloride,** $MnCl_4$, have not been isolated in the solid state, although possibly solutions of these substances have been obtained.[5]   A cold concentrated solution of hydrochloric acid dissolves MnO_2, Mn_2O_3, or Mn_3O_4, forming a dark brown solution, and, when MnO_2 alone is used, chlorine is evolved, slowly at ordinary temperatures, more rapidly on heating.

According to Pickering,[6] this solution contains only $MnCl_3$ and not $MnCl_4$, and, when treated with KCl or NH_4Cl, may be made to yield double salts of the formula $MnCl_3.2KCl$.[7]   When the solution of the dioxide is diluted with

[1] Dawson and Williams, *Zeitsch. physikal. Chem.*, 1899, **31**, 63.
[2] W. Jaeschke and J. Meyer, *Zeitsch. physikal. Chem.*, 1913, **83**, 281- 89.
[3] Thomsen, *Thermochemische Untersuchungen*, iii. 270, 271; Sabatier, *Bull. Soc. chim.*, 1894, [iii.], **11**, 546.
[4] See Haute, *Annalen*, **66**, 280; Rammelsberg, *J. prakt. Chem.*, 1854, **65**, 181; Pickering, *Trans. Chem. Soc.*, 1879, **35**, 672; v. Hauer, *J. prakt. Chem.*, 1855, **63**, 436; J. Süss, *Zeitsch. Kryst. Min.*, 1912, **51**, 248–68.
[5] Pickering, *loc. cit.*; also Fisher, *Trans. Chem. Soc.*, 1878, **33**, 409; Christensen, *J. prakt. Chem.*, 1887, [ii.], **35**, 57, 161, 541.
[6] Pickering, *Trans. Chem. Soc.*, 1879, **35**, 654.
[7] Neumann, *Monatsh.*, 1894, **15**, 489; Rice, *Trans. Chem. Soc.*, 1898, **73**, 258.

water, a part of the manganese is precipitated as $MnO_2.H_2O$, the rest remaining in solution as $MnCl_2$.[1]

Chlorine is evolved when the dark brown solution is heated, thus :—
$$2MnCl_3 = 2MnCl_2 + Cl_2.$$

When manganese dioxide is treated with ether saturated with HCl gas, a dark green solution results, which on diluting with ether turns violet or blue. Nicklès[2] thought this solution contained $MnCl_4$, while Franke[3] gave the contained chloride the formula $MnCl_2.MnCl_4$. However, Meyer and Best[1] came to the conclusion that no $MnCl_4$ was present, only $MnCl_3$, because it yields double salts with the hydrochlorides of pyridene and quinoline solely of the type $MnCl_3.2RHCl$, nearly all the manganese being precipitated in this form.[4] A solution of HCl gas in absolute alcohol produces similar green solutions with MnO_2, Mn_2O_3, or potassium permanganate, the solution thus obtained containing much more oxide than the ethereal solution.

The following double salts, derivatives of $MnCl_3$, have been prepared :—

$MnCl_3.2NH_4Cl$ separates as a violet-brown crystalline mass when MnO_2 is slowly stirred into a strongly cooled solution of HCl, previously saturated with chlorine, and then a solution of NH_4Cl·is added.

$MnCl_3.2KCl$, similarly prepared, using KCl instead of NH_4Cl.

$MnCl_3.2RbCl$, prepared as described below.

$MnCl_3.2CsCl$, a brown, easily decomposable precipitate.

$MnCl_4.MnCl_3.5KCl$, prepared as below.

Derivatives of the higher *tetrachloride*, $MnCl_4$, have undoubtedly been prepared.[1] Thus when 5 grams of $KMnO_4$ are warmed with 150 c.c. of glacial acetic acid until energetic action begins, and then gaseous hydrogen chloride is passed into the solution, an almost black crystalline precipitate of *potassium manganichloride*, $MnCl_4.2KCl$, separates out.

The same compound may be prepared[5] by adding calcium permanganate and a concentrated solution of potassium chloride to a 40 per cent. aqueous solution of hydrochloric acid cooled with ice and salt, when it forms small, dark red crystals.

This substance is unstable in moist air, rapidly losing chlorine ; it may, however, be kept for some time in dry air.

The corresponding *ammonium* and *rubidium salts* were prepared in the same way.

If to the liquid before treating with gaseous hydrogen chloride potassium acetate be added, then gaseous hydrogen chloride passed in for a short time only, there separates out $MnCl_4.MnCl_3.5KCl$; when, however, the liquid is completely saturated with HCl we get Neumann's salts of the formula $MnCl_3.2KCl$ instead (Meyer and Best).

Weinland and Dinkelacker[5] isolate from the solutions from which the double salts of quadrivalent manganese have separated, double salts of tervalent manganese of the type $MnCl_3.2KCl$ by adding excess of the alkali chlorides in concentrated aqueous solution. They describe the salts $MnCl_3.2RbCl$, $MnCl_3.2CsCl$, $MnCl_3.2NH_4Cl$.

[1] Meyer and Best, *Zeitsch. anorg. Chem.*, 1899, **22**, 169.
[2] Nicklès, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 169 ; 1867, [iv.], **10**, 318.
[3] Franke, *J. prakt. Chem.*, 1888, [ii.], **36**, 31, 451.
[4] See, however, Holmes and Manuel, *J. Amer. Chem. Soc.*, 1908, **30**, 1192-93.
[5] Weinland and Dinkelacker, *Zeitsch. anorg. Chem.*, 1908, **60**, 173-77.

The absorption spectra of solutions of $MnCl_3$ and $MnCl_4$ have been studied by Jaeschke and Meyer.[1]

Permanganic oxychloride, MnO_3Cl.—Dumas [2] was the first to obtain this substance, which he believed to be $MnCl_7$ from the manner of preparation; it was Aschoff [3] who first analysed the substance and showed that its formula was MnO_3Cl. To prepare the body, fused sodium chloride is slowly added to a solution of potassium permanganate in concentrated sulphuric acid, when a green gas is evolved, which at 0° C. condenses to a greenish-brown liquid. Its formation in this way may be explained as follows :—

The $KMnO_4$ dissolves in the sulphuric acid with the production of $(MnO_3)_2SO_4$, (see p. 289), and the $NaCl$ is then acted on by the sulphuric acid to produce HCl gas, which then reacts on the $(MnO_3)2SO_4$, thus :—

$$(MnO_3)_2SO_4 + 2HCl = 2(MnO_3)Cl + H_2SO_4.$$
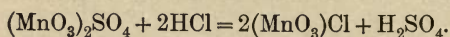
From its mode of preparation it may be regarded as an acid chloride of permanganic acid, $HMnO_4$ or $HO.MnO_3$, and when acted on by water it is decomposed into permanganic acid, thus :—

$$Cl.MnO_3 + H_2O = HO.MnO_3 + HCl.$$
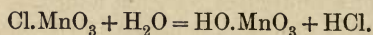
However, permanganic acid, $HO.MnO_3$ is soon decomposed by the free hydrogen chloride, with the production of free chlorine and hydrated MnO_2.

When permanganic oxychloride is exposed to the air, it emits a purple-red vapour, which acts violently on the mucous membrane and smells like the oxides of chlorine, so that even a very minute quantity of any chloride contained in commercial permanganate may be readily detected by cautiously dissolving in concentrated sulphuric acid.

Permanganic oxychloride explodes violently when heated.

Manganous chlorate, $Mn(ClO_3)_2$, is only known in solution, being apparently produced when $MnSO_4$ is added to $Ba(ClO_3)_2$. However, on concentrating the colourless solution, decomposition sets in, chlorine, oxygen, and hydrated manganese dioxide being produced.[4]

Manganous perchlorate, $Mn(ClO_4)_2$, is obtained [5] by mixing together solutions of $MnSO_4$ and $Ba(ClO_4)_2$, in the form of large deliquescent needles soluble in water and in absolute alcohol.

Manganese and Bromine.

Manganous bromide, $MnBr_2$, may be obtained by methods analogous to those used in producing the chloride. Thus when the powdered metal is heated in bromine vapour we get the substance formed, which after fusing appears as a reddish mass and when ignited in air decomposes completely into bromine and Mn_3O_4.[6]

When dry bromine is added to finely divided manganese under dry

[1] Jaeschke and Meyer, *Zeitsch. physikal. Chem.*, 1913, **83**, 281–89.
[2] Dumas, *Ann. Chim. Phys.*, 1827, [ii.], **36**, 81.
[3] Aschoff, *Pogg. Annalen*, 1860, **111**, 217.
[4] Wächter, *J. prakt. Chem.*, 1843, **30**, 321.
[5] Serullas, *Ann. Chim. Phys.*, 1831, [ii.], **46**, 305.
[6] Gorgeu, *Bull. Soc. chim.*, 1888, [ii.], **49**, 664 ; *Compt. rend.*, 1888, **106**, 743.

ether,[1] a series of compounds such as $MnBr_2.Et_2O$, $MnBr_2.3Et_2O$ are obtained. On heating, Et_2O is lost, and anhydrous $MnBr_2$ is left as a white powder.

In a hydrated form it may be easily produced by dissolving manganous carbonate in hydrogen bromide, and evaporating at a gentle heat, when $MnBr_2 + 4H_2O$ separates out as small monoclinic tablets or needles, isomorphous [2] with $MnCl_2 + 4H_2O$. The crystals are more deliquescent than the corresponding chloride, melt when heated in their water of crystallisation, and have a piercing taste. According to Thomsen,[3] the heat of formation in aqueous solution is given by $(Mn,Br_2,Aq.) = 106,120$ calories. Berthelot gives:—

$$[Mn,Br_2 \text{ (gas)}] = 114,400 \text{ calories,}$$
$$[Mn,Br_2 \text{ (liquid), Aq.}] = 107,000 \text{ calories.}$$

The tetrahydrate melts at $64.3°$ C., and loses water in so doing,[4] giving a rose-red powder of the probable composition $MnBr_2.2H_2O$.

A hexahydrate,[5] $MnBr_2.6H_2O$, is formed when the tetrahydrate is heated to its melting-point, and the dihydrate thus produced as a rose-red powder is filtered off, and the residual liquid cooled to $0°$ C.

Saunders [6] describes the double salts such as $2MnBr_2.MgBr_2 + 12H_2O$ and $MnBr_2.2MgBr_2 + 12H_2O$.

Manganese tetrabromide, $MnBr_4$ (Manganese Tribromide, $MnBr_3$). —Nicklès [7] states that when Mn_3O_4, Mn_2O_3, and MnO_2 are treated with fuming hydrobromic acid dissolved in ether a green solution is obtained similar to the green solution of manganese trichloride (which see). Dilution with dry ether causes the green solution to change to violet. The solution disolves gold.

Manganese bromate has not been isolated.

Manganese and Iodine.

Anhydrous manganous iodide, MnI_2, may be obtained [8] by adding iodine to finely divided manganese covered with anhydrous ether. The action is completed by warming on the water-bath. Anhydrous MnI_2 can also be obtained [9] by dehydrating the hydrated iodide *in vacuo*, without heating (at $80°$ C. iodine is evolved). The substance forms a white powder, which soon becomes discoloured; it is completely soluble in water, combines energetically with gaseous ammonia and is soluble in liquid ammonia.[10] Berthelot gives:—

$$[Mn,I_2 \text{ (gas)}] = 89,800 \text{ calories.}$$

[1] Ducelliez and Raynaud, *Compt. rend.*, 1914, **158**, 576-78 ; *Bull. Soc. chim.*, 1914, [iv.], **15**, 273-75.
[2] Marignac, *Arch. Sci. phys. nat.*, **36**, 207.
[3] Thomsen, *Thermochemische Untersuchungen*, iii. 271.
[4] Lescœur, *Ann. Chim. Phys.*, 1894, [vii.], **2**, 78, 104.
[5] Kusnetzoff, *J. russ. phys. Ges.*, 1887, **29**, 288, 330 ; *Zeitsch. anorg. Chem.*, 1898, **18**, 387.
[6] Saunders, *Amer. Chem. J.*, **14**, 127.
[7] Nicklès, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 169 ; 1867, [iv.], **10**, 318 ; *Compt. rend.*, 1867, **65**, 107. See also Meyer and Best, *Zeitsch. anorg. Chem.*, 1899, **22**, 182.
[8] F. Ducelliez, *Bull. Soc. chim.*, 1913, [iv.], **13**, 815-16.
[9] W. Peters, *Ber.*, 1909, **42**, 4826 ; *Zeitsch. anorg. Chem.*, 1912, **77**, 137.
[10] Franklin and Kraus, *Amer. Chem. J.*, 1898, **20**, 828.

Hydrated manganous iodide may be obtained by dissolving manganous carbonate in aqueous hydriodic acid, and evaporating, when rose-coloured deliquescent crystals are obtained, of composition $MnI_2.4H_2O$, which become brown on exposure to air, and in the absence of air may be heated to their melting-point without decomposition. When ignited in the presence of air, purple fumes of iodine are evolved and a residue of Mn_3O_4 is left.

According to Thomsen,[1] the heat of formation of manganous iodide in aqueous solution is : $(Mn,I_2,Aq.) = 75,700$ calories (76,200, Berthelot).

Several other hydrates have been isolated [2] in addition to the tetrahydrate $MnI_2.4H_2O$. Thus when a solution of manganous iodide is saturated at 0° C. and then is cooled to $-5°$ C., first of all the tetrahydrate $MnI_2.4H_2O$ separates, and after this prismatic colourless columns, having the composition $MnI_2.6H_2O$. This hexahydrate decomposes at $-2·7°$ into the tetrahydrate.

A hydrate having the composition $MnI_2.9H_2O$ is obtained by cooling a solution of the concentration $MnI_2.9H_2O$ to $-20·5°$, when it slowly separates in the form of tablets, melting at $-9·3°$ C. Lescœur [3] describes hydrates of the composition $MnI_2.H_2O$ and $MnI_2.2H_2O$. P. Kusnetzoff [4] describes a basic manganese iodide, $MnI_2.MnO.6H_2O$.

Manganese tri-iodide, MnI_3 (existence doubtful), may exist in the dark solution obtained by allowing aqueous HI to act on MnO_2 at low temperatures, the solution on warming yielding MnI_2 and free iodine.

When the oxides Mn_2O_3, Mn_3O_4, or MnO_2 are covered with dry ether, and the solution saturated with gaseous hydrogen iodide, unstable solutions are formed similar to those obtained in the same manner when hydrogen chloride and bromide act in ethereal solution on the oxides of manganese.[5] (See $MnCl_3$, $MnBr_4$, pp. 272 and 275.)

Manganese iodate, $Mn(IO_3)_2$, may be obtained by precipitating $NaIO_3$ with manganese acetate, or by treating $Mn(NO_3)_2$ dissolved in concentrated nitric acid with $NaIO_3$, and evaporating at 60°-70° C.

Obtained by the first method it forms a pale red crystalline powder, whereas obtained by the second method it forms small, shining, red crystals only very sparingly soluble in water or HNO_3—1 part of salt dissolving in 200 of water.

Manganese tetriodate, $Mn(IO_3)_4$, has not been isolated in a pure state, but derivatives of it are known; thus when hydrated manganese dioxide is boiled with iodic acid and potassium iodate, a brownish-violet, insoluble crystalline powder, of the composition $Mn(IO_3)_4.2KIO_3$, is deposited.[6] Berg also describes the ammonium compound $(NH_4IO_3)_4.Mn(IO_3)_4$ as a brick-red crystalline powder prepared in a similar manner to the potassium derivative, and $Ba(IO_3).Mn(IO_3)_4$ as yellowish-brown crystals.

$Mn_2(IO_3)_6$ ($= Mn(IO_3)_2.Mn(IO_3)_4$) is also described by Berg as consisting of delicate grey-blue needles or as violet-brown crystals.

[1] Thomsen, *Thermochemische Untersuchungen*, iii. 271.
[2] See Kusnetzoff, *J. russ. phys. Ges.*, 1900, **32**, 290.
[3] Lescœur, *Ann. Chim. Phys.*, 1894, [vii.], **2**, 103, 110.
[4] P. Kusnetzoff, *Chem. Zentr.*, 1913, i. 1659.
[5] See Nicklès, *Ann. Chim. Phys.*, 1865, [iv.], **5**, 161 ; 1867, [iv.], **10**, 318 ; *Compt. rend.*, 1867, **65**, 107.
[6] Berg, *Compt. rend.*, 1899, **128**, 673.

MANGANESE AND OXYGEN.

Manganese forms a numerous series of oxides and oxy-acids, of which the following have the simplest constitution :—

Oxides.		*Oxy-acids.*
Manganese monoxide,	MnO.	
Trimanganese tetroxide,	Mn_3O_4.	
Manganese sesquioxide,	Mn_2O_3.	
Manganese dioxide,	MnO_2.	Manganous acid,* H_2MnO_3.
Manganese trioxide,	MnO_3.	Manganic acid,* H_2MnO_4.
Manganese heptoxide,	Mn_2O_7.	Permanganic acid, $HMnO_4$.

* Only known in solution.

A number of oxides between Mn_2O_3 and MnO_2 also exist, having the general form $xMnO_2.yMnO$.

The oxide, Mn_3O_4, appears to act as a compound of the monoxide and sesquioxide, or of the dioxide and monoxide, and so has the probable composition $MnO.Mn_2O_3$, or $MnO_2.2MnO$.

The tetroxide, MnO_4, does not appear to exist (Thorpe and Hambly), although Franke described it some years ago.

Manganese monoxide, MnO, is a powerful basic oxide, reacting with acids to form *manganous salts*, MnX_2 ($X = NO_3$, $\frac{1}{2}SO_4$, etc.).

The sesquioxide, Mn_2O_3, is only weakly basic, producing an unstable series of *manganic salts*, MnX_3, which are easily reduced to MnX_2.

The tetroxide, Mn_3O_4, when dissolved in acids usually produces a mixture of MnX_2 and MnX_3 salts, but sometimes MnX_2 and MnO_2 are produced therefrom.

Manganese dioxide, MnO_2, is a weak acidic oxide, producing with oxides more basic than itself a series of salts known as *manganites*, of general formula $xMnO_2.yRO$. When MnO_2 is dissolved in acids, salts of the type MnX_4 are not in general produced ; although it is possible that a few salts of this type exist, yet their isolation is very doubtful (see MnO_2).

The acidic character is still more developed in the case of manganese trioxide, MnO_3. MnO_3 is very unstable, but combines with water to form the acid $H_2Mn_2O_8$, together with MnO_2. It does not form salts, but the existence of $(MnO_3)_2SO_4$ is probable. The *manganates*, X_2MnO_4, H_2MnO_4, of which MnO_3 may be regarded as the anhydride just as SO_3 is the anhydride of H_2SO_4, are as a class very unstable. They are isomorphous with the sulphates and chromates, X_2SO_4 and X_2CrO_4.

Manganese heptoxide, Mn_2O_7, is also very unstable and strongly acidic. It combines with water to form the powerful acid $HMnO_4$, known as permanganic acid. This acid yields stable salts which are isomorphous with the perchlorates.

Manganese monoxide (*Manganous Oxide*, MnO) **and its Salts.**—This oxide occurs native in small quantities in bright green hexagonal crystals, forming the mineral *manganosite*, which occurs in Sweden.

Preparation.—(1) When equal parts of manganous chloride, $MnCl_2$, sodium carbonate, Na_2CO_3, with a little ammonium chloride, NH_4Cl, are heated to redness in a platinum crucible, manganous carbonate is first formed, and then decomposes into $MnO + CO_2$, the NH_4Cl preventing the formation of higher oxides. The fused mass is lixiviated, washed, and dried.[1]

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[1] Liebig and Wöhler, *Pogg. Annalen*, 1831, **21**, 584.

(2) MnO may be also prepared by heating Mn_3O_4 or MnO_2 to redness in a stream of hydrogen or carbon monoxide, finally igniting and cooling in nitrogen gas in order to remove occluded hydrogen.[1]

(3) When manganese carbonate, $MnCO_3$, or manganese oxalate, MnC_2O_4, is heated strongly in absence of air, and finally ignited in hydrogen, we also get MnO produced in a pure form.[2]

Deville[3] obtained MnO in the form of bright green, regular octahedral crystals, by heating MnO_2 in hydrogen containing a little HCl gas.

(4) Manganese which has been prepared by the distillation of its amalgam, when heated in a stream of carbon monoxide, CO, to 350°–500° C. suddenly ignites and burns to MnO,[4] according to the equation $Mn + CO = MnO + C$. The carbon monoxide is so rapidly absorbed by the burning metal that a partial vacuum ensues even when the gas is being introduced in a rapid stream. Strongly ignited or fused manganese reacts only very slowly when ignited with carbon monoxide; also the ferro-manganese alloys react very slowly indeed with this gas.

Properties.—Natural manganosite, MnO, forms a hexahedral mass, giving a bright green fracture; in thin plates it appears ruby-red by transmitted light; it possesses a hardness of 5 to 6 and a specific gravity of 5·18.[5]

Crystalline MnO, prepared by Deville's process (see above), forms transparent, bright green regular octahedra, with a diamond-like lustre and a specific gravity 5·09. The amorphous MnO, prepared by the methods indicated above, forms a grass-green non-hygroscopic powder.

MnO, prepared by reducing higher oxides of manganese in CO or H_2 at as low temperatures as possible (say 260°), ignites and burns in air when heated to only 140°,[6] while specimens prepared from the oxalate by heating to 200°–420° are pyrophoric, oxidising to Mn_2O_3 when ignited and heated for a short time in air. When heated for some hours, however, the resulting product has the composition $2MnO.3MnO_2$. The denser forms of MnO when ignited gently in air also oxidise, but without actually catching fire, Mn_3O_4 being produced. When pure, MnO does not oxidise on exposure to air; but when traces of potash are present, oxidation gradually occurs.[7]

MnO melts at a white heat in absence of air. It is not reduced by heating in hydrogen or carbon monoxide, or with carbon at 500°–600°; but when heated in a stream of hydrogen to over 1200° or with carbon to 1100°–1200° C., it is reduced to metallic manganese.[8] Even at very high temperatures it does not evolve oxygen gas. When heated in hydrogen sulphide it forms MnS.

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[1] Forchhammer, *Thomson's Annals Phil.*, 1820, 16, 130; 1821, 17, 50; Turner, *Pogg. Annalen*, 1828, 14, 211; Wright and Luff, *J. Chem. Soc.*, 1878, 33, 522; Moissan, *Ann. Chim. Phys.*, 1880, [v.], 21, 232; Weeren, *Inaug. Dissert.* (Halle, 1890); G. Charpy, *Compt. rend.*, 1909, 148, 560–61.

[2] Scheele, *Opuscula*, I., 227; Arfvedson, *Pogg. Annalen*, 1824, 1, 50; Bachmann, *Zeitsch. Phys. Math.*, 4, 312, 6, 172; Liebig, *Annalen*, 95, 116.

[3] Deville, *Compt. rend.*, 1861, 53, 199.

[4] Guntz, *Bull. Soc. chim.*, 1892, [iii.], 7, 276, 278; *Compt. rend.*, 1892, 114, 115. Charpy, *Compt. rend.*, 1909, 148, 560–61.

[5] Blomstrand, *Ber.*, 1875, 8, 130.

[6] Moissan, *Ann. Chim. Phys.*, 1880, [v.], 21, 232.

[7] Gorgeu, *Compt. rend.*, 1888, 106, 743; *Bull. Soc. chim.*, 1888, [ii.], 49, 664; Wright and Menke, *Trans. Chem. Soc.*, 1880, 37, 28; Scheele. *Opuscula*, I., 227; Liebig, *Annalen*, 95, 116.

[8] Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 1–35; Moissan, *loc. cit.*; Greenwood, *Trans. Chem. Soc.*, 1908, 93, 1491.

MnO readily dissolves in acids producing manganous salts, MnX_2 (X = Cl, NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, etc.).

The heat of the formation of MnO is given by Le Chatelier as 90,000 calories.[1]

Manganous hydroxide, $Mn(OH)_2$, occurs in Sweden as the mineral *pyrochroïte*, forming a pearl-white mass, appearing flesh-coloured through transmitted light. It may be obtained as a white precipitate by adding caustic alkali to a solution of a manganous salt.

It oxidises rapidly in the air, turning brown, and producing first the oxide Mn_3O_4, and finally Mn_2O_3. To obtain it pure, it is precipitated in the absence of oxygen, and dried at a gentle heat in a stream of hydrogen. Thus prepared it may form a pyrophoric white powder, which, when touched with red-hot charcoal, glows at the point of contact, the oxidation then spreading rapidly through the whole mass.

The following practical details regarding the preparation of crystalline $Mn(OH)_2$ are given by de Schulten:[2] 300 grams KOH purified by alcohol are dissolved in 500 c.c. of water in a flask, and all the air in the liquid is removed by boiling and passing into the flask a stream of hydrogen or coal gas. After cooling, a solution of 15 to 17 grams of crystallised manganous chloride, $MnCl_2.4H_2O$, dissolved in 15 c.c. water is added, and the whole is heated to 160° C., so that a clear solution is obtained, which, on cooling, solidifies to a crystalline mass. This mass is then washed in an atmosphere of hydrogen, first with air-free water, then with alcohol, and finally with ether, and then it is dried at a gentle heat in a stream of hydrogen. The mass so produced consists of regular hexagonal prisms of about 0·2 mm. diameter, which are perfectly transparent, but of a reddish tinge. The specific gravity at 13° C. was 3·258. When perfectly pure they only change very slowly in air ; when impure, however, rapid oxidation occurs, the white mass going brown or black. The solubility of the hydroxide in water is given as $2\cdot15 \times 10^{-5}$ gram.-mol. per litre at 18° C.[3]

When aqueous ammonia is added to a solution of a manganous salt, the hydroxide is not precipitated, as it is soluble in ammonia solution.

However, the resulting solution rapidly absorbs oxygen from the air, and after some time the manganese is completely precipitated as hydrated Mn_2O_3 or Mn_3O_4.[4] It should be noted that solutions of double manganous ammonium salts are scarcely altered in air if free ammonia is absent, owing to the fact that the presence of NH_4 ions hinders the oxidation process.

Herz[5] proved that when manganous hydroxide, $Mn(OH)_2$, is treated with an ammonium salt it dissolves to an extent directly proportional to the concentration of the NH_4 ions in the solution, complex ions containing ammonium and manganese being formed.

Thomsen[6] gives the heat of formation as (Mn,O,H_2O) = 94,700 calories ; the heat of neutralisation by H_2SO_4 is 26,480 calories ; by HNO_3 it is 22,950 calories ; by HCl it is 22,950 calories ; by $H_2S_2O_6$ it is 22,780 calories.

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[1] Le Chatelier, *Compt. rend.*, 1896, **122**, 80.

[2] De Schulten, *Compt. rend.*, 1887, **105**, 1265.

[3] O. Sackur and E. Fritzmann, *Zeitsch. Elektrochem.*, 1909, **15**, 842–46 ; Tamm, *Zeitsch. physikal. Chem.*, 1910, **74**, 496–502, gives the solubility as 2×10^{-4} mol. per litre.

[4] Gorgeu, *Compt. rend.*, 1877, **84**, 177.

[5] W. Herz, *Zeitsch. anorg. Chem.*, 1899, **21**, 242 ; 1899, **22**, 279.

[6] Thomsen, *Thermochemische Untersuchungen*, 1883, iii. 270.

Manganous Salts.—The manganous salts, MnX_2, are well crystallised as a rule, and usually have a faint rose-colour.

The cause of this coloration has been the subject of much discussion. Fromherz and Brandes [1] considered it to be due to a trace of manganic or higher oxidation product, because by repeated precipitation of manganous salts with K_2CO_3, followed by solution in H_2SO_4 or HCl, at last perfectly colourless crystals of $MnSO_4$ or $MnCl_2$ were obtained. Gorgeu, [2] however, appears to have proved that the pink colour is characteristic of manganous salts, while the colourless crystals are impure—the presence of only 0·8 per cent. of nickel rendering the manganous salts colourless. He showed that amorphous manganous salts are really colourless, but yield coloured crystals.

The manganous salts are usually soluble in water, forming solutions neutral to litmus; those salts which are insoluble in water readily dissolve in hydrogen chloride. In neutral solutions they only oxidise slightly on exposure to air, but in alkaline solution they show a great tendency to oxidise into manganic salts: they reduce Fehling's solution, forming manganese tartrate.

Manganous salts, especially when combined with organic acids, can serve as oxygen "transferers," taking the oxygen from the air, giving it up to oxidisable organic bodies, and again taking up more oxygen from the air. Bertrand [3] made a study of the circumstances in which this action takes place, and came to the conclusion that the oxidising action of Lakkase, the ferment in the Chinese Lacquer tree, *Rhus vernicifera*, is due to the presence of organic manganese salts, since no less than 2·5 per cent. of the ash consists of manganese.

The action of manganese salts as "driers" of linseed oil in this connection is similar.

As regards the *absorption spectra* of manganous salts, see Jaeschke and Meyer. [4]

Trimanganic tetroxide (*Mangano-Manganic Oxide, Red Oxide of Manganese*), Mn_3O_4.—This oxide occurs native as *hausmannite*, forming brownish black acute tetragonal pyramids.

Preparation.—(1) This substance is formed as a red powder when MnO is heated in contact with air; also when the higher oxides such as MnO_2 or Mn_2O_3 are very strongly heated in contact or out of contact with air, when the final composition of the product approximates to the formula Mn_3O_4. Dittmar, [5] who studied this question, showed that the composition of the product obtained by heating MnO_2 in a mixture of oxygen and nitrogen varied very considerably according to the partial pressure of the oxygen; thus if the partial pressure of the oxygen was about 0·19 atmosphere the substance obtained finally had the composition Mn_3O_4, while if the pressure is greater than 0·26 atmosphere the product has the composition Mn_2O_3.

Gorgeu [6] showed that finely powdered Mn_3O_4 can be oxidised to $xMnO.yMnO_2$, and ultimately to Mn_2O_3 by heating in air.

(2) When manganese carbonate or oxalate is ignited in air, Mn_3O_4 is

[1] *Schweigger's J. Chem. Phys.*, **44**, 327.
[2] Gorgeu, *Ann. Chim. Phys.*, 1853, [iii.], **42**, 70.
[3] Bertrand, *Compt. rend.*, 1896, **122**, 1132.
[4] W. Jaeschke and J. Meyer, *Zeitsch. physikal. Chem.*, 1913, **83**, 281–89.
[5] Dittmar, *J. Chem. Soc.*, 1864, 294. See also Meyer and Rötgers, *Zeitsch. anorg. Chem.*, 1908, **57**, 104–12.
[6] Gorgeu, *Compt. rend.*, 1888, **106**, 743.

ultimately produced. Wright and Luff,[1] who studied the effects of heating $MnCO_3$ in air, found that when the heating is continued for a very long time and the temperature kept very high (at a white heat) only Mn_3O_4 is produced. If, however, the temperature be not kept very high, the product invariably contains more oxygen than corresponds to Mn_3O_4.

(3) Manganese in a powdered form gradually oxidises itself to Mn_3O_4 when left in air at ordinary temperatures, the action being more rapid when heat is employed.[2]

The manganese tetroxide prepared by the preceding methods is an amorphous red powder, but several methods exist for obtaining it in a crystalline form. For example, Deville[3] showed that if the powder is heated to redness in a slow current of gaseous hydrochloric acid it is converted into crystals of hausmannite. Debray[4] obtained it in a crystalline form by heating to bright redness a mixture of K_2SO_4 and $MnSO_4$. Other methods are : igniting MnO and $CaCl_2$,[5] keeping molten $MnCl_2$ in an atmosphere laden with moisture,[6] melting amorphous Mn_3O_4 with borax.[7]

Properties. — Crystalline Mn_3O_4 forms brown tetragonal pyramids, $a : c = 1 : 1.1537$; its specific gravity is 4.856. Amorphous Mn_3O_4 usually forms a reddish powder, of specific gravity 4.718 (Rammelsberg).

The oxide can be heated to a very high temperature without change ; according to Meyer and Rötgers,[8] Mn_3O_4 is stable in air up to 1300°, while in oxygen at atmospheric pressure it is converted at 650°–900° C. into Mn_2O_3 ; it is reduced to MnO when heated with hydrogen, carbon monoxide, or carbon. Reduction by carbon monoxide begins at 240° C., by hydrogen at 255° C., and by carbon at 430° C.[9] When heated to whiteness with carbon, it is reduced to manganese. (See MnO.)

The heat of formation is 328,000 calories.[10] Mn_3O_4 dissolves in concentrated hydrochloric acid on gently warming, evolving chlorine :—

$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2.$$
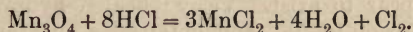
When fused with alkalies, the oxide produces alkaline manganates, R_2MnO_4.

Mn_3O_4 is not a simple basic oxide giving rise to a series of salts ; its behaviour towards acids indicates that it is a compound oxide whose composition may be either $MnO.Mn_2O_3$, or $2MnO.MnO_2$. The following is the evidence upon which this view is founded :[11] The oxide dissolves slowly in cold concentrated sulphuric acid, forming a red solution which is a mixture of both manganous and manganic sulphates ; acetic acid dissolves one-third of the manganese as manganous acetate, leaving behind Mn_2O_3 ;[12] a boiling

[1] Wright and Luff, *Trans. Chem. Soc.*, 1878, **33**, 520.
[2] See Ruff and Gersten, *Ber.*, 1913, **46**, 400–13.
[3] Deville, *Compt. rend.*, 1861, **53**, 199.
[4] Debray, *Compt. rend.*, 1861, **52**, 985.
[5] Kuhlmann, *Compt. rend.*, 1861, **52**, 1283.
[6] Gorgeu, *Compt. rend.*, 1883, **96**, 1144.
[7] Nordenskjöld, *Pogg. Annalen*, 1861, **114**, 612.
[8] R. J. Meyer and K. Rötgers, *Zeitsch. anorg. Chem.*, 1908, **57**, 104–12.
[9] Wright and Luff, *Trans. Chem. Soc.*, 1878, **33**, 520 ; *Ber.*, 1878, **11**, 2143. G. Charpy, *Compt. rend.*, 1909, **148**, 560–61.
[10] Le Chatelier, *Compt. rend.*, 1896, **122**, 80. Ruff and Gersten, *Ber.*, 1913, **46**, 400–13, give 329,000 ± 740 calories.
[11] See Pickering, *Trans. Chem. Soc.*, 1879, **35**, 654 ; Rammelsberg, *Ber. Berl. Akad.*, 1885, 97 ; Franke, *J. prakt. Chem.*, 1887, [ii.], **36**, 31, 166, 451 ; Christensen, *J. prakt. Chem.*, 1883, [ii.], **28**, 1.
[12] Gorgeu, *Bull. Soc. chim.*, 1903, [iii.], **29**, 1111, 1167.

solution of NH_4Cl dissolves out MnO, leaving behind Mn_2O_3;[1] these three facts all support the constitution $MnO.Mn_2O_3$:—

$$MnO.Mn_2O_3 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O,$$
$$MnO.Mn_2O_3 + 2CH_3.COOH = Mn(CH_3COO)_2 + Mn_2O_3 + H_2O.$$
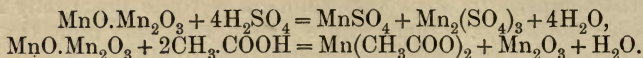
On the other hand, the following facts speak for the constitution $2MnO.MnO_2$: when the oxide is *heated* with dilute sulphuric acid, or with nitric acid, a manganous salt and MnO_2 are formed :— [2]

$$2MnO.MnO_2 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O,$$
$$2MnO.MnO_2 + 2H_2SO_4 = 2MnSO_4 + MnO_2 + 2H_2O,$$
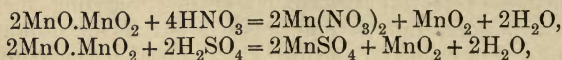
the MnO_2 then reacting with the H_2SO_4, forming $MnSO_4$ and O :—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$
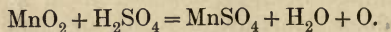
The reactions of the oxide with potassium iodide, KI, also suggest the formula $2MnO.MnO_2$ (see Pickering).

The following scheme illustrates these transformations in constitution :—[3]

$$MnO.Mn_2O_3$$

$$Mn_3O_4$$

$$2MnO.MnO_2.$$
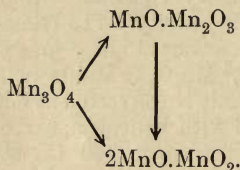
(See also below under Manganese Sesquioxide, Mn_2O_3, which exhibits similar behaviour.)

Hydroxides corresponding to Trimanganic Tetroxide, $Mn_3O_4.xH_2O$.— Several of these appear to exist. Veley[4] heated hydrated forms of manganese oxides in hydrogen to $200°$ and obtained a substance of approximate composition $8Mn_3O_4.3H_2O$. Gorgeu[5] describes yellowish-green hydrates of Mn_3O_4 produced by shaking aqueous solutions of manganese salts with alkali in the presence of air, while Otto[6] produces hydrates of the same oxide by heating MnO_2 with excess of an ammoniacal solution of $MnCl_2$.

Manganese sesquioxide (*Manganic Oxide*), Mn_2O_3.—Manganese sesquioxide occurs naturally as *braunite*, forming obtuse tetragonal pyramids of semi-metallic lustre, and possessing a brownish-black colour and a specific gravity of $4·752$.

Preparation.—The preparation of this oxide has been referred to under the oxide just discussed. The substance is obtained artificially by igniting any of the oxides of manganese in pure oxygen or in a mixture of oxygen and nitrogen, provided the mixture contains more than 26 per cent. of oxygen.[7] The change $MnO_2 \rightarrow Mn_2O_3$ begins in air at $530°$ and is complete in eighty-six

[1] H. Rose, *Ber. Berl. Akad.*, Mai, 1848.
[2] Turner, *Pogg. Annalen*, 1828, **14**, 211 ; Berthier, *Ann. Chim. Phys.*, 1822, **20**, 187 ; Forchhammer, *Ann. Phil.*, 1820, **16**, 130 ; 1821, **17**, 50.
[3] Caven and Lander, *Systematic Inorganic Chemistry*, (1911), p. 306.
[4] Veley, *Trans. Chem. Soc.*, 1882, **41**, 56.
[5] Gorgeu, *Compt. rend.*, 1887, **84**, 177.
[6] Otto, *Annalen*, 1855, **93**, 372.
[7] See Dittmar, *Trans. Chem. Soc.*, 1864, 294 ; also Meyer and Rötgers, *Zeitsch. anorg. Chem.*, 1908, **57**, 104–12.

hours; in dry O it begins at 565°. Manganese sesquioxide is also produced by heating MnO_2 in a stream of ammonia gas :— [1]

$$2NH_3 + 6MnO_2 = N_2 + 3Mn_2O_3 + 3H_2O.$$
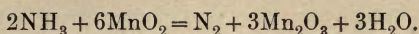
Properties.—The amorphous oxide is a black powder of specific gravity 4·325. The natural oxide, *braunite*, forms brownish-black, lustrous, very hard, octahedra, of specific gravity 4·752.

At a white heat the oxide loses oxygen and is converted into Mn_3O_4.

According to Meyer and Rötgers,[2] the change $Mn_2O_3 \rightarrow Mn_3O_4$ begins in air about 940° and is complete in twelve hours. In dry oxygen at atmospheric pressure the reaction $Mn_2O_3 \rightarrow Mn_3O_4$ begins at 1090°. In oxygen at 650°–900° Mn_3O_4 is converted into Mn_2O_3. It is soluble in cold concentrated hydrogen chloride, forming a brown liquid probably containing $MnCl_3$. It also dissolves in concentrated sulphuric acid, forming a reddish liquid, which evolves oxygen on warming and then contains $MnSO_4$.

Manganic oxide is a basic oxide producing a series of *manganic* salts; the salts are, however, few in number and are unstable, being readily reducible to manganous salts.

Manganic sulphate, $Mn_2(SO_4)_3$, unites with alkali sulphates to form a series of well-crystallised alums.

Many of the reactions of Mn_2O_3 with acids and potassium iodide seem to indicate that it possesses the constitution $MnO.MnO_2$.[3] For example, when boiled with dilute sulphuric acid or nitric acid some MnO_2 separates and MnO goes into solution as $MnSO_4$ or $Mn(NO_3)_2$. It is very probable, however, that manganic oxide has the constitution of a true sesquioxide, but that when heated with acids a separation takes place into MnO, which dissolves, and MnO_2, which remains behind :—

$$Mn_2O_3 \rightleftharpoons MnO.MnO_2.$$
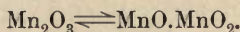
(See also Manganic Tetroxide as regards this point.)

Manganese sesquioxide is, according to Liesegang,[4] sensitive to light—a fact which has been put to practical use by Lumière Brothers.[5]

Hydroxide of manganic oxide, MnO(OH).—This substance occurs naturally as *manganite*, forming steel-grey or black tetragonal crystals of specific gravity 4·3. The mineral resembles pyrolusite (MnO_2) in appearance, but is distinguishable therefrom by giving a brown and not a black streak when rubbed on unglazed white porcelain. Heated to 270°–320° C. in air it oxidises into MnO_2.[6]

Artificially the substance may be prepared by allowing manganese hydroxide to oxidise in moist air, by passing chlorine into water containing suspended manganese carbonate, or by decomposing manganic sulphate with water.[7]

As thus produced it is a dark brown powder, with pigment properties.

[1] Michel and Grandmougen, *Ber.*, 1893, **26**, 2565.
[2] Meyer and Rötgers, *loc. cit.*
[3] Pickering, *Trans. Chem. Soc*, 1879, **35**, 654 ; Christensen, *J. prakt. Chem.*, 1883, [ii.], **28**, 1.
[4] Liesegang, *Phot. Archiv*, 1893, **34**, 133.
[5] A. and L. Lumière, *Phot. Archiv*, 1892, **33**, 177.
[6] Gorgeu, *Compt. rend.*, 1888, **106**, 743, 1101.
[7] Carius, *Annalen*, 1856, **98**, 53 ; Franke, *J. prakt. Chem.*, [ii.], **36**, 451.

It loses water when heated above 100° C.   It is soluble in hot nitric acid, forming manganous nitrate and manganese dioxide, thus :—

$$2MnO(OH) + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + 2H_2O.$$
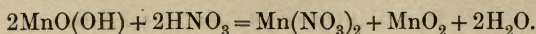
When warmed with concentrated sulphuric acid to about 100° it dissolves to form manganic sulphate, $Mn_2(SO_4)_3$, without the evolution of oxygen.

Manganic salts, MnR_3, are all very unstable, and are decomposed by water.   The fluoride, sulphate, and some phosphates have been isolated, while manganic potassium alum separates in violet octahedra on crystallising the solution obtained by dissolving Mn_3O_4 in strong sulphuric acid, and after adding potassium sulphate.   (See also above, under Mn_2O_3.)

MANGANESE DIOXIDE.
(*Manganese Peroxide, Black Oxide of Manganese.*)
Formula, MnO_2.

This, the most important ore of manganese, occurs native as *pyrolusite* and as *polianite*.   Pyrolusite occurs abundantly at Ilmenau in Thuringia, near Mährisch-Trubau in Moravia, also in Bohemia, in the Caucasus, in France, Spain, and on the Lahn, and in Devonshire.   In America it occurs in large deposits at Vermont, near San Francisco, in New Brunswick, Nova Scotia, and in New Zealand.

Pyrolusite is usually mixed with other manganese ores, such as manganite and psilomelane $(Mn,Ba)O.M2nO_2$, and almost invariably is contaminated with lime, ferric oxide, carbonates, and traces of cobalt and nickel oxides.

Preparation.—(1) Artificially pure MnO_2 may be obtained by heating the nitrate.   Pure $MnCO_3$ is dissolved in as small a quantity as possible of dilute nitric acid, and the solution of $Mn(NO_3)_2$ thus obtained is evaporated to a syrup, and warmed until red fumes appear ; the clear liquid is then decanted from the lower oxides which separate out, and heated in another vessel at 155°–162° in an oil bath for forty to sixty hours, when the dioxide is obtained in a crystalline form.   The product is then well washed with boiling water, dried over H_2SO_4, and heated to 180°–200° until all the water is removed.   The pure MnO_2 thus obtained resembles natural pyrolusite.[1]

(2) If $MnCO_3$ be heated in air to 260° C., and the product well washed with very dilute cold HCl, pure MnO_2 remains (Forchhammer).

Moissan heats 1 part of $MnCO_3$ to 300° C. with 2 parts of melted $KClO_3$, and then thoroughly washes the mass after cooling, when pure MnO_2 is left as a residue.[2]

(3) Many attempts have been made to obtain pure MnO_2 by precipitating manganese salts.   Thus a brown precipitate approximating to hydrated MnO_2 in composition can be obtained by the aid of a large number of oxidising agents—*e.g.* by treating with bromine water in the presence of sodium acetate or ammonia,[3] by sodium hypochlorite,[4] potassium permanganate,

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[1] Gorgeu, *Bull. Soc. chim.*, 1890, [iii.], **4**, 16 ; *Compt. rend.*, 1879, **88**, 796.
[2] Moissan, *Ann. Chim. Phys.*, 1880, [v.], **21**, 232 ; Göbel, *Schweigger's J. Chem. Phys.*, 1833, **67**, 77.
[3] Wright and Menke, *Trans. Chem. Soc.*, 1880, **37**, 41.
[4] R. Phillips, *Phil. Mag.*, 1829, **5**, 214.

sodium chlorate and nitric acid, persulphate and mineral acid,[1] ozone,[2] etc. The outcome of a very large amount of work on the subject, however, seems to be, firstly, that products of constant composition can only be obtained from acidified solutions,[3] and secondly, that pure MnO_2 cannot be obtained by any of the precipitation methods,[4] since hydrated MnO_2 very readily loses part of its oxygen, forming mixtures of the composition $xMnO + yMnO_2$.

Thus, the product obtained by the reduction of permanganic acid by $MnSO_4$ and by the precipitation of permanganic acid in the presence of hydrated MnO_2 varies in composition from $15MnO_2 + MnO$ to $5MnO_2 + MnO$.

In certain cases of precipitation, however, all the manganese is present as MnO_2, but the product combines with other bases present, forming manganites, which remain to contaminate the resulting product.

Thus, Volhard's[5] method of adding excess of $KMnO_4$ solution to $MnSO_4$ solution in the presence of nitric acid, gives all the manganese as MnO_2 accompanied by about 3 per cent. of K_2O, which could not be removed by washing, and which was undoubtedly chemically combined. When the precipitation is carried out at $80°$ C. in the presence of $ZnSO_4$, a similar result is obtained.

The oxide precipitated from $Mn(NO_3)_2$ by HNO_3 and $NaClO_3$,[6] or by ammonium persulphate,[7] contains slightly less than the theoretical percentage of oxygen for MnO_2, the former precipitate containing 98 per cent. of the manganese as MnO_2.

Colloidal manganese dioxide.—By treating manganic hydroxide with hot nitric acid,[8] or by precipitating $KMnO_4$ with sodium thiosulphate or hydrogen peroxide,[9] it yields hydrated manganese dioxide, which can be made to dissolve in water yielding a brown solution which has been called "*manganous acid*," H_2MnO_3 or H_4MnO_4; the solution is acid to litmus and may be kept without alteration for weeks, but a trace of acid or alkali causes an instant precipitation—evidently a colloidal solution of MnO_2 has been thus produced.[10]

Properties.—*Pyrolusite* forms iron-black, opaque, brittle crystals of the rhombic system. It possesses a specific gravity $4·82$, hardness 2 to $2·5$, is a good electrical conductor, and in contact with metals becomes strongly negatively electrified. *Polianite* forms tetragonal crystals of steel-grey colour, of specific gravity $4·84$ to $4·88$, and of hardness 5 to $5·5$.

The heat of formation of artificial MnO_2 is 126,000 calories according to Le Chatelier,[11] $2MnO + O_2 = 2MnO_2 + 42,800$ calories (Berthelot), and 39,200 calories (Sackur and Fritzmann).[12] The specific heat is $0·159$.

When heated to moderate redness Mn_2O_3 is formed, the decomposition

[1] Marshall, *Trans. Chem. Soc.*, 1891, **59**, 771 ; Baubigny, *Compt. rend.*, 1902, **135**, 1110 ; 1903, **136**, 449, 1325, 1662.

[2] Jannasch and Gottschalk, *Ber.*, 1904, **37**, 3111.

[3] Rupp, *Zeitsch. anal. Chem.*, 1903, **42**, 732.

[4] Gorgeu, *Compt. rend.*, 1890, **110**, 960, 1134.

[5] Volhard, *Annalen*, **198**, 321 ; Wright and Menke, *Trans. Chem. Soc.*, 1880, **37**, 39 ; Baubigny, *Compt. rend.*, 1903, **136**, 1662–64. See this vol., p. 268.

[6] Gooch and Austin, *Amer. J. Sci.*, 1898, [iv.], **5**, 260 ; *Zeitsch. anorg. Chem.*, 1898, **18**, 339. [7] von Knorre, *Zeitsch. angew. Chem.*, 1901, **14**, 1149.

[8] Gorgeu, *Ann. Chim. Phys.*, 1862, [iii.], **66**, 153.

[9] Bredig and Marck, *Gedenkboek aangeboden ann J. M. van Bemmelen*, 1910, p. 342.

[10] See Spring, *Ber.*, 1883, **16**, 1142 ; *Bull. Soc. chim.*, 1887, [ii.], **48**, 170 ; Eugen Deiss, *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 69–77 ; Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1898, **29**, 562. [11] Le Chatelier, *Compt. rend.*, 1896, **122**, 80.

[12] O. Sackur and E. Fritzmann, *Zeitsch. Elektrochem.*, 1909, **15**, 842–46.

beginning[1] at about 390° C. Heated to whiteness, Mn_3O_4 results.[2] (See pp. 280–283.)

According to Meyer and Rötgers,[3] the change $MnO_2 \rightarrow Mn_2O_3$ begins in air at 530°, in dry oxygen at 565°, and is complete in about eighty-six hours. At 940° in air and 1090° in dry oxygen the further change $Mn_2O_3 \rightarrow Mn_3O_4$ begins and is completed in twelve hours; the oxide Mn_3O_4 can be heated to a temperature of 1300° in air without further decomposition.

Sackur and Fritzmann[4] calculate the dissociation pressure of manganese dioxide at 18° C. to be $6\cdot3 \times 10^{-23}$ atmospheres.

According to Askenasy and Klonowski,[5] the dissociation pressure of artificially prepared MnO_2 is given by the following table :—

Temperature.	Dissociation Pressure.
° C.	mm.
382	23
448	125
478	200
536	1040

The oxidation potential for MnO_2 depends upon the activity of the solution, but the normal potential is given as $1\cdot35$ volts by Haehnel.[6]

When manganese dioxide is heated in hydrogen or carbon monoxide reduction to MnO takes place. Reduction with carbon begins at about 390°, in hydrogen at about 190°, and in CO at about 87°. (See also Reduction of MnO and Mn_3O_4.) When heated in gaseous ammonia it forms Mn_2O_3.[7] When mixed with potassium chlorate, oxygen is evolved at a considerably lower temperature than from pure $KClO_3$ alone, MnO_2 remaining unchanged together with KCl and a little chlorine. This reaction is discussed under "Preparation of Oxygen," Vol. VII.

Manganese dioxide reacts with acids to form salts corresponding to MnO ; with cold concentrated hydrogen chloride it forms a solution which probably contains $MnCl_3$, but which, when heated, evolves chlorine with the production of $MnCl_2$. (See Chlorine, p. 55 ; Manganese Trichloride, p. 272.)

With hot concentrated sulphuric acid $MnSO_4$ is formed and oxygen is evolved, the action taking place, according to Carius,[8] in two stages :—

(1) At 110° :—

$$2MnO_2 + 3H_2SO_4 = Mn_2(SO_4)_3 + 3H_2O + O.$$
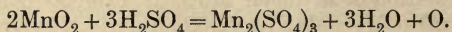
(2) At the boiling-point of sulphuric acid :—

$$Mn_2(SO_4)_3 = 2MnSO_4 + SO_3 + O.$$
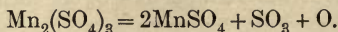
When heated with sulphuric acid and oxidisable agents, MnO_2 acts as an oxidising agent; for example, it completely oxidises oxalic acid, $H_2C_2O_4$, to water and carbon di-oxide. Dilute nitric acid does not dissolve MnO_2 ; but when

[1] Wright and Luff, *Ber.*, 1878, **11**, 2144.
[2] See Berthier, *Ann. Chim. Phys.*, 1822, **20**, 187 ; Schneider, *Pogg. Annalen*, **107**, 605 ; Dittmar, *J. Chem. Soc.*, 1864, **17**, 294 ; Christensen, *J. prakt. Chem.*, 1883, [ii.], **28**, 1.
[3] Meyer and Rötgers, *Zeitsch. anorg. Chem.*, 1908, **57**, 104–12.
[4] O. Sackur and E. Fritzmann, *loc. cit.*
[5] P. Askenasy and S. Klonowski, *Zeitsch. Elektrochem.*, 1910, **16**, 104–14.
[6] Haehnel, *Zeitsch. Elektrochem.*, 1909, **15**, 834–42.
[7] Michel and Grandmougen, *Ber.*, 1893, **26**, 2565.
[8] Carius, *Annalen*, 1856, **98**, 53.

oxidisable bodies are present, solution takes place with formation of $Mn(NO_3)_2$. When hydrogen peroxide, H_2O_2, is brought into contact with MnO_2, it is decomposed, the MnO_2 apparently remaining unchanged (see Hydrogen Peroxide, Vol. II.). With hydrogen peroxide in the presence of a mineral acid a manganous salt is formed and oxygen evolved.

Freshly precipitated MnO_2 dissolves to an appreciable extent in concentrated hydrogen peroxide solution at $-20°$ C., forming, according to Bredig and Marck,[1] the manganous salt of hydrogen peroxide; this salt,

$$Mn\big<^O_O|||,\text{ is isomeric with manganese dioxide, }Mn\big<^O_O.$$
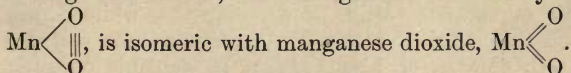
When heated with magnesium chloride, $MnCl_2$ and MgO are formed, while chlorine is evolved. When heated with alkalis, MnO_2 unites to form a class of bodies known as *Manganites* (discussed below) of the general formula xMO.yMnO.

According to this, it would appear that manganese dioxide possesses feebly acidic properties. However, it also, apparently, possesses feebly basic properties as well; for, although in general it does not react with acids to produce oxy-salts of the corresponding type MnX_4, but rather manganous salts, MnX_2 (see above, Reactions with Acids), with evolution of oxygen, yet *manganese tetrachloride*, $MnCl_4$, has been obtained by the action of dry hydrogen chloride gas on manganese dioxide suspended in carbon tetrachloride. It is unstable, but forms complex salts, such as K_2MnCl_6.[2]

Again, Fremy[3] states that the salt $Mn\big<^O_{SO_4}$ is formed by acting on hydrated MnO_2 with concentrated sulphuric acid and allowing to stand in air. By adding $MnSO_4$ to a solution of red lead in acetic acid Schönbein[4] obtained a liquid which probably contained manganese tetra-acetate, $Mn(C_2H_3O_2)_4$, as the solution was a strong oxidising agent. However, this substance has not as yet been isolated in a pure state.

Uses.—The oxide has long been used in the form of pyrolusite to remove the colour from glass tinged by compounds of iron; hence pyrolusite has been known as *savon des verriers*, and the name "pyrolusite" is due to this use of the mineral, being derived from πῦρ, fire, and λύω, I wash. Pyrolusite is also used as the main source of metallic manganese, also for preparing manganese compounds, and for making chlorine in the manufacture of bleaching powder (Weldon's process).

Constitution.—This has been the subject of much controversy. Manganese dioxide is not a peroxide in the sense of giving hydrogen peroxide, H_2O_2, with acids. Richarz[5] attributes to it the formula of a simple polyoxide, viz. $O=Mn=O$. However, reactions are known which indicate that it has a much more complex structure than this. Thus Guyard[6] (1864) and Volhard[7] (1879) regarded it as the permanganate of manganous oxide, $(MnO)_3Mn_2O_7$, this conception being based on its formation by the action of potassium permanganate on manganous sulphate solution:—

$$3MnSO_4 + 2KMnO_4 + 2H_2O = (MnO)_3Mn_2O_7 + K_2SO_4 + 2H_2SO_4.$$
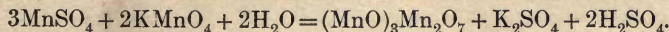
[1] Bredig and Marck, *loc. cit.*   [2] Meyer and Best, *Zeitsch. anorg. Chem.*, 1900, **22**, 169.
[3] Fremy, *Compt. rend.*, 1876, **82**, 475.   [4] Schönbein, *J. prakt. Chem.*, 1858, **74**, 319.
[5] Richarz, *Ber.*, 1888, **21**, 1675.   [6] Guyard, *Bull. Soc. chim.*, 1864, **1**, 89.
[7] Volhard, *Annalen*, 1879, **198**, 318.

Laspeyres[1] considered it to be manganous manganate, because, among other reasons, it is precipitated as manganous manganate when barium permanganate reacts with manganous sulphate :—

$$BaMnO_4 + MnSO_4 = MnMnO_4 + BaSO_4.$$
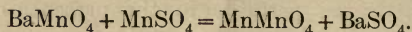
Both of these reactions, however, can be explained as due to the direct oxidation of a manganous salt at the expense of a manganate or permanganate, which are thereby reduced to the dioxide stage. Elliot and Storer consider it to be a basic manganic manganate ($Mn_2O_3.MnO_3 = Mn_3O_6$), while Spring and Lucion[2] (1890) regard the simple formula MnO_2 as quite incorrect, but regard such formulæ as $MnO.MnO_3$, or $3MnO.Mn_2O_7$ as possible ones; in other words, the molecular constitution of manganese dioxide is unknown.

Bredig[3] believes that he has obtained an oxide $Mn\begin{smallmatrix}O\\ \parallel\parallel\parallel \\ O\end{smallmatrix}$ isomeric with ordinary manganese dioxide, $Mn\begin{smallmatrix}O\\ \\ O\end{smallmatrix}$, by acting on manganous salts with H_2O_2.

Hydrates of manganese dioxide.—Precipitated manganese dioxide (see above, p. 284) always contains water, but it is doubtful whether any definite and stable hydroxides of manganese dioxide have been obtained. When, by means of oxidising agents, the precipitation takes place in such a way that most of the manganese is in the form of MnO_2, the mass first precipitated usually approximates in composition to $MnO_2.H_2O$. However, this body loses water merely on standing in dry air[4] and passes into a product of approximate composition $3MnO_2.2H_2O$, which Franke[5] (1887) regards as polymanganic acid :—

$$(HO)_2Mn\begin{smallmatrix}O\\ \\ O\end{smallmatrix}\rangle Mn\begin{smallmatrix}O\\ \\ O\end{smallmatrix}\rangle Mn(OH_2).$$

When, however, the whole of the manganese is not precipitated as MnO_2, it appears possible to obtain hydroxides which are stable for many hours within strictly defined temperature limits, such precipitated hydroxides having the general formula $xMnO_2.yMnO.zH_2O$.[6]

For Weldon's recovery process, see under Chlorine, p. 58.

The Manganites.—Manganese dioxide combines with a number of oxides more basic than itself to form bodies which may be regarded as salts of manganous acid. However, the composition of these compounds appears to depend largely upon the amount of alkali which is present. Risler[7] describes a whole series of manganites of the general composition $MO.5MnO_2$, where M = Ca, Ba, Sr, Zn, and Pb. Among the best known may be mentioned :—

Calcium manganite, $CaO.5MnO_2$, is thrown down as a brownish-black precipitate when manganous nitrate solution is added to an excess of a solution of bleaching-powder. Of special practical importance are the calcium

[1] Laspeyres, *J. prakt. Chem.*, 1876, [ii.], **13**, 176.
[2] Spring and Lucion, *Bull. Soc. chim.*, 1890, [3], **3**, 4.
[3] Bredig and Marck, *Gedenkboek aangeboden ann J. M. van Bemmelen*, 1910, 342–43.
[4] Wright and Menke, *Trans. Chem. Soc.*, 1880, **37**, 22.
[5] Franke, *J. prakt. Chem.*, 1887, [ii.], **36**, 166, 451.
[6] See Veley, *Trans. Chem. Soc.*, **37**, 581 ; 1882, **41**, 56.
[7] Risler, *Bull. Soc. chim. Paris*, 1878, [ii.], **30**, 110. See also Rousseau, *Compt. rend.*, 1886, **102**, 616 ; **103**, 261 ; and 1891, **112**, 525.

manganites, CaO,MnO_2 and $CaO.2MnO_2$,[1] which are found in Weldon mud, obtained by oxidising precipitated manganese hydroxide in the presence of air.

Potassium manganite, $K_2O.5MnO_2$, is a yellow precipitate obtained by passing CO_2 gas through a solution of potassium manganate, K_2MnO_4.

Besides these a very large number of other manganites have been described, some of them occurring naturally, *e.g.* psilomelan, varvicit, credernite, etc.

According to Gorgeu,[2] MnO_2 withdraws 7 per cent K_2O and 4·1 per cent. Na_2O from dilute solutions of K_2CO_3 and Na_2CO_3, forming manganites of the approximate composition $M_2O.15MnO_2$. Neutral solutions of salts of Ca, Ba, Ag, Mn are also decomposed by MnO_2, which renders the solutions acid and combines with the bases.

Deiss[3] considers that the so-called manganites must, in many cases, be regarded as adsorption compounds of manganese dioxide and bases.

Manganese trioxide, MnO_3.—The preparation of this substance has been described by Franke,[4] and is best carried out as follows:—6 grams of potassium permanganate are dissolved in 100 c.c. of *cold* concentrated sulphuric acid. Next, dry anhydrous sodium carbonate is placed in a dry distilling-flask surrounded by cold water, and connected with two U-tubes surrounded by a freezing mixture of ice and salt. The first U-tube is usually filled with fragments of glass in order to condense better the fumes coming over, while the second U-tube contains a little dilute sulphuric acid. The green solution of $KMnO_4$ in sulphuric acid is now placed in a dropping-funnel fitted into the distilling-flask, and is allowed to fall drop by drop upon the sodium carbonate at the bottom of the flask; as each drop falls a pink cloud is formed, which partly condenses in the first U-tube as a purple fume on the glass fragments, being carried forward by the CO_2 gas generated; part passes on and is dissolved in the sulphuric acid in the second tube. The following action takes place:—

$$2(MnO_3)_2SO_4 + 2Na_2CO_3 = 2Na_2SO_4 + 4MnO_3 + 2CO_2 + O_2.$$
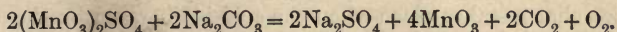
According to another view, the sulphuric acid contains the anhydride of permanganic acid, namely, Mn_2O_7, in solution, and the MnO_3 owes its existence to the spontaneous decomposition of this substance, thus:—

$$2Mn_2O_7 = 4MnO_3 + O_2.$$
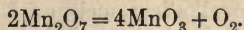
A very small quantity only of MnO_3 is thus obtainable as a reddish brown amorphous mass of quite extraordinary tinctorial power, appearing red when seen in thin layers, and dark red, almost black, in thicker layers. It is very deliquescent, and volatilises again at 50° C., forming a purple fume which has an extremely irritating effect on the bronchial passages, causing coughing. It slowly decomposes at ordinary temperatures, but is moderately stable if kept surrounded by ice and salt.

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[1] See Weldon, *Chem. News*, 1869, **20**, 109; *Moniteur scientif.*, 1874, [3], **4**, 891; *Ber.*, 1875, **8**, 168; Lunge and Zahorski, *Zeitsch. angew. Chem.*, 1892, 631; Wiernik, *Zeitsch. angew. Chem.*, 1894, 257. A detailed description of Weldon's process is to be found in Lunge's *Sulphuric Acid and Alkali Manufacture*, vol. iii., and in Geoffrey Martin's *Industrial Inorganic Chemistry*.
[2] Gorgeu, *Ann. Chim.*, 1862, [iii.], **66**, 161; Volhard, *Annalen*, 1879, **198**, 231.
[3] Eugen Deiss, *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 69–77.
[4] Franke, *J. prakt. Chem.*, 1887, [ii.], **36**, 31, 35. See also Thorpe and Hambly, *Trans. Chem. Soc.*, 1888, **53**, 175; Lankshear, *Proc. Chem. Soc.*, 1912, **28**, 198; *Zeitsch. anorg. Chem.*, 1913, **82**, 97–102.

When heated it decomposes into crystalline MnO_2 and oxygen. It dissolves slowly in water, forming a solution of bright red colour. Thorpe and Hambly state that the substance is decomposed by water, yielding permanganic acid, $HMnO_4$, and MnO_2, thus :—

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$
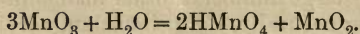
According to Franke (*loc. cit.*), manganic acid, H_2MnO_4, is first produced, but this rapidly decomposes to O and MnO_2, and a di-permanganic acid, $H_2Mn_2O_7$. Whichever view is adopted, it may be concluded that manganic acid is an unstable substance.

MnO_3 dissolves in concentrated sulphuric acid, forming first a yellow, then a green solution (which Franke considers to contain $(MnO_3)_2SO_4$), with separation of some MnO_2. It also dissolves in caustic soda or potash, forming a green solution of sodium or potassium manganate, Na_2MnO_4, or K_2MnO_4.

MnO_3 is an extremely powerful oxidising agent, liberating iodine from KI and acting on mercury like ozone.

Manganese trioxide is the anhydride of mánganic acid.

MANGANIC ACID AND MANGANATES.

Manganic acid, H_2MnO_4, itself has not been isolated and is very unstable. A solution of MnO_3 in water possibly contains manganic acid, H_2MnO_4, but it is rapidly decomposed by water to permanganic acid, $HMnO_4$, and MnO_2 :—

$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O.$$
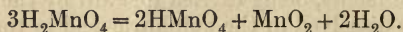
It is evidently, therefore, a very unstable body.

A similar change takes place when the acid is liberated by the addition of a strong mineral acid to a solution of a manganate.

The salts of manganic acid are known as *manganates* and possess the general formula M_2MnO_4, where M stands for a monovalent metal.

Preparation of the manganates.—The manganates are formed by heating MnO_2 with caustic alkalies, such as KOH, NaOH, $Ca(OH)_2$, to a temperature of about 150° C. if air is excluded, or to a higher temperature when air or an oxidising agent (such as $KClO_3$) is present :—

$$MnO_2 + 2KOH + O = K_2MnO_4 + H_2O.$$
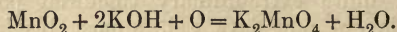
Manganates are also formed by the partial reduction of permanganates in alkaline solution by small quantities of reducing agents, such as alcohol, sulphuretted hydrogen, sodium thiosulphate, etc. (See below, under "General Properties.") Also the cautious heating of permanganates causes the evolution of oxygen and the formation of manganates. Thus when potassium permangante is heated to 240° C., we get :—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$
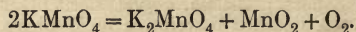
General Properties.—The manganates of Na, K, Rb, Cs, Ag, Tl, Ca, Ba, Sr, are all known, being obtained either as just described, or, when insoluble, by precipitating K_2MnO_4 solution with a suitable salt of the metal. These manganates are all dark bluish-green substances, which are isomorphous with the sulphates, selenates, and chromates, all these substances having

apparently the same arrangement of atoms in their molecules, which leads, according to Mitscherlich, to identity of crystalline form :—

$$\begin{matrix} M \\ \\ M \end{matrix} \Big\rangle Mn \Big\langle \begin{matrix} O \\ \\ O \end{matrix} \qquad \begin{matrix} M \\ \\ M \end{matrix} \Big\rangle S \Big\langle \begin{matrix} O \\ \\ O \end{matrix} \qquad \begin{matrix} M \\ \\ M \end{matrix} \Big\rangle Se \Big\langle \begin{matrix} O \\ \\ O \end{matrix} \qquad \begin{matrix} M \\ \\ M \end{matrix} \Big\rangle Cr \Big\langle \begin{matrix} O \\ \\ O \end{matrix}$$

$$\text{Manganates.} \qquad \text{Sulphates.} \qquad \text{Selenates.} \qquad \text{Chromates.}$$
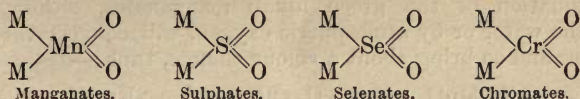
According to Retgers [1] (1891), the manganates, as regards their crystalline form, may be divided into two chief groups : the first group, consisting of the manganates of K, Rb, Cs, and Tl, forms rhombic, weakly doubly refracting, pseudo-hexagonal columns ; while the other group, consisting of the manganates of Li, Na, and silver, differs from the preceding group in some important respects.

The alkali manganates are soluble in water, but are decomposed by it [2] with precipitation of MnO_2 and formation of permanganates unless free alkali is present (see below). The manganates of barium, strontium, etc., are insoluble in water.

In alkaline solution the alkaline manganates are strong oxidising agents ; consequently their solutions are decolourised, with precipitation of MnO_2, by easily oxidisable bodies such as ferrous salts, arsenious oxide or arsenites, sulphites, sulphuretted hydrogen, and the like.

When chlorine is passed into a solution of an alkali manganate it changes it completely into permanganate, thus :— [3]

$$K_2MnO_4 + Cl = KCl + KMnO_4.$$
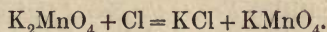
When hydrochloric acid is added to a solution of a manganate, chlorine is evolved owing to the oxidation of the acid, $MnCl_3$ being formed simultaneously.

The alkali manganates form bright green solutions, stable in the presence of free alkali, but decomposing rapidly in neutral or acid solutions, or even when the alkaline solutions are diluted with much water.

Thus if a green alkaline solution of potassium manganate, K_2MnO_4, is diluted with water, or has CO_2 passed through it, or is made weakly acid, the liquid changes in colour from green to blue, and finally to violet, owing to the formation of permanganate, thus :—

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO.$$
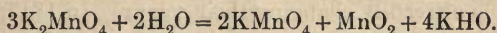
According to Caven and Lander,[4] it is doubtful whether or not pure water can effect this change ; but in the absence of other acid, carbonic acid derived from the air will bring it about. Caven and Lander attribute the change to the hydrolysis of the manganate and the self-oxidation and reduction of the resulting manganic acid, according to the equations :—

$$3Na_2MnO_4 + 3H_2O + 3CO_2 = 3H_2MnO_4 + 3Na_2CO_3,$$
$$3H_2MnO_4 = 2HMnO_4 + MnO_2 + 2H_2O.$$
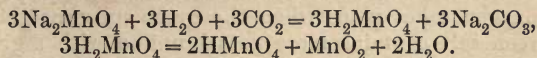
Ammonium salts, in the presence of excess of free ammonia, will also cause the green manganates to decompose into red permanganates. Thus, if a crystal of ammonium sulphate, $(NH_4)_2SO_4$, be placed in the green manganate solution it becomes surrounded with a red zone of permanganate.

[1] Retgers, *Zeitsch. physikal. Chem.*, 1891, **8**, 6.
[2] Retgers, *Rec. trav. chim. Pays-Bas*, 1891, **10**, 1.
[3] Städeler, *J. prakt. Chem.*, 1868, **103**, 107.
[4] Caven and Lander, *Systematic Inorganic Chemistry*, 1911, p. 309.

The salts of the other alkali metals do not, in general, effect this curious decomposition.[1]

Direct oxidation of the green alkali manganates, either by oxygen dissolved in the water or by atmospheric oxygen, will convert them into red permanganates and so bring about a colour change, thus :—

$$2Na_2MnO_4 + H_2O + O = 2NaMnO_4 + 2NaOH.$$
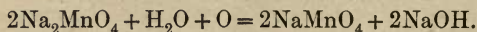
Manganates are also formed when permanganates are partially reduced in alkaline solution by the addition of small quantities of such reducing agents as alcohol, sodium thiosulphate, etc., to the red permanganate solution, previously made alkaline. A striking change of colour ensues, the red solution gradually turning first blue and then green.

It should be noted that when an alkaline solution of permanganate is exposed to the air the reducing action of organic matter contained in the atmosphere will usually cause the liquid to change from red through blue to green. On adding acid or much water, the liquid again goes through the reverse colour change, owing to the re-formation of permanganate.

These facts explain the curious properties of "mineral chameleon," described by writers of the eighteenth century. The history of this "mineral chameleon" is interesting. Glauber in 1656, in his book entitled *The Prosperity of Germany*,[2] states that when manganese dioxide is fused with caustic potash "fixed saltpetre," the product, when dissolved in water gave "a most delicate purple fiery liquor" which, on keeping, turns blue, red, and green. Half a century later, in a book entitled *Key to the Secret Cabinet of Nature's Treasury* (1705), by an unknown author, we find the statement that when saltpetre and manganese dioxide are fused together and the mass treated with water, a solution is obtained which is initially green, then becomes blue, violet, and finally rose-red. This is the converse series of colour changes recorded by Glauber. Next, Pott in 1740 investigated the colour changes, under the belief that he was describing them for the first time.

The fact that pyrolusite, saltpetre, and potash when fused together produce a green solution which became blue, violet, and red on adding water was well known to Scheele,[3] who gave the green compound the name *Chamœleon minerale*—a term which had previously been applied to other substances capable of readily changing their colour. In 1817, when Chevillot and Edwards[4] published a correct view of its composition, they showed that the green substance was a definite compound of potash with an acid of manganese, and is always formed when excess of alkali is employed; and that, on the other hand, when the manganese is in excess, the result of the fusion with potash is the formation of the red body (*i.e.* potassium permanganate), which they succeeded in obtaining in a crystalline state. They proved that an absorption of oxygen takes place when the green substance changes to red, and that the green salt contains more potash united with a given weight of manganese than the red (views which are now expressed by the formulæ K_2MnO_4 for the green manganate, and $KMnO_4$ for the red permanganate). Forchhammer,[5] in 1820, investigated the salts, and ascribed the difference in colour as due to two distinct acids.

[1] See Retgers, *Rec. trav. chim. Pay-Bas*, 1891, **10**, 1 ; also Santi, *Boll. chim. farm.*, 1904, **43**, 673.   [2] See Packe's translation, 1687, p. 353.
[3] Scheele, *Opuscula*, I., 227 ; *Crell's Neuesten Entdech.*, 1781, i. 112, 140.
[4] Chevillot and Edwards, *Ann. Chim. Phys.*, 1817, [ii.], **4**, 287.
[5] Forchhammer, *Ann. Phil.*, 1807, **16**, 130 ; 1808, **17**, 150.

Mitscherlich,[1] in 1832, however, was the first who gave the exact composition of manganic and permanganic acid, attributing to manganic acid the formula H_2MnO_4 and to permanganic acid the formula $HMnO_4$—views universally accepted at the present day.

The following are some of the more important manganates :—

Potassium manganate K_2MnO_4.—This is prepared[2] by dissolving 2 parts of KOH in a little water, adding 1 part of $KClO_3$ and 2 parts of finely divided MnO_2. The mixture is dried, heated nearly to redness, and the fused mass, when cold, is treated with a little cold water, the green solution thus obtained being allowed to stand until clear, and is then decanted and evaporated *in vacuo* :—

$$2KOH + MnO_2 + O = K_2MnO_4 + H_2O.$$
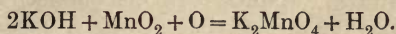
In the absence of an oxidising agent we get :—

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O.$$
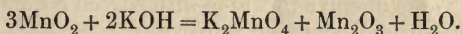
The substance may also be prepared by boiling a saturated solution of potassium permanganate, $KMnO_4$, with sodium hydroxide solution of specific gravity 1·33.

P. Askenasy and S. Klonowski[3] studied the oxidation of the lower oxides of manganese by heating them with potassium hydroxide in an atmosphere containing oxygen. The results obtained, starting with manganese dioxide or manganic oxide, Mn_2O_3, were practically identical. In both cases the quantity of manganate formed increases as the temperature rises up to the point at which the pressure of the oxygen is equal to the dissociation pressure of the manganate ; at a temperature higher than this the manganate is gradually decomposed.

In air the best temperature is about 600° C., and in oxygen it is about 700° C. 60 to 70 per cent. of the potassium hydroxide is convertible into manganate when excess of manganese oxide is used ; extending the time of heating beyond one hour does not increase the yield to any great extent. The absorption of oxygen begins at 240° C. somewhat slowly, and increases as the temperature increases.

The dissociation pressures of the purest potassium manganate which could be prepared are as tabulated below :—[3]

Temperature.	Dissociation Pressure.	Temperature.	Dissociation Pressure.
° C.	mm.	° C.	mm.
410	2	616	235·5
454	5	652	568
548	40	668	763
586	109		

[1] Mitscherlich, *Pogg. Annalen*, 1832, **25**, 287.
[2] See Thénard, *Compt. rend.*, 1856, **42**, 382 ; Luboldt, *J. prakt. Chem.*, **77**, 315 ; Aschoff, *Uebermangansaure, etc.* (Berlin, 1861) ; *J. prakt. Chem.*, 1860, 167 ; also Mitscherlich, *loc. cit.*
[3] Askenasy and Klonowski, *Zeitsch. Elektrochem*, 1910, **16**, 104–14. See also O. Sackur, *Ber.*, 1910, **43**, 381–88, 448–553 ; 1911, **44**, 777 ; Auger, *Compt. rend.*, 1910, **150**, 470–72, **151**, 69–70.

Potassium manganate forms dark green crystals, isomorphous with potassium sulphate and chromate ; it is soluble without decomposition in cold water containing potassium hydroxide, but dissolves in pure water with decomposition to $KMnO_4$ and MnO_2. It is decomposed by dilute acids (including CO_2) to potassium permanganate and a manganous salt, thus :—

$$5K_2MnO_4 + 4H_2SO_4 = 4KMnO_4 + MnSO_4 + 3K_2SO_4 + 4H_2O.$$
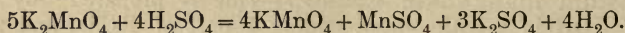
The absorption spectrum is given by Jaeschke and J. Meyer.[1] A complex potassium mangani-manganate, $5K_2O.Mn_5O_{11}$, is described by Sackur[2] and also by V. Auger.[2]

Sodium manganate, $Na_2MnO_4.10H_2O$, is obtained by boiling MnO_2 with sodium nitrate solution for a long time (say sixteen hours), filtering, and evaporating ; forms colourless crystals isomorphous with Glauber's salt, $Na_2SO_4.10H_2O$.[3] These dissolve in water with partial decomposition to form a green solution which has deodorising properties.

Mixter[4] gives the following thermal values :—

$$Mn + 3O + Na_2O = Na_2MnO_4 + 169,000 \text{ calories,}$$
$$MnO_2 + O + Na_2O = Na_2MnO_4 + 49,400 \text{ calories.}$$
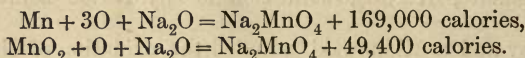
A complex sodium mangani-manganate of formula $2Na_2O.Mn_2O_5$, has been described by Sackur[2] and also by Auger.[2]

Barium manganate, $BaMnO_4$, is obtained by igniting barium nitrate with manganese dioxide, or by adding powdered manganese dioxide to a molten mixture of potassium chlorate and barium hydroxide.

It forms a dark green powder, insoluble in water, unchanged by air, but decomposed by acids. Specific gravity = 4·85. It has been used as a green pigment.

Manganese heptoxide, Mn_2O_7.—This oxide was first prepared by Thénard,[5] and its composition was first determined by Aschoff.[6] Terreil[7] further investigated the substance.

Preparation.—Pure potassium permanganate free from chlorine is gradually added to well-cooled concentrated sulphuric acid (density = 1·845). The salt readily dissolves, forming an intense olive-green liquid. The liquid is strongly cooled in a freezing mixture, and a few drops of water are added, when the Mn_2O_7 gradually deposits as a dark reddish brown liquid, which does not solidify at – 20°. Any quantity of $KMnO_4$ up to 20 grams may be used without danger.

It should be noticed that, according to Wohler,[8] when a quantity of concentrated sulphuric acid is poured on a larger amount of potassium per-

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[1] J. Jaeschke and J. Meyer, *Zeitsch. physikal. Chem.*, 1913, **83**, 281–89.

[2] O. Sackur, *Ber.*, 1910, **43**, 381–88, 448–553 ; 1911, **44**, 777 ; Auger, *Compt rend.*, 1910, **150**, 470–72 ; **151**, 69–70.

[3] Gentele, *J. prakt. Chem.*, 1861, **82**, 58; Funk, *Ber.*, 1900, **33**, 3696, could not obtain this substance by Gentele's method, and doubts its existence. See also Sackur, *Ber.*, 1910, **43**, 381–88, 448–53.

[4] William G. Mixter, *Amer. J. Sci.*, 1910, [iv.], **30**, 193–201.

[5] Thénard, *Compt. rend.*, 1856, **42**, 382 ; see also Chevillot and Edwards, *Ann. Chim.*, **8**, 337.

[6] Aschoff, *Pogg. Annalen*, 1860, **111**, 217.

[7] Terreil, *Bull. Soc. chim.*, 1862, p. 40.

[8] Wöhler, *Ann. Chim. Phys.*, 1853, **86**, 373.

manganate, the Mn_2O_7 set free decomposes violently, red fumes are evolved, oxygen and ozone are liberated, and dark brown specks of oxides of manganese float about in the air. Consequently caution is needed in the preparation of the substance, else explosion may ensue.

For other methods of preparation see Terreil[1] and Lovén[2] (1892). The latter uses 25 to 50 grams of $KMnO_4$ to 25 to 50 c.c. of concentrated sulphuric acid, and allows the whole to stand for some hours in the desiccator, when the liquid Mn_2O_7 separates out and may be filtered off from the pasty mass left behind.

Properties.—Thénard and Terreil describe Mn_2O_7 as a dark olive-green liquid, possessing a metallic lustre and a peculiar smell, resembling that of ozone. It has a specific gravity 2·4, does not solidify at $-20°$ C., may be heated in a vacuum to $65°$ without visible vapour rising, but over $65°$ the liquid explodes with a loud report, smashing the vessel in which it is contained, the explosion being accompanied by a vivid flash of light. When heated rapidly it may explode at $30°-40°$ C., but Terreil states that it may be heated safely to $65°$ C. provided that the heating is carried out slowly, but explosion takes place above $70°$. This last authority also states that it may be partially volatilised in the form of a violet vapour, which has an unpleasant "metallic" smell.

According to Lovén,[2] it is stable in dry air, and may be kept several days without change ; in moist air, however, or when left exposed to the atmosphere it gradually decomposes, evolving bubbles of ozonised oxygen, accompanied by violet fumes of permanganic acid. It rapidly absorbs moisture, and dissolves in water with the evolution of so much heat that partial decomposition ensues, forming a deep violet liquid, which is, presumably, a solution of permanganic acid : $Mn_2O_7 + H_2O + Aq. = 2HMnO_4 + Aq. + 12,000$ calories (Lovén). Concentrated sulphuric acid dissolves it, forming an olive-green solution which, according to Franke, contains the sulphate, $(MnO_3)_2SO_4$, it being formed according to the equation :—

$$2KMnO_4 + 2H_2SO_4 = (MnO_3)_2SO_4 + K_2SO_4 + 2H_2O.$$
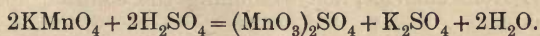
On adding water this decomposes into the heptoxide, thus :—

$$(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4.$$
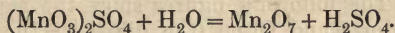
This green solution in sulphuric acid on heating evolves MnO_3, which can be collected (see Preparation of MnO_3, p. 289).

Manganese heptoxide is a powerful oxidising agent. Carbon and all organic matter cause its instant decomposition, with inflammation. Paper causes it to explode violently, while a drop of fat produces a white flame. Alcohol, ether, etc., also causes violent inflammation and detonations ; but, curiously enough, acetic acid dissolves it without instant decomposition, producing a violet-coloured solution. Other reducing agents such as sulphur, phosphorus, hydrogen, carbon disulphide, potassium sulphite solution, etc., all cause the substance to decompose instantly, usually with inflammation followed by explosion.

[1] Terreil, *Bull. Soc. chim.*, 1862, p. 40.
[2] Lovén, *Mitt. aus Chalmer's Inst.*, *Gothenburg* ; *Ber.*, 25, (1892), Ref. 620.

PERMANGANIC ACID AND PERMANGANATES.

Permanganic acid, $HMnO_4$.—*Preparation.*—(1) It may be produced in solution by allowing Mn_2O_7 to dissolve slowly in water, which it does with partial decomposition.[1] According to Lovén,[2] solutions containing 20 per cent. of $HMnO_4$ may be thus prepared, decomposition occurring when the concentration exceeds this:—

$$Mn_2O_7 + H_2O = 2HMnO_4.$$
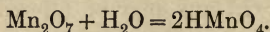
(2) Another method of preparing permanganic acid is to precipitate a solution of barium permanganate, $Ba(MnO_4)_2$, with the calculated quantity of sulphuric acid,[3] and decant from the precipitated $BaSO_4$:—

$$Ba(MnO_4)_2 + H_2SO_4 = BaSO_4 + 2HMnO_4.$$
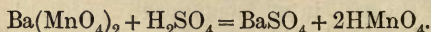
(3) Morse and Olsen [4] prepare a solution of pure permanganic acid by electrolysing a concentrated solution of potassium permanganate in a porous earthenware cell, the anodic space being separated from the cathodic by a porous earthenware diaphragm (so that the escaping hydrogen does not reduce the permanganic acid), while the potassium hydroxide formed in the cathodic space is removed from time to time.

(4) Permanganic acid is also formed when manganous salts (excepting the halides) are oxidised by certain agents, *e.g.* warming with lead peroxide and nitric acid; with potassium bromate and dilute sulphuric acid;[5] with bismuthic oxides and nitric acid;[6] or with ammonium persulphate, silver nitrate, and nitric acid.[7]

Properties.—A deep red liquid is thus obtained, appearing blue by reflected light and possessing an unpleasant metallic taste. The acid has a very characteristic absorption spectrum, showing dark bands in the green and yellowish green parts of the spectrum.[8] Owing to this fact, the presence of 1,250,000 parts of manganese in solution may be detected in the presence of copper or iron compounds by boiling with lead dioxide or with red lead and dilute nitric acid free from chlorine, and examining the solution spectroscopically for permanganate.

$HMnO_4$ is a strong mineral acid, having a strength nearly equal to that of nitric acid; this is shown by the electrolytic conductivities of solutions of permanganic acid. The following figures show the results of some careful determinations by Morse and Olsen (the dilution = the number of litres in which 1 gram-molecule is dissolved):— [9]

Dilution	16	32	64	128	256	512	1024
μ	352·3	361·2	371·6	375·0	374·7	376·6	377·3

[1] Aschoff, *Pogg. Annalen*, 1860, **111**, 217.
[2] Lovén, *Mitt. aus Chalmer's Inst., Gothenburg*; *Ber.*, **25**, (1892), Ref. 620; *Zeitsch. physikal. Chem.*, 1895, **17**, 374.
[3] Mitscherlich, *Pogg. Annalen*, 1832, **25**, 287; Aschoff, *loc. cit.*
[4] Morse and Olsen, *Amer. Chem. J.*, 1900, **23**, 431.
[5] Vitali, *Boll. chim. farm.*, 1898, **37**, 545.
[6] Schneider, *Dingl. Poly. J.*, 1888, **269**, 224.
[7] Marshall, *Chem. News*, 1901, **83**, 76.
[8] For the spectrum see Stokes, *Phil. Mag.*, 1853, [iv.], **6**, 401; Hoppe-Seyler, *J. prakt. Chem.*, 1863, **90**, 303; Lecoq de Boisbaudran, *Spectres lumineux*, p. 108; John E. Purvis, *Proc. Camb. Phil. Soc.*, 1909, **15**, 247–56; Merton, *Trans. Chem. Soc.*, 1911, **99**, 637; Hartley, *Trans. Chem. Soc.*, 1912, **101**, 826.
[9] Morse and Olsen, *loc. cit.*

Lovén's [1] conductivity determinations agree approximately with those of Morse and Olsen, and as a result he calculates for the acid the *avidity* 0·82.

Measurements on the conductivities of permanganates gave similar results,[2] from which it appears that permanganic acid is undoubtedly a strong monobasic acid.

The acid is unstable in solution. It decomposes on exposure to light or when heated, with evolution of oxygen and separation of hydrated manganese dioxide. The solution, therefore, is a very powerful oxidising agent, and in consequence it destroys the colour of litmus, without reddening it, and produces a brown stain on the skin.

When a solution of permanganic acid is evaporated to dryness, even *in vacuo* over H_2SO_4, it is for the most part decomposed into oxides of manganese, but Hünefield [3] claims that he obtained the acid in indigo-like crystals (doubtful).

The rate of decomposition of weak solutions of permanganic acid is considerably increased by the presence of hydrated manganese dioxide,[4] which apparently exercises a catalytic effect on the decomposition. When the solution is skaken with a reducing gas such as hydrogen or carbon monoxide, the gas is rapidly absorbed and a quantity of oxygen gas is simultaneously evolved.[5]

Lovén [6] shows, however, that very dilute solutions, containing only ·5 per cent. to 1 per cent. of $HMnO_4$ are stable, and can even be boiled without loss of oxygen.

The decomposition of the acid in the presence of sulphuric acid has been studied by Gooch and Danner.[7] They show that it increases with the concentration of the sulphuric acid and the length of time for which it acts. With 10 per cent. sulphuric acid the decomposition is insignificant after eight hours, but amounted to 4 per cent. after five days.

In the presence of 50 per cent. of H_2SO_4, however, 2 per cent. of the $HMnO_4$ underwent immediate decomposition, 15 per cent. in eight hours, 50 per cent. in five days, while heating at 80° C. for one and half hours also decomposed 50 per cent. of the acid.

Many substances decompose permanganic acid with evolution of oxygen ; for example, hydrogen peroxide reacts at ordinary temperatures, thus :—

$$2HMnO_4 + 5H_2O_2 = 2MnO + 6H_2O + 5O_2.$$
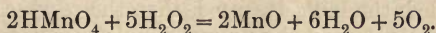
At lower temperatures, viz. $-12°$ C., decolorisation takes place, without evolution of oxygen, which makes probable the formation of such an oxide as H_2O_3.

Hydrochloric acid also destroys permanganic acid, being oxidised by it with the evolution of chlorine :—

$$HMnO_4 + 7HCl = MnCl_2 + 4H_2O + 5Cl.$$
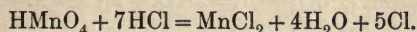
The Permanganates.—The salts of permanganic acid form a numerous and well-defined series of compounds, which are isomorphous with the

[1] Lovén, *loc. cit.*

[2] Bredig, *Zeitsch. physikal. Chem.*, 1893, **12**, 233 ; 1894, **13**, 217 ; Franke, *ibid.*, 1895, **16**, 475.　　　　　　　[3] Hünefield, *Schweigger's J.*, **60**, 133.

[4] See Morse and pupils, *Amer. Chem. J.*, 1896, **18**, 401 ; 1898, **20**, 521 ; *Ber.*, 1897, **30**, 48 ; 1900, **23**, 313 ; Olsen, *Amer. Chem. J.*, 1903, **29**, 242.

[5] Victor Meyer and Recklinghausen, *Ber.*, 1896, **29**, 2549 ; Hirtz and Meyer, *Ber.*, 1896, **29**, 2828.

[6] Lovén, *Mitt. aus Chalmer's Inst., Gothenburg* ; *Ber.*, **25**, (1892), Ref. 261.

[7] Gooch and Danner, *Amer. J. Sci.* (Sill.), 1892, [iii.], **44**, 301.

perchlorates, $RClO_4$; they are all purple-red and soluble in water, the silver salt $AgMnO_4$ being one of the most sparingly soluble permanganates known. The permanganates are all powerful oxidising agents. They are decomposed by most reducing agents: even ammonia decomposes them with formation of oxides of manganese, $xMnO_2.yMnO$. Concentrated nitric acid, also hydrochloric acid, decomposes permanganates.

According to A. Skrabal,[1] the evolution of oxygen in the decomposition of permanganates is principally due to the reaction:—$Mn^{II} + Mn^{VII} \rightarrow Mn^{III} \rightarrow Mn^{II} + O_2$; Sirkar and Dutta,[2] however, regard it as due to the reaction $Mn^{IV} \rightarrow Mn^{II} + O_2$.

The following are some of the more important permanganates:—

Potassium permanganate, $KMnO_4$, is perhaps the most important salt of permanganic acid.

Preparation.[3]—Two parts of potassium hydroxide, KOH, and 1 part of potassium chlorate, $KClO_3$, are melted together in a crucible, and 2 parts of finely divided MnO_2 are gradually added, after first removing the flame from the crucible. Heating is then continued with stirring until the mass sets to a hard mass, the temperature being then increased for a short time to redness.

The following change occurs:—

$$2KOH + MnO_2 + O = K_2MnO_4 + H_2O.$$
$$\underset{\substack{\text{From} \\ \text{KClO}_3.}}{} \quad \underset{\substack{\text{Potassium} \\ \text{manganate.}}}{}$$
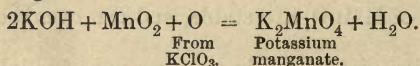
On cooling, the mass is broken up into fragments and boiled with about 40 parts of water to every 1 part of $KClO_3$ used (in order to use sufficient water to prevent crystals separating on cooling), and a rapid stream of carbon di-oxide gas is then sent into the boiling liquid until a drop of the latter when placed on a piece of filter-paper makes a red stain without showing green at the edges. When this occurs, all the manganate has been turned into permanganate, thus:—

$$3K_2MnO_4 + 3H_2O + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3 + 3H_2O.$$
$$\underset{\substack{\text{Potassium} \\ \text{manganate.}}}{} \qquad \underset{\substack{\text{Potassium} \\ \text{permanganate.}}}{}$$
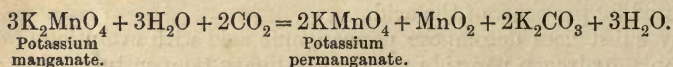
The solution is cooled, the bulk decanted, then the residue is filtered through glass wool from the MnO_2, and the united liquids are evaporated until a drop placed on a cold surface rapidly crystallises. After standing twenty-four hours the bulk of the $KMnO_4$ has separated, a further crop of crystals being obtained from the mother liquors. 100 grams MnO_2 yield 30 grams $KMnO_4$. In this preparation chlorine may replace the carbon di-oxide:—[4]

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4.$$
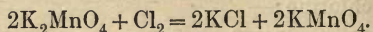
$KMnO_4$ is also formed by electrolysing KOH solution with a manganese or ferro-manganese anode,[5] also by electrolysing solutions of manganates.[6]

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[1] Skrabal, *Zeitsch. anorg. Chem.*, 1910, **68**, 48–51.
[2] Sirkar and Dutta, *Zeitsch. anorg. Chem.*, 1910, **67**, 225; *Proc. Chem. Soc.* 1909, 249.
[3] Böttger, *J. prakt. Chem.*, **90**, 169; see also Wöhler, *Pogg. Annalen*, **27**, 626; v. Gräger, *J. prakt. Chem.*, 1865, **96**, 169; Béchamp, *Ann. Chim.*, 1859, [iii.], **57**, 293; for technical preparation see Brock and Hurter, *J. Soc. Chem. Ind.*, 1894, **13**, 394; Eng. Pat., 7512/93. [4] Städeler, *J. prakt. Chem.*, 1868, **103**, 107.
[5] White, *J. Physical Chem.*, 1906, **10**, 502; see also Lorenz, *Zeitsch. anorg. Chem.*, 1896, **12**, 393; 1902, **33**, 25, and the German patents, 101,710; 105,008 (1898).
[6] See Askenasy and Klonowski, *Zeitsch. Elektrochem.*, 1910, **16**, 170–76; Brand and Ramsbottom, *J. prakt. Chem.*, 1910, [ii.], **82**, 336–96.

Properties.—The substance forms dark purple rhombic crystals, which, when freshly prepared, show a green metallic lustre, which on exposure to air becomes steel-blue. The crystals when crushed form a red powder. The crystals are isomorphous with potassium perchlorate, $KClO_4$, $a : b : c = 0.79523 : 1 : 0.6478$; they have specific gravity $= 2.71$. The solubility of potassium permanganate in water is as follows :— [1]

Temperature, °C.	0°	9.8°	19.8°	24.8°	34.8°	45°	55°	65°
Grams $KMnO_4$ in 100 grams H_2O	2.83	4.31	6.34	7.59	10.67	14.58	19.33	25.03

a deep purple solution being formed. This solution slowly decomposes in presence of traces of organic matter with separation of manganese dioxide.

Thomsen [2] gives the heat of formation as $(K_2, Mn_2, O_8) = 389,650$ calories, and heat of solution as $-20,790$ calories.

When solid potassium permanganate is heated to 240°, it is decomposed thus :—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$
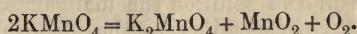
With concentrated sulphuric acid Mn_2O_7 is produced, which dissolves in excess of acid to $(MnO_3)_2SO_4$ (see p. 295), the solution on heating breaking up into MnO_2, oxygen, and water, the final product being $MnSO_4$ if the heating be continued long enough.

A mixture of $KMnO_4$ with sulphur or phosphorus is very inflammable and explodes violently on percussion; a mixture of $KMnO_4$ with charcoal burns like tinder.

An acid solution of potassium permanganate is decomposed by hydrogen peroxide, half the oxygen evolved coming from the peroxide and half from the permanganate, according to the equation : —

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$
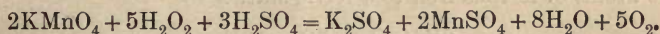
A considerable discussion has arisen on the nature of this reaction, for which reference must be made to the literature quoted below.[3] Potassium permanganate is a valuable oxidising agent, being used both in analytical work and in the preparation of organic oxidisation products. Three stages in the reduction of potassium permanganate may be distinguished, according as potassium manganate, manganese dioxide, or a manganous salt is produced —the complete reduction being represented by the last stage—as represented in terms of the oxide, thus :—

$$\underset{\text{Permanganate.}}{Mn_2O_7} \rightarrow \underset{\text{Manganate.}}{2MnO_3 + O} \rightarrow \underset{\substack{\text{Manganite}\\\text{(Manganese dioxide).}}}{2MnO_2 + 3O} \rightarrow \underset{\substack{\text{Manganous}\\\text{salts.}}}{2MnO + 5O.}$$
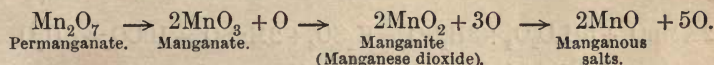
The first stage takes place readily in alkaline solution, the second in alkaline or neutral solution, and the last usually in the presence of free acid.

Thus green alkali manganate, *e.g.* K_2MnO_4, is produced by the action of mild reducing agents on potassium permanganate in alkaline solution (see p. 290); in a neutral solution, or by more vigorous reduction induced by heating, hydrated manganese dioxide is precipitated, which can be further reduced to manganous salts; *e.g.* when dilute $KMnO_4$ solution is added to excess of alkali sulphide solution and free alkali, the hydrated MnO_2 first precipitated

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[1] Baxter, Boylston, and Hubbard, *J. Amer. Chem. Soc.*, 1906, **28**, 1336 ; Patterson, *ibid.*, p. 1734.

[2] Thomsen, *Thermochemische Untersuchungen*, vol. iii. p. 271.

[3] See Balyer and Villiger, *Ber.*, 1900, **33**, 2488 ; Bach, *Ber.*, 1901, **34**, 3851.

is reduced to the more stable manganous sulphide, the alkali sulphide being simultaneously oxidised to sulphate.

In acid solution, however, these three successive stages of reduction are hard to follow, since the stable condition of soluble manganous salt is rapidly reached, although in some cases the formation of hydrated manganese dioxide can be observed.[1]

The following examples with sulphites show these changes well :— [2]

$$2KMnO_4 + K_2SO_3 + 2KOH = 2K_2MnO_4 + K_2SO_4 + H_2O,$$
(Excess of alkaline permanganate)   (Manganate formed)

$$2KMnO_4 + 3K_2SO_3 + H_2O = 2MnO_2 + 3K_2SO_4 + 2KOH,$$
(Excess of sulphite)   (Manganese dioxide formed)

$$2KMnO_4 + 5H_2SO_3 = 2MnSO_4 + 2KHSO_4 + H_2SO_4 + 3H_2O.$$
(In acid solution)   (Manganese salt produced)

It will be seen that in *acid* solution the manganese of the permanganate is converted into a salt corresponding to the monoxide MnO, five atoms of oxygen being rendered available, thus :—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

This equation may be derived from the more simple expression :—

$$2KMnO_4 = K_2O + 2MnO + 5O.$$

Now, as 2 molecules of $KMnO_4$ are capable of yielding up 5 atoms of oxygen to any oxidisable body *in acid solution*, and since, according to the equation $2FeO + O = Fe_2O_3$, 2 atoms of *ferrous* iron are oxidised to the *ferric state* by *1* atom of oxygen, it follows that 2 molecules of $KMnO_4$ will oxidise 10 atoms of ferrous iron to a ferric state :—

$$2KMnO_4 \rightarrow 5O \rightarrow 10\overset{..}{Fe}.$$

The following equation, representing the oxidation of ferrous sulphate to ferric sulphate, shows this :—

$$2KMnO_4 + 10\overset{..}{Fe}SO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5\overset{...}{Fe}_2(SO_4)_3 + 8H_2O.$$

In a similar manner, since 1 atom of oxygen will oxidise 1 molecule of oxalic acid, thus $H_2C_2O_4 + O = H_2O + 2CO_2$, it follows that $2KMnO_4$, with its 5 atoms of available oxygen in acid solution, will oxidise 5 molecules of oxalic acid :—

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

The complete oxidation [3] is carried out at 60°, as at lower temperatures the intermediate stage of reduction of the permanganate may be reached. In an exactly similar manner, the 5 available atoms of oxygen from $2KMnO_4$ react with H_2O_2, thus :—

$$H_2O_2 + O = H_2O + O_2,$$

the complete equation being, therefore :—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O,$$

[1] See Skrabal, *Zeitsch anorg. Chem.*, 1910, **68**, 48–51 ; Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 1204–07.

[2] See Caven and Lander, *Systematic Inorganic Chemistry*, 1911, p. 310.

[3] For conditions of accuracy, see K. Schröder, *Zeitsch. öffentl. Chem.*, 1910, **16**, 270–83, 290–305 ; W. C. Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 1204–07.

half the oxygen coming from the permanganate and half from the peroxide. Hence in acidified solution $KMnO_4$ is of great use in analytical work.

Ferrous iron, however, cannot be accurately estimated by titration with potassium permanganate in the presence of a chloride or of hydrochloric acid, unless very special precautions are observed. Friend[1] attributes this to the reaction taking place in two stages—namely, a partial reduction of the permanganate resulting in the oxidation of some of the iron to $FeCl_3$, with the simultaneous formation of an unstable perchloride of manganese. The latter substance then oxidises more ferrous iron to the ferric condition, according to the equation :—

$$MnCl_{(x+2)} + xFeCl_2 \rightleftharpoons MnCl_2 + xFeCl_3,$$
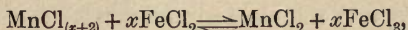
until equilibrium is established. If special precautions are taken, it is possible to secure reasonably accurate results ;[2] but it is less trouble to use potassium bichromate for the estimation of iron, as this reagent is not affected by the presence of hydrogen chloride. Hydrogen fluoride has a somewhat similar disturbing effect upon the permanganate method of estimating iron.[3]

The above remarks do not apply to the estimation of oxalic acid with permanganate—a reaction which proceeds easily and accurately in the presence of hydrogen chloride.

Sodium permanganate, $NaMnO_4.3H_2O$, is obtained in a similar manner to the potassium salt. It may also be formed by the reaction between silver manganate and sodium chloride :—

$$AgMnO_4 + NaCl = AgCl + NaMnO_4.$$
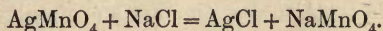
It is very soluble in water and so crystallises with difficulty.

Condy's Disinfecting Fluid.—According to Roscoe and Schorlemmer,[4] Hofmann was the first to show that manganates and permanganates were valuable disinfectants, being, like all powerful oxidising agents, extremely strong germicides and deodorisers.

The application of manganates and permanganates for this purpose is now an important branch of chemical industry. For disinfecting purposes it is not essential to employ the well-crystallised pure salts used in the laboratory ; instead the commercial article may consist of a mixture of sodium manganate and permanganate, which, according to Roscoe and Schorlemmer,[4] is made as follows :—

1500 kilos of soda-ash are mixed with 350 kilos of powdered MnO_2 and heated to dull redness in a flat vessel for two days. The mass thus obtained contains about 26 per cent. of sodium manganate, and can be used as such. More usually, however, the substance is lixiviated with water and concentrated to the most convenient degree for use. If the solution is to be completely converted into permanganate, it is neutralised with sulphuric acid and the solution concentrated until sodium sulphate

[1] Friend, *Trans. Chem. Soc.*, 1909, **95**, 1228.
[2] See T. W. Harrison and T. M. Perkin, *Analyst*, 1908, **33**, 43 ; W. Colet Birch, *Chem. News*, 1909, **99**, 61, 73 ; G. C. Jones and J. H. Jeffrey, *Analyst*, 1909, **34**, 306 ; Friend, *loc. cit.*, and *Proc. Chem. Soc.*, 1909, **25**, 224 ; Barnebey, *J. Amer. Chem. Soc.*, 1914, **36**, 1429.
[3] Müller and Koppe, *Zeitsch. anorg. Chem.*, 1910, **68**, 160.
[4] Roscoe and Schorlemmer, *Treatise on Chemistry*, 1907, vol. ii. p. 1118.

separates in a crystalline form. The crystals are then separated and the liquid further evaporated.[1]

Ammonium permanganate, NH_4MnO_4,[2] may be prepared by titrating a strong solution of ammonium chloride, NH_4Cl, with silver manganate, $AgMnO_4$, filtering and evaporating at ordinary temperatures over sulphuric acid :—

$$AgMnO_4 + NH_4Cl = AgCl + NH_4MnO_4.$$
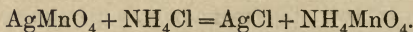
It may also be made by decomposing $BaMnO_4$ with $(NH_4)_2SO_4$, also by decomposing $KMnO_4$ with NH_4Cl.

Ammonium permanganate is isomorphous with $KMnO_4$, which it resembles in appearance. It is very soluble, and also unstable, decomposing with explosion when rapidly heated or subjected to percussion. When gently heated it decomposes into ammonium nitrate, oxides of nitrogen, and a complex oxide of manganese, which analyses as $22MnO_2.MnO$.

Silver permanganate,[3] $AgMnO_4$, is obtained by mixing warm solutions of silver nitrate and potassium permanganate. It forms large regular monoclinic crystals. It is one of the least soluble of the permanganates, 1 part dissolving in 190 parts of water at 15° C. ; it is much more soluble in boiling water, but the solution decomposes when heated.

Calcium permanganate, $CaMnO_4.5H_2O$, is a deliquescent crystalline mass prepared by decomposing $AgMnO_3$ by means of $CaCl_2$.

Barium permanganate, $BaMnO_4$, may be prepared by suspending barium manganate, $BaMnO_4$, in water and then passing in a stream of carbon dioxide until it is completely converted into permanganate, filtering from MnO_2, and evaporating. Also by the action of silver permanganate on barium chloride.

The substance forms small, hard, almost black rhombic octahedra, which are soluble in water.

Strontium permanganate may be similarly prepared.

The permanganates of lithium, magnesium, zinc, lead, lanthanum, and luteo-cobaltic permanganates have, among others, been prepared.

Manganese and Sulphur.

Manganese monosulphide, MnS, is found native as " manganese-blende " or " alabandite," often occurring in cubes and octahedra, as a steel-grey crystalline mass, of specific gravity 3·95. It is found in veins in coal mines in Transylvania, Freiberg, Mexico, and some other localities.

Artificially it may be produced by heating manganous oxide or carbonate in a stream of sulphuretted hydrogen in a porcelain tube, when it forms a dark grey powder which can be fused at a high temperature; on cooling it sets to a greyish crystalline powder. Moissan[4] obtained it in green octahedra by heating manganous sulphide with a little sulphur in the electric furnace. Schneider[5] obtained MnS in a crystalline state by melting together

[1] Hofmann, *Report Exhib.*, 1862, p. 109.
[2] Mitscherlich, *Pogg. Annalen*, 1832, **25**, 287 ; Aschoff, *loc. cit.*, 1860, **III**, 217 ; Böttger, *J. prakt. Chem.*, 1863, **90**, 169.
[3] Mitscherlich, *Pogg. Annalen*, 1832, **25**, 310 ; Böttger, *loc. cit.*
[4] Mourlot, *Compt. rend.*, 1895, **121**, 202 ; *Ann. Chim. Phys.*, 1899, [vii.], **17**, 548.
[5] Schneider, *Pogg. Annalen*, 1874, **151**, 449.

sulphur, 12 parts; anhydrous $MnSO_4$, 1 part; and anhydrous K_2CO_3, 12 parts; extracting with water, and drying the residue in a stream of hydrogen. Sidot [1] produces crystalline MnS out of amorphous by heating it in a stream of H_2S to a white heat. Ordinary precipitated MnS may be dehydrated by gently warming in a stream of hydrogen sulphide or hydrogen.

According to the method of preparation, the substance appears as a light or dark green, and sometimes almost black, powder. When prepared by heating together $MnSO_4$ and carbon, it is a dark steel-grey powder with a feeble metallic lustre. Sidot's crystalline MnS forms hexagonal yellowish-green prisms, while Schneider's crystalline forms consisted of needles which appeared to be built up of regular octahedra, and had the appearance of a bright green crystalline powder.

The powder obtained by heating MnO in H_2S, or by dehydrating precipitated MnS by warming in a stream of sulphuretted hydrogen, oxidises at ordinary temperatures in the air, slowly turning brown. It has even been known to ignite spontaneously in air.[2] The sulphide obtained in a crystalline form by heating in the electric furnace is not so oxidisable.[3] When ignited in air, MnS gives Mn_3O_4. Heated in steam, we get Mn_3O_4, H, and H_2S produced:—

$$3MnS + 4H_2O = Mn_3O_4 + 3H_2S + H_2.$$
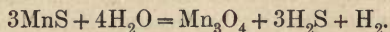
It dissolves in dilute acids, evolving H_2S. Easily oxidisable samples of MnS yield with chlorine manganous chloride and sulphur chlorides, but the other varieties are not rapidly attacked by this element.

When a solution of a manganous salt is treated with a solution of ammonium sulphide or other alkali sulphide, a light flesh-coloured precipitate of MnS is thrown down. This substance oxidises rapidly in air at ordinary temperatures, acquiring a brown tint in so doing; it readily dissolves in acids evolving sulphuretted hydrogen; when precipitated in the absence of air, filtered, dried at 70° C. in CO_2, and extracted with carbon disulphide to get rid of any free sulphur, it has the composition MnS and specific gravity 3·55.[4] Seen under the microscope, it consists of small transparent crystals. However, when this pink precipitate is left in contact with a freshly prepared ammonium sulphide solution for nine days,[5] when it is suspended in a dilute solution of hydrogen sulphide and exposed to a temperature of 0° C., or when simply heated to 320° for thirty minutes in an indifferent atmosphere, it passes completely into a green crystalline sulphide. This green modification also consists of microscopic crystals, possessing a specific gravity of 3·74 to 3·63.

Olsen and Rapalje [6] assert that, besides the red and green modification, a grey modification exists, and that the ordinary flesh-coloured precipitate produced by ammonium sulphide is really a mixture of this grey modification and the red variety, and that the sulphide thrown down by sodium sulphide solution does not contain the grey form and does not become green when left in contact with excess of sodium sulphide solution.

The heat of formation of precipitated MnS is given by Thomsen [7]

[1] Sidot, *Compt. rend.*, 1868, **66**, 1257.
[2] O. Binder, *Zeitsch. anal. Chem.*, 1908, **47**, 144.
[3] Mourlot, *Ann. Chim. Phys.*, 1899, [vii.], **17**, 551.
[4] Antony and Donnini, *Gazz. chim. ital.*, 1893, **23**, i. 560.
[5] Antony and Donnini, *loc. cit.* See also Villiers, *Compt. rend.*, 1895, **120**, 322.
[6] Olsen and Rapalje, *J. Amer. Chem. Soc.*, 1904, **26**, 1615.
[7] Thomsen, *Thermochemische Untersuchungen*, vol. iii. p. 271.

as $(Mn,S,xH_2O) = 46,400$ calories, $(Mn(OH)_2,H_2S,Aq.) = 10,700$ calories.
Wologdine and Penkiewitsch [1] give the molecular heat of formation of MnS as
70,535 and 62,901 calories.

Manganous sulphide unites with the sulphides of the alkali metals to
produce a number of double compounds. [2]

Thus the compound $3MnS.K_2S$ is obtained when anhydrous manganese
sulphate is slowly heated to redness with 3 parts K_2CO_3, $0·2$ part lamp-black,
and excess of sulphur ; after extracting the mass with water it remains as a
dark red crystalline mass.

Compounds of the formulæ $3MnS.Na_2S$ and $2MnS.Na_2S$ have also been
described.

Trimanganic tetrasulphide, Mn_3S_4, is formed, according to Gautier
and Hallopeau, [3] when rhodanite, $MnSiO_3$, is heated to whiteness in the
vapour of CS_2.   It is a metallic-looking mass, which reacts with water,
slowly in the cold but rapidly on heating, yielding H_2S and a hydroxide
of manganese.

Manganese disulphide, MnS_2, is found native at Kalinka in Hungary,
as the mineral hauerite, occurring in regular reddish brown metallic-looking
octahedra, specific gravity $3·463$; according to Sénarmont, [4] it may be made
as a brick-red amorphous powder by heating $MnSO_4$ with potassium poly-
sulphide in a sealed tube to $160°-170°$.

Manganous sulphate, $MnSO_4$, is best prepared [5] free from iron by
heating a mixture of MnO_2 and concentrated sulphuric acid to redness in a
crucible, whereby the iron sulphate is converted into insoluble oxide.   The
mass is lixiviated, and then the filtrate is heated with a little manganous
carbonate in order to precipitate any traces of iron in the liquid.

Cobalt or copper, if present, may be precipitated by passing H_2S into
the boiling liquid.

The anhydrous salt remains on heating the water-rich crystalline
substance cautiously to $280°$ C. [6]   According to the results of Cottrell, [7]
and Richards and Fraprie, [8] the salt cannot be dehydrated at $180°$, nor
even when heated for thirty minutes at $350°$, the last traces of water being
completely removed only when the salt is heated for five minutes at
$450°$ C.   It then forms a white, bitter powder, of specific gravity $3·282$
(Thorpe and Watts), which is decomposed at a bright red heat, leaving
red oxide of manganese.

The heat of formation is given by Thomsen [9] as $(Mn,O_2,SO_2) = 178,790$
calories, and the heat of solution as $+13,790$ calories.

Anhydrous manganese sulphate is very soluble in water, 1 part dissolving
in $1·78$ parts of water to form a syrupy solution.   This solution when heated
to $102·1°$ C. deposits crusts, which again dissolve in the cold, showing that
the solubility diminishes as the temperature increases [10] (see p. 305).

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[1] S. Wologdine and B. Penkiewitsch, *Compt. rend.*, 1914, **158**, 498–99.
[2] Völker, *Annalen*, 1846, **59**, 35 ; Schneider, *J. prakt. Chem.*, 1874, [ii.], **9**, 209 ; **10**, 55.
See Brunner, *Arch. Sci. phys. nat. Genève*, **22**, 68 ; *Chem. Zentr.*, 1889, ii. 554.
[3] Gautier and Hallopeau, *Compt. rend.*, 1889, **108**, 806.
[4] Sénarmont, *J. prakt. chem.*, 1850, **51**, 385 ; *Ann. Chim. Phys.*, 1850, [iii.], **30**, 140.
[5] See Muck, *Zeitsch. Chem.*, 1869, 626 ; Brunner, *Pogg. Annalen*, 1857, **101**, 264.
[6] Thorpe and Watts, *Trans. Chem. Soc.*, 1880, **37**, 113.
[7] Cottrell, *J. Physical Chem.*, 1900, **4**, 637.
[8] Richards and Fraprie, *Amer. Chem. J.*, 1901, **26**, 75.
[9] Thomsen, *Thermochemische Untersuchungen*, vol. iii. p. 271.
[10] Brandes, *Pogg. Annalen*, 1830, **20**, 556.

Mulder,[1] using the hydrate $MnSO_4.4H_2O$ (see p. 307), found the solubility as follows :—

Temperature, ° C.	Parts of $MnSO_4$ dissolved in 100 of Water.	Temperature, ° C.	Parts of $MnSO_4$ dissolved in 100 of Water.
0	55·4	50	74·8
5	58·2	54	75·3
10	63·8	63·5	61·3
20	66·3	64	61·5
25	68·5	85	61·3
30	70·4	90	60·3
35	71·9	95	57·9
40	73·1	100	52·9
45	74·0	...	...

According to this, there is a maximum of solubility at about 54°. According to Etard,[2] the solubility increases up to 55° and thereafter decreases from 55°–145° C. The changes are probably due to the formation of different hydrates.

These numbers do not seem to be in agreement with those published by Roscoe and Schorlemmer,[3] who assert that the solubility of the monohydrate, $MnSO_4.H_2O$, decreases as the temperature rises, so that a *maximum* of solubility exists at 27° C. According to these authorities, the solubility in water is as follows :—

Temperature, ° C.	0°	9°	15°	27°	50°	70°	100°
Grams of $MnSO_4$ in 100 grams H_2O	53·2	59·3	61·1	66	59·5	52	33·3

Linnebarger's [4] results are interesting. He gives the following data :—
100 parts H_2O dissolve of anhydrous $MnSO_4$:—

Temperature, °C.	120°	132°	141°	146°	155°	170°
Parts of $MnSO_4$	67·18	63·16	41·18	38·83	26·49	16·15

His data regarding the solubility of some of the different hydrates are given in the following table (p. 306).

Linnebarger's results do not agree with those of Cottrell,[5] and Richards and Fraprie,[6] who believe Linnebarger made errors by not completely dehydrating his salt. Some of Richards and Fraprie's results are placed in brackets in the table.

[1] G. J. Mulder, *Scheikund. Verhandel.* 3 *Deel.*, 3 *Stuck. Rotterdam*, 1864, 135.
[2] Etard, *Compt. rend.*, 1888, 106, 208.
[3] Roscoe and Schorlemmer, *Treatise on Chemistry*, 1907, vol. ii. p. 1124.
[4] Linnebarger, *Amer. Chem. J.*, 1893, 15, 225.
[5] Cottrell, *J. Physical Chem.*, 1900, 4, 637.
[6] Richards and Fraprie, *Amer. Chem. J.*, 1901, 26, 75.

SOLUBILITIES OF HYDRATES OF MANGANESE SULPHATE.

Temp. °C.	$MnSO_4, 7H_2O.$ $MnSO_4$ in 100 parts $H_2O.$	$MnSO_4, 6H_2O.$ $MnSO_4$ in 100 parts $H_2O.$	$MnSO_4, 5H_2O.$ $MnSO_4$ in 100 parts $H_2O.$	$MnSO_4, 4H_2O.$ $MnSO_4$ in 100 parts $H_2O.$	$MnSO_4, 3H_2O.$ $MnSO_4$ in 100 parts $H_2O.$	$MnSO_4, 2H_2O.$ $MnSO_4$ in 100 parts $H_2O.$	$MnSO_4, H_2O.$ $MnSO_4$ in 100 parts $H_2O.$
− 10	50·11	...	...	...	...	...	...
− 8	50·43	...	...	...	...	...	...
− 5	51·62	...	...	...	...	...	...
− 4	...	55·87	...	...	...	...	...
0	53·53	64·21	58·05	...	...	...	...
2·2	...	...	...	57·88	...	...	...
2·5	...	...	62·41	...	...	...	...
3	...	66·87	...	...	...	...	...
4	...	...	64·22	...	...	...	...
5	54·78	67·49	...	...	54·68	...	...
7	56·62	...	66·83	...	...	...	...
7·3	...	...	...	61·78	...	...	...
9	...	70·88	...	...	...	...	...
10	59·91	...	68·05	...	...	...	...
11	...	...	...	64·01	...	...	...
12	...	...	...	...	60·56	...	...
15	64·34	72·45	72·33	67·12	...	...	...
16	...	...	...	...	63·41	...	...
19	...	...	...	...	65·12	...	...
20	66·61	74·35	75·16	69·93	...	...	...
25	67·14	75·38	78·63 (65·19 Richards and Fraprie)	72·33 (66·38)[1]	66·85	..	...
30	...	76·24	79·16	74·67	67·38	...	...
32	...	...	80·88	...	...	...	...
34	...	77·02	82·04	(68·2)[1]	...	...	...
35	68·51	77·23	...	...	68·31	68·88	...
35·5	...	...	...	78·81	...	...	...
37	...	...	83·91	...	...	...	...
38	...	78·41	...	...	...	...	...
40	...	...	84·63	79·63	70·63	75·31	...
42	...	...	85·27	...	...	77·63	...
45	70·33	...	86·16	83·06	...	80·07	...
47·7	...	...	86·95	...	...	...	...
48	...	...	...	84·33	71·89	...	87·98
50	...	...	...	...	...	83·16	..
52	...	...	...	86·16	...	...	...
53	...	...	88·89	...	72·81	...	86·10
54	73·06	...	89·08	...	...	...	...
55	...	...	...	...	...	86·27	...
56	...	...	...	88·19	...	...	...
57	...	...	...	...	73·17	...	...
58	72·94	...	...	...	...	...	...
65	...	...	...	...	...	...	84·33
72	...	...	...	...	...	...	82·73
78	...	...	...	...	...	...	79·13
90	...	...	...	...	...	...	75·63
100	...	...	...	...	...	...	71·27
106	...	...	...	...	...	...	70·14
115	...	...	...	...	...	...	69·78
117	...	...	...	...	...	...	68·81

[1] Richards and Fraprie, *loc. cit.*

Anhydrous $MnSO_4$ is insoluble in absolute alcohol, and dissolves only in 500 parts of a 55 per cent. alcoholic solution.[1]

Hydrates of Manganous sulphate.[2]—This substance unites with water to form a considerable number of hydrates. When a solution of the salt is evaporated, below 8° C. the heptahydrate, $MnSO_4.7H_2O$, separates, but between 8° and 27° the pentahydrate, $MnSO_4.5H_2O$, is obtained, and above 27° the monohydrate, $MnSO_4.H_2O$, separates. At 30° a tetrahydrate, $MnSO_4.4H_2O$, crystallises out.

According to Schieber, the only hydrates obtainable are those with 7, 5, 4 and 1 molecules of water. The following particulars have been published about these hydrates :—

$MnSO_4.7H_2O$ occurs in nature as the mineral mallardite, forming monoclinic pale red crystals, which separate out from solution from $-4°$ to $+6°$ (Brandes), or under 0° (Schieber).

The crystals are isomorphous with $FeSO_4.7H_2O$, and melt at 19° C. changing into the monohydrated form $MnSO_4.H_2O$. Left exposed to the air, they lose 18·6 per cent. of water between 12·5° and 15° C., changing to an opaque mass. Alcohol partially deprives the crystals of water of crystallisation, cold absolute alcohol taking up 2 molecules of water, and boiling alcohol splitting off still more (Brandes).

$MnSO_4.5H_2O$ crystallises out of water between 15° and 20° C., in forms resembling $CuSO_4.5H_2O$. It may also be obtained by treating $MnSO_4.7H_2O$ with cold absolute alcohol (see above) or by precipitating a saturated solution of $MnSO_4$ with alcohol. It forms triclinic needles or leaves which, according to Thomsen,[3] possess a heat of solution $= 40$ calories, while the heat of formation is given by $(Mn,O_2,SO_2,5H_2O) = 192,540$ calories.

$MnSO_4.4H_2O$ crystallises out of solution between 25°–31° C. in pale red, transparent, rhombic prisms; while between 35°–40° a small portion separates as monoclinic crystals. The crystals lose water on exposure to air, and when heated to 241° C. yield up nearly all their water, being thereby converted into a white powder. Cold alcohol does not deprive the crystals of water, but boiling alcohol takes up 1 molecule of H_2O.

The heat of solution is given by Thomsen[4] as 2240 calories.

$MnSO_4.H_2O$ occurs naturally as the mineral szmikite, which has a specific gravity 3·15. It is produced gradually by exposure of the preceding hydrates to dry air. It may be also produced by heating $MnSO_4.5H_2O$ to 150° C., and also by rapidly boiling a solution of $MnSO_4$, when it separates as a yellowish-red powder of specific gravity 2·845 to 2·893.

Thomsen[5] determined the heat of formation as :—

$$(Mn,O_2,SO_2,H_2O) = 184,760 \text{ calories,}$$
$$(MnSO_4,H_2O) = 5970 \text{ calories.}$$

The heat of solution is given by the same authority as 7820 calories.

When heated to 280° it loses all its water, giving anhydrous $MnSO_4$. The last traces of water are only expelled from the monohydrate at 450° C.

[1] Brandes, *Pogg. Annalen*, 1830, **20**, 556.
[2] Regarding these, see Schieber, *Monatsh.*, 1898, **19**, 280 ; Cottrell, *loc. cit.* ; Richards and Fraprie, *loc. cit.* ; Lescœur, *Ann. Chim. Phys.*, 1895, [vii.], **4**, 220.
[3] Thomsen, *Thermochemische Untersuchungen*, vol. iii. p. 271.
[4] Thomsen, *Ber.*, 1873, **6**, 710 ; *J. prakt. Chem.*, 1878, [ii.], **18**, 1.
[5] Thomsen, *J. prakt. Chem.*, 1878, [ii.], **17**, 165.

For the absorption spectra of manganous sulphate see Jaeschke and Meyer.[1]

Double Sulphates.—Finely crystallised double sulphates are obtainable by allowing mixed solutions of manganous sulphate and the alkali sulphates to crystallise together,[2] these double salts being of the types $MnSO_4.M_2SO_4.4H_2O$, and $MnSO_4.M_2SO_4.6H_2O$, M being here a monovalent element like Na, K, Rb, Cs, etc.

Lang describes the compound $2MnSO_4.(NH_4)_2SO_4$.[3]

Manganous sulphate also crystallises with the sulphates of the metals of the magnesium group (Mg, Zn, Fe, Cu), forming a complex set of salts, the proportions and crystalline form of which vary with the amount of hydrated water present.

An acid salt, $MnSO_4.H_2SO_4$, and a basic salt, $3MnO.2SO_3.3H_2O$, are also known.[4]

Manganous aluminium sulphate, $MnSO_4.Al_2(SO_4)_3.24H_2O$, has been found as the mineral *apjohnite* in Algoa Bay, South Africa.[5]

Manganic sulphate, $Mn_2(SO_4)_3$, was made by Carius[6] by intimately mixing together MnO_2 and H_2SO_4 (concentrated) into a thin paste, and heating to 138°, whereby a green liquid is obtained and oxygen is evolved.

From this liquid the manganic sulphate separates out as an amorphous powder, which is freed from the concentrated sulphuric acid by placing it on a porous porcelain plate while still hot, and then rubbing together the residue six to eight times in a hot mortar with concentrated nitric acid, removing the acid after each operation by placing on a porous tile. Finally the nitric acid is removed by heating rapidly to 130°. All these operations must be very rapidly carried out, as manganic sulphate is very deliquescent, and consequently must be carefully protected from atmospheric moisture.

It is a dark green, amorphous powder, stable at 160°, but on heating to higher temperatures is decomposed into $MnSO_4$, oxygen, and sulphur tri-oxide.

Exposed to air it deliquesces into a viscid clear violet liquid, which decomposes gradually, the hydrated oxide $Mn_2O_3.H_2O$ gradually separating out. Excess of water and acids, when added to the salt, decomposes it in a similar manner, a considerable amount of heat being simultaneously evolved.

The substance, however, is soluble in cold concentrated sulphuric acid, forming a pale violet solution. When, however, this solution is heated to a high temperature, decomposition sets in, oxygen being evolved and $MnSO_4$ formed. The substance is insoluble in concentrated nitric acid.

Manganic sulphate is a powerful oxidising agent, rapidly oxidising organic bodies, and when heated with them causes them to ignite and burn almost explosively. The absorption spectrum is described by Jaeschke and Meyer.[7]

Franke[8] describes an acid salt of the formula $Mn_3(SO_4)_3,H_2SO_4,4H_2O$.

Manganese Alums.—Manganese forms a series of alums, of the general

[1] W. Jaeschke and J. Meyer, *Zeitsch. physikal. Chem.*, 1913, **83**, 281–89.
[2] See Mallet, *Trans. Chem. Soc.*, 1900, **77**, 221 ; 1902, **81**, 1549 ; Schreinemakers, *Chem. Weekblad*, 1909, **6**, 131–36.
[3] Walther Lang, *D.R.P.* 189,178, 1902.
[4] Schulz, *Dissertation* (Berlin, 1868) ; Gorgeu, *Compt. rend.*, 1882, **94**, 1425.
[5] See Dana's *System. Mineral.*, 6 edition, p. 955 ; Kane, *Pogg. Annalen*, 1838, **44**, 471.
[6] Carius, *Annalen*, 1856, **98**, 53 ; see also Franke, *J. prakt. Chem.*, 1887, [ii.], **36**, 451.
[7] Jaeschke and Meyer, *Zeitsch. physikal. Chem.*, 1913, **83**, 281–89.
[8] Franke, *J. prakt. Chem.*, 1887, [ii.], **36**, 451.

formula $R'_2SO_4.Mn_2(SO_4)_3.24H_2O$.[1] They crystallise in pink or red octahedra, but are unstable, being decomposed by water. In the presence of sulphuric acid, however, these alums are stable so long as the temperature is kept low. The rubidium and cæsium manganese alums have been prepared pure (see below), but, apparently, the potassium and ammonium salts are extremely unstable and have not been obtained pure : the salts produced by adding potassium or ammonium sulphate to manganic sulphate and concentrating the solution invariably contain less water than true alums. Lepierre[2] describes an anhydrous *ammonium manganic sulphate*, $(NH_4)_2SO_4.Mn_2(SO_4)_3$, as consisting of violet crystals of specific gravity 2·56 insoluble in sulphuric acid, ether, or benzene, and decomposed by water and also by heating, the decomposition in the latter case taking place according to the equation :—

$$(NH_4)_2SO_4.Mn_2(SO_4)_3 = O + SO_3 + (NH_4)_2SO_4.2MnSO_4.$$
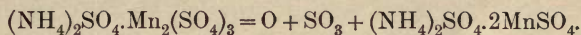
Manganic cæsium alum, $Cs_2SO_4.Mn_2(SO_4)_3.24H_2O$, is obtained[3] by dissolving cæsium sulphate and manganic acetate (made by acting on manganese acetate dissolved in glacial acetic acid with $KMnO_4$) in dilute sulphuric acid and cooling to $-20°$ C. ; also by electrolysing[4] at $10°-15°$ C., in the anodic compartment of an electrolysed cell, a mixture of $MnSO_4$ and Cs_2SO_4 dissolved in dilute sulphuric acid.

Coral-red crystals, decomposed by water, and melting at 40° C. in its water of crystallisation.

Manganic rubidium alum,[5] $Rb_2SO_4.Mn_2(SO_4)_3.24H_2O$, obtained in a manner similar to those employed in preparing the cæsium alum, closely resembles the latter, but is more unstable, decomposing at 15° C.

Manganous sulphite,[6] $MnSO_3.3H_2O$, may be obtained by passing sulphur dioxide into water containing manganous carbonate in suspension and boiling the solution until saturated, allowing the salt to crystallise out in a closed vessel; also by treating a solution of $MnSO_4$ in water with sodium sulphite solution acidified with acetic acid.

Rhombic prisms. Sparingly soluble in water, 1 part dissolving in 10,000 cold and 5000 parts of hot water. It is very soluble in a solution of sulphur dioxide in water, insoluble in alcohol and ether, and easily decomposed by acids. It is unaltered by exposure to air.

By allowing the substance to crystallise out at 100° C. the monohydrated form, $MnSO_3.H_2O$ is obtained. The same substance was isolated by Denigès[7] by decomposing manganous aniline disulphite with boiling water. A sulphite, $MnSO_3.3H_2O$, was obtained by treating a solution of $MnSO_4$ in water with a solution of sodium sulphite acidified with acetic acid.

Sulphur dioxide acts on a boiling hot mixture of MnO_2 in water, forming a mixture of manganous sulphite and manganous dithionate (see p. 310).

A number of double salts of manganese sulphite have been isolated. Among these may be mentioned :—

[1] Christensen, *Zeitsch. anorg. Chem.*, 1901, **27**, 328.
[2] Lepierre, *Compt. rend.*, 1895, **120**, 924.
[3] See Christensen, *loc. cit.*
[4] Piccini, *Zeitsch. anorg. Chem.*, 1898, **17**, 355 ; 1899, **20**, 12.
[5] Christensen, *loc. cit.*
[6] See Gorgeu, *Compt. rend.*, 1882, **94**, 1425 ; 1883, **96**, 341 ; Rammelsberg, *Pogg. Annalen*, 1846, **67**, 245 ; Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, **4**, 81 ; Denigès, *Bull. Soc. chim.*, 1892, [iii.], **7**, 569, 571.
[7] Denigès, *loc. cit.*

$K_2SO_3.MnSO_3$, hexagonal tablets, produced by evaporating $MnSO_3$ in $KHSO_3$ solution containing $NaOH$; also $K_2SO_3.2MnSO_3$; $Na_2SO_3.MnSO_3.H_2O$; $Na_2SO_4.4MnSO_3$; and $(NH_4)_2SO_3.MnSO_3$.

Manganous dithionate, $MnS_2O_6.3H_2O$, is obtained on passing sulphur dioxide through water in which MnO_2 (or hydrated Mn_2O_3)[1] is suspended, adding a little baryta water finally so long as a precipitate of $BaSO_4$ is formed, in order to remove the small amount of $MnSO_4$ which is always simultaneously produced. The crystals are rhombic, easily soluble, having a heat of solution = 1930 calories, and a heat of formation[2] given by $(Mn,O_2,2SO_2,6H_2O)$ = 188,600 calories.

The salt is employed for making dithionic acid (see Sulphur, Vol. VII.).

An acid salt, $H_2Mn(S_4O_6)_2$, is also known.[3]

MANGANESE AND SELENIUM.

Manganese selenide, $MnSe$, is precipitated by hydrogen selenide, H_2Se, from a solution of manganese acetate, and may be obtained in a crystalline form by melting it at a high temperature and allowing it to solidify ;[4] also by reducing manganese selenate, $MnSeO_4$, by means of carbon in the electric furnace ; also by heating Mn in Se vapour.[5] It forms cubic crystals of specific gravity 5·59, easily decomposed by mineral acids.

Diacon prepares prismatic $MnSe$ by acting on $MnCl_2$ with H_2Se at a red heat.

According to Fabre,[5] the heat of formation of the crystallised salt is 31,140 calories, and of the amorphous 27,500 calories.

Manganese Selenites. — Normal anhydrous manganous selenite, $MnSeO_3$, does not appear to have been described. The *monohydrate*, $MnSeO_3.H_2O$, was obtained by Nilson[6] as a white, voluminous, amorphous precipitate by adding neutral $MnSO_4$ to a solution of K_2SeO_3. On standing in the liquid the precipitate decreased in volume and changed into yellowish-red four-sided tablets. The *dihydrate*, $MnSeO_3.2H_2O$, has also been obtained by precipitating $MnSO_4$ with the acid potassium selenate, $KHSeO_3$,[6] also by treating $MnCO_3$ with H_2SeO_3.[7] The substance easily melts, and when heated oxidises, SeO_2 rapidly escaping and oxide of manganese being formed.

The acid selenite, $MnO.2SeO_2$, has been obtained both in an anhydrous form and also combined with water.[8]

Manganic selenite, $MnSe_2O_6$, obtained by Laugier[9] by heating hydrated MnO_2 with SeO_2 in a sealed tube to 140° C., formed small green prisms, dissolving in HCl, evolving chlorine. Can be heated to 600° without losing SeO_2. Laugier also describes hydrated selenites of the formulæ $Mn_2O_3.3SeO_2.5H_2O$ and

[1] Carpenter, *Trans. Chem. Soc.*, 1902, **81**, 1.
[2] Thomsen, *J. prakt. Chem.*, 1878, [ii.], **17**, 165.
[3] Curtius, *J. prakt. Chem.*, 1881, [ii.], **24**, 239 ; Curtius and Henkel, *ibid.*, 1888, **37**, 148.
[4] Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1025.
[5] Fabre, *Thèse*, 1886 ; Wedekind and Veit, *Ber.*, 1911, **44**, 2663.
[6] Nilson, *Nova Acta R. Soc. Upsala*, 1875 ; *Jahresber.*, 1874, p. 208 ; 1875, p. 163.
[7] Muspratt, *Annalen*, 1849, **70**, 274.
[8] Nilson, *loc. cit.* Boutzoureano, *Ann. Chim. Phys.*, 1889, [vi.], **18**, 316 ; *Bull. Soc. chim.*, 1887, [ii.], **48**, 209.
[9] Laugier, *Compt. rend.*, 1887, **104**, 1508 ; *Bull. Soc. chim.*, [ii.], 1887, **47**, 915. Marino and Squintani, *Atti R. Accad. Lincei*, 1911, [v.], **20**, i. 447.

$Mn_2O_3.3SeO_2.4H_2O$. These, on heating, lose water and are converted into $Mn_2O_3.2SeO_2$ and into $MnSeO_4$ respectively.

Manganous selenates.—$MnSeO_4$, was obtained by Laugier [1] by heating the selenite $MnSe_2O_6$ to 600°. It formed a rose-red powder soluble in water.

It may be obtained [2] in the form $MnSeO_4.2H_2O$ by evaporating a solution of the selenate at 50°–60° C., when it forms crystalline crusts, or sometimes small needles consisting of rhombic tablets. The salt is fairly stable in air, and has a specific gravity of 2·949 (Topsöe), 3·006 (Petterson). When a solution is evaporated, some brown manganese hydroxide separates.

The *pentahydrate*, $MnSeO_4.5H_2O$, may be obtained by allowing the solution of manganous selenate to evaporate at ordinary temperatures. It exists as pale red, transparent triclinic crystals; stable in air; specific gravity, 2·388; soluble in water, the solution decomposing on standing or heating, depositing dark-coloured hydrated manganese oxides.

An *ammonium manganous selenate*, $(NH_4)_2SeO_4.MnSeO_4.6H_2O$, consisting of pale red crystals, soluble in water, and of specific gravity 2·093, was described by Topsöe [2] in 1870.

MANGANESE AND TELLURIUM.

Manganese telluride, MnTe, has been prepared by heating together manganese and tellurium in an evacuated bomb-tutel.[3] It is a crystalline substance, with silvery lustre; readily decomposed by mineral acids.

MANGANESE AND BORON.

Manganese diboride, MnB_2, may be prepared by heating together manganese carbide, Mn_3C, and boron oxide, B_2O_3:—[4]

$$Mn_3C + 3B_2O_3 + 8C = 3MnB_2 + 9CO;$$
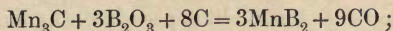
also by igniting a mixture of manganese thermit and boron,[5] or by reducing manganese oxides with boron.[6] Non-magnetic grey-black crystals, decomposed by water at 100°, by caustic alkalies at still lower temperatures, and by gaseous HCl at a low red heat.

It dissolves in acids at ordinary temperatures and has the density 6·9. Heat of formation for 1 gram = 2487 calories.[4] It is not more magnetic [7] than metallic manganese.

Manganese monoboride, MnB, is prepared [8] by reducing Mn_3O_4 with boron at a white heat in a magnesia crucible; also in the electric furnace; also by direct union of Mn and B. Black crystalline powder, specific gravity 6·2, has similar properties to the diboride, but is magnetic [6] and dissolves more easily in acids. Chlorine gives a chloride $2MnCl_2.BCl_3$.

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[1] Laugier, *loc. cit.*

[2] Topsoe, *Selens. Salte, Kopenhagen*, 1870, 19.

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

[4] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [v.], 9, 65.

[5] Matignon and Trannoy, *Compt. rend.*, 1905, 141, 190 ; Jassonneix, *Bull. Soc. chim.*, 1906, [iii.], 35, 102.

[6] Wedekind, *Ber.*, 1905, 38, 1228 ; *Zeitsch. Elektrochem.*, 1905, 11, 850 ; *Zeitsch. physikal. Chem.*, 1909, 66, 614–32 ; Jassonneix, *Eighth Inter. Cong. Appl. Chem.*, 1912, 2, 165–70.

[7] J. Hoffmann, *Zeitsch. anorg. Chem.*, 1910, 66, 361–99 ; *Chem. Zeit.*, 1910, 34, 1045–46, 1349–50.

[8] See Jassonneix, *Compt. rend.*, 1904, 139, 1209 ; Wedekind, *loc. cit.*

Manganous borate, $MnH_4(BO_3)_2$, is precipitated [1] when a solution of a manganous salt is added to borax solution.   Dried at 100° it forms a white powder.   Decomposed by water to $Mn(OH)_2$.   Soluble in excess of $MgSO_4$ solution.   Heated to redness it yields the metaborate, $Mn(BO_2)_3$.   The precipitated borate is used in the manufacture of drying oils and varnishes, the commercial salt being of indefinite composition.

The borate, $Mn_3(BO_3)_2$, has been obtained by Ouvrard.[2]

The borate MnB_4O_7 and its hydrated forms, $MnB_4O_7.3H_2O$ and $MnB_4O_7.5H_2O$, have also been described.[3]   The latter compound, heated to 120° C., loses $2H_2O$, but readily reabsorbs water and sets to a hard mass.

Both the hydrated salts readily yield their manganese to hot oils, producing quick-drying varnishes.

MANGANESE AND CARBON.

Manganese carbide, Mn_3C, is obtained [4] by heating Mn_3O_4 with charcoal or calcium carbide in an electric furnace to between 1500° and 3000° C.   The substance when heated to very high temperatures in the electric furnace is decomposed again at a temperature lower than that at which carbon volatilises, the manganese volatilising and the C remaining as graphite.[5]   It has the specific gravity 6·89, and is decomposed by water or moist air, yielding equal volumes of methane and hydrogen :—

$$Mn_3C + 6H_2O = CH_4 + H_2 + 3Mn(OH)_2.$$
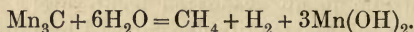
The substance burns in oxygen and is readily attacked by fluorine and chlorine.   Le Chatelier,[6] gives the heat of formation of the carbide as 10,400 calories, taking the carbon in the form of diamond as regards thermal data. From graphite the heat of formation is 9,340 calories.   Ruff and Gersten give 12,900 $\pm$ 2140 calories, and give the molecular heat of combination to Mn_3O_4 as 410,900 + 740 calories.   Needle-like pseudo-hexagonal prisms, possessing angles 59° 22′ to 59° 50′ and 60° 15′ to 60° 29′.[7]

The maximum solubility of carbon in manganese at 2000° C. is 6·72 per cent., corresponding with the carbide Mn_3C.   The carbide Mn_3C freezes at 1217° C.[8]   Density 6·888.   It is readily oxidised.   Manganese does not take up carbon when heated in sugar charcoal for twelve hours at 1100° C.

When manganese [9] is heated in a current of methane to 600°–900° C., carbides are formed containing from 8–20 per cent. carbon.

Manganous carbonate, $MnCO_3$, occurs naturally as *manganese spar* in rose-coloured crystals, also in *rhodochrosite* or *dialogite*.   It forms an isomorphous constituent of dolomite and chalybite.   These minerals all crystallise in the same form as calc spar, viz. in rhombohedra ; however, one

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[1] See Hartley and Ramage, *Trans. Chem. Soc.*, 1893, **63**, 133.

[2] Ouvrard, *Compt. rend.*, 1900, **130**, 335 ; see also Mallard, *Compt. rend.*, 1887, **105**, 1263.

[3] Guertler, *Zeitsch. anorg. Chem.*, 1904, **40**, 268 ; Endemann and Paisley, *Zeitsch. angew. Chem.*, 1903, **16**, 176 ; *Amer. Chem. J.*, 1903, **29**, 68–73

[4] Moissan, *Ann. Chim. Phys.*, 1896, [vii.], **9**, 286 ; *Compt. rend.*, 1893, **116**, 349 ; Ruff and Gersten, *Ber.*, 1913, **46**, 400–13.

[5] Gin and Leleux, *Compt. rend.*, 1898, **126**, 749.

[6] Le Chatelier, *Compt. rend.*, 1896, **122**, 80.

[7] Spencer, *Mng. Mag.*, London, 1903, **13**, 296.

[8] A. Stadeler, *Metallurgie*, 1908, **5**, 260–67, 281–88.

[9] S. Hilpert and J. Paunescu, *Ber.*, 1913, **46**, 3479–86.

mineral, *manganocalcite* $(Mn,Ca,Mg)CO_3$, is known which crystallises in the same form as aragonite.

The carbonate may be obtained artificially by heating together $MnCl_2$ and Na_2CO_3 to 150° C. in a sealed tube.[1] Thus obtained, it forms an amorphous pale rose-coloured powder. It may be obtained crystallised in rhombohedra [2] by heating $MnSO_4$ with urea to 180°. Thomsen [3] gives the heat of formation of precipitated $MnCO_3$ (see below) as follows :—

$$(Mn,C,O_3) = 210,840 \text{ calories}; \quad (Mn,O_2,CO) = 181,840 \text{ calories}.$$
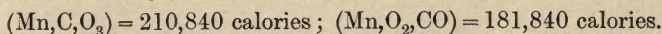
Le Chatelier [4] showed that the heat of formation of mineral $MnCO_3$, prepared from Mn and CO_2, was 27,000 calories, which is considerably more than that of the precipitated carbonate which, according to Berthelot,[5] is given by the equation :—

$$Mn_2O_2 + 2CO_2 \text{ (solution)} = Mn_2O_2((CO_2)_2 + 27,200 \text{ calories}).$$
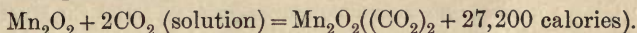
The powder has the density 3·65 ; when heated in air in a dry state, it gives first MnO, which over 425° oxidises to Mn_2O_3.[6] Heated to 200° C. with water and oxygen, it yields some Mn_3O_4.

Hydrated manganous carbonate, $MnCO_3.H_2O$, is thrown down as a white precipitate on adding sodium carbonate solution to a solution of a manganous salt.[7] When the dilution is greater than 1 : 200, the carbonate begins to decompose hydrolytically, with separation of $Mn(OH)_2$. It is also gradually decomposed by boiling water into $Mn(OH)_2$, and the same action takes place when the carbonate is boiled with caustic alkalies, the decomposition being only partial in the latter case at ordinary temperatures. The substance dissolves in 7680 parts of cold water and in 3840 parts of water saturated with carbon dioxide.

It turns brown with partial oxidation [8] when exposed to air in a moist state.

MANGANESE AND CYANOGEN.

Manganous cyanide, $Mn(CN)_2$, has not yet been isolated in a pure state.[9]

Potassium manganous cyanide,[10] $KCN.Mn(CN)_2$, is thrown down as a green precipitate when a concentrated solution of manganous acetate is warmed with solid potassium cyanide. When washed with air-free water and kept dry over H_2SO_4, it may be preserved unaltered. When the green precipitate produced as above is allowed to stand in the solution of KCN it gradually disappears, its place being taken by dark blue crystals of :—

Potassium manganocyanide, $4KCN.Mn(CN)_2.3H_2O$.—The same substance may be produced by heating manganous carbonate with a solution of KCN to a temperature of 40°–50°. The salt forms efflorescent deep violet-blue tetragonal tablets. Addition of water decomposes it into KCN and $KCN.Mn(CN)_2$.

[1] Sénarmont, *Compt. rend.*, 1849, **28**, 693.
[2] Weinschenk, *Zeitsch. Kryst. Min.*, 1890, **17**, 486.
[3] Thomsen, *Thermochemische Untersuchungen*, vol. iii. p. 271.
[4] Le Chatelier, *Compt. rend.*, 1896, **122**, 80.
[5] Berthelot, *Compt. rend.*, 1883, **96**, 88 ; *Ann. Chim. Phys.*, 1883, [v.], **30**, 543.
[6] Gorgeu, *Bull. Soc. chim.*, 1888, [ii.], **49**, 668.
[7] Joulin, *Ann. Chim.*, 1873, [4], **30**, 248 ; *Bull. Soc. chim.*, 1873, [ii.], **19**, 338.
[8] Gorgeu, *Compt. rend.*, 1889, **108**, 950, 1006 ; *Bull. Soc. chim.*, 1889, [iii.], **1**, 605, 612.
[9] Fittig and Eaton, *Annalen*, 1868, **145**, 157.
[10] Fittig and Eaton, *loc. cit.* ; also Christensen, *J. prakt. Chem.*, 1885, [ii.], **31**, 163 ; Descamps, *Compt. rend.*, 1868, **66**, 628.

Potassium manganicyanide,[1] $3KCN.Mn(CN)_3$, is produced by allowing a solution of the preceding salt to oxidise in air. Dark red prisms. Boiled with water, it is decomposed, precipitating all the manganese as hydrated manganese oxide. When a solution of this salt is treated with potassium amalgam, it is again reduced to potassium manganocyanide.

Manganocyanic acid, $H_4Mn(CN)_6$, is stated to have been isolated by Descamps[2] by treating lead manganocyanide with H_2S. Easily decomposable, yellow crystals.

Among other salts which have been prepared may be mentioned :[3] *sodium manganocyanide*, $4NaCN.Mn(CN)_2$; *sodium manganicyanide*, $3NaCN.Mn(CN)_3$; *ammonium manganocyanide*, $NH_4CN.Mn(CN)_2$; *calcium manganocyanide*, $2Ca(CN)_2.Mn(CN)_2$; *calcium manganicyanide*, $3Ca(CN)_2.2Mn(CN)_3$; *potassium cupro-manganocyanide*, $K_2Cu_2Mn(CN)_6$; *sodium cupro-manganocyanide*, $Na_2Cu_2Mn(CN)_6$; *ammonium cupro-manganocyanide*, $(NH_4)_2Cu_2Mn(CN)_6$, etc.

Manganese thiocyanate, $Mn(SCN)_2$, is obtained from $MnSO_4$ and barium thiocyanate, $Ba(SCN)_2$. The anhydrous salt is yellow, while the hydrate, $Mn(SCN)_2.3H_2O$, is green. Aqueous solutions when concentrated are green, but become pink when diluted.[4]

MANGANESE AND SILICON.

Manganese Silicides.—Several of these apparently exist.

Manganese silicide, Mn_2Si, is formed[5] by heating together manganese and silicon in the electric furnace ; also by igniting a mixture of SiO_2, manganese oxide, and aluminium; also by heating together potassium silicofluoride, copper, sodium, and red oxide of manganese. It forms a hard, brittle mass, steel-grey in colour, with a pronounced metallic lustre and a specific gravity of 6·4 at 15° C. Water at ordinary temperatures does not attack the substance, but steam does at a red heat, also oxygen and chlorine at a red heat. Fluorine gas attacks it at ordinary temperatures. Hydrochloric acid dissolves it, forming gelatinous silicic acid and manganous salts. Alkalies energetically react with the substance when heated with it.

Manganese monosilicide, $MnSi$, forms hard, lustrous, tetrahedral crystals possessing a specific gravity of 5·9. HNO_3 and H_2SO_4, either concentrated or dilute, hot or cold, do not attack the substance (Lebeau). Concentrated HCl only attacks it.

A *disilicide*, $MnSi_2$, has also been described,[6] consisting of octahedral crystals of specific gravity 5·24. A fourth silicide, Mn_3Si_2,[7] has been described, but is probably impure Mn_2Si.

Doubt has been thrown on the existence of these silicides as definite compounds, but Doerinckel,[8] from a study of the melting-point curve of mixtures

[1] Christensen, *loc. cit.* ; see also J. Meyer, *Zeitsch. anorg. Chem.*, 1913, **81**, 385–405.
[2] Descamps, *Ann. Chim.*, 1881, [v.], **24**, 185.
[3] Fittig and Eaton, *loc. cit.* ; P. Straus, *Zeitsch. anorg. Chem.*, 1895, **9**, 6.
[4] See Porret, *Trans. Roy. Soc.*, 1814, p. 527 ; *Annals of Philosophy*, 1819, **13**, 356. Grotthus, *Schweigger's J. Chem. Phys.*, **20**, 225 ; **32**, 272. Meitzendorff, *Pogg. Annalen*, 1842, **56**, 63. Kumakow and Weimann, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 518. Grossmann, *Ber.*, 1905, **37**, 559.
[5] See Vigouroux, *Compt. rend.*, 1895, **121**, 771 ; 1905, **141**, 722. Lebeau, *Comp. rend.*, 1903, **136**, 89, 231 ; *Bull. Soc. chim.*, 1903, [iii.], **29**, 797 ; *Ann. Chim. Phys.*, 1904, [viii.], **1**, 553.   [6] De Chalmot, *Amer. Chem. J.*, 1896, **18**, 536 ; Lebeau, *loc. cit.*
[7] Gin, *Compt. rend.*, 1906, **143**, 1229.
[8] Doerinckel, *Zeitsch. anorg. Chem.*, 1906, **50**, 117.

of the two former silicides, came to the conclusion that the two compounds Mn_2Si and $MnSi$ existed.

Manganous silicates occur naturally as isomorphous components of several minerals. *Rhodonite* or mangano-metasilicate, $MnSiO_3$, occurs in light red, transparent, triclinic crystals of specific gravity 3·55. It may be obtained artificially by fusing together[1] MnO and SiO_2. According to Ginsberg,[2] the melting-point is 1218° and density 3·350. It is isomorphous with calcium silicate (wollastonite). Its heat of formation is given by Le Chatelier[3] as $(MnO,SiO_2) = 5400$ calories. Wologdine[4] gives 7725 calories. *Tephroite*, manganous orthosilicate, Mn_2SiO_4, is also a naturally occurring mineral, crystallising in rose-red, brown, or grey tetragonal forms of specific gravity 4·06 to 4·12, and often occurs associated with rhodonite.

Manganese granite, Spessartin, $3(2MnO.SiO_2) + 2Al_2O_3.3SiO_2$, was made artificially by Gorgeu[5] by heating to bright redness kaolin and $MnCl_2$ in a stream of steam. Yellow crystals of specific gravity 4·05. Gorgeu[6] also describes the double compound $Mn_2SiO_4.MnCl_2$.

Manganese silicofluoride,[7] $MnSiF_6.6H_2O$, has been obtained from $MnSO_4$ and $BaSiF_6$, also from $MnCO_3$ and H_2SiF_6. Large pink crystals soluble in hot water, from which they may be crystallised. Stable in air. Specific gravity at 17·5° C. is 1·9038.

MANGANESE AND THE ELEMENTS OF THE NITROGEN GROUP.

Manganese and Nitrogen.—*Pentamangandinitride,* Mn_5N_2, is produced when finely divided manganese is heated to redness in a stream of nitrogen.[8] It has the probable structure

$$\begin{matrix} Mn & & & & Mn \\ & \diagdown & & & \diagup \\ & & N—Mn—N & & , \\ & \diagup & & & \diagdown \\ Mn & & & & Mn \end{matrix}$$
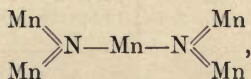
although Haber and van Oordt doubt this, regarding it as a mixture of Mn_3N_2 with oxides of Mn.[9]

The substance has a dull metallic lustre, and is only feebly magnetic;[10] with water and alkalies it yields ammonia; treated with a solution of ammonium chloride, it yields hydrogen and ammonia, thus:—

$$Mn_5N_2 + 20NH_4Cl = 2H_2 + 12NH_3 + 5MnCl_2.2NH_4Cl.$$
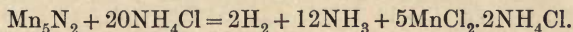
When ignited in ammonia gas, this substance yields:—[8]

Trimangandinitride, Mn_3N_2 ($Mn=N—Mn—N=Mn$), which is also formed merely by heating finely powdered manganese or manganese amalgam in a stream of ammonia to 800° C.[11] It acts chemically in much the same manner as Mn_5N_2, and when heated to redness in a stream of nitrogen it absorbs

[1] See Gautier and Hallopeau, *Compt. rend.*, 1889, **108**, 806 ; Doerinckel, *Metallurgie*, 1911, **8**, 201. [2] A. S. Ginsberg, *Zeitsch. anorg. Chem.*, 1908, **59**, 346–63.
[3] Le Chatelier, *Compt. rend.*, 1896, **122**, 80.
[4] S. Wologdine, *Compt. rend*, 1913, **157**, 121–23.
[5] Gorgeu, *Compt. rend.*, 1883, **97**, 320, 1303.
[6] Gorgeu, *Compt. rend.*, 1884, **98**, 107.
[7] Stolba, *Ber. Böhm. Ges. Wiss.*, Central Blatt, 1883, p. 292.
[8] Prelinger, *Monatsh.*, 1894, **15**, 391.
[9] Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1905, **44**, 373.
[10] Wedekind and Veit, *Ber.*, 1908, **41**, 3769–73.
[11] Henderson and Galletly, *J. Soc. Chem. Ind.*, 1908, **27**, 387–89.

some gas, being thereby converted into the pentanitride.   It is strongly magnetic.[1]

Heptamangandinitride, Mn_7N_2, obtained by the action of ammonia on manganese heated with the oxy-hydrogen blowpipe, has stronger magnetic properties[1] than either of the above nitrides.   It is readily attacked by acids and alkalies.

A quantitative investigation of the absorption of nitrogen by metallic manganese was made by Shukoff.[2]   He showed that manganese began to absorb nitrogen rapidly at 850°–875° C., and that the resulting product, containing 12 per cent. of nitrogen, exhibits magnetic properties almost as intense as those of iron.

Manganous nitrate, $Mn(NO_3)_2$, may be obtained by dissolving $MnCO_3$ in dilute nitric acid, or by acting on MnO_2 with HNO_3 in the presence of a reducing agent.   It crystallises out as colourless, deliquescent needles of formula[3] $Mn(NO_3)_2.6H_2O$, which melt at 25·8°, are readily soluble in alcohol, and possess the specific gravity 1·8199 at 21°.[4]   Heat of formation is given by Thomsen[5] as $(Mn,O_2,2NO_2,6H_2O) = 157,700$ calories.   Heat of solution $= -6150$ calories $(Mn(OH)_2,3HNO_3,Aq.) = 22,950$ calories.

The crystals heated to 129·5° boil, yielding, gradually, MnO_2;[4] heated to 200°, they decompose into MnO_2 and oxides of nitrogen.[6]

A second hydrate, $Mn(NO_3)_2.3H_2O$, is obtainable[7] by evaporating a solution of manganous nitrate in strong nitric acid in a vacuum.   It melts at 35·5° C.   The solubility curves[8] of both hydrates cut at about 25°.   Funk[8] gives the following data as regards solubility :—

Hydrate.	Temperature, ° C.	Parts of $Mn(NO_3)_2$ in 100 parts of Solution.	Molecules Water to 1 Molecule $Mn(NO_3)_2$.
$Mn(NO_3)_2 + 6H_2O$	− 29	42·29	13·57
	− 26	43·15	13·11
	− 21	44·30	12·50
	− 16	45·52	11·91
	− 5	48·88	10·40
	0	50·49	9·75
	+ 11	54·50	8·31
	+ 18	57·33	7·40
	+ 25·8	62·37	6·00 M.P.
	+ 25·5	65·92	5·35
	+ 27	65·66	5·21
	+ 29	66·99	4·90
	+ 30	67·38	4·82
$Mn(NO_3)_2 + 3H_2O$	+ 34	71·31	4·01
	+ 35·5	76·82	3·00 M.P.

[1] Wedekind and Veit, *loc. cit.*
[2] I. I. Shukoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 457–59.
[3] Hannay, *Trans. Chem. Soc.*, 1878, **33**, 273 ; Millon, *Compt. rend.*, 1842, **14**, 905.
[4] Ordway, *Amer. J. Sci.* (Sill.), 1859, [ii.], **27**, 16.
[5] Thomsen, *Thermochemische Untersuchungen*, vol. iii. p. 271.
[6] Deville, *Ann. Chim. Phys.*, 1853, [iv.], **38**, 10.
[7] Schultz-Sellack, *Zeitsch. Chem.*, 1870, 646.   [8] Funk, *Ber.*, 1899, **32**, 100.

Ditte[1] also describes a *monohydrate*, $Mn(NO_3)_2.H_2O$, obtained by dissolving the strongly heated nitrate in hot concentrated HNO_3 until saturated, and then cooling. On warming, the monohydrate melts, beginning to decompose at 140° C., and being completely decomposed at 190°–200°. Fused with nitric anhydride, it yields the *anhydrous salt*, $Mn(NO_3)_2$, which forms pink crystals, having heat of solution 12,930 calories, completely decomposing at 200° C.

Rüdorff,[2] from measurements on the depression of the freezing-point of aqueous solutions of the nitrate, came to the conclusion that in solution the substance existed as $Mn(NO_3)_2.12H_2O$.

Lescœur[3] investigated the vapour tensions of the various hydrates and their solutions.

Gerlac[4] gives the following data regarding the specific gravity of solutions of the salt in water :—

Specific gravity .	.	1·052	1·107	1·165	1·230	1·302	1·381	1·466	1·558
Per cent. $Mn(NO_3)_2.6H_2O$		10	20	30	40	50	60	70	80
Per cent. $Mn(NO_3)_2$.		6·237	12·474	18·711	24·948	31·185	37·422	43·659	49·896
(in 100 parts solution).									

A basic nitrate, $2MnO.N_2O_5.3H_2O$, has been described.[5]

<div align="center">MANGANESE AND PHOSPHORUS.</div>

Manganese Phosphides.—Several of these are known :—

Mn_3P is formed by heating manganese and phosphorus together to a dull red heat, when combination takes place with the evolution of heat and light.[6] It is an amorphous powder, specific gravity, 4·94, insoluble in HCl, very soluble in HNO_3. Rose[7] obtained the phosphide as a black metallic powder by heating $MnCl_2$ in gaseous hydrogen phosphide.

Struve[8] obtained a brittle substance resembling cast iron by heating manganese pyrophosphate mixed with sugar charcoal in a crucible filled with charcoal. This composition varied between Mn_3P_2 and Mn_2P. This product dissolved with inflammation in HNO_3, but was only partially soluble in HCl and H_2SO_4.

Merkel and Wöhler[9] obtained a mixture of phosphides by igniting together MnO_2, bone-ash, sand, and lamp-black. The composition agreed with Mn_5P_2 ; but as part was soluble in HCl and part insoluble, they regarded the substance as a mixture of two phosphides, viz. Mn_3P_2 (soluble in HCl), and Mn_7P_2 (insoluble in HCl). Metal-rich phosphides have also been obtained from $Mn_3(PO_4)_2$ by the thermit process.[10]

Granger[11] obtained the phosphide Mn_3P_2 by heating to redness in a stream of hydrogen gas $MnCl_2$ and P, placed in two different boats. It

[1] Ditte, *Compt. rend.*, 1879, **89**, 641 ; *Ann. Chim. Phys.*, 1879, [v.], **18**, 320. See also Guntz and Martin, *Bull. Soc. chim.*, 1909, [iv.], **5**, 1004–11.

[2] Compare Jones and Basset, *Amer. Chem. J.*, 1905, **33**, 563.

[3] Lescœur, *Ann. Chim. Phys.*, 1896, [vii], **7**, 423.

[4] Gerlac, *Zeitsch. anal. Chem.*, 1889, **28**, 477 ; see also Jones and Basset, *loc. cit.*

[5] Gorgeu, *Compt. rend.*, 1882, **94**, 1426.

[6] A. Schrötter, *Ber. Wien. Akad.*, 1849, **1**, 305. See, however, Wedekind and Veit, *Ber.*, 1907, **40**, 1268.

[7] H. Rose, *Pogg. Annalen*, **24**, 335.

[8] Struve, *Bull. Acad. Sci. Petrograd*, 1860, i. 470.

[9] Merkel and Wöhler, *Annalen*, 1853, **86**, 371.

[10] See Matignon and Trannoy, *Compt. rend.*, 1905, **141**, 190.

[11] Granger, *Compt. rend.*, 1897, **124**, 190.

formed fine, strongly refractive needles, which dissolved in aqua regia but was not soluble in nitric acid. When heated, it slowly oxidised.

Wedekind and Veit [1] obtained a magnetic compound, Mn_5P_2, by Granger's method. The same authors obtained the phosphide Mn_5P_2 by heating manganese with red phosphorus in an atmosphere of hydrogen, thus obtaining lustrous magnetic needles, of specific gravity 5·12, soluble in warm nitric acid.

Manganese phosphide, MnP, [2] obtained by heating together manganese and phosphorus, forms a black inodorous powder, which burns on heating in air; it is insoluble in HCl, but soluble in HNO_3. The substance is magnetic, losing magnetic properties between 18°–26° C.

A *higher phosphide*, MnP_2, is obtained [3] as a black powder by heating Mn and red P in an exhausted sealed tube, first to 400° C. and then to 600° C. Heated in H to 400° C., it is reduced to MnP.

MANGANESE PHOSPHATES.

A great many of these exist.

Manganous Phosphates. [4] — *Normal manganous orthophosphate*, $Mn_3(PO_4)_2.xH_2O$, is obtained with 14 molecules of water by precipitating manganese sulphate with Na_2HPO_4 solution. Thus obtained, it forms a white amorphous precipitate, soluble in mineral acids and also in certain solutions of salts. When kept over sulphuric acid, it loses 7 molecules of water, producing the heptahydrate, $Mn_3(PO_4)_2.7H_2O$. Heated at 100°, $Mn_3(PO_4)_2.6H_2O$ is formed.

Salts containing 9 to 11 molecules of water, also $7H_2O$ and $3H_2O$, are obtained by decomposing $MnHPO_4.xH_2O$ by water and drying under different conditions. *Anhydrous* $Mn_3(PO_4)_2$ is obtained by heating any of the above-mentioned hydrates, also by heating manganese pyrophosphate in dry hydrogen:—[5]

$$3Mn_2P_2O_7 = 2Mn_3(PO_4)_2 + P_2O_5.$$
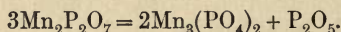
Many acid salts have been described; *e.g.* $MnHPO_4.3H_2O$ is obtained [6] by precipitating a solution of $MnSO_4$ with slight excess of Na_2HPO_4, dividing the precipitate and solution into two equal portions, adding HCl or HNO_3 to one portion until the precipitate first redissolves, and then mixing the two solutions. In the course of two days the precipitate changes into $MnHPO_4.3H_2O$. It forms very pale red rhombic six-sided tablets, losing at 100° five-sixths of its water of crystallisation, the rest being given up at 200° C.

Besides this compound, such *acid salts* as $MnH_4P_2O_8.2H_2O$ and $Mn_3P_2O_8.MnHPO_4.xH_2O$ have been described, along with numerous hydrated forms. Also a number of *double salts* are known.

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[1] Wedekind and Veit, *Ber.*, 1907, **40**, 1268.

[2] Wedekind, *Zeitsch. physikal. Chem.*, 1909, **66**, 614–32; Hilpert and Dieckmann, *Ber.*, 1911, **44**, 2831–35; 1914, **47**, 780–84.

[3] Hilpert and Dieckmann, *Ber.*, 1914, **47**, 780–84.

[4] These salts have been investigated extensively by the following authors (among others): Heintz, *Pogg. Annalen*, 1849, **74**, 450. Debray, *Ann. Chim. Phys.*, 1861, [iii.], **61**, 434; *Compt. rend.*, 1861, **52**, 44; 1864, **59**, 40. Bödecker, *Ann. Chim. Phys.*, 1861, [iii.], **61**, 433. Erlenmeyer, *Annalen*, 1877, **190**, 191, 208. Viard, *Compt. rend.*, 1899, **129**, 412. Dakin, *Zeitsch. anal. Chem.*, 1900, **39**, 784.

[5] Struve, *Bull. Acad. Sci. Petrograd*, 1860, i. 239; *J. prakt. Chem.*, 1860, **79**, 345.

[6] Bödecker, *loc. cit.*; Erlenmeyer and Heinneich, *loc. cit.*; Debray, *loc. cit.*

Thus, *ammonium manganous orthophosphate*,[1] $NH_4MnPO_4.H_2O$, is produced by treating $MnCl_2$ with $Na_2NH_4PO_4$.

Manganous wagnerite, $Mn_3(PO_4)_2.MnCl_2$, was obtained [2] by heating ammonium phosphate to redness with excess of $MnCl_2$, extracting with water, and crystallising.

Manganous apatite, $3Mn_3(PO_4)_2.MnF_2$, and also the *bromide*,[3] $3Mn_3(PO_4)_2.MnBr_2$, is produced by melting 5 parts of manganese fluoride, MnF_2, or $MnBr_2$, with 5 parts of ammonium phosphate. Double salts with $Fe_3(PO_4)_2$, and sodium potassium and ammonium phosphates have also been described.

Manganous Pyrophosphates. — The normal manganous salt, $Mn_2P_2O_7.3H_2O$, is a white amorphous powder obtained [4] by precipitating $MnSO_4$ with $Na_4P_2O_7$. It is soluble in excess of a solution of $Na_4P_2O_7$, and still more easily soluble in $K_4P_2O_7$ solution. Heated to 120° C., it gives $Mn_2P_2O_7.H_2O$; and when ignited, $Mn_2P_2O_7$.

The anhydrous salt may also be obtained by heating $MnHPO_4.3H_2O$ or $MnNH_4PO_4.H_2O$. It is a white powder of specific gravity 3·585 at 20° C. Heated to whiteness in hydrogen $Mn_3P_2O_8$ is obtained. The acid salt $MnH_2P_2O_7.4H_2O$ is produced [5] by acting on $Mn_2P_2O_7$ with oxalic acid.

Various double salts are known,[6] *e.g.* $K_2MnP_2O_7$ (obtained by melting together MnO and KPO_3); $K_2MnP_2O_7 + 8H_2O$; $Mn_2P_2O_7.2K_4P_2O_7.10H_2O$; $K_2MnP_2O_7.MnO$; $MnNa_2P_2O_7$ (flesh-coloured prisms); $3Mn_2P_2O_7.2Na_4P_2O_7$. $24H_2O$, $NH_4NaMnP_2O_7.3H_2O$.

Manganous Metaphosphates. — *Manganous dimetaphosphate*, $MnP_2O_6.4H_2O$, is obtained [7] by treating a solution of $(NH_4)_2P_2O_6$ with excess of $MnCl_2$. Red crystals which, when ignited, yield $Mn(PO_3)_2$—a reddish-white difficultly fusible powder, insoluble in water and dilute acids, but soluble in concentrated sulphuric acid.

Manganous trimetaphosphate, $Mn_3(P_3O_9)_3.11H_2O$, separates when $MnCl_2$ solution is mixed with sodium trimetaphosphate.[8] Triclinic prisms, very sparingly soluble in hot and cold water, but more soluble in hot hydrochloric acid.

Manganous hexametaphosphate separates as an oily precipitate when solutions of $MnSO_4$ and sodium hexaphosphate are mixed.[9] Dries in air to a light rose-coloured glass, and at 100° to a reddish-grey powder. When ignited, it melts to a glass. Insoluble in water.[10]

Manganic Phosphates. — *Neutral manganic orthophosphate*, $Mn(PO_4).H_2O$, was obtained [11] as a greenish-grey precipitate by heating

[1] See Braun, *Zeitsch. anal. Chem.*, 1868, **7**, 340; Gibbs, *Chem. News*, 1873, **28**, 51; Dakin, *Zeitsch. anal. Chem.*, 1900, **39**, 784.
[2] Deville and Caron, *Ann. Chim. Phys.*, 1863, [iii.], **67**, 459.
[3] Ditte, *Compt. rend.*, 1883, **96**, 846.
[4] Schwarzenberg, *Annalen*, 1848, **65**, 150. See also Heintz, Bödecker, Debray.
[5] Pahl, *Ber.*, 1873, **6**, 1465; *Oefvers. af. Sv. Vet. Akad. Förh.*, 1873, **29**, 45.
[6] Ouvrard, *Compt. rend.*, 1888, **106**, 1729; *Ann. Chim. Phys.*, 1889, [vi.], **16**, 313; Pahl, *loc. cit.*
[7] Fleitmann, *Pogg. Annalen*, 1849, **78**, 257; Madrell, *Annalen*, 1847, **61**, 58; Tammann, *J. prakt. Chem.*, 1892, [ii.], **45**, 423.
[8] Lindbom, *Lund's Univers.-Arskr.*, 1874.
[9] H. Rose, *Pogg. Annalen*, 1849, **76**, 4, 18.
[10] Lüdert, *Zeitsch. anorg. Chem.*, 1893, **5**, 15–41.
[11] Christensen, *J. prakt. Chem.*, 1883, [ii.], **28**, 22.

manganic acetate with orthophosphoric acid solution. The manganic acetate is made by allowing 4–5 grams of hydrated Mn_3O_4 to be acted on by 150–200 c.c. glacial acetic acid in the cold, and then heating and filtering. Laspeyres[1] probably obtained the same substance by digesting MnO_2 with phosphoric acid at 100°–110° C. and precipitating with water.

Both manganic oxide and the dioxide dissolve in a concentrated solution of phosphoric acid, evolving in the latter case oxygen, and forming a deep violet solution from which violet-coloured crystals separate. This substance is decomposed by water, alkalies precipitating manganic hydroxide. Its absorption spectrum is described by Jaeschke and Meyer.[2] When the violet solution is evaporated, *manganic metaphosphate*, $Mn(PO_3)_3.H_2O$,[3] separates as a powder.

The *acid pyrophosphate*, $MnHP_2O_7$, has been obtained[4] by dissolving the neutral manganic orthophosphate in melted orthophosphoric acid, heating for 24 hours at 170°–190°.

The double phosphates $MnKP_2O_7$ and $Mn_4P_6O_{21}.14H_2O$, as well as other double phosphates, have been prepared.[5]

MANGANESE AND ARSENIC.

Arsenic combines with manganese at 500° C. with incandescence, producing arsenides.[6]

The *arsenide* MnAs is stable only below 400°–450° C. It has specific gravity 5·5. It may be also obtained by the action of $AsCl_3$ on manganese, incandescence taking place at 500° C. Regarding its magnetism, see p. 267.[6]

The *arsenide* Mn_2As is stable at high temperatures and may be produced from MnAs by heating in absence of air. Grey body. Regarding its magnetic properties, see p. 267.[6]

The *arsenide* Mn_3As_2 is obtained by heating manganese and arsenic to 700°–800° in a stream of hydrogen. Regarding its magnetism, see p. 267.[6]

Manganese Arsenates. — Several of these are known. The *acid manganous arsenate*, produced by saturating arsenic acid with $MnCO_3$, separates from solution as sparingly soluble rectangular tablets.[7] Its monohydrate, $HMnAsO_4.H_2O$, has been obtained.[8] The substance readily dissolves in arsenic acid, giving rise to the salt $H_4Mn(AsO_4)_2$, which crystallises out as rectangular plates.

Neutral manganous arsenate is obtained by precipitating $MnCl_2$ solution with sodium arsenate. When $MnSO_4$ is heated with neutral sodium arsenate to 175°, the compound $Mn_3(AsO_4)_2.H_2O$ is obtained as brown needles. The *pyro-arsenate*, $Mn_2As_2O_7$, is described by Lefèvre.[9] Other double

[1] Laspeyres, *J. prakt. Chem.*, 1877, [ii.], **15**, 320.

[2] W. Jaescke and J. Meyer, *Zeitsch. physikal. Chem.*, 1913, **83**, 281–89.

[3] Hermann, *Pogg. Annalen*, 1848, **74**, 303 ; Barbier, *Compt. rend.*, 1902, **135**, 1054, 1109 ; Auger, *Compt. rend.*, 1901, **133**, 94.

[4] Christensen, *loc. cit.* ; Schjerning, *J. prakt. Chem.*, 1892, [ii.], **45**, 515.

[5] Schjerning, *loc. cit.*

[6] See Wedekind, *Zeitsch. Elektrochem.*, 1905, **11**, 850 ; *Ber. Deut. physikal. Ges.*, 1906, **4**, 412 ; *Ber.*, 1911, **44**, 2663–70. G. Arrivaut, *7th Intern. Congr. Appl. Chem.*, 1909, sect. ii. 100–03. Hilpert and Dieckmann, *Ber.*, 1911, **44**, 2378–85. P. Schoen, *Metallurgie*, 1911, **8**, 739–41.

[7] See Schiefer, *Zeitsch. Ges. Naturw. Berlin*, 1864, **23**, 347 ; Coloriano, *Compt. rend.*, 1886, **103**, 273.   [8] Otto, *J. prakt. Chem.*, 1834, **2**, 414.

[9] Lefèvre, *Compt. rend.*, 1890, **110**, 405 ; *Ann. Chim. Phys.*, 1892, [vi.], **27**, 29 ; Reichard, *Ber.*, 1898, **31**, 2165 ; Stavenhagen, *J. prakt. Chem.*, 1895, **51**, 36.

arsenates which should be mentioned are *ammonium manganous arsenate*, $MnNH_4AsO_4.6H_2O$, and *manganarsenwagnerite*, $Mn_3(AsO_4)_2.MnCl_2$.[1]

Manganic arsenate, $Mn_2(AsO_4)_2.2H_2O$, has been obtained in the same way as manganic phosphate. It forms a grey powder. Several double salts with alkali arsenates have been obtained.[2]

Manganous arsenite, $Mn_3(AsO_3)_2.5H_2O$, obtained by precipitating a manganous salt solution with neutral ammonium arsenite, is a pale rose-coloured precipitate, which rapidly darkens in air.

MANGANESE AND ANTIMONY.

Manganese antimonide, MnSb, has been prepared by direct union, also by igniting antimony with manganese-thermit purified by treating with bromine. Black, strongly magnetic,[3] crystalline powder of specific gravity 5·6, soluble in hot HCl and HNO_3. Loses its magnetism between 320°–330° C. The antimonide Mn_2Sb is also known.

Manganous antimonate, $Mn(SbO_3)_2$, is a white, sparingly soluble precipitate obtained by precipitating $MnCl_2$ with $KSbO_3$.[4]

MANGANESE AND BISMUTH.

Manganese bismuthide, MnBi,[5] is prepared by heating bismuth with manganese amalgam in an atmosphere of hydrogen, also by the interaction of manganese-thermit and bismuth. Silver-white in colour.[5] Loses its magnetism between 360°–380° C. Readily attacked by acids except concentrated hydrochloric acid.

[1] Stein, *Annalen*, 1850, **74**, 218.
[2] Lefèvre, *Compt. rend.*, 1890, **110**, 405 ; *Ann. Chim. Phys.*, 1892, [vi.], **27**, 29 ; Reichard, *Ber.*, 1898, **31**, 2165 ; Stavenhagen, *J. prakt. Chem.*, 1895, **51**, 36.
[3] Hilpert and Dieckmann, *Ber.*, 1911, **44**, 2831-35. Wedekind and Fetzer, *Ber.*, 1907, **40**, 1266 ; *Zeitsch. physikal. Chem.*, 1909, **66**, 614-32.
[4] Rammelsberg, *Pogg. Annalen*, 52, 193 ; Ebel, *Ber.*, 1889, **22**, 3044 ; Senderens, *Bull. Soc. chim.*, 1899, [iii.], **21**, 56.
[5] Hilpert and Dieckmann, *Ber.*, 1911, **44**, 2831-35 ; Wedekind and Veit, *Ber.*, 1911, **44**, 2663-70.

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