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INORGANIC CHEMISTRY.
VOLUME IX. PART II.

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A TEXT-BOOK OF INORGANIC CHEMISTRY.

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[*Frontispiece*

THE PERIODIC TABLE *

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

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

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VOLUME IX. PART II.

IRON AND ITS COMPOUNDS.

BY
J. NEWTON FRIEND,
D Sc (B'ham), Ph.D (Wurz), F I C.

With Frontispiece and 8 Illustrations.

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GENERAL INTRODUCTION TO THE SERIES.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

J. NEWTON FRIEND.

March 1925.

PREFACE.

THE position occupied by iron amongst the elements is unique. Indeed, it is not too much to say that, without abundant supplies of this metal, civilisation as we know it to-day would not be possible.

Owing to the importance of iron and the enormous amount of research that has been carried out upon it and upon its compounds, it was felt that the subject deserved a separate book in this series, and, as has already been mentioned in the Preface to Part I. of this volume, Part II. was accordingly assigned to it. As the work progressed, however, it became evident that the amount of matter requiring treatment could not be efficiently condensed into a single book, and it has therefore been decided to again subdivide this volume, namely into Parts II. and III.—the former to deal with the chemistry of Iron and its Compounds, and the latter to be devoted to a study of the Metallurgical Chemistry of Iron. Only in this way did it appear possible for iron to receive the detailed and careful treatment it so well deserves.

The literature relating to iron is extraordinarily voluminous, but it is believed that the references given in the text are reasonably complete. In almost every case the original memoirs have been consulted, and although it is too much to hope that the references are entirely free from error, it is believed that any such errors will be relatively few and of minor importance.

The addition of the *Table of Dates of Issue of Journals* (pp. xviii–xxv) will, it is hoped, enhance the value of this volume. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the Library of the Chemical Society by Mr F. W. Clifford and his Staff.

The Author desires to express his sincere thanks to Mr H. F. V. Little, B.Sc., D.I.C., who wrote the section on the Atomic Weight of Iron; to Mr R. H. Vallance, B.Sc., A.I.C., who has carefully read through the whole of the work in proof; to Mr G. C. Lloyd and his Staff at the Iron and Steel Institute; and particularly to Mr F. W. Clifford and his Staff at the Library of the Chemical Society for their generous assistance.

J. N. F.

March 1921.

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Iron and Selenium—Selenides—Selenites—Selenates—Double Selenates.
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LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

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

ABBREVIATED TITLE.	JOURNAL.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Geol. Mag.	Geological Magazine.
Int. Zeitsch. Metallographie	Internationale Zeitschrift fur Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-koniglichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch fur Mineralogie.
Jahresber.	Jahresbericht uber die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift fur Naturwissenschaft.
J. Amer. Chem Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal fur Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal fur praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbucher.
Mém. Paris Acad.	Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France.
Mon. scient.	Moniteur scientifique.
Monatsh.	Monatshefte fur Chemie und verwandte Theile anderer Wissenschaften.
Münch. Med. Wochenschr.	Munchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Öfvers. K. Vet.-Akad. Forh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Pfluger's Archiv	Archiv fur die gesammte Physiologie des Menschen und der Thiere.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Pharm. Post	Pharmazeutische Post.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin)
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824–1877).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil Soc Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal fur Chemie und Physik.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.

ABBREVIATED TITLE.	JOURNAL.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Koniglich bayerischen Akademie der Wissenschaften zu Wien.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Techn. Jahresber.	Jahresbericht uber die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mém. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau International des Poids et Mesures.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedermann's Annalen der Physik und Chemie (1877–1899).
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift fur analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift fur angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift fur anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift fur Chemie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift fur Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift fur Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift fur Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift fur Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift fur physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift fur physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift fur wissenschaftliche Photographie, Photophysik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS.

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

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

* First series known as *Bulletin de Pharmacie.*

Year	Amer. J Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm	Bull. Soc. chim.	Compt. rend.	Dingl. Poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon.* Scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	43–45	7–8	31–34	...	...	35–38	16	...	...	7, 8	120	18–20	...	...	
31	19, 20	.	46–48	...	35–39	...	..	39–42	17	...	...	9, 10	121	21–23	...	...	
32	21, 22	1–4	49–51	(3) 1, 2	40–43	...	..	43–47	18	...	...	11 (3) 1	122	24–26	1	. .	
33	23, 24	5–8	52–55	3, 4	44–47	.	...	48–50	19	..	...	2, 3	123	27–30	2	...	
34	25–27	9–12	56–57	5, 6	48–50	...	..	51–54	20	1–3	.	4, 5	124	31–33	.	...	
1835	28, 29	13–16	58–60	7, 8	(2) 1–4	...	1	55–58	21	4–6	...	6, 7	125	34–36	...	.	
36	30, 31	17–20	61–63	9, 10	5–8	...	2, 3	59–62	22	7–9	..	8, 9	126	37–39	..	. .	
37	32, 33	21–24	64–66	11, 12	9–12	...	4, 5	63–66	23	10–12		10, 11	127	40–42	3	...	
38	34, 35	25–28	67–69	13, 14	13–16	...	6, 7	67–70	24	13–15		12, 13	128	43–45	.	.	
39	36, 37	29–32	70–72	15, 16	17–20	...	8, 9	71–74	25	16–18	...	14, 15	129	46–48	. .		
1840	38, 39	33–36	73–75	17, 18	21–24	...	10, 11	75–78	26	19–21	..	16, 17	130	49–51	.	.	
41	40, 41	37–40	(3) 1–3	19, 20	25–28	...	12, 13	79–82	27	22–24	.	18, 19	131	52–54	..	...	
42	42, 43	41–44	4–6	(4) 1, 2	29–32	...	14, 15	83–86	(3) 1, 2	25–27	...	20, 21	132	55–57	..	...	
43	44, 45	45–48	7–9	3, 4	33–36	. .	16, 17	87-90	3, 4	28–30	...	22, 23	133	58–60	4	...	
44	46, 47	49–52	10–12	5, 6	37–40	...	18, 19	91–94	5, 6	31–33	...	24, 25	134	61–63	...	...	
1845	48–50	53–56	13–15	7, 8	41–44	...	20, 21	95–98	7, 8	34–36	...	26, 27	135	64–66	...	..	
46	(2) 1, 2	57–60	16–18	9, 10	45–48	...	22, 23	99–102	9, 10	37–39		28, 29	136	67–69			
47	3, 4	61–64	19–21	11, 12	49–52	...	24, 25	103–106	11, 12	40–42		30, 31	137	70–72	...	1	
48	5, 6	65–68	22–24	13, 14	53–56	...	26, 27	107–110	13, 14	43–45		32, 33	138	73–75	...	1, 2	1
49	7, 8	69–72	25–27	15, 16	57–60	...	28, 29	111–114	15, 16	46–48	...	34, 35	139	76–78	...	2, 3	2, 3
1850	9, 10	73–76	28–30	17, 18	61–64	...	30, 31	115–118	17, 18	49–51	...	36, 37	140	79–81	...	3	4, 5
51	11, 12	77–80	31–33	19, 20	65–68	...	32, 33	119–122	19, 20	52–54	...	(4) 1, 2	141	82–84	5	4	6, 7
52	13, 14	81–84	34–36	(5) 1, 2	69–72	...	34, 35	123–126	21, 22	55–57	..	3, 4	142	85–87	. .	5	8, 9
53	15, 16	85–88	37–39	3, 4	73–76	...	36, 37	127–130	23, 24	58–60	..	5, 6	143	88–90	...	6	10, 11
54	17, 18	89–92	40–42	5, 6	77–80	...	38, 39	131–134	25, 26	61–63	...	7, 8	144	91–93	6, 7	7	12–14
1855	19, 20	93–96	43–45	7, 8	81–84	...	40, 41	135–138	27, 28	64–66	...	9, 10	145	94–96	7	8	15–18
56	21, 22	97–100	46–48	9, 10	85–88	...	42, 43	139–142	29, 30	67–69	...	11, 12	146	97–99	8	9	19 22
57	23, 24	101–104	49–51	11, 12	89–92	...	44, 45	143–146	31, 32	70–72	(1) 1	13, 14	147	100–102	9	10	23–27
58	25, 26	105–108	52–54	13, 14	93–96	1	46, 47	147–150	33, 34	73–75	2	15, 16	148	103–105	9	11	28–33
59	27, 28	109–112	55–57	15, 16	97–100	1	48, 49	151–154	35, 36	76–78	3	17, 18	149	106–108	9, 10	12	34–38

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

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

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

* See footnote, p. xix.

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

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Week-blad.	Chem Zeit.	Compt. rend.
1890	12	39, 40	15	256–260	19–21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
91	13	41, 42	16	261–266	22–24	19, 20	229	24	5, 6	63, 64	8, 9	...	15	112, 113
92	14	43, 44	17	267–271	25–27	(9) 1, 2	230	25	7, 8	65, 66	10, 11		16	114, 115
93	15	45, 46	18	272–277	28–30	3, 4	231	26	9, 10	67, 68	12, 13	.	17	116, 117
94	16	47, 48	19	278–283	(7) 1–3	5, 6	232	27	11, 12	69, 70	14, 15	...	18	118, 119
1895	17	49, 50	20	284–288	4–6	7, 8	233	28	13, 14	71, 72	16, 17	...	19	120, 121
96	18	(4) 1, 2	21	289–293	7–9	9, 10	234	29	15, 16	73, 74	18, 19	...	20	122, 123
97	19	3, 4	22	294–298	10–12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299–303	13–15	13, 14	236	31	19, 20	77, 78	22, 23	.	22	126, 127
99	21, 22	7, 8	24	304–309	16–18	15, 16	237	32	21, 22	79, 80	24, 25	...	23	128, 129
1900	23, 24	9, 10	25	310–313	19–21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
01	25, 26	11, 12	26	314–319	22–24	19, 20	239	34	25, 26	83, 84	28, 29	...	25	132, 133
02	27, 28	13, 14	27	320–325	25–27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	..	26	134, 135
03	29, 30	15, 16	28	326–329	28–30	3, 4	241	36	29, 30	87, 88	32, 33		27	136, 137
04	31, 32	17, 18	29	330–337	(8) 1–3	5, 6	242	37	31, 32	89, 90	34, 35	...	28	138, 139
1905	33, 34	19, 20	30	338–343	4–6	7, 8	243	38	33, 34	91, 92	36, 37	...	29	140, 141
06	35, 36	21, 22	31	344–350	7–9	9, 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
07	37, 38	23, 24	32	351–357	10–12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	4	31	144, 145
08	39, 40	25, 26	33	358–363	13–15	13, 14	246	41	3, 4	97, 98	42, 43	5	32	146, 147
09	41, 42	27, 28	34	364–371	16–18	15, 16	247	42	5, 6	99, 100	44, 45	6	33	148, 149
1910	43, 44	29, 30	35	372–377	19–21	17, 18	248	43	7, 8	101, 102	46, 47	7	34	150, 151
11	45, 46	31, 32	36	378–385	22–24	19, 20	249	44	9, 10	103, 104	48, 49	8	35	152, 153
12	47, 48	33, 34	37	386–394	25–27	(11) 1, 2	250	45	11, 12	105, 106	50, 51	9	36	154, 155
13	49, 50	35, 36	38	395–401	28–30	3, 4	251	46	13, 14	107, 108	52, 53	10	37	156, 157
14	Publication ceased	37, 38	39	...	...	5, 6	252	47	15, 16	109, 110	54, 55	11	38	158, 159
1915		39, 40	40	.	...	...	253	48	17, 18	111, 112	56, 57	12	39	160, 161
16	...	41, 42	41	...	...	..	254	49	19, 20	113, 114	58, 59	13	40	162, 163
17	...	43, 44	42	...	...	...	255	50	21, 22	115, 116	60, 61	14	41	164, 165
18	...	45, 46	43	...	...	...	..	51	23, 24	117	62, 63	15	42	166, 167
19	. .	47, 48	44	...	...	...	...	52	25, 26	118, 119	64, 65	16	43	168, 169

Year	Dingl. Poly. J.	Gazzetta.	J. Amer. Chem Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc	J. Soc. Chem. Ind.	Monatsh.	Mon.* Scient.	Nature.	Phil Mag.
1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279–282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283–286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287–290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291–294	24	16	65, 66	. .	29, 30	.	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295–298	25	17	67, 68	...	(6) 1, 2	..	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299–302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303–306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307–310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311–314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
01	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
02	317	32	24	81, 82	. .	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
03	318	33	25	83, 84	..	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
04	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
06	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
07	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
08	323	38	30	95, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
09	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89, 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102–104	37, 38

* See footnote, p. xix.

Year	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-Chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem
1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	..	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	..	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186		11	57, 58, 59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	.	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	..	13	60, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	15	64, 65, 66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	1	16	66, 67	19	109	20	Continued as Annalen der Physik.	39	13	22–25	6, 7	32–34	32–35
01	196, 197	2	17	68, 69	20	110	21		40	14	26–29	7	34–36	36–38
02	198, 199	3	18	69, 70	21	111	22		41	15	29–33	8	36, 37	39–42
03	200–202	4	19	71, 72	22	112	23		42	16	33–37	9	37–39	43–46
04	203	5	20	72, 73, 74	23	113	24		43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
06	206	7	22	A. 77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
07	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
08	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
09	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
13	212, 213	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
1915	215, 216	16	Publication of matter of scientific interest now abandoned.	...	34	..	35		54	28	90–93	21	55	89, 90
16	216, 217	17		...	35	...	36		55	29	94–98	22	...	91, 92
17	217	18		...	36, 37	...	37		56	30	99–101	23	..	92
18	217	...		.	37	...	38		57	31	102–104	24	No issue*	92
19	...	...		...	38	...	39		58	32	105–109	25		...

* Remainder of vol. 55 appeared in 1920.

A TEXTBOOK OF
INORGANIC CHEMISTRY.

VOL. IX. PART II.
IRON AND ITS COMPOUNDS.

CHAPTER I.
THE EARLY HISTORY OF IRON.

THE important part played by iron in the development of modern civilisation renders a study of the history of this metal one of peculiar interest. In whichever direction we turn we are confronted by articles of iron, large and small, essential and ornamental. It is iron in some form or other that constitutes the framework both of our railways and of our mercantile marine. Without these rapid means of transport the huge populations of London and our larger cities could not be fed and supplied with the necessaries of civilised life as we know it to-day. Again, reinforced concrete,[1] the building material of the future, owes what strength and adaptability it possesses almost entirely to its iron frame, and as our supplies of building stone become depleted we shall be driven to placing increased reliance upon this material. Of all the metals known to science, iron takes the foremost place in the service of man. Indeed, the wonderful progress that has been made during the last hundred years would not have been possible had not the earth possessed an abundant supply of iron or its ores.

At the dawn of the human era man would seize upon any stones, branches, or other hard materials lying at hand for purposes of offence, defence, or the chase. Later on it would occur to him to improve upon the natural shapes by chipping, and he would soon discover that flint is particularly amenable to such treatment. Thus would originate the flint weapons and tools which have been discovered in large quantities in modern times, and which antiquaries have made use of to throw interesting light upon the manner in which primitive man lived during what has been aptly termed the *Stone Age*.

In all probability during his search for suitable stones early man occasionally stumbled across meteoric iron. Finding that it did not crack on being hammered,[2] that it possessed great tenacity and admitted of being rubbed to a fine, hard edge, he would prepare from it his most valued weapons.

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[1] See Friend, *Trans. Concrete Inst.*, 1917–18, 9.

[2] The impression shared by many writers, namely, that meteoric iron is usually brittle and unworkable in the cold, appears to be erroneous (Zimmer, *J. Iron Steel Inst.*, 1916, II., 306).

This does not constitute the beginning of what antiquaries term the *Iron Age*, for man at this period did not recognise any relationship between metallic iron and the red or brown earthy hæmatites around him. He regarded the iron merely as a particularly useful but unfortunately rare kind of stone, and not as a substance that he could manufacture for himself.

Interesting side-lights on the customs of prehistoric man are afforded by the behaviour of his modern representatives in uncivilised countries. Thus Ross in his Arctic explorations in 1818 came across certain Eskimos who carried knives consisting of blades of meteoric iron set into bone handles.[1] The pieces of metal had been detached with great labour from the softest of three masses of metal of meteoric origin at Melville Bay, and had then been cold worked with stone hammers.

It has been urged that meteoric iron is too scarce to have ever been used to any appreciable extent by prehistoric man. This is hardly the case, however, for some 246 tons of the metal are known to science,[1] and in prehistoric times meteoric iron would be even more plentiful than now inasmuch as the accumulations derived from meteoric showers of the previous ages could be drawn upon. As the metal, owing to its nickel content, is usually highly resistant to corrosion, it would not decay so rapidly by exposure as the ordinary manufactured metal.

Ages elapsed before man discovered that certain " stones," on being heated in a fire, yielded a new " stone " capable of being hammered into useful shapes, and differing from the original stone in most of its other properties. This new product is now called copper or bronze, according to its composition. At first, no doubt, it was a matter of accident whether bronze or copper was produced. In districts such as Cornwall, where copper and tin ores occur in association, they would be reduced together as one and the same, yielding what may be termed a " natural bronze." In Hungary, where copper ores are associated with those of antimony, early implements consist of an alloy of copper containing up to 4 5 per cent. of antimony. Similarly Egyptian implements contain arsenic, whilst those from Germany contain nickel.[2]

The discovery that bronze is not obtained from a single ore but from a mixture of at least two ores represents a high standard of metallurgical knowledge, soon to be followed, if not indeed already preceded, by the discovery of iron. The question now arises as to how many years iron—whether native, meteoric, or manufactured—has been known to and used by different peoples. Just as the nations to-day differ in the relative degrees of their civilisations, so in past ages some of the peoples were living in their stone age whilst others were using implements of bronze and yet others had become familiar with iron. Thus Britain was passing through her stone period at a time when iron was already known in Assyria, in Egypt, and probably also in China.[3] Again, at the time of the Roman invasion of Britain the southern tribes used bronze implements and were familiar with iron, whilst the northern tribe of Brigantes was still in their stone age. Iron was known in Egypt at least some 3500 B.C.,[1] although it did not come into common use probably until the fifth or sixth century B.C. Possibly the iron found its way thither from Ethiopia, where iron smelting was probably practised at an earlier date than in Egypt. During blasting operations within the Great Pyramid at Gizeh in 1837, an iron tool was found, which, if coeval with the pyramid, proves that iron was known in Egypt at the time of the Fourth Dynasty —that is, some 5500 years ago.[2]

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[1] Zimmer, *loc. cit.*

[2] Gowland, *Huxley Memorial Lecture for* 1912, Royal Anthropological Institute.

[3] See Brough, *J. Iron Steel Inst.*, 1906, I., 233.

The first general group of iron tools found in Egypt dates back to the time of the Assyrian Invasion of 666 B.C., and was found at Thebes. The Assyrians themselves appear to have made chain mail about 900 B.C.[3]

The Israelites were familiar with iron, and several interesting allusions to the metal occur in Holy Writ.[4] Og, King of Bashan, *c.* 1200 B.C., is stated to have had an iron bedstead.[5] It is generally accepted that iron was introduced into Palestine about this time by the Philistines,[6] who were a far more cultured race than the Israelites, with whom they were constantly coming into conflict.

The oldest examples of iron used in Palestine are two wedge-shaped lumps found in the famous water passage at Gezer.[7] The passage was sealed up about 1450 to 1250 B.C., several hundred years before the use of iron became general in Palestine; but although these are simply stray pieces of metal, they show that iron was known prior to these dates. Excavations at Gezer, Lachish, and Megiddo have brought to light numerous tools, weapons, and ornaments of iron, dating in some cases as far back as the time of David, namely, about 1000 B.C. An interesting example is that of a ring cemented to a finger-bone by rust, showing that it had been used for personal adornment.[8]

It is not improbable that India acquired her knowledge of iron from Babylon[9]; at any rate iron was worked in India at an early date. From a passage in the *Black Yajuveda* it would appear that some form of iron cannon was used in the Vedic Age, namely between 2000 and 1000 B.C.[10] Between 500 and 200 B.C. iron appears to have been in quite common use, particularly for war weapons.

The famous pillar at Delhi has frequently been described, and owing to a regrettable series of errors the date of 912 B.C. has repeatedly been assigned to it. In reality it only dates back to about A.D. 300. It is 23 feet 8 inches in height, 22 feet being vertically above ground and 20 inches below. Its upper diameter is 12½ inches; its lower, 16½ inches; whilst its total weight is approximately 6 tons.[11] The legend connected with this famous pillar asserts that the metal had been driven so deep into the ground that it had pierced the head of the king of serpents who supports the earth. It had thus a remarkably sure foundation. A Rajah doubted this and ordered the pillar to be dug up, with the result that its end was observed to be moist with the serpent's blood. On attempting to replace the pillar, however, it was found impossible to transfix the wily reptile, and the pillar, in consequence, remained loose and shaky,[1] symbolic of the Rajah's faltering faith. It has been suggested that the city of Delhi owes its name to the pillar, the Hindoo term being *Dhelli*, or unstable. Sanskrit authorities are inclined to the opinion, however, that the word Delhi means the *Heart's Delight*, and has nothing whatever in common with the pillar. A remarkable feature of the pillar is its freedom from rust. This is no doubt due to some peculiarity of its surface layer, for pieces broken away appear to rust with ease.[2] Hadfield[3] analysed one such sample, and found it to contain :—

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[1] Petrie (*ibid.*, 1912, I., 182) gives 7000 to 6000 B.C., but his system of chronology is different.

[2] See J. V. Day, *Proc. Phil. Soc. Glasgow*, April 12, 1871; also King and Hall, *Egypt and Western Asia in the Light of Recent Discoveries* (S.P.C.K., 1907).

[3] Louis, *Proc. Durham Phil. Soc.*, 1911, 4, Part 2.

[4] See Gen. iv. 22; Deut. iv. 20; Num. xxxv. 16, etc.

[5] Deut. iii. 11.

[6] See 1 Sam. xiii. 19–22; Josh. xvii. 16–18; Judges i. 19, iv. 3.

[7] Macalister, *Palestine Exploration Fund, Quarterly Statement*, 1908, p. 101.

[8] See Handcock, *The Archæology of the Holy Land* (Unwin, 1916), p. 210.

[9] V. Smith, *J. Iron Steel Inst.*, 1912, I., 183.

[10] Neogi, *J. Roy. Soc. Arts*, 1914, 63, 43.

[11] Hadfield, *J. Iron Steel Inst.*, 1912, I, 134.

Carbon . . .	0·080 per cent.
Silicon . . .	0·046 ,,
Sulphur . . .	0·006 ,,
Phosphorus . .	0·114 ,,
Manganese . .	0 000 ,,

The high phosphorus and low carbon, sulphur, and manganese contents all tend towards reduction of corrodibility, but do not suffice to explain the general immunity of the pillar from corrosion. It has been suggested[4] that the employment of stone anvils may have siliconised the surface and thus rendered it less susceptible to corrosion.

Turning now to Europe, it appears that Greece was the first country to use iron, namely, about 1400 B.C.[5] Homer (B.C. 880) was thoroughly familiar with the metal, and frequently alludes to it in both his *Iliad* and *Odyssey*. Iron, gold, and bronze are repeatedly mentioned as indicative of wealth at the time of the Trojan war, which was fought at the transition of the Grecian bronze and iron ages, namely, *c.* 1400 to 1200 B.C.

It is an interesting observation that although Homeric agricultural implements were made of iron, the weapons were made of bronze with but two exceptions.[6] The explanation appears to be that when iron was first made its quality was uncertain. Warriors, therefore, refrained from using it until artificers had gained sufficient experience to produce a reliable metal.

It is said that Pheidon deposited in the Heræum certain iron bars that had, prior to his time, namely, B.C. 600, served as money ; and Waldstein, during his excavations at this site, discovered a bundle of iron rods which are believed to be the remains of Pheidon's gift.

The close of the Minoan age in Crete, *c.* 1400 to 1100 B.C., was the period of transition from bronze to iron in that island, and coincides with the Homeric age referred to above.

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[1] This is not actually the case, for the pillar is very firmly fixed in the ground.

[2] See Desch, *J. West Scotland Iron Steel Inst*, 1914, *21*, 176.

[3] Hadfield, *loc. cit.*

[4] Carulla, *J. Iron Steel Inst.*, 1908, I., 85.

[5] Montelius, *J. Iron Steel Inst.*, 1900, II., 514.

[6] Lang, *The World of Homer* (Longmans, 1910), chapter x.

The Romans, several centuries later, were skilled metallurgists, and developed to a remarkable extent the iron resources of their empire. Pliny, who compiled his famous *Natural History* nearly two thousand years ago, gives a considerable amount of information relative to the ores of iron and the properties of the metal. He discourses at considerable length upon the tendency of the metal to rust. "Nature," he writes,[1] "in conformity with her usual benevolence, has limited the power of iron by inflicting upon it the punishment of rust, and has thus displayed her usual foresight in rendering nothing in existence more perishable than the substance which brings the greatest dangers upon perishable mortality."

Pliny was also aware of the fact that some kinds of iron are less resistant to corrosion than others, and specifically mentions[2] a species that "is more particularly liable to rust." He further states[3] "that there is in existence at the city of Zeugma, upon the Euphrates, an iron chain by means of which Alexander the Great constructed a bridge across the river; the links of which that have been replaced are attacked with rust, while the original links are totally exempt from it."

This passage is remarkable as being a very early, if not indeed the earliest, statement of the relative corrodibilities of two kinds of iron.

The Britons were familiar with iron for at least a century prior to the Roman invasion of 55 B.C., South Wales being regarded as possibly the early home of the iron trade.[4] Cæsar mentions that the Britons used iron bars for currency, probably employing them for purposes of exchange, marriage portions, etc., in a similar manner to that in which the *loggoh kullutty*[5] (iron spade-like articles) of the natives of Central Africa or the iron ingots of Cambodia are used at the present day. Some of the bars may be seen in the British Museum,[6] whilst others, found near Worcester, are lodged in the Museum of that city.[7] In appearance they resemble swords, having a flat and slightly tapering blade, with blunt edges, and a rude kind of handle formed by turning up the edges at one end. Two of the bars were examined by Gowland, who gives the following analyses:—

	Bar A.	Bar B.
Carbon	trace per cent.	0·08 per cent.
Silicon	0·09 ,,	0 02 ,,
Phosphorus	0 69 ,,	0 35 ,,
Manganese	nil.	nil.
Nickel	0·23 ,,	nil.

Bar A, examined under the microscope, revealed a structure similar to that exhibited by meteoric iron, whilst Bar B resembled iron produced by direct reduction from ore and forged from a bloom.

The bars have lost somewhat in weight in consequence of rusting, but, making allowances for this, the weights appear originally to have approximated to 309 grams or to some multiple or sub-multiple of this amount. In all, six different denominations have been found, of the following presumed standard weights:—

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[1] Pliny, book 34, chap. xl. Translated by Bostock and Riley, 1857.

[2] Pliny, *ibid.*, chap. xli.

[3] Pliny, *ibid.*, chap. xliii.

[4] Wilkins, *The History of the Iron, Steel, Tinplate, and Other Trades of Wales* (Merthyr Tydfil, 1903).

[5] Schweinfurth, *The Heart of Africa* 1868–71, (Sampson Low), vol i. p. 125.

[6] R. A. Smith, *Proc. Soc. Antiq.*, 1905, 20, 179; 1915, 27, 69, 76; *Archæological J.*, 1913, 19, (4), 421.

[7] Friend, *Trans. Worcestershire Nat. Club*, 1919, 7, Part 2.

Quarter unit	77 grams.
Half unit	154·5 ,,
Unit	309 ,,
Unit and one half	463·5 ,,
Double unit	618 ,,
Quadruple unit	1236 ,,

The reason for choosing the third weight, namely 309 grams, as the unit, and not the smallest weight, namely 77 grams, lies in the fact that in the Cardiff Museum is a bronze weight, which was found in association with enamelled bronze ornaments of Late Celtic character, near Neath in Glamorganshire. On the top of this weight is engraved the figure 1, and it weighs 309 grams. Another similar weight made of basalt, and also marked with a 1, is to be found (or was, prior to 1914) in the Mainz Museum.

These relics suggest that not merely was there a standard British weight corresponding to 309 grams, but that the same standard had been adopted throughout a large portion of Europe.

Boadicea was familiar with the use of iron, and the wheels of the early British war chariots were encircled with iron tyres, as is proved by remains found in Yorkshire, although it is very doubtful if they were fitted with scythes for laming hostile infantry, as was at one time believed. Undoubtedly many of the weapons wielded by Boadicea's troops against the Romans, A.D. 61, were also made with or strengthened by iron.

During Roman times a considerable iron trade was established in Britain. In A.D. 120 Hadrian established an arms factory at Bath, where iron from the Forest of Dean was worked.[1] But in the unsettled periods immediately succeeding the Roman occupation the industry lapsed, to be revived again shortly before the Norman Conquest. This latter invasion produced such an upheaval in the country that the trade again declined until about the fourteenth century.

In 1350 or thereabouts cast iron was produced in Sussex, which county was at that period one of England's most important centres of the iron industry. The introduction of cast iron made it possible to utilise our ores to far greater advantage than would otherwise have been the case, and constituted an important advance in the metallurgy of iron. It was in the little Sussex village of Buxted that

> "Master Huggett and his man John,
> They did cast the first cannon,"

and many of the village churches and churchyards are graced by iron tombstones which date back several centuries.

Prior to 1653 there were 42 iron forges in Sussex, and 27 furnaces. The industry employed some 50,000 men and furnished the main supply of ordnance for national defence. About this time, however, the fuel shortage began to be serious, the supply of charcoal becoming very scarce. Before 1664 the number of furnaces was reduced to 11, and in 1667 the forges numbered only 18. It was not until 1809, however, that the last Sussex forge was extinguished, namely at Ashburnham.

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[1] See Scrivenor, *History of the Iron Trade* (Longmans, 1854).

Towards the close of the eighteenth century there was considerable improvement in the trade in other parts of the country, for coke was now being used. In 1790 England possessed no fewer than 81 coke and 25 charcoal furnaces. In 1917 the total number of blast furnaces was 496, and of these an average of 324 were in blast at any moment during the year. The enormous growth in the output of pig iron since 1740 is well illustrated by the following table.

PRODUCTION OF PIG IRON IN THE UNITED KINGDOM.[1]

Year.	Pig Iron. Tons.	Year.	Pig Iron. Tons.
1740	17,350	1870	5,963,515
1788	63,300	1880	7,749,233
1806	243,851	1890	7,905,000
1820	368,000	1900	8,908,570
1830	677,417	1910	10,216,745
1840	1,396,400	1913	10,260,315
1850	2,249,000	1918	9,072,000
1860	3,889,752	1919	7,398,000

The output for 1913 constituted a record up to the outbreak of war in 1914, in which latter year the production fell by about 10 per cent. and remained at approximately 9 million tons until 1919—the latest returns available at the time of writing,—in which year there was a marked decline in production.

The world's production in tons of coal, iron ore, pig iron, and steel for 1913—the last year for which complete records are available—is given in the following table,[2] and indicates the enormous quantities of fuel, ore, and metal annually handled, and their consequent importance to modern civilisation.

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[1] Compiled from data supplied by the *Statistical Reports* for 1916 and 1918 of the Iron, Steel, and Allied Trades Federation, and from the *J. Iron Steel Institute.*

[2] *Statistical Report* for 1916.

[TABLE.

Country.	Coal.	Iron Ore.	Pig Iron	Steel.
United Kingdom .	287,412,000	15,997,328	10,260,315	7,663,876
Canada . . .	15,012,000	307,634	1,015,118	1,042,503
Newfoundland .	. .	868,102	. .	. .
Australia . .	11,322,000	. .	46,563	. .
New Zealand . .	1,888,000	. .	. .	. .
Union S. Africa .	10,733,000	. .	. .	. .
India . . .	16,208,000	370,845	. .	. .
Tunis (exports to U.K.) . . .	. .	279,071	. .	. .
Austria-Hungary	* 17,519,000 † 36,179,000	5,318,631	2,380,864	2,625,879
Belgium . .	22,842,000	149,450	2,484,690	2,466,630
France . . .	40,844,000	21,918,000	5,311,316	4,635,166
Algeria . . .	. .	1,349,000	. .	. .
Holland . . .	1,873,000	. .	. .	. .
Germany . .	*191,511,000 † 87,116,000	35,941,285	19,291,920	18,958,819
Italy. . . .	701,000	603,116	426,755	933,500
Russia . . .	33,369,000	8,077,000	4,557,000	4,837,000
Portugal . . .	. .	49,182	. .	. .
Spain . . .	4,293,000	9,861,668	424,774	241,995
Norway . . .	. .	78,936	. .	. .
Sweden . . .	364,000	7,475,571	730,257	590,887
United States . .	569,960,000	61,980,437	30,966,152	32,321,618
China . . .	2,185,000	. .	. .	. .
Brazil . . .	. .	. .	. .	. .
Greece . . .	. .	310,078	. .	. .
Total . .	1,351,331,000	170,935,334	77,895,724	76,317,873

* Coal. † Lignite.

CHAPTER II.

THE MINERALOGY OF IRON.

NEXT to aluminium, iron is the most abundant and widely distributed metal in the crust of the earth.[1] It is seldom found free in nature owing to the extreme readiness with which it combines with moist air to form the hydrated oxide known as rust. Such ferruginous minerals as contain a sufficiently high percentage of iron, possess a suitable chemical composition, and occur in nature in large quantity, are termed *ores* and are used for the commercial extraction of iron. Owing to their economic importance the ores of iron have been studied with unusual care, and the suitability of the more important types for metallurgical purposes is discussed in Part III. of this volume.

The various minerals containing iron may be conveniently classified according to the state of the chemical combination of the iron, and the system adopted here is schematically represented as follows:—

1. Native Iron.
2. Oxides
   - Magnetites, Fe_3O_4.
   - Hæmatites
     - Red, anhydrous ores, Fe_2O_3.
     - Red-brown, hydrated ores, $Fe_2O_3.xH_2O$.
3. Carbonates—spathic ores, $FeCO_3$.
4. Sulphides—pyrites.
5. Miscellaneous Minerals.

NATIVE IRON.

As has already been mentioned, iron seldom occurs in the free state in nature on account of the readiness with which it oxidises on exposure to a moist atmosphere. Native iron is frequently of meteoric origin,[2] and contains varying quantities of alloyed nickel.[3] Usually the nickel ranges from 1 to 10 per cent., but the metallic particles contained in the meteorite which fell near Middlesbrough in 1881 possessed no less than 21·32 per cent. of nickel,[4] whilst the Santa Catharina siderite[5] contained 34 per cent., and Oktibbeha County siderite 60 per cent. of nickel. Owing largely to the presence of this element, meteoric iron presents a whitish fracture, and resists corrosion extraordinarily well.[1]

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[1] See this series, Vol. I., 3rd edition, p. 8.

[2] Meteorites consisting mainly of metallic iron alloyed with nickel are termed *siderites*. *Siderolites* differ from the above in containing stony matter as well as native metal. *Aerolites* consist essentially of stony matter.

[3] On the structure of meteoric iron see Fraenkal and Tammann, *Zeitsch. anorg. Chem.*, 1908, 60, 416; Osmond and Cartaud, *Compt. rend.*, 1903, 137, 1057.

[4] See *J. Iron Steel Inst.*, 1883, II., 716.

[5] Discovered in 1875. Described by Lunay, *Compt. rend.*, 1877, 85, 84. Regarded by some as of terrestrial origin.

The following analyses of meteorites, arranged in chronological order, will prove of interest as illustrating the variation in composition that has been met with by different investigators :—

Number . .	1.	2.	3.	4.	5.	6.	7.
Date when found	1913	1906	1906	1904	1892	1881	1876
Locality . .	Mt. Edith, West Australia.	Muonion-alusta, North Sweden	Perry-ville, Missouri.	Okauo, Japan.	Williams-town, Kentucky	Middles-bro', (Yorks)	Rowton, (Shrop-shire).
Weight . .	355 lbs.	16·5 lbs	38 lbs	10·4 lbs	68·2 lbs.	3 lbs. 8½ oz	6·85 lbs
Density .	7·86	7·9	7·61	7·98	8·1	..	..
Analysis :—							
Fe . .	89·500	91·20	89·015	94·85	91·54	76·99	91·15
Ni .	9·450	8·02	9·660	4·44	7·26	21·32	8·67
Co .	0·625	0·69	0·545	0·48	0·52	1·69	0·34
Cr . .	..	0·01	..	.	0·05		..
Cu . .	0·013	0·01	0·025	trace	0·03	.	trace
P . . .	0·316	0·05	0·365	0·23	0·12	..	..
C . .	0·017	..	0·015	..	0·004	.	..
Si . .	0·005	..	0·003	..	trace	..	..
S . . .	0·005	..	0·002	..	0·17	..	..

1. Foote, *Amer. J. Sci.*, 1914, 37, 391.
2. Hogborn, *Zeitsch. Kryst. Min*, 1914, 53, 408.
3. G. P. Merrill, *Proc. U.S. National Museum*, 1912, 43, 595 ; *Engineering and Mining J.*, 1913, 95, 350. 0·370 per cent. of ferric oxide was also present.
4. Chikashige and Hiki, *Zeitsch anorg. Chem.*, 1912, 77, 197.
5. E E. Howell, *Amer. J. Sci*, 1908, (4), 25, 49
6. Flight, *Jahrb. Min.*, 1884, 2, Ref. 28. The analysis of the metallic portion is given only. Of the remaining constituents 60 per cent. were soluble silicates and 40 per cent. insoluble.
7. See Flight, *Jahrb. Min.*, 1884, 2, Ref. 28 ; also *An Introduction to the Study of Meteorites*, 1908, p. 66.

It will be observed that all of the meteorites contain, in addition to nickel, a small quantity of cobalt, whilst the carbon content is extremely small. Carbon is sometimes present in meteoric iron in the form of minute diamonds.[2] The Rowton specimen is interesting as being the first siderite observed to fall in Great Britain, and may be seen in the Natural History Museum, South Kensington. The Perryville siderite is the first recorded instance of the presence of ruthenium in meteoric iron. In addition to traces of this element, traces of iridium, palladium, and platinum were detected.

The largest known meteoric mass is the Ahnighito, brought by Peary from Western Greenland in 1895. It now lies in the New York Museum, and weighs 36½ tons.

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[1] A magnificent collection of meteorites is contained in the South Kensington Natural History Museum, London, and a full account of them is given in the little handbook, printed by order of the trustees, entitled *An Introduction to the Study of Meteorites*, 1908 The reader is also referred to *Meteorites*, by Farrington (Chicago, 1915), and to *Handbuch der Mineralchemie*, by Rammelsberg (Leipzig, 1860).

[2] See Friedel, *Compt. rend.*, 1892, 115, 1037 ; Foote, *Amer. J. Sci.*, 1891, 42, 413.

In 1870 Nordenskiöld found some large masses of iron containing 1 or 2 per cent. of nickel at Ovifak in Western Greenland.[1] They weighed 9000, 20,000, and 50,000 lbs. respectively, and, though formerly regarded as meteoric, are now believed to be of terrestrial origin,[2] having been reduced from basalt by some natural process.

Grains of **Awaruite**, an alloy of nickel and iron, have been found in the sands of certain New Zealand and Canadian rivers, containing as much as 67·6 per cent. nickel.[3] **Souesite**[4] and **Josephinite**[5] are names given to similar alloys,[6] the former from British Columbia, and the latter found enclosed within water-worn pebbles in Josephine and Jackson Counties, Oregon, U.S.A. An alloy containing some 7 per cent. of nickel is frequently termed **kamasite**[7]; one corresponding to the formula Fe_5Ni_3 (38 per cent. Ni), **taenite**[8]; and FeNi (60 per cent. nickel), **octibbehite.**[9]

Native iron has been found in the coal measures of Missouri,[10] at depths ranging from 35 to 51 feet, which preclude the possibility of meteoric origin. Most probably the metal has been formed by reduction. The fragments of iron weighed on the average 0·5 gram, but a larger mass of 45·4 grams was also discovered. The metal was soft (hardness on Mohs' scale[11] 4), malleable, and, on fracture, silver-white in appearance. Different specimens yielded the following analyses :—

	I.	II.	III.
Fe . .	99·16	99·39	97·10 per cent.
SiO_2 .	0·37	0·31	1·65 ,,
C . .	0·065	?	?
P . .	0·207	0·13	0·176 ,,

In no case was cobalt, nickel, or copper present. The densities ranged from 7·43 to 7·88.

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[1] Analyses are given by Winkler (*Zeitsch. Kryst. Min.*, 1903, 37, 286) of a weathered sample of the metal. F. Wohler (*Jahrb. Min*, 1879, p. 832) gives an analysis of the metal itself See also Nordenskiold, *Compt. rend.*, 1893, 116, 677; Moissan, *ibid.*, p. 1269; Tornebohm, *Jahrb. Min.*, 1879, p 173.

[2] C. Winkler, *Chem. Zentr.*, 1900, I, 1307; *Zeitsch. Kryst. Min.*, 1903, 37, 286; C. Benedicks, *Metallurgie*, 1911, 8, 65.

[3] Skey, *Trans. N. Zealand Inst*, 1885, 18, 401; Johnston, *Summary Report Geol. Survey, Canada, for 1910*, 1911, p. 256

[4] G. C. Hoffmann, *Amer. J. Sci.*, 1905, (4), 19, 319.

[5] Melville, *Amer. J. Sci.*, 1892, (3), 43, 509.

[6] These names might very well be dispensed with, and all three alloys—Josephinite, Souesite, and Awaruite—known by the earlier name of Awaruite. See Jamieson, *Amer. J. Sci.*, 1905, (4), 19, 413.

[7] See Cohen and Weinschenk, *Jahrb. Min.*, 1892, II., Ref. 244.

[8] See Fletcher, *Min. Mag.*, 1908, 15, 147; 1899, 12, 171.

[9] Taylor, *Amer J. Sci.*, 1857, 24, 293.

[10] Allen, *Amer. J. Sci.*, 1897, (4), 4, 99.

[11] Mohs' scale of hardness is indicated by the following substances, arranged in order of their ascending hardnesses :—

1. Talc.
2. Rock salt.
3. Calcite.
4. Fluorspar.
5. Apatite.
6. Orthoclase.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

The dust showers which at various times have fallen in Italy and Sicily frequently contain grains of metallic iron. Similar grains are found in the sands of the Sahara desert, and it is not improbable that the dust showers referred to are terrestrial phenomena, the sand being transported from the desert by cyclones.[1] In numerous other places small grains of iron have been found, and a terrestrial origin is ascribed to the metal in all of these cases.

Traces of metallic iron have been found [2] in basaltic rocks, such as those from the Giant's Causeway. They were detected by pulverising the rock, separating the magnetic grains, and subjecting them to the action of an acidulated solution of copper sulphate in the field of a microscope. Small depositions of copper in crystalline bunches indicated the presence of traces of native iron. Grains of native iron mixed up with limonite and organic matter have been found in petrified wood.[2] Iron crystallises in the cubic system, its cleavage being octahedral. Hardness 4·5; density, when pure, 7·86 (mean value).

A specimen of what may be termed "native cast iron" is stated by Inostzanzeff[3] to have been obtained from Russian Island, Vladivostok. Analysis showed it to contain

Iron	93·87 per cent.
Carbon (free)	2·87 ,,
Carbon (combined) . . .	0·33 ,,
Silicon	1·55 ,,

and small quantities of manganese, sulphur, etc. In micrographical structure, as well as in composition, the metal resembled cast iron, and it is supposed to have been formed by the interaction of coal and iron ore in a sedimentary rock induced by the heat from an intruded igneous rock.

A carbide of iron occurs as **Cohenite** $(Fe, Co, Ni)_3C$, in meteorites in distorted crystals, probably belonging to the cubic system.[4] It possesses a metallic lustre, is tin-white in colour when pure, becoming bronze-yellow upon exposure to air. Hardness 5 5 to 6; density 6·977.[5]

MAGNETITES.

Magnetite or **Lodestone,** Fe_3O_4 or $Fe_2O_3.FeO$, is the richest form of iron ore, containing when pure 72·4 per cent. of metal. Magnetite crystals are usually octahedra and dodecahedra, and are well developed in some chlorite schists. Good crystals have been found at Nornmark in Wermland. They are not scratched by a knife, their hardness on Mohs' scale ranging from 5·5 to 6 5, and their density from 4·9 to 5·2. Magnetites in the massive form are widely distributed, occurring in large quantities in India, Sweden, South Africa, Russia,[6] Siberia, Canada, and the United States. The Indian deposits [7] are located in the Madras Presidency, and are estimated at milliards of tons, but, owing to the scarcity of fuel, they have not been worked on a large scale. Of even greater magnitude are the American deposits in the neighbourhood of Lake Superior, which form the largest source of iron ore in the world. The metal in these ores ranges from 55 to 65 per cent.

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[1] Tacchini, *Compt. rend.*, 1880, 90, 1568.

[2] See Dana, *A System of Mineralogy* (Wiley, 1889), p. 16.

[3] Inostzanzeff, *Zeitsch. Kryst. Min.*, 1911, 50, 61.

[4] Spencer, *Min. Mag.*, 1902, 13, 296.

[5] Weinschenk, *Annalen K. naturhist. Museum*, Wien, 1889, 4, 94; Cohen and Weinschenk, *ibid.*, 1891, 6, 131.

[6] See Bogdanowitsch, *Stahl und Eisen*, 1912, 32, 990.

[7] See V. Ball, *Economic Geology of India.*

Some of the Swedish magnetites are very pure,[1] and are used in the manufacture of Swedish iron, which is noted for its high quality. As the name implies, magnetite possesses magnetic properties, sometimes exhibiting polarity. Specimens possessing the most powerful magnetism are found in Siberia and the Harz Mountains. It is on account of this property that the ores can be concentrated magnetically on a commercial scale. The colour varies from brownish grey to iron black. When compact, the mineral is opaque, but translucent dendrites have been found in mica, exceedingly thin, and ranging in colour from almost colourless to pale smoky brown. The mineral has a subconchoidal fracture which is bright when fresh. It is fusible only with difficulty; soluble in hydrochloric acid.

According to Nicander, the name **magnetite** is derived from Magnes, the shepherd, who discovered it in consequence of his shoe-nails being drawn from their soles as he drove his flocks to pasture. More probably the name is derived from Magnesia, a town in Asia Minor, where magnetite was discovered.

A pseudomorph of magnetite has been described under the name of **dimagnetite**,[2] which crystallises in elongated prisms, black in colour and possessed of feeble lustre. It occurs implanted on crystals of magnetite, is magnetic, and probably has an analogous composition to magnetite. Several varieties of magnetite are known in which the ferrous or ferric, or even both, irons are more or less replaced by other metals. The more important of these are:—

Chromite, chromo-ferrite, sidero-chrome, or **chrome iron ore,** $FeO.Cr_2O_3$, in which the ferric oxide of magnetite is replaced by chromium sesqui-oxide. This ore constitutes the main source of chromium compounds, and, on account of its infusibility,[3] is sometimes utilised in furnaces for linings. Chromite is widely distributed, being found in Sweden,[4] Germany, Northern Caucasus,[5] India, Canada, the United States,[6] Rhodesia, New Caledonia, Turkey and Greece. Rhodesia yields more chrome iron ore than any other country, the production in 1912 amounting to 61,857 tons.[7] Chromite occurs in small quantities in most meteorites.[8] The ore resembles magnetite in appearance, having a black colour and a similar crystalline form.[9] It sometimes exhibits magnetic properties; hardness 5·5; density 4·3 to 4·6. It leaves a brown streak.

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[1] See Fuchs and de Launay, *J. Iron Steel Inst.*, 1894, I., 408, from *Traité des Gîtes Minéraux et Metallifères*, vol. i. pp. 708–712.

[2] Shepard, *Amer. J. Sci.*, 1852, (2), 13, 392.

[3] W. H. Patterson gives the melting-point of various chrome iron ores as ranging from 1545° to 1730° C. (*J. Iron Steel Inst.*, *Carnegie Schol. Memoirs*, 1914, 6, 238).

[4] See Tegengren, *Teknisk Tidskrift*, 1913, 43, 26.

[5] In the province of Kuban (Besdorodko, *Jahrb. Min.*, 1912, 34, 783).

[6] See report by Phalen, *U.S. Geol. Survey*, 1912; *Mineral Resources for* 1911, Part I., p. 979.

[7] Diller, *U.S. Geol. Survey, Mineral Resources for* 1913, Part I., p. 57 *et seq.*

[8] See analyses by Tassin, *Proc. U.S. National Museum*, 1908, 34, 685.

[9] On the origin of chromite see Pratt, *Amer. J. Sci.*, 1899, (4), 7, 281.

Acids do not attack chromite, but fusion with alkali hydrogen sulphates effects its decomposition. The Grecian ore, which occurs mainly in the Eastern Provinces and in the island of Skyros, is particularly refractory on account of the impurities it contains. Chrome iron ores containing some Fe_2O_3 may be regarded as mixtures of chromite and chromitite (p. 17). Platiniferous chromites are found in the Urals.[1]

Franklinite, $(Mn, Zn)O.Fe_2O_3$, is a magnetite in which the ferrous oxide is more or less replaced by zinc oxide and manganous oxide, which latter imparts a red colour to the ore. It is found in New Jersey, U.S.A., in large black octahedra, and in recognition of its zinc content is frequently called **zincite.** It is slightly magnetic. Hardness 5·5 to 6·5. Density 5·07 to 5·2. It is infusible in the blowpipe; soluble in concentrated hydrochloric acid.[2]

Ilmenite, titanic iron ore or ferrous titanite, $FeO.TiO_2$, is the ore in which titanium was first discovered. It takes its name from the Ilmen Mountains. In the massive form it occurs in Norway, whilst in Canada, the United States, India, and New Zealand, it is met with as sand. Well-formed crystals are rare, but differ from those of the preceding minerals in that they belong to the hexagonal system, and not to the cubic. They have almost the same angles (viz. 94° 29′) as those of hæmatite (viz. 94° 0′) (*vide infra*).

Ilmenite is faintly but decidedly magnetic; hardness 5·5; density 4·8. It usually contains from 26 to 30 per cent. of titanium, although specimens have been found containing considerably more and considerably less than this amount. The density falls with increase of titanium, and the axial ratio $a : c$ likewise falls, indicating an increase in the vertical axis, c. This is well illustrated by the following data:—[3]

TiO_2. Per cent.	Density.	Axial Ratio, $a \cdot c$.
5·66	5·041	1 : 1·368
21·58	4·910	1 : 1·3716
47 68	4·852	1 : 1·3772
49·68	4 614	1 : 1·379
57·23	..	1 : 1·3851

The formula for ilmenite may also be written as $Fe_2O_3.Ti_2O_3$, and, on account of the difficulty of determining the state of oxidation of the titanium, it is not easy to decide, from chemical considerations alone, which formula is correct,[4] although the balance of chemical evidence appears to support the formula $FeO.TiO_2$.[5] The mineral crystallises, however, in the rhombohedral-tetartohedral division of the hexagonal system, and the axial ratio in no case[1] lies between that of hæmatite, Fe_2O_3,

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[1] Vogel, *Jahresber.*, 1873, p. 291; Duparc and Rubies, *Anal. Fis. Quim.*, 1913, 11, 367.

[2] Berthier, *Ann. Mines*, 1819, 4, 489; Seyms, *Amer. J. Sci*, 1876, 12, 210. For analyses see Stone, *Zeitsch. Kryst. Min.*, 1888, 14, 291.

[3] Doby and Melczer, *Zeitsch. Kryst. Min.*, 1904, 39, 526; Sustschinsky, *ibid.*, 1903, 37, 57.

[4] Manchot and Heffner, *Zeitsch. anorg. Chem.*, 1912, 74, 79.

[5] Koenig and Pfordten, *Ber.*, 1889, 22, 1485.

$$a : c = 1 : 1\cdot359,$$

and that of artificial titanium sesqui-oxide, Ti_2O_3, namely

$$a : c = 1 : 1\cdot316,$$

as it might be expected to do if it were an isomorphous mixture of $Fe_2O_3.Ti_2O_3$. This lends strong support to the view that the mineral is a titanite of ferrous iron, namely $FeTiO_3$.[2]

Other varieties of this mineral are known as **kibdelophane**[3] and **crichtonite,**[4] containing about 30 per cent. of titanium; **menaccanite,**[5] **hystastite**, and **uddevallite,** containing some 25, 15 to 20, and 10 per cent. of titanium respectively.

In **Geikielite,** from Ceylon, part of the iron is replaced by magnesium, thus $(Mg, Fe)O.TiO_2$. Density 3 976. Axial ratio,[6]

$$a : c = 1 : 1\cdot370.$$

It is isomorphous with **senaite,** $(Fe, Mn, Pb)O.TiO_2$,[7] which is likewise hexagonal, having axial ratios

$$a : c = 1 : 0\cdot997.$$

The crystals are black, thin crystals showing a greenish colour by transmitted light.

Bixbyite, $FeO.MnO_2$, occurs as brilliant black, cubic crystals, possessed of metallic lustre.[8] The composition of bixbyite might also be written as $Fe_2O_3.Mn_2O_3$. If such were correct, however, the mineral might be expected to crystallise in the hexagonal system, and belong to the hæmatite group.

Magnesio-ferrite or **magno-ferrite,** $MgO.Fe_2O_3$, is a variety of magnetite in which the ferrous oxide has been replaced by magnesia.[9] It crystallises in regular octahedra, and resembles magnetite in colour and general appearance. It is magnetic; hardness 6 to 6·5; density 4·57 to 4·65. It has been found around the fumaroles of Vesuvius. Hydrochloric acid attacks it only with difficulty.

In **Ludwigite** part of the magnesium oxide is replaced by ferrous oxide, and boric oxide is associated with the ferric oxide. Thus $(Mg, Fe)O.Fe_2O_3.B_2O_3$,[10] or perhaps $3MgO.B_2O_3 + FeO.Fe_2O_3$.

HÆMATITES.

The hæmatites consist essentially of ferric oxide, Fe_2O_3, and may be divided into two groups according as they are anhydrous or contain combined water. The former are usually red in colour, whence the word "hæmatite," from the Greek *haima*, blood.[1] The hydrated hæmatites vary in colour from red to dark brown, according to the amount of water they contain. Perfectly pure anhydrous ferric oxide contains 70 per cent. of iron, but the red hæmatites used in this country for commercial purposes average more nearly 60 per cent. of metal. The crystalline variety is known as **specular iron ore, iron glance** or **looking-glass ore,** and is obtained mainly from metamorphic rocks, but also occurs as a product of volcanic heat—as, for example, in Italy, some very beautiful crystals being found in the neighbourhood of Etna and Vesuvius. The ore is found in France, Switzerland, and elsewhere in Europe, fine specimens having been obtained from St Gothard. The island of Elba[2] has long been famous for its beautiful crystals, even Ovid (43 B.C. to A.D. 18) drawing attention to them. Other sources are India, Canada, Mexico, and the United States of America.

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[1] See the foregoing table.

[2] Penfield and Foote, *Amer. J. Sci.*, 1897, (4), 4, 108; *Zeitsch. Kryst. Min.*, 1897, 28, 596.

[3] Rammelsberg, *Pogg. Annalen*, 1858, 104, 497.

[4] Marignac, *Ann. Chim. Phys.*, 1845, 14, 50

[5] From Menaccan near Helston in Cornwall. Found as sand in a stream.

[6] Sustschinsky, *loc. cit.*

[7] Hussak and Reitinger, *Zeitsch. Kryst. Min.*, 1903, 37, 550; Hussak and Prior, *Min. Mag.*, 1898, 12, 30.

[8] Penfield and Foote, *Amer. J. Sci.*, 1897, (4), 4, 105.

[9] Rammelsberg, *Pogg. Annalen*, 1859, 107, 451.

[10] Schaller, *Amer. J. Sci.*, 1910, (4), 30, 146; Mallard, *Bull. Soc. Min.*, 1888, 11, 310; Renard, *Bull. Acad. roy. Belg.*, 1885, 9, 547.

The crystals belong to the hexagonal system; hardness 5·5 to 6·5; density 4·5 to 5·3.

Micaceous iron ore is the name given to crystalline ferric oxide exhibiting a foliated structure of dark grey scales that glisten like mica. No mica, however, is present in the ore. It is found in the Lake Superior district, U.S.A., but the finest crystals come from Elba. Prior to the European war of 1914 micaceous ore was raised in Devonshire[3] and sent to Germany under the name of **shining ore.** Hardness 6; density 5·2.

An octahedral variety is known as **martite.** It is black in colour, sometimes appearing bronzed, but it has a reddish brown streak, which serves to distinguish it from magnetite, as also the fact that it is not magnetic, or at best only very feebly so. Hardness 6 to 7; density 4·35 to 5·33. Martite is probably a pseudomorph of magnetite—that is, it may have been derived from that mineral by oxidation, without appreciable alteration of the crystalline form. This change may be effected in the laboratory by prolonged heating of magnetite in the blowpipe.[4]

A hard, compact, nodular variety of hæmatite is found in Cumberland in the carboniferous limestone series of Cleator Moor, in Furness in North Lancashire, and to a less extent in Devonshire, and from its shape is termed **kidney ore.** The ore is very low in phosphorus, and is particularly valuable for making Bessemer pig iron—that is, pig iron suitable for the manufacture of steel by the acid Bessemer process. The Furness ore appears to have been worked in prehistoric times.

The colour of the ore varies from red to iron-black, and exhibits quite a metallic appearance. When scratched or powdered the colour becomes bright red. The Brixham ore is used in the manufacture of paint.

Softer, earthy forms of red hæmatite are also found in Cumberland, the colours of which vary from bright to dull red.[5] They are known as **ruddle** or sometimes as **puddle ore,** as they are used for lining the hearths of puddling furnaces. Spain and America likewise yield large quantities of earthy red hæmatite.

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[1] The jeweller's *bloodstone* is not hæmatite, however, but a variety of chalcedony.

[2] See H. Scott, *J. Iron Steel Inst.*, 1895, I., 141.

[3] See J. S. Martin, *Trans. Manchester Geol. Soc.*, 1895, 23, 162; Worth, *Trans. Devon Assoc.*, 1875, 7, 225.

[4] Friedel, *Bull Soc. franc. Min.*, 1894, 17, 150.

[5] See J. L. Shaw, *J. Iron Steel Inst.*, 1892, I., 306.

Immense deposits of a variety known as **red fossil ore** occur in the United States, containing from 30 to 50 per cent. of iron and from 0·4 to 0·7 of phosphorus. **Red ochre** is another form of anhydrous ferric oxide, but the term is also used for a variety of turgite.

Hæmatite ores, rich in iron, are found in China.[1]

The problem of the origin of the hæmatites has been the subject of much discussion. The view is largely held that, in the instance of Cumberland and Lancashire, the hæmatite has gradually replaced the calcium carbonate, molecule by molecule. This is supported by the fact that the ore and rock appear to have "grown together," as the miners express it, the ore gradually passing into the limestone and possessing precisely similar stratifications and dip. Again, casts of mollusca and other fossils characteristic of carboniferous limestone have been found in the hæmatite, as well as crystals of hæmatite pseudomorphic with calcite.[2] It does not follow, however, that all hæmatites are necessarily formed in this way; local conditions must always be taken into consideration. Admitting for the sake of argument the foregoing or metasomatic origin of the north-country hæmatites, the next point of interest is to determine how this molecular substitution could have taken place. The formation of anhydrous ferric oxide would appear to postulate an application of heat in some way or other, and volcanic activity seems to be the most easy way by which such heat might be forthcoming. It seems possible, therefore, that the carboniferous strata were overlain by ferruginous Permian and Triassic deposits. Waters, charged with ferrous iron in solution by passage through these deposits, percolated through the limestone beneath, dissolving out the calcium carbonate and leaving ferrous carbonate. This slowly oxidised, and under the influence of heat yielded anhydrous ferric oxide.[3]

Red hæmatite has been found at Torquay, apparently pseudomorphic with pyrites, which is remarkable, for, although pyrites is frequently oxidised to limonite, it is indeed rarely that it is converted into anhydrous hæmatite. It is suggested that pyrites was converted into ferric chloride by the action of sea water, and that this reacted with limestone to yield anhydrous ferric oxide[4] in some such manner as that indicated above.

Chromitite occurs as dull, magnetic crystals, resembling magnetite, and has a mean composition represented by the formula $Fe_2O_3.Cr_2O_3$.[5]

As already stated, **hydrated hæmatites**[6] usually differ from the anhydrous in colour. As the percentage of water increases the colour changes from bright red to dark brown. **Turgite,**[7] or **hydro-hæmatite,**

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[1] A. Bordeaux gives a description of the Chinese mineral resources, *Trans. Canadian Mining Institute*, 1913, 16, 351.

[2] See Goodchild, *Trans. Cumberland Assoc.*, 1882, Part vii, p. 116; *Proc. Geol. Assoc.*, 1889, 11, 62; Kimball, *Amer. J. Sci.*, 1891, (3), 42, 231; Shaw, *Trans. Fed. Inst. Min. Eng.*, 1892, 3, 580; Kendall, *The Iron Ores of Great Britain and Ireland*, 1893, p. 303.

[3] Compare de Launay, *Compt. rend.*, 1897, 124, 689; *Ann. Mines*, 1897, 12, 178; Kimball, *Amer. J. Sci.*, 1891, 42, 231.

[4] Solly, *Min. Mag.*, 1889, 8, 183.

[5] Jovitschitsch, *Bull. Soc. franç. Min.*, 1912, 35. 511; *Monatsh.*, 1909, 30, 39.

[6] For a detailed study of these see Posnjak and Merwin, *Amer. J. Sci.*, 1919, 47, 311.

[7] See Samoiloff (*Zeitsch. prakt. Geol.*, 1903, 11, 302) for an account of the turgite ores of Russia.

$2Fe_2O_3.H_2O$, is a common ore which contains about 5 per cent. of water. It occurs as an earthy deposit frequently known as **red hæmatite** and as **red ochre**; it is also found in a compact, fibrous condition, and in botryoidal and stalactitic forms, similar to limonite, for which ore it has frequently been mistaken. It may usually be distinguished by its redder colour, its red streak, and its greater hardness. Hardness 5 to 6; density 3·56 to 4·7. When heated in a tube it splinters in a characteristic manner, which serves to distinguish it from limonite and other ores of analogous composition.

One of the most important of the brown hæmatites is **limonite,** $2Fe_2O_3.3H_2O$, which contains some 15 per cent. of water. It is found in mammillary and stalactitic forms of various shades of brown. It also occurs in concretionary form. The name "limonite" is derived from the Greek *leimon,* a meadow, and was first used [1] to designate the bog ores (see below).

Limonite is found in relatively small quantity in the Forest of Dean, where iron ores were worked in Roman times. It is called **brush ore,** locally, when it occurs in stalactitic, reniform or compact masses, containing some 80 per cent. of ferric oxide or 56 per cent. of metallic iron; and **smith ore** when incoherent and containing only 54 to 58 per cent. of ferric oxide (38 to 41 per cent. of iron).[2]

Fine varieties of earthy limonite, more or less contaminated with clay, etc., are known as **ochres, siennas,** and **umbers,** the colour of the last-named being darker, probably on account of the presence of manganese. Ochres and umbers are found in several parts of England, notably in Derbyshire, Oxfordshire, Devon, and Cornwall. The name **umber** is derived from Umbria, a town now known as Spoleto, in Italy, where umber was first obtained. **Sienna** likewise received its name from the Italian town of the same name. **Turkey umbers** are acknowledged to be the finest. They really come from Cyprus, but received their name through having been imported from Constantinople at a time when their true origin was unknown. Siennas are found in the Harz, in Tuscany, and in America.[3]

Large deposits of brown hæmatite occur in Northamptonshire, the beds extending into Lincolnshire and Oxfordshire. The ore is abundant in the U.S.A.

A fibrous variety of limonite is known as **wood iron ore.**

Goethite, $Fe_2O_3.H_2O$, is named after the famous German poet, Goethe, who was also a mineralogist of considerable repute. It occurs as black or brown rhombic crystals, the parameters of which are

$$a : b : c = 0{\cdot}66 : 1 : 1{\cdot}089.$$

The crystals are usually blackish brown in colour, but appear red by transmitted light. They yield a red streak; hardness 5 to 5·5; density 4·0 to 4·4.

Goethite contains some 63 per cent. of iron. It has been found in Somerset, Cornwall, and Gloucester, some very fine crystals coming from Lostwithiel in Cornwall. On the Continent it has been found in numerous districts such as Saxony, Nassau, etc., whilst quantities are present in U.S.A. Other names for the ore are **pyrrho-siderite,** and **rubinglimmer.** Acicular varieties are known as **needle iron stone** and **onegite,** the latter occurring in quartz in a similar manner to the penetrating needles of rutile so frequently met with. Aventurine oligoclase or sunstone owes its beautiful internal reflective powers to the presence of crystals of hæmatite or Goethite. A velvety variety of Goethite is known as **sammet-blende,** from the German *Sammet,* velvet. A variety of Goethite occurs as fine red scales which may be recognised under the microscope by their dichroism. This serves also to distinguish them from hæmatite. **Lepidocrite** is a form of Goethite presenting a fibro-scaly structure.

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[1] By Hausmann, *Handbuch Min.,* 1813.

[2] J. W. Watson, *The Geologist,* 1858, I, 217, 265.

[3] Classification and analyses of ochres are given by Gin, *Compt rend. Assoc franç. Av. Sci.,* 1895, 23, (2), 512. For analyses of ochres, umbers, and siennas see Hurst, *Chem. News,* 1889, 59, 172.

Hydrogoethite, $3Fe_2O_3.4H_2O$, has been found in Russia [1] in thin red veins in limonite. Under the microscope it is seen to consist of transparent plates or needles, with a distinct cleavage.

Limnite,[2] $Fe_2O_3.3H_2O$, and **xantho-siderite,** $Fe_2O_3.2H_2O$, closely resemble limonite in appearance, but are usually slightly lighter in colour and contain more water. The former name is derived from the Greek *limne,* a marsh, and the ores are frequently termed **bog** or **lake ore.** They are found in different localities, such as Ireland, Sweden, and America. They consist of deposits of hydrated ferric oxide, probably oxidised from ferrous salts and thrown out of solution by lowly organisms.[3] Large deposits of chromiferous brown hæmatite, containing about 2 per cent. of chromium, occur in Greece [4] and in Cuba.[5] Xanthosiderite also occurs in crystalline form as golden needles.[6]

Laterite is a similar mineral, which is found in India, and contains varying quantities of iron and aluminium hydroxides.[7]

Minette is a brown hæmatite found in Luxemburg, Lorraine, and Rhineland. It consists of oolitic grains bound together by a cement of chalk, clay, or silica, and may contain anything from 0·5 to 2·0 per cent. of phosphorus.[8] Minette is therefore largely used in basic steel manufacture. Brown hæmatites also occur in Russia, Poland, and China. Spain exports large quantities of hæmatite, which vary in colour from red in the almost anhydrous " rubio " ores to brown.[9]

Esmeraldaite, $Fe_2O_3.4H_2O$, occurs as pod-shaped inclusions in limonite in Esmeralda Country, Nevada. It is glassy, brittle, and possesses a yellowish-brown streak.[10]

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[1] Zemjatschensky, *Zeitsch. Kryst. Min.*, 1892, 20, 184; Samoiloff, *Zeitsch Kryst Min.*, 1901, 35, 272.

[2] Hermann, *J. prakt Chem* , 1842, 27, 53; J. D Dana, *Mineralogy*, 1868, p. 178

[3] Mumford has isolated an iron bacillus from Bridgewater Canal Tunnels, Worsley, Lancs. It precipitates iron as a mixture of oxides corresponding to bog ore (*Proc. Chem. Soc.*, 1913, 29, 79). See also Ellis, *Iron Bacteria* (Methuen, 1920); Raumer, *Zeitsch anal. Chem.*, 1903, 42, 590; *Iron Bacteria,* Harder, U.S. Geol. Survey, Professional Paper, No. 113, 1920.

[4] H. K. Scott, *J. Iron Steel Inst* , 1913, I , 447.

[5] See D. A. Willey, *Engineering Magazine,* 1913, 44, 867; J. S. Cox, *Bull. Amer. Inst. Mining Eng.*, 1911, p. 199, etc.

[6] Schmid, *Pogg. Annalen,* 1851, 84, 495.

[7] The word *laterite* is derived from the Latin *later,* a brick, since the mineral is often used for building purposes. For analyses of Indian laterite see Warth, *Geol Mag* , 1903, 10, 154; *Chem. News,* 1903, 87, 256; Bauer compares laterite and bauxite, Al_2O_3 $3H_2O$ (*Jahrb. Min* , 1898, ii. 163).

[8] See E. Schroedter, *J. Iron Steel Inst.*, 1889, I., 114; Wandesleben, *ibid.*, 1892, II 655.

[9] See Gill, *J. Iron Steel Inst.*, 1882, I., 63.

[10] Eakle and Schaller, *Bull. Dept. Geol., Univ. California,* 1901, 2, 315.

Many minerals are known in which ferric oxide is associated with other metallic oxides. Thus **Arizonite** or ferric titanite, $Fe_2O_3.3TiO_2$, is a dark, steel-grey mineral found in Arizona.[1]

Plumbo-ferrite, (Pb, Fe, Cu) $O.Fe_2O_3$, occurs in Sweden and elsewhere as hexagonal plates, in appearance like molybdenite, but yielding a pale red streak.[2]

Cuprous ferrite, $CuFeO_2$ or $Cu_2O.Fe_2O_3$, occurs as the mineral **delafossite** in Arizona.[3] It yields tetragonal crystals,

$$a : c = 1 : 1·94 ;$$

of hardness 5·5 ; black, with black streak, and non-magnetic.

CARBONATES.

These consist essentially of ferrous carbonate, $FeCO_3$, the purest form of which is **spathic iron ore**, which occurs both in the crystalline and the massive form. It is mined in Russia, Poland, the Balkans, Styria (Austria), Westphalia, and other parts of Germany. Its phosphorus content is low, but a considerable quantity of manganese is present. It is usually of a light brown colour and is possessed of a pearly lustre.

Styrian ore is obtained by quarrying, there being three kinds of veins, each several yards in thickness, the richest of which contains some 45 per cent. of metallic iron. In 1913 the production of ore amounted to 1,950,000 tons. It is estimated that the reserve of rich ore exceeds 200 million tons. It is practically free from sulphur, contains 0·01 per cent. of phosphorus and 2·23 per cent. of manganese.[4]

When crystalline, spathic ore is known as **siderite** or **chalybite**. The crystals belong to the hexagonal system

$$a = 0·81715,$$

and Cornwall has yielded many fine specimens.[5]

The theoretical percentage of metallic iron is 48·3. Hardness 3·5 to 4·5; density 3·7 to 3·9. It is brown or grey in colour and leaves a white streak. It readily oxidises when wet, being converted into limonite. Siderite from East Pool Mine, Cornwall, has been found containing cobalt, nickel, and even indium and rubidium in small quantity.[6]

The spathic ores of the Brendon Hills, West Somerset, were at one time worked largely for the manufacture of Spiegeleisen, as they contained some 12 per cent. of manganese, probably as carbonate, since ferrous and manganese carbonates are isomorphous.[7] The ore was worked in early times, perhaps by the Romans.

Staffordshire, West Yorkshire, and South Wales, yield an **argillaceous iron ore,** also known as **clay iron stone,** which contains some 10 per cent. of clay and from 30 to 40 per cent. of metallic iron. The Staffordshire ore has many local names ; when found in concretionary and globular masses it is called **sphaero-siderite.** It contains about 0 25 per cent. of phosphorus. **Cleveland iron stone** is one of the lowest grades of ore worked for iron in this country, and contains about 33 per cent. of metallic iron. It occurs in bands in the Middle Lias, the most important band being nearly 20 feet thick. Its phosphorus content is high, averaging 0·75 per cent. The bluish-green colour of the ore is due to ferrous silicate. Traces of zinc, gallium, nickel, and cobalt have been detected in the ore.[1]

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[1] Palmer, *Amer. J. Sci.*, 1909, (4), 28, 353.

[2] Igelstrom, *Jahrb. Min.*, 1896, I, Ref 15; from *Geol. För. Förh.*, 1894, 16, 594.

[3] Rogers, *Amer. J. Sci.*, 1913, (4), 35, 290.

[4] Nagel, *Iron Age*, 1914, 94, 482.

[5] Hutchinson, *Min. Mag.*, 1903, 13, 209.

[6] Hartley and Ramage, *Trans. Chem. Soc.*, 1897, 71, 533.

[7] See Morgans, *Trans. S. Wales Inst. Eng.*, 1870, 6, 79: *Quart. J. Geol. Soc.*, 1869, 25, 255.

Under the microscope the ore has an appearance suggestive of oolitic limestone, from which it has very probably been formed by molecular replacement of the calcium carbonate by ferrous carbonate, through the infiltration of waters containing the latter in solution.[2]

Beneath the brown hæmatite ores of Northamptonshire, an impure unaltered ferrous carbonate deposit occurs which is bluish or greenish-grey in appearance. The depth at which it lies represents the depth to which weathering or oxidation of the upper layers has occurred.

A clay iron stone containing some 35 per cent. of iron has been worked from Roman times, if not earlier, in the Weald of Sussex and Kent, charcoal being used as the fuel.

In Linlithgow and Lanark a clay iron stone occurs, impregnated with some 15 per cent. of carbonaceous matter. It is also found in North Staffordshire and in South Wales, and is known as **blackband iron stone.** The carbonaceous material present is often sufficient to allow the ore to be calcined without the further addition of fuel. A product containing 50 to 70 per cent. of iron is yielded.

An ore, containing magnesium carbonate in the proportion represented by the formula $2FeCO_3.MgCO_3$, is known as **sidero-plesite,** and has been found at Salzburg and in Nova Scotia.[3] **Pistomesite,** $FeCO_3.MgCO_3$, is found at Salzburg and Piedmont; and **mesitite,**[4] $FeCO_3.2MgCO_3$, at Piedmont. **Ankerite** is $2CaCO_3.MgCO_3.FeCO_3$.

SULPHIDES.

Iron pyrites, pyrite, marquisite, or **mundic** is the name given to a brass-coloured sulphide of iron to which the formula FeS_2 is usually ascribed. It often occurs in coal, and is known by miners as "brass" or "fool's gold." The spontaneous combustion of coal is frequently facilitated by the oxidation of iron pyrites to iron sulphate.[5] It often crystallises in cubes, the faces showing striations; but a very characteristic form is the pentagonal dodecahedron, usually termed the pyritohedron. Hardness 6 to 6·5; density 4·8 to 5·2. It leaves a greenish or brownish-black streak.

Peruvian pyrites is called **stone of the Incas,** because the ancient sovereigns of Peru attributed great virtues to it. Rings, amulets, mirrors, etc., were made of it. A century ago iron pyrites was used in this country to a considerable extent for feminine ornaments.[1]

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[1] See *The Geology of North Cleveland,* by Barrow (Mem. Geol Survey), 1885; *The Jurassic Rocks of Britain,* by Fox-Strangways (Mem. Geol. Survey), 1892, vol. i.; *The Iron Ores of Great Britain,* by Dick (Mem. Geol. Survey); also Scrivenor, *Min Mag.,* 1903, 13, 348.

[2] Sorby, *Proc. Geol. Polytech. Soc. West Riding,* 1856–7, 3, 460; *Proc. Geol. Soc.,* 1878–9, p. 56.

[3] Louis, *Trans. New Zeal. Inst.,* 1878–9, 5, 50.

[4] Breithaupt, *Pogg. Annalen,* 1827, 11, 170, 1847, 70, 148; Gibbs, *ibid.,* 1847, 71, 566, Ettling, *Annalen,* 1853, 99, 203.

[5] See this series, Volume VII

Pyrites occurs in rocks of all ages, both eruptive and sedimentary. In some cases it is evidently an original mineral, whilst in others it has been formed as a secondary product. Large quantities are found in Spain and are used in the manufacture of sulphuric acid, ferrous sulphate, and ferric oxide.

Iron pyrites is found in masses in the " twenty-inch " coal seam of the Forest of Dean, the masses being locally called " dogs." It is common in coal measures generally, having probably been formed by the reducing action of organic matter on waters charged with iron sulphate in solution. **Explosive pyrites** is the name given to a variety of pyrites found in Cork, which decrepitates violently upon application of gentle heat. The decrepitation is due to the presence of carbon dioxide under high pressures confined in minute cavities in the mineral.[2] Decrepitation usually begins at about 30° to 35° C., and it has been suggested that the explosions which sometimes occur in domestic grates may be due to the presence in the coal of this variety of pyrites. Frequently metals other than iron are associated with pyrites, chief among which are copper, nickel, cobalt, tin, gold, thallium, and silver.

When oxidised by weathering, the final product of pyrites is hydrated ferric oxide or rust, as stated above, but the method of oxidation depends upon circumstances. In the absence of carbon dioxide or carbonates, it is usual for oxidation to ferrous sulphate to first take place ; whence the mineral copperas or melanterite (see below). This, in course of time, oxidises to limonite. In the presence of carbon dioxide, however, it appears that the sulphate is not first formed, but the readily oxidisable carbonate, which is then converted into limonite.[3]

The presence of pyrites in mineral veins is frequently betrayed by the brown, rusty appearance of the upper parts of the deposits. This is well exemplified in the case of certain copper lodes, the iron of the contained copper pyrites having become converted into hydrated ferric oxide or rust. Such weathered zones are known as *gozzans,* and frequently present a cavernous or honeycombed appearance, due to the removal of pyritic material. In France the gozzan is termed the *chapeau de fer*, and in Germany *der eiserne Hut,* and an old adage states that [4]

" A Lode that wears no iron hat
Is never likely to be fat."

Marcasite or **white iron pyrites** is the name given to a rhombic variety of pyrites which occurs in concretions, known locally as " fairy balls " and " thunderbolts." Its crystallographic elements are [5]

$$a : b : c = 0{\cdot}7662 : 1 : 1{\cdot}2342.$$

The exterior of the nodules is often brownish, but when broken open they exhibit a radiating structure, usually pale yellow in colour, although pure marcasite is probably tin-white in appearance.[1] It rapidly tarnishes, and it is difficult to keep a fracture bright for museum purposes. Concretions of marcasite are found in chalk and in many clays. Hardness 6 to 6 5 ; density 4·7 to 4·8.[2]

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[1] See *Gems*, by Castellani, translated by Brogden (London, 1871).

[2] Blount, *Trans. Chem. Soc*, 1885, 47, 593.

[3] J. W. Evans, *Min Mag.*, 1900, 12, 371. See also Weed and Penrose, *J. Geology*, 1894, 2, 288.

[4] See Rudler, *A Handbook to a Collection of the Minerals of the British Islands*, 1905 (H.M S.O., Wyman, London).

[5] Prior, *Min. Mag.*, 1903, 13, 217.

Owing to its jagged outline marcasite is frequently known as **cockscomb pyrites** and **spear pyrites.**

Cobalt-nickel pyrites, $(Fe, Co, Ni)S_2$, has been found in Westphalia as small cubic crystals, steel-grey in colour, giving a greyish-black streak.[3] Density 4·7 ; hardness 5 to 5·5. **Iron nickel pyrites,** $(Fe,Ni)S_2$, occurs in Norway [4] and in the Sudbury district, Ontario.[5]

Pyrrhotite or **magnetic pyrites,**[6] Fe_7S_8 or $5FeS.Fe_2S_3$, is slightly redder than ordinary pyrites, from which, however, it may be readily distinguished, both on account of its magnetic properties and by its greater softness. Hardness 3·5 to 4·5 ; density 4·4 to 4 7. It occurs in Cornwall, in the lavas of Vesuvius, and in various other parts of Europe ; in Canada and the U.S.A. Two varieties are known : namely α-pyrrhotite, which is rhombic ; and β-pyrrhotite, which is hexagonal.

Troilite, FeS, is brownish in colour, and occurs in nodules in most meteorites containing iron. Hardness 4 ; density 4·7 to 4·8.[7]

Copper pyrites or **chalcopyrite,** $Cu_2S.Fe_2S_3$, is a brass-coloured sulphide which crystallises in the tetragonal system, but is isomorphous with pyrites, since its crystallographic elements are [8]

$$a : c = 1 : 0{\cdot}9853.$$

It yields a greenish-black streak ; hardness 3·5 to 4 ; density 4·1 to 4·3. It should contain some 34·6 per cent. of copper and 30·5 per cent. of iron ; but the percentage of iron is frequently higher, due probably to admixture of iron pyrites. Copper pyrites constitutes the most important copper ore in Cornwall. It is found also in Scotland, Sweden, and many other parts of Europe, in Australia, and the U.S.A. **Barnhardtite,** $2Cu_2S.Fe_2S_3$, resembles the previous ore in appearance, and receives its name from the place of its discovery, namely, Barnhardt's Land.[9] A varying mixture of sulphides of iron and copper is present in the mineral known variously as **erubescite, Bornite,** and **horseflesh ore.** The name Bornite was given in honour of Ignatius von Born, who had charge of the mineral collection in Vienna. It is not a happy name, however, since it is liable to be confused with bournonite, a thio-antimonite of copper and lead. Its copper content ranges from 50 to 70 per cent., and its iron from 6 to 20 per cent. When fresh its fracture is reddish brown, but it tarnishes rapidly, yielding peacock colours. Crystalline forms (cubic) occur in Cornwall, chiefly at the Carn Brea, Tincroft, and Cook's Kitchen mines near Redruth.

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[1] H. N. Stokes, *U S. Geol. Survey*, Bulletin No. 186, 1901.

[2] The chemical constitution of marcasite is discussed on p. 141. The surface characters of pyrites and marcasite, as examined through the microscope, are described by Poschl, *Zeitsch. Kryst. Min.*, 1911, 48, 572.

[3] Henglein, *Centr. Min.*, 1914, p. 129.

[4] Vogt, *Zeitsch. Kryst. Min.*, 1895, 24, 139.

[5] T. L. Walker, *Amer. J. Sci.*, 1894, (3), 47, 312.

[6] See Breithaupt, *J. prakt. Chem.*, 1835, 4, 265 ; Rammelsberg, *Pogg. Annalen*, 1864, 121, 337.

[7] Haidinger, *Sitzungsber. K. Akad. Wiss. Wien*, 1863, (2), 47, 283 ; Smith, *Amer. J. Sci* , 1855, 19, 156 ; Meunier, *Ann. Chim. Phys.*, 1869, 17, 36.

[8] Prior, *Min. Mag.*, 1903, 13, 217.

[9] Genth, *Amer. J. Sci.*, 1855, 19, 17 ; 1859, 28, 247.

Hardness 3; density 4·4 to 5·5. The usually accepted formula, Cu_3FeS_3, was based on analyses of Cornish crystals, but the Canadian mineral[1] corresponds more closely to Cu_5FeS_4.

In this connection it is interesting to note that Roman coins and other bronze objects which were thrown into certain thermal springs as votive offerings and have since been examined are found to have become partially converted into various sulphides of copper, including chalcopyrite and erubescite.

A double sulphide of copper and iron known as **Chalmersite,** $CuFe_2S_3$, occurs in the ore deposits of the Prince of Wales Sound, Alaska,[2] and in small quantities in Brazil.[3] It is massive, pale yellow in colour, and strongly magnetic, which latter property enables it to be readily separated from the copper pyrites with which it is intimately associated. Density 4·04 to 4 68. The crystals are rhombic,

$$a : b : c = 0{\cdot}5734 : 1 : 0{\cdot}9649,$$

and isomorphous with copper glance.

Cubanite, $CuS.Fe_2S_3$, is a bronze-coloured mineral found[4] in Cuba, whence its name. Hardness 4, density 4 0 to 4 2.[5]

A black variety of blende, occurring in Cornwall[6] and elsewhere, is known as **marmatite,**[7] and has the composition corresponding to $4ZnS.FeS$.

Pentlandite, a double sulphide of iron and nickel approximating to $2FeS.NiS$, occurs as cubic, bronze-coloured crystals in Argyllshire, Inveraray, and Cornwall. Hardness 3·5 to 4; density 4·6.

Arsenical pyrites[8] or **mispickel,** $FeS_2.FeAs_2$, containing 34 per cent. of iron, occurs in rhombic crystals, with frequent twinning, and of the following parameters:—

$$a : b : c = 1{\cdot}7588 : 1 : 1{\cdot}4793.$$

It is a grey mineral; hardness 5·5 to 6; density 6 to 6·4. It is found in Devon and Cornwall (where it is worked on a small scale), Silesia, Norway, Sweden, and U.S.A., and constitutes an important source of arsenic. If cobalt is also present the mineral is known as **glaucodote.**[9] When struck with a hammer, mispickel possesses the characteristic odour of arsenic and is hence known by Cornish miners as **arsenical mundic** or simply as **arsenic.** The ore readily oxidises, and when weathered gives rise to arsenates such as scorodite, etc. (see below).

Pacite[10] consists of rhombic crystals of $FeS_2.4FeAs_2$.

A double sulphide of iron and chromium, $FeS.Cr_2S_3$, occurs as the rare mineral **daubreelite**[11] associated with troilite. It possesses a brilliant metallic lustre, is black in colour, but not magnetic. Density 5·0.

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[1] Harrington, *Amer. J. Sci.*, 1903, (4), 16, 151. See also analyses by Kraus and Goldsberg, *ibid.*, 1914, (4), 37, 539.

[2] Johnston, *Econ. Geol.*, 1917, 12, 519.

[3] Hussak, *Centr. Min.*, 1906, p. 332; 1902, p. 69.

[4] Breithaupt, *Pogg. Annalen*, 1843, 59, 325.

[5] Scheidhauer, *Pogg Annalen*, 1845, 64, 280; Schneider, *J. prakt Chem*, 1895, (2), 52, 555.

[6] Church, *J. Chem Soc.*, 1866, 19, 130, Collins, *Min. Mag.*, 1879, 3, 91.

[7] Boussingault, *Pogg. Annalen*, 1829, 17, 399.

[8] See analyses and crystallographic studies by Scherer, *Zeitsch. Kryst. Min.*, 1893, 21, 354.

[9] Breithaupt and Plattner, *Pogg. Annalen*, 1849, 77, 127; Breithaupt, *J. prakt. Chem.*, 1835, 4, 258. See also Fletcher, *Min Mag*, 1904, 14, 54.

[10] Breithaupt, *Berg- und Hutten-mannische Zeitung*, 1866, 25, 167.

[11] J. L. Smith, *Amer. J. Sci.*, 1876, 12, 109; 1878, 16, 270.

MISCELLANEOUS MINERALS CONTAINING IRON.

Copperas or **melanterite**, $FeSO_4.7H_2O$, occurs in nature as the result of the oxidation of pyrites or marcasite. It yields greenish, monoclinic crystals, of hardness 2, and density when pure 1·832. A rhombic variety of the heptahydrate is known as **tauriscite.** Heat decomposes the heptahydrates, yielding at 200° to 250° C. the monohydrate, $FeSO_4.H_2O$, found in nature as **ferropalladite,**[1] and at high temperatures, ferric oxide. Copperas is isomorphous with **Boothite,** $CuSO_4.7H_2O$, and with **pisanite,**[2] $(Fe, Cu)SO_4.7H_2O$, which latter occurs in California as blue, transparent crystals. Copperas has also been found as a bluish green crust on limonite in Carinthia.[3] Its density is 1·8 to 1 95. The isomorphism of these minerals is evident from the following data :—[4]

	$a : b : c$	β
Melanterite . . .	1·1828 : 1 : 1·5427	75° 44′.
Pisanite . . .	1·1670 : 1 : 1·5195	75° 30′.
Boothite . . .	1·1622 : 1 : 1·5000	74° 24′.

All these minerals lose 6 molecules of water at 200° to 250° C.

Salvadorite, $FeSO_4.2CuSO_4.21H_2O$, appears to be a dimorphous variety of pisanite.[5] A ferric sulphate, $Fe_2(SO_4)_3.9H_2O$, occurring in hexagonal prisms in Coquimbo is known as **Coquimbite.**[6] It is white to yellowish brown in colour. **Janosite**[7] is a greenish yellow efflorescence occurring in Hungary, and possessed of the same composition. It crystallises in rhombic plates. The decahydrate, $Fe_2(SO_4)_3.10H_2O$, occurs as monoclinic crystals in **quenstedtite. Ferronatrite** (see p. 162), $Na_3Fe(SO_4)_3.3H_2O$, occurs as a greenish-white mineral in Chili.[8]

Halotrichite[9] or ferrous alum, $FeSO_4.Al_2(SO_4)_3.24H_2O$, occurs in several localities, including Persia, where it is used by the natives for making ink. In Baluchistan it occurs as a white inflorescence on decomposed slate, and is used for dyeing, its local name being **khaghal.**[10] It has recently been found in Elba in fibrous masses, white or faintly blue in colour, and possessed of a silky lustre. Density 1·90 ; hardness 2·5. Analysis shows a slight deficit of water due to partial dehydration in dry air.[11]

Other sulphates are **copiapite,**[12] $3Fe_2O_3.8SO_3.27H_2O$ [13] ; **amarantite,**[14] $Fe_2O_3.2SO_3.7H_2O$; **fibroferrite,**[15] $Fe_2O_3.2SO_3.10H_2O$; **castanite,**[16]

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[1] Scharizer, *Zeitsch. Kryst. Min.*, 1903, 37, 529.

[2] Pisani, *Compt. rend.*, 1859, 48, 807.

[3] Leitmeier, *Centr. Min.*, 1917, p. 321. See also Horn, *Amer. J. Sci.*, 1914, (4), 37, 40.

[4] Schaller, *Bull. Dept Geol. Univ. California*, 1903, 3, 191.

[5] Hertz, *Zeitsch. Kryst. Min.*, 1896, 26, 16.

[6] Rose, *Pogg Annalen*, 1833, 27, 310.

[7] Bockh and Emszt, *Abstr. Chem. Soc.*, 1905, ii. 536

[8] Mackintosh, *Amer. J Sci*, 1889, 38, 244.

[9] Rammelsberg, *Pogg. Annalen*, 1848, 43, 399 ; Clark, *Amer. J. Sci.*, 1884, 28, 24.

[10] Hooper, *J. Asiatic Soc. Bengal*, 1903, 72, 236.

[11] Millosevich, *Atti R. Accad. Lincei*, 1915, (5), 24, ii 501.

[12] Smith, *Amer. J. Sci.*, 1854, 18, 375 ; Manasse, *Jahrb. Min.*, 1913, I, Ref. 386 ; Darapsky, *Jahrb. Min*, 1890, 1, 62 ; Mackintosh, *Amer. J Sci.*, 1889, 38, 242, Scharizer, *Zeitsch Kryst. Min.*, 1913, 52, 372.

[13] Formula given by Wirth and Bakke, *Zeitsch. anorg. Chem.*, 1914, 87, 13. See also p. 161.

[14] In allusion to its red colour (Mackintosh, *Amer. J Sci.*, 1889, 38, 242).

[15] Rose, *Pogg Annalen*, 1833, 27, 316 ; Prideaux, *Phil Mag*, 1841, 18, 397 ; Manasse, *Zeitsch. Kryst. Min.*, 1911, 49, 202.

[16] Darapsky, *Jahrb. Min.*, 1890, 2, 267.

$Fe_2O_3.2SO_3.8H_2O$; **botryogen**,[1] $FeO.MgO.Fe_2(SO_4)_3.18H_2O$; **roemerite**,[2] $FeSO_4.Fe_2(SO_4)_3 12H_2O$; **planoferrite**,[3] $Fe_2O_3.SO_3.15H_2O$; **paposite**,[4] $2Fe_2O_3.3SO_3.10H_2O$. Iron associated with tellurium occurs as **durdenite**,[5] $Fe_2O_3.3TeO_2.4H_2O$, in Honduras, and as **emmonsite**[6] in Colorado.

Rhabdite is a crystalline phosphide of iron approximating in composition to $(Ni, Fe)_3P$. It is found in meteorites in the form of minute tetragonal prisms.[7] Density 6·3 to 6·8.

Vivianite,[8] $Fe_3(PO_4)_2.8H_2O$, occurs as monoclinic crystals, isomorphous with erythrite, $Co_3(AsO_4)_2.8H_2O$, and perhaps also with annabergite, $Ni_3(AsO_4)_2.8H_2O$. Its crystallographic elements are:—

$$a : b : c = 0{\cdot}7489 : 1 : 0{\cdot}7017. \quad \beta = 75^\circ\ 34'.$$

Some specimens obtained from Cornwall are beautifully crystallised, possessing a pale, bluish green tint. Others are nodular, deep blue in colour, pulverulent, and sometimes enclose crystals of dark brown colour, which exhibit a reddish hue by reflected light. Both the green and the brown specimens yield the same results upon analysis, so that their difference in colour is most probably due to a difference in the degree of oxidation of a small portion of the iron. The crystals offer a very perfect cleavage parallel to the clino-pinacoid. The pure mineral is probably colourless, the tints usually observed being due to some of the iron becoming oxidised. The density ranges from 2·6 to 2·7. Some good crystals have yielded the value of 2·587.[9]

The mineral was discovered by Vivian, in Cornwall, whence its name.

An earthy variety found in peat mosses is known as **blue iron earth.**

In **paravivianite**, from Russia,[10] part of the iron is replaced by manganese and magnesium, thus $(Fe, Mn, Mg)_3(PO_4)_2.8H_2O$. **Kertschenite**, $(Fe, Mn, Mg)O.Fe_2O_3.P_2O_5.7H_2O$, likewise found in Russia, occurs as very dark green crystals.

Tamanite,[11] the same mineral as **anapaite**, $(Ca, Fe)_3(PO_4)_2.4H_2O$,[12] occurs in pale greenish crystalline masses.

An anhydrous mixed phosphate of manganese, calcium, and divalent iron occurs as **Graftonite**, $(Fe, Mn, Ca)_3(PO_4)_2$, which occurs as salmon-coloured, monoclinic crystals, the crystallographic elements of which are

$$a : b : c = 0{\cdot}886 : 1 : 0{\cdot}582. \qquad \beta = 66^\circ.$$

Triphyllite, $Li\ (Fe, Mn)PO_4$, occurs as light green, rhombic crystals, which become dark through oxidation.[13]

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[1] Haidinger, *Pogg Annalen*, 1828, 12, 491; Scharizer, *loc. cit.* The mineral described as *Palacheite* (Eakle, *Bull. Dep Geol. Univ. California*, 1903, 3, 231) is the same as botryogen (Eakle, *Amer. J. Sci.*, 1903, (4), 16, 379.

[2] Grailich, *Sitzungsber. K. Akad. Wiss. Wien*, 1858, 28, 272. Scharizer, *loc. cit.*

[3] Darapsky, *Zeitsch Kryst. Min.*, 1898, 29, 213.

[4] Darapsky, *Jahrb. Min.*, 1890, I., Mem. 49.

[5] Dana and Wells, *Amer. J. Sci.*, 1890, 40, 80.

[6] Hillebrand, *Zeitsch. Kryst. Min.*, 1887, 12, 492 ; *Proc. Colorado Soc.*, 1885, 2, i. 20; *Amer. J Sci.*, 1904 (4), 18, 433.

[7] Flight, *Phil. Trans*, 1882, 173, 891.

[8] See Rath, *Pogg. Annalen*, 1869, 136, 405; Fisher, *Amer. J. Sci.*, 1850, 9, 84; Flight, *Chem. News*, 1870, 22, 260; Dudley, *Amer. J. Sci.*, 1890, 40, 120.

[9] Katzer, *Tscher. Min. Mitt.*, 1897, 16, 504.

[10] Popoff, *Centr. Min*, 1906, p. 112

[11] Popoff, *Zeitsch Kryst. Min.*, 1903, 37, 267.

[12] Sachs, *Sitzungsber. K. Akad. Wiss Berlin*, 1902, p. 18

[13] Penfield, *Amer. J. Sci.*, 1900, (4), 9, 20. See also Penfield and Pratt, *ibid.*, 1895, (3), 50, 387.

Ludlamite is a green hydrated form of ferrous phosphate found in Cornwall[1] and elsewhere. On heating it disintegrates into bluish green plates, in contradistinction to vivianite which turns white and exfoliates under similar treatment.

Ferric phosphate occurs in nature as **phospho-siderite**, $4FePO_4.7H_2O$, and **strengite**, $FePO_4.2H_2O$. Possibly these two minerals are the same.[2]

A basic ferric phosphate, known as **Dufrenite**,[3] $Fe_2(OH)_3.(PO_4)$, is found as rhombic crystals, dark green in colour, and named after Dufrénoy, the French mineralogist. Hardness 3·5 to 4; density 3·2 to 3·4. A ferric phosphate, $Fe_2O_3.P_2O_5.6H_2O$ or $FePO_4.3H_2O$, occurs in monoclinic needles as **Koninckite** in Belgium.[4]

Beraunite[5] is $FePO_4.2Fe_2(PO_4)(OH)_3.4H_2O$, and occurs in reddish brown monoclinic crystals. **Childrenite**[6] is a hydrated phosphate of iron and aluminium with a little manganese. It crystallises in yellow or brown rhombic prisms. When more manganese is present the mineral is called **eophosphorite**.[7]

Lölingite, $FeAs_2$, occurs in Saxony and Norway in rhombic crystals. Hardness 5 to 5·5; density 6·8 to 8·7. Greyish in colour, it gives a greyish black streak. When heated in an open tube a white sublimate of arsenious oxide or "white arsenic" is obtained; in the absence of air metallic arsenic is volatilised to a dark sublimate.

Leucopyrite, $FeAs.FeAs_2$, resembles the previous mineral in appearance, hardness, and density.

Berthierite,[8] $FeS.Sb_2S_3$, occurs in elongated rhombic prisms of density 4 to 4·3; hardness 2 to 3. It has a steely appearance. Heated in air, oxides of sulphur and antimony are evolved. It is readily soluble in hydrochloric acid, evolving hydrogen sulphide.

Scorodite,[9] $FeAsO_4.2H_2O$, occurs as pale green or brown rhombic crystals of density 3·1 to 3·3; hardness 3·5 to 4. It owes its name (Greek *skorodon*, garlic) to the fact that, when heated, it emits the characteristic odour of arsenic. It occurs in Cornwall, and in a readily oxidisable form as a deposit from certain geysers in Yellowstone Park,[10] U.S.A. A hydrated arsenate of iron and aluminium is known as **Liskeardite**.[11]

A basic arsenate, $2FeAsO_4.Fe(OH)_3.5H_2O$, is known as **iron sinter**, or **pharmaco-siderite** in consequence of the poisonous character of arsenic (Greek *pharmakon* poison). It crystallises in small, green cubic crystals, for which reason it is also known as **cube ore**.[12]

A hydrated arsenate of iron and calcium from Yukon is termed **Yukonite**. Its composition approximates to[13] $(Ca_3,Fe_2)As_2O_8.2Fe(OH)_3.5H_2O$. It is brownish black, resinous, and amorphous. Density *c*. 2·65.

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[1] Maskelyne and Flight, *J. Chem. Soc.*, 1871, 24, 1; Fukuchi, *Beitr. Min Japan*, 1912, No. 4, 192. [2] Bruhns and Busz, *Zeitsch. Kryst. Min.*, 1890, 17, 555.

[3] Kinch and Butler, *Min Mag*, 1887, 7, 65; Kinch, *ibid.*, 1889, 8, 112.

[4] Cesàro, *Amer. J. Sci.*, 1885, 29, 342

[5] Streng, *Jahrb. Min.*, 1881, 1, 102; Wherry, *Proc. U.S. National Museum*, 1914, 47, 501.

[6] Church, *J. Chem. Soc.*, 1873, 26, 103; Lévy, *Brandes J.*, 1823, 16, 274; Drugman, *Min. Mag.*, 1915, 17, 193.

[7] Brush and Dana, *Amer J. Sci.*, 1878, 16, 35; Drugman, *loc. cit.*

[8] Berthier, *Ann. Chim. Phys.*, 1827, 35, 351; *Pogg. Annalen*, 1827, 11, 478.

[9] Bournon, *Phil. Trans.*, 1801, p. 191; Damour, *Ann. Chim. Phys.*, 1844, 10, 412.

[10] Hague, *Amer. J. Sci.*, 1887, (3), 34, 171.

[11] Maskelyne, *Nature*, 1878, 18, 426; Flight, *Trans. Chem Soc.*, 1883, 43, 140.

[12] See W. Phillips, *Trans Geol. Soc.*, 1811, 1, 23; Hartley, *Min. Mag.*, 1899, 12, 152.

[13] Tyrrell and R. P. D. Graham, *Trans. Roy. Soc. Canada*, 1913, (3), 7, § 4.

Ferrous antimonate, $2FeO.Sb_2O_5$ or $FeSbO_3$, is found in the cinnabar gravels of Tripuhy, and is termed **Tripuhyte.** It is dull, greenish yellow in colour, possessing a canary-yellow streak. When heated, antimony oxide vaporises, leaving ferric oxide behind. Density 5·82.[1] **Derbylite** is ferrous antimonate associated with titanate, $2FeSbO_3.5FeTiO_3$. It crystallises in the rhombic system, its elements being [2]

$$a : b : c = 0{\cdot}96612 : 1 : 0{\cdot}55025.$$

It is black in colour, with a resinous lustre.

An ortho-silicate of iron, termed **fayalite** or **iron olivine,** Fe_2SiO_4, was first found on Fayal Island in the Azores. It had crystallised in tabular rhombs of Fe_2SiO_4, very similar to the ferrous silicate present in certain slags.[3] The axial ratios [4] are

$$a : b : c = 0{\cdot}46000 : 1 : 0{\cdot}58112.$$

It is quite possible that it was simply a lump of slag from a ship's ballast. Fayalite has also been found at Rockport.[5]

Olivine, $Fe_2SiO_4 + xMg_2SiO_4$, is a variable mixture of ferrous and magnesium ortho-silicates, olive green in colour, and of density about 3·3 to 3·5. It is a common constituent of rocks.

Anthophyllite, or magnesium iron metasilicate, $(Mg, Fe)SiO_3$, crystallises in the rhombic system. A pure iron anthophyllite, $FeSiO_3$, has been found at Rockport, but is rare.[6] It is white to light brown in colour.

Sodium ferric metasilicate is found as **acmite**[7] or **ægirite,**[8] $Na_2Fe_2(SiO_3)_4$. Its crystals are blackish green in colour, and possess the following crystallographic elements:—[9]

$$a : b : c = 1{\cdot}1044 : 1 : 0{\cdot}6043. \qquad \beta = 73^\circ\ 27'.$$

Hydrated ferric metasilicates are found as **Müllerite,** $Fe_2O_3.3SiO_2.2H_2O$,[10] and **nontronite,** $Fe_2O_3.3SiO_2.5H_2O$.[11]

Astrolite, $(Al, Fe)_2Fe(Na, K)_2(SiO_3)_5.H_2O$, a metasilicate of aluminium, iron, and alkali metals, occurs in Saxony [12] as small spherical balls, with radially fibrous structure.

Glauconite, the green constituent of many rocks, if pure, would be represented by the formula $KFe(SiO_3)_2.H_2O$, that is, potassium ferric metasilicate.[13]

Cronstedtite occurs in Cornwall, associated with vivianite. It is also met with in association with Hisingerite in acicular needles in cavities in iron pyrites. Its usual structure is fibrous and radiating, and it consists essentially of ferrous silicate and hydrated ferric oxide.[1]

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[1] Hussak and Prior, *Min. Mag.*, 1897, 11, 302.

[2] Hussak and Prior, *ibid.*, 176.

[3] Gmelin, *Pogg. Annalen*, 1840, 51, 160; Hidden and Mackintosh, *Amer. J. Sci.*, 1891, 41, 439.

[4] Soellner, *Zeitsch. Kryst. Min.*, 1911, 49, 138.

[5] Warren, *Amer. J. Sci.*, 1903, (4), 16, 337; Penfield and Forbes, *ibid.*, 1896, (4), 1, 129; *Zeitsch. Kryst. Min.*, 1896, 26, 143.

[6] Warren, *Amer. J. Sci.*, 1903, (4), 16, 337.

[7] Greek ἀκμή, a point, referring to the sharp points of the crystals.

[8] Ægir was the Icelandic *Neptune.*

[9] Palache and Warren, *Amer. J. Sci.*, 1911, (4), 31, 533.

[10] Zambonini, *Zeitsch. Kryst. Min.*, 1899, 32, 157.

[11] See Kovář, *ibid.*, 1899, 31, 523.

[12] Reinisch, *Centr. Min.*, 1904, p. 108.

[13] Glinka, *Zeitsch. Kryst. Min.*, 1898, 30, 390; Clarke, *Monograph U.S. Geol. Survey*, 1903, 43, 243.

Hisingerite likewise occurs in Cornwall, as dark brown, amorphous, reniform masses. Its hardness is 2·75, and density 1·74. It yields a conchoidal fracture and leaves a rust-brown streak.[2] Its composition [3] approximates to $Fe_2O_3.2SiO_2.2H_2O$.

Other silicates are **pinguite,**[4] $2Fe_2O_3.6SiO_2.3H_2O+xH_2O$; **hoeferite,**[4] $2\ Fe_2O_3.4SiO_2.7H_2O$.

Numerous other silicates are known in which iron is one of the constituent metals. As a source of iron they are all useless for commercial purposes, since the percentage of the metal is low.

Wolframite, $(Fe, Mn)WO_4$, is a black mineral associated with cassiterite in Cornwall and elsewhere. It yields monoclinic crystals which may be distinguished by their lustre and perfect single cleavage. Hardness 5·5; density 7·3.[5]

Ferritungstite, $Fe_2O_3.WO_3.6H_2O$, an alteration product of Wolframite, is a pale ochre, which under the microscope is seen to consist of hexagonal plates.[6]

Ferrous chloride is present in **rinneite,** $FeCl_2.3KCl.NaCl$, which occurs in large, lenticular masses in beds of rock salt at Wolkramshausen in the Harz, and as a kieserite-rinneite rock in Hanover.[7] It crystallises in the hexagonal system, and when a hot, saturated solution is allowed to cool, potassium chloride separates out.

Douglasite,[8] $FeCl_2.2KCl.2H_2O$, occurs in the Stassfurt deposits, associated with carnallite. Density 2·16.

Ferric chloride has been found as a brown incrustation on lava, particularly in the neighbourhood of Vesuvius. It is then known as **molysite,** $FeCl_3$. In combination with alkali chlorides, ferric chloride is found as **kremersite,**[9] $KCl.NH_4Cl.FeCl_3.H_2O$, and **Erythrosiderite,** $2KCl.FeCl_3.H_2O$, both minerals being found in minute quantities in the neighbourhood of Vesuvius.

Lagonite is an ochre-coloured incrustation consisting of iron borate, $Fe_2O_3.3B_2O_3.3H_2O$. It occurs as an incrustation by lagoons in Tuscany.[10] A natural nitride of iron has been found in the lava of Etna, as the mineral **siderazote.**[11]

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

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[1] Steinmann, *Schweigger's J.*, 1821, 32, 69; Maskelyne and Flight, *J. Chem. Soc*, 1871, 24, 1.

[2] Church, *J. Chem. Soc.*, 1870, 23, 3.

[3] Church, *loc. cit.*, Clarke, *Amer. J. Sci*, 1887, 34, 133.

[4] Katzer, *Tsch. Min. Mitt.*, 1895, 14, 483.

[5] Analyses are given by Wherry, *Proc U.S. National Museum*, 1914, 47, 501.

[6] Schaller, *Amer. J. Sci*, 1911, (4), 32. 161.

[7] Boeke, *Chem Zeit.*, 1908, 32, 1228; *Jahrb Min.*, 1911, I., 48; Rinne and Kolb, *Centr. Min*, 1911, p. 337. Schneider (*Centr Min.*, 1909, p. 503) found a higher sodium chloride content, but this appears to have been due to the mechanically admixed salt.

[8] Precht, *Ber.*, 1881, 13, 2328.

[9] Kremers, *Pogg. Annalen*, 1851, 84, 79.

[10] Bechi, *Amer. J. Sci.*, 1854, 17, 129.

[11] Silvestri, *Pogg. Annalen*, 1876, 157, 165.

Name	Composition.	Density.	Hardness Mohs' Scale.	Remarks
Acmite Ægirite	$Na_2Fe_2(SiO_3)_4$	3·5–3·6	6–6·5	Monoclinic.
Amarantite	$Fe_2O_3\ 2SO_3\ 7H_2O$	2·0	2·1	Triclinic.
Anapaite	$FeCa_2(PO_4)_2.4H_2O$	..	..	Pale green
Ankerite	$2CaCO_3\ MgCO_3.FeCO_3$	2·9–3	3·5–4	Hexagonal.
Anthophyllite	$(Mg, Fe)SiO_3$	5·5–6	3·1–3·2	Rhombic.
Argillaceous iron ore	See Clay iron stone	.	..	..
Arizonite	$Fe_2O_3.3TiO_2$	4·25	5·5	..
Arsenic Arsenical mundic Arsenical pyrites	$FeS_2.FeAs_2$	6–6·4	5·5–6	Rhombic.
Astrolite	$(Fe, Al, Na, K)SiO_3.H_2O$	2·78	3·5	? rhombic.
Awaruite	Alloy of Fe and Ni	8·1	5	67–74 per cent. Ni.
Barnhardtite	$2Cu_2S\ Fe_2S_3$	4·5	3·5	Massive Bronze yellow Conchoidal fracture.
Beraunite	$FePO_4.2Fe_2(PO_4)(OH)_3.4H_2O$	2·8–2·9	..	Monoclinic.
Berthierite	$FeS\ Sb_2S_3$	4–4·3	2–3	Rhombic.
Bixbyite	$FeO.MnO_2$	4·95	6–6·5	Cubic.
Blackband	Carbonaceous $FeCO_3$	..	.	..
Blue iron earth	Earthy variety of vivianite	..	.	.
Bog ore	Hydrated Fe_2O_3	.	..	Brown, earthy.
Bornite	Sulphides of Fe and Cu	4·4–5·5	3·3	Cubic, also massive.
Botryogen	Essentially ferric sulphate	2·0–2·1	2–2·5	Monoclinic.
Brush ore	Variety of limonite	..	..	Stalactitic and reniform.
Castanite	$Fe_2O_3\ 2SO_3\ 8H_2O$	2·1	3	Monoclinic.
Chalcopyrite	See Copper pyrites	..	..	..
Chalmersite	$CuFe_2S_3$	4–4·7	3·5	Rhombic and massive. Pale yellow.
Chalybite	See Spathic ore	..	..	..
Childrenite	Hydrated phosphate of Fe and Al	3·1–3·2	4·5–5	Rhombic.
Chrome iron ore	See Chromite	..	..	..
Chromite	$FeO\ Cr_2O_3$	4·3–4·6	5·5	Cubic.
Chromitite	$Fe_2O_3\ Cr_2O_3$	3·1	..	Cubic Magnetic, like magnetite.
Chromoferrite	See Chromite	..	.	..
Clay iron stone	Impure $FeCO_3$	..	.	Earthy. 30–40 per cent. Fe.
Cleveland iron stone	Variety of clay iron stone	..		About 33 per cent Fe.
Cobalt-nickel pyrites	$(Fe, Co, Ni)S_2$	4·7	5–5·5	Cubic.
Cockscomb pyrites	Variety of marcasite	..	..	..
Cohenite	$(Fe, Co, Ni)_3C$	6·977	5·5–6	Cubic.
Copiapite	$3Fe_2O_3\ 8SO_3\ 27H_2O$	2·1	2·5	Monoclinic.
Copper pyrites	$Cu_2S.FeS_2$	4·1–4·3	3·5–4	Tetragonal.
Copperas	$FeSO_4.7H_2O$	1·83	2	Monoclinic.
Coquimbite	$Fe_2(SO_4)_3.9H_2O$	2	2–2·5	Hexagonal.
Crichtonite	$FeTiO_3$	4·7–4·8	.	About 30 per cent. Ti.
Cronstedtite	$4FeO.2Fe_2O_3.3SiO_2\ 4H_2O$	3·3–3·4	3·5	Acicular needles.
Cubanite	$CuS.Fe_2S_3$	4–4·2	4	Cubic.
Cube ore	See Iron sinter	..	..	..
Daubreelite	$FeS.Cr_2S_3$	5	..	Massive, black Non-magnetic.
Delafossite	$CuFeO_2$	..	5·5	Tetragonal.
Derbylite	$2FeSbO_3.5FeTiO_3$	4·53	5	Rhombic.
Dimagnetite	Fe_3O_4	5·79	5·5–6·5	Cubic.
Douglasite	$FeCl_2\ 2KCl.2H_2O$	2·16	..	Monoclinic.
Dufrenite	$Fe_2(OH)_3PO_4$	3·2–3·4	3·5–4	Rhombic.
Durdenite	$Fe_2O_3.3TeO_2.4H_2O$	..	2–2·5	Greenish yellow. Massive.

Name.	Composition	Density.	Hardness. Mohs' Scale.	Remarks.
Emmonsite	Hydrated ferric tellurite	..	5	? monoclinic
Eophosphorite	Variety of childrenite richer in Mn	3·1–3·2	5	Rhombic.
Erubescite	See Bornite	..	..	..
Erythrosiderite	$2KCl.FeCl_3.H_2O$	..	..	Red, rhombic crystals
Esmeraldaite	$Fe_2O_3.4H_2O$	2·58	2·5	Coal black, vitreous
Fayalite	See Iron olivine	..		..
Ferritungstite	$Fe_2O_3.WO_3.6H_2O$	..	..	? hexagonal.
Ferronatrite	$Na_3Fe(SO_4)_3.3H_2O$	2·5	2	Hexagonal
Fibroferrite	$Fe_2O_3.2SO_3.10H_2O$	..	..	Straw-yellow fibres. Silky lustre.
Franklinite	See Zincite	..	..	..
Geikielite	$(Mg, Fe)O.TiO_2$	3·976	..	Hexagonal.
Glaucodote	$(Co, Fe)AsS$	5·9–6	5	Rhombic.
Goethite	$Fe_2O_3.H_2O$	4–4·4	5–5·5	Rhombic.
Graftonite	$(Fe, Mn, Ca)_3(PO_4)_2$	3·67	..	Monoclinic.
Halotrichite	$FeSO_4.Al_2(SO_4)_3.24H_2O$	1·90	2·5	Mono- or tri-clinic, fibrous
Hisingerite	$Fe_2O_3.2SiO_2.2H_2O$	1·74	2·75	Dark brown, massive.
Hoeferite	$2Fe_2O_3.4SiO_2.7H_2O$	2·3–2·4	1–3	Green, earthy.
Horse-flesh ore	See Bornite	..	..	..
Hydrogoethite	$3Fe_2O_3.4H_2O$	3·7	4	Red.
Hydrohematite	See Turgite	..	..	..
Hystatite	$FeTiO_3$	5	..	15–20 per cent. Ti.
Ilmenite	$FeO.TiO_2$	4·5–5	5–6	Hexagonal.
Iron glance	See Specular ore	.		..
Iron, native	Fe	7·3–7·8	4·5	Cubic
Iron olivine	Fe_2SiO_4	4–4·2	6·5	Rhombic.
Iron pyrites	See Pyrites	..	..	..
Iron sinter	$2FeAsO_4.Fe(OH)_3.5H_2O$	2·8–3	2·5	Cubic.
Janosite	$Fe_2(SO_4)_3.9H_2O$	2·51–2·55	2–2·5	Rhombic.
Josephinite	Alloy of Fe and Ni	..	..	72 per cent. Ni.
Kamasite	Alloy of Fe and Ni	..	.	7 per cent. Ni.
Kibdelophane	$FeTiO_3$	4·6–4·7		About 30 per cent. Ti
Kidney ore	Fe_2O_3	..	.	Reniform, massive.
Koninckite	$FePO_4.3H_2O$	2·3	3·5	Monoclinic.
Kremersite	$KCl.NH_4Cl.FeCl_3.H_2O$	..		Cubic.
Lagonite	$Fe_2O_3.3B_2O_3.3H_2O$	..		Brown incrustation
Lake ore	See Bog ore	..	..	..
Laterite	Similar to limnite	..	..	..
Lepidocrite	Fibro-scaly goethite	..	..	..
Leucopyrite	$FeAs.FeAs_2$	6·8–7·4	5–5·5	Rhombic.
Limnite	$Fe_2O_3.3H_2O$	2·7	..	Light brown, earthy.
Limonite	$2Fe_2O_3.3H_2O$	5–5·5	3·6–4	Brown, earthy.
Liskeardite	Hydrated arsenate of Fe and Al	..	..	White, massive. Structure fibrous.
Lodestone	See Magnetite	..	..	..
Lölingite	$FeAs_2$	6·8–7·4	5–5·5	Rhombic.
Looking-glass ore	See Specular ore	..	..	..
Ludlamite	$7FeO.2P_2O_5.9H_2O$	3·1	3–4	Monoclinic.
Ludwigite	$(Fe, Mg)O.Fe_2O_3.B_2O_3$	3·9–4	5	Rhombic.
Magnesioferrite	$MgO.Fe_2O_3$	4·57–4·65	6–6·5	Cubic.
Magnetic pyrites	$4FeS.Fe_3S_4$	4·4–4·7	3·5–4·5	Two varieties, hexagonal and rhombic.
Magnetite	Fe_3O_4	4·9–5·2	5·5–6·5	Cubic.
Magnoferrite	See Magnesioferrite		..	..
Marcasite	FeS_2	4·7–4·8	6–6·5	Rhombic.
Marmatite	$FeS.4ZnS$	3·9–4·1	.	Cubic.
Martite	Fe_2O_3	4·3–5·3	6–7	Cubic. Probably a pseudomorph of magnetite.

Name.	Composition.	Density.	Hardness Mohs' Scale.	Remarks.
Melanterite	See Copperas	..	.	..
Menaccanite	See Ilmenite	..	..	..
Mesitite	$FeCO_3$ $2MgCO_3$	3·3–3·4	3·5–4	Hexagonal.
Micaceous iron ore	Fe_2O_3	5·2	6	Foliated variety of specular iron.
Minette	Hydrated Fe_2O_3	..	..	..
Mispickel	See Arsenical pyrites	..	..	..
Molysite	$FeCl_3$	..	..	Brown incrustation.
Mundic	See Pyrites	..	.	..
Needle iron stone	See Goethite	..	..	An acicular variety.
Nontronite	Fe_2O_3 $3SiO_2.5H_2O$	2·15	..	Yellow, earthy.
Ochre	Variety of limonite	..	.	Yellow, earthy.
Octibbehite	Alloy of Fe and Ni	..	.	60 per cent Ni.
Olivine	Fe_2SiO_4 Mg_2SiO_4	3·3–3·5	6·5–7	Rhombic.
Onegite	See Goethite	..	..	An acicular variety.
Pacite	$FeS_2.4FeAs_2$	6·3	..	Rhombic.
Pentlandite	$2FeS.NiS$	4·6	3·5–4	Cubic.
Pharmaco-siderite	See Iron sinter	..	..	..
Phosphosiderite	$2FePO_4.7H_2O$	2·76	3·75	Rhombic.
Pinguite	$2Fe_2O_3.6SiO_2.Aq.$	2·73	1	Yellow-green, earthy.
Pisanite	$(Fe, Cu)SO_4.7H_2O$	1·95	.	Monoclinic.
Pistomesite	$FeCO_3$ $MgCO_3$	3·4	..	Hexagonal.
Planoferrite	$Fe_2O_3.SO_3.15H_2O$	..	..	Rhombic.
Plumbo-ferrite	$(Pb, Fe, Cu)O.Fe_2O_3$	..	..	Hexagonal.
Puddle ore	Fe_2O_3	..	.	Red, earthy.
Pyrites	FeS_2	4·8–5·2	6–6·5	Cubic.
Pyrrho-siderite	See Goethite	..	.	..
Pyrrhotite	See Magnetic pyrites	..	..	..
Quenstedtite	$Fe_2(SO_4)_3.10H_2O$	2·1	2·5	Monoclinic.
Red fossil ore	Fe_2O_3	..	.	Red, earthy.
Red hæmatite	Generic name for anh. Fe_2O_3. Also given to turgite	..	..	..
Red ochre	See Turgite and Red hæmatite	..	..	..
Rhabdite	$(Ni, Fe)_3P$	6·3–6·8	..	Tetragonal.
Rinneite	$FeCl_2.3KCl$ $NaCl$	..	..	Hexagonal.
Roemerite	$FeSO_4.Fe_2(SO_4)_3.12H_2O$	2·2	3–3·5	Triclinic.
Rubinglimmer	See Goethite	..	..	..
Ruddle	Fe_2O_3	..	..	Red, earthy.
Sammet-blende	Velvety variety of Goethite	..	.	..
Scorodite	$FeAsO_4.2H_2O$	3·1–3·3	3·5–4	Rhombic
Senaite	$(Fe, Mn, Pb)O$ TiO_2	4·8	..	Hexagonal.
Shining ore	Micaceous iron ore	..	..	A Devonshire variety.
Siderazote	Fe_2N	..	..	Thin coating on lava. Non-crystalline.
Siderite	See Spathic ore	..	..	..
Sidero-chrome	See Chromite	..	..	..
Sidero-plesite	$2FeCO_3.MgCO_3$	3·6–3·7	..	Hexagonal.
Sienna	$Fe_2O_3.Aq$	..	..	An earthy variety of limonite containing Mn.
Smith ore	Variety of limonite	..	..	..
Souesite	Alloy of Fe and Ni	8·2	..	75 per cent. Ni.
Spathic ore	$FeCO_3$	3·7–3·9	3·5–4·5	Hexagonal.
Spear pyrites	Variety of marcasite	..	..	..
Specular iron ore	Fe_2O_3	4·5–5·3	5·5–6·5	Hexagonal.
Sphæro-siderite	Variety of clay iron stone	.	..	Concretionary.
Strengite	$FePO_4$ $2H_2O$	2·7–2·8	..	Rhombic.

Name.	Composition.	Density.	Hardness. Mohs' Scale.	Remarks.
Tænite	Alloy of Fe and Ni	..	..	43 per cent. Ni.
Tauriscite	$FeSO_4.7H_2O$	..	..	Rhombic.
Titanic iron ore	$FeTiO_3$	4·5–5	5–6	Hexagonal.
Triphylite	$Li(Fe, Mn)PO_4$	3·58	..	Rhombic.
Tripuhite	$2FeO Sb_2O_5$	5·82	.	Yellow.
Troilite	FeS	4·7–4·8	4	Massive. Possibly hexagonal.
Turgite	$2Fe_2O_3 H_2O$	3·5–4·7	5–6	Red, earthy.
Uddevalite	$FeTiO_3$	4·8	..	About 70 per cent. Ti.
Umber	Fe_2O_3 Aq.	..	..	Dark brown, earthy.
Vivianite	$Fe_3(PO_4)_2.8H_2O$	2·6–2·7	1·5–2	Monoclinic.
White iron pyrites	See Marcasite	..	..	..
Wolframite	$(Fe, Mn)WO_4$	7·3	5·5	Monoclinic.
Wood iron ore	Variety of limonite	..	..	Fibrous
Xantho-siderite	$Fe_2O_3 2H_2O$	2·7	2·5	Acicular.
Yukonite	$(Ca_3, Fe_2)As_2O_8 2Fe(OH)_3.5H_2O$	2·65	..	Dark, resinous, massive
Zincite	$(Mn, Fe)O.Fe_2O_3$	5–5·2	5·5–6·5	Cubic.

Other Sources of Iron.—It should be mentioned that iron is a minor constituent in an indefinite number of other minerals and rocks. Thus, it is present in small quantities in **serpentine, biotite, hornblende, garnets,** etc. Indeed, the mean percentages of ferrous and ferric oxides in British and American igneous rocks have been calculated to be as follow:—[1]

	Fe_2O_3.	FeO.
British rocks	5·34	2·40
American rocks	2·65	3·35

so that the total amount of iron distributed throughout the igneous rocks of the world is very considerable.

Further, the brown and red colours of soil, clay, and sandstone are largely due to iron; [2] sea, spring, and river waters contain dissolved iron compounds; and the metal also enters into the animal and vegetable organism, being an essential constituent of hæmoglobin and chlorophyll. Spectroscopic examination of light from the sun and many fixed stars,[3] reveals the presence of iron, thus showing that the metal is widely diffused throughout the universe.

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[1] Harker, *Geol. Mag.*, 1899, 6, 220.

[2] On the ferruginous colouring matters of soils see Spring, *Rec. Trav. Chim.*, 1898, *17*, 202.

[3] Lockyer, *Proc. Roy. Soc.*, 1897, *61*, 148, 213.

CHAPTER III.

PREPARATION AND PROPERTIES OF PURE IRON.

Preparation.—1. One of the earliest methods of obtaining a pure iron consists in reducing ferrous chloride by heating in an atmosphere of hydrogen.[1] The iron is deposited in the form of cubic crystals of microscopic size.

2. Reduction of iron oxide, carbonate, or oxalate in a current of hydrogen results in the formation of a very pure iron. The reaction is fairly rapid at 600° C., but higher temperatures are more efficient, whilst at lower temperatures the product is usually contaminated with ferrous oxide (see p. 109).

3. Iron may be reduced from its salts by means of zinc. Thus at high temperatures ferrous chloride is reduced by zinc vapour,[2] whilst aqueous solutions of ferrous salts are reduced by metallic zinc at their boiling-points,[3] yielding finely divided iron.

4. An exceptionally pure form of reduced iron has been obtained by Lambert and Thomson[4] by reduction of pure, colourless crystals of ferric nitrate.[5] The crystals were first converted into oxide or basic nitrate by ignition in an iridium boat.[6] The whole was then introduced into a silica tube and heated in an electric resistance furnace to just above 1000° C. in a current of pure hydrogen gas, obtained by the electrolysis of barium hydroxide solution.

5. *Electrolytic Iron.*—Iron may be obtained in a high state of purity by electrolysing a mixed solution containing 20 per cent. of ferrous sulphate (calculated as $FeSO_4.7H_2O$) and 5 per cent. of magnesium sulphate ($MgSO_4.7H_2O$). Some 25 grams of sodium hydrogen carbonate are added to every 6 litres of the solution, whereby a skin of ferric hydroxide forms on the surface of the bath and protects the liquid from oxidation. A precipitate settles to the bottom and is allowed to remain undisturbed. An anode of wrought iron is employed, the cathode being made of copper, thinly silvered and iodised, and maintained in rotation. The best results are obtained with a current density of 0·3 ampere per sq. decimetre of cathode, and a temperature of 15°

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[1] Peligot, *Compt. rend.*, 1844, 19, 670.

[2] Poumarède, *Compt. rend.*, 1849, 29, 518.

[3] Capitaine, *Compt. rend*, 1839, 9, 737; Davis, *Chem. News*, 1874, 30, 292.

[4] Lambert and J. C. Thomson, *Trans. Chem. Soc.*, 1910, 97, 2426.

[5] Prepared as indicated on p. 177.

[6] Richards (*Proc. Amer. Acad.*, 1900, 35, 253) prepared pure iron in a somewhat analogous manner, but used vessels of platinum instead of iridium. He states that his iron invariably contained traces of platinum and that a trace of this metal remained after dissolving the iron in acid.

to 18° C. The bath is kept continuously at work, and 20 to 25 grams of carbonate are added every three or four days.

Both the magnesium sulphate and the sodium hydrogen carbonate appear to be essential constituents of the bath, and the good quality of the metal is attributed to the small concentration of hydrogen ions which prevents the deposited iron from containing occluded hydrogen.[1]

Numerous attempts have been made to prepare iron by the electrolysis of ferrous chloride, but with this salt an elevated temperature is essential for good results, namely, 60° to 70° C. The current density at the cathode should not exceed 0·4 ampere per sq. decimetre, and the quality of the deposit is improved by rotation of the cathode.[2]

According to Noyes, the minimum potential required for the electrolysis of an aqueous solution of a ferrous salt at 20° C. is 0·66 volt, when electrodes of electrolytic iron are employed.[3] This value falls by 0·007 volt per degree rise in temperature up to 110° C., when it attains a minimum. Further rise in temperature necessitates an increased voltage.

Hicks and O'Shea[4] recommend the electrolysis of a 5 per cent. solution of ferrous chloride to which ammonium chloride has been added in sufficient quantity to establish the ratio

$$FeCl_2 : NH_4Cl = 1 : 2.$$

Any ferric chloride present is reduced to ferrous by shaking with reduced iron. A thin copper plate serves as cathode, is cleaned with dilute nitric acid, rubbed with cotton-wool and sand, and finally washed with potassium cyanide and then with water. Swedish iron constitutes the anode, and is placed in a porous cell to prevent the spongy carbon, which normally separates from the metal, from reaching the cathode. The sulphur in the metal passes into solution as sulphate, and requires removal at intervals with the anode liquor. A current of 0·08 to 0·2 ampere per sq. decimetre of cathode surface is recommended, the voltage being 0·7. The iron content of the bath should not fall below the equivalent of about 4 per cent. of ferrous chloride.

Skrabal[5] obtained a very pure iron by electrolysis of a solution of ferrous ammonium oxalate, the metal being deposited on a cathode of platinum foil. The electrode thus prepared was now used as anode in an acidified solution of ferrous sulphate, an E.M.F. of 0·4 volt being employed, the cathode again consisting of platinum foil. The metal thus obtained was white and crystalline ; it dissolved slowly in warmed, dilute sulphuric acid, leaving no residue, and evolving a pure, odourless hydrogen. To prevent oxidation of the bath, the electrolysis was carried out in an atmosphere of carbon dioxide, and the cathode separated from the anode by means of a porous diaphragm. Excellent results were also obtained[1] with ferrous ammonium sulphate. With this salt a concentration of 70 grams of the hexahydrate $(NH_4)_2SO_4.FeSO_4.6H_2O$ per litre is recommended, with a maximum cathode current density of 0·5 ampere per sq. decimetre, working at a temperature of 15° to 18° C.,[2] or not less than 26 grams per litre, with a cathodic current density of 0·2 to 0·65 ampere per sq. decimetre, the surface of the bath being protected from oxidation by a layer of solid paraffin, a stirrer being employed, and the wrought-iron anodes enclosed in linen bags;[3] or a saturated solution, with a current density of 1 ampere at 30° C.[4] Acidified solutions of ferrous sulphate have been used under various conditions, the best results being obtained, according to Pfaff, with a current density of 2 amperes per sq. decimetre at the cathode, a temperature of 70° C., and a concentration of at least two equivalents of ferrous sulphate per litre and 0·01 equivalent of sulphuric acid.[5]

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[1] Maximowitsch, *Zeitsch. Elektrochem.*, 1905, **11**, 52; Ryss and Bogomolny, *ibid*, 1906, **12**, 697. Lenz electrolysed a solution of ferrous and magnesium sulphates in 1870, using magnesium carbonate to maintain neutrality. His metal was not very satisfactory, being obtained as a hard, grey deposit containing a considerable quantity of occluded gases, mainly hydrogen, nitrogen, and oxides of carbon (*Bull. Soc. chim.*, 1870, (2), **13**, 551).

[2] Ryss and Bogomolny, *loc. cit.*; Pfaff, *Zeitsch. Elektrochem.*, 1910, **16**, 217.

[3] Noyes, *Compt. rend.*, 1919, **169**, 971.

[4] Hicks and O'Shea, *Electrician*, 1895, p. 843; *Chem. Zentr.*, 1896, I., 293.

[5] Skrabal, *Ber.*, 1902, **35**, 3404. See also Watts and Li, *Trans. Amer. Electrochem. Soc.*, 1914, **25**, 529.

Electrolytic iron deposited from solution at ordinary pressures and temperatures is apt to be admixed with ferric hydroxide, and to contain hydrogen[6] and carbon. The last-named element is commonly derived from the oxalates or tartrates in the baths, when these are used, and as the result of transfer from the anodes. The carbon may be free, combined as carbide, or present as occluded carbon monoxide or dioxide.

Electrolytic iron is frequently brittle, a property that is usually attributed to occluded hydrogen,[7] but there are probably other auxiliary causes.[8]

Iron has also been obtained from solutions of its salts in organic solvents by electrolysis between platinum electrodes. A solution of ferric chloride in methyl chloride conducts electricity well, and may be used for the purpose.[9] Produced in this way, however, the metal is particularly liable to be contaminated with carbon.[10]

Electro-deposition of Iron on Copper.—Deposits of iron are frequently applied to engraved copper plates to harden their surfaces and thus increase their life for printing purposes. Various solutions are recommended for this purpose. A simple one[11] yielding good results consists of

Ferrous ammonium sulphate . .	1 lb.	or 100 grams.
Water	1 gallon	,, 1 litre.

This solution must be perfectly neutral for use. Another useful mixture contains ferrous chloride and ammonium chloride in molecular proportions to the extent of 50 to 60 grams per litre, or

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[1] Skrabal, *Zeitsch. Elektrochem.*, 1904, 10, 749.

[2] Ryss and Bogomolny, *loc. cit.*

[3] Amberg, *Zeitsch. Elektrochem.*, 1908, 14, 326.

[4] Pfaff, *loc. cit.*; A. Muller, *Metallurgie*, 1909, 6, 145; Burgess and Hambuechen, *Electrochem. Ind.*, 1904, 2, 184; Klein, *Bull. Soc. Encourag. Industrie nat.*, 1868, 15, 286.

[5] Pfaff, *loc. cit.*; Lee, *Dissertation*, Dresden, 1906.

[6] See Kremann and Breymesser, *Monatsh.*, 1917, 38, 359, etc.

[7] See Coulson, *Trans. Amer. Electrochem. Soc.*, 1917, 32, 238; Guillet, *J. Iron Steel Inst.*, 1914, II., 66.

[8] W. E. Hughes, *J. Iron Steel Inst.*, 1920, I, 321.

[9] Timmermans, *Bull. Soc. chim. Belg*, 1906, 20, 305.

[10] Archibald and Piguet, *Trans. Roy. Soc. Canada*, 1917–18, (3), 11, 107.

[11] See *Electroplating*, Barclay and Hainsworth (Arnold, 1912).

$FeCl_2.2NH_4Cl$.	½ lb.,	or 50 grams.
Water	1 gallon,	,, 1 litre.[1]

This works well with a current density of 0·15 to 0·17 ampere per sq. decimetre, the initial density being 0·2 ampere until a thin deposit has been obtained on the cathode. Voltage 0·7. The anodes should consist of pure Swedish charcoal iron. These become covered with a black carbonaceous slime after a time, and require cleaning. It is desirable that the anodic area should somewhat exceed that of the cathode.

Electro-deposition of Copper on Iron.—It is frequently desirable to protect iron by coating it superficially with copper. The following bath is recommended[2] for the electro-deposition of this metal upon iron:—

Copper sulphate	60 grams.
Sodium hydroxide	50 ,,
Sodium potassium tartrate	159 ,,
Water	1000 ,,

with a cathode density of 0·1 to 0·5 ampere per sq. decimetre and an anode density not exceeding 1·04 amperes. As this bath evolves no dangerous fumes, it is preferable to cyanide baths.

Physical Properties of Pure Compact Iron.—The properties of iron are affected to such a remarkable and unique extent by the presence of small quantities of alloying elements, chief amongst which is carbon, that these phenomena are an important study in themselves. It is not intended in this section, therefore, to deal with the physical properties of any commercial iron other than the chemically pure and compact metal. For a discussion of the physical and metallurgical properties of various types of commercial iron and its alloys, the reader is referred to Part III. of this volume. Pure iron is a white metal which can be readily machined in a lathe, and even cut with a knife. It crystallises according to the cubic system,[3] but crystals are rare, the metal being usually massive. Dendritic crystals may be obtained artificially with branches parallel to the cubic axes.[4] Shock apparently assists or induces crystallisation in iron.[5]

Pure iron, prepared by reducing ferrous chloride with hydrogen at temperatures up to about 800° C., usually separates in small hexahedra, although it sometimes yields rhombic dodecahedra and tetrakishexahedra.[6] The mechanical properties of the individual crystals of iron vary with the crystallographic orientation. For example, the metal is brittle in the direction of the planes of cleavage, but exhibits considerable plasticity in other directions.[7] In compact iron the crystals are separated from each other by an amorphous cement, which acts as a binding agent. The metal is ductile and malleable. It possesses considerable tenacity, a wire 2 mm. in diameter being capable of supporting 250 kgms.[8] This value is greatly influenced by the presence of alloying elements, particularly carbon.[9]

[1] Hicks and O'Shea, *Electrician*, 1895, p. 843.

[2] Brown and Mathers, *J. Physical Chem.*, 1906, **10**, 39.

[3] Wohler, *Pogg. Annalen*, 1832, **26**, 182, Fuchs, *Annalen*, 1852, **84**, 257.

[4] Capitaine, *Compt. rend.*, 1839, **9**, 737; *Ann. Chim. Phys.*, 1841, (3), **2**, 126.

[5] Kohn, *Repertoire de chimie appliquée*, 1858, **1**, 55.

[6] Osmond and Cartaud, *Chem. Zentr.*, 1902, I., 848—from *Ann. Mines*, 1900, **17**, 110: 1900, **18**, 113.

[7] Osmond and Frémont, *Compt. rend.*, 1905, **141**, 361.

[8] Baudrimont, *Ann. Chim. Phys.*, 1850, (3), **30**, 311.

[9] See this volume, Part III.

At a low temperature, such as that of liquid air, pure iron is very brittle;[1] indeed most alloys of iron, with the exception of those containing nickel, lose in ductility as the temperature falls.

The *density* of the metal varies somewhat according to its mechanical history, the usual values obtained for the pure metal ranging from 7·85 to 7·88.[2]

As a rule the density of a metal decreases with cold working, and iron appears to be no exception. Iron filings are less dense than the compact metal from which they are obtained,[3] as indicated by the following data:—

	Density.
Pure compact iron . . .	7·8558
Filings from ditto . . .	7·8172
Decrease in density . . .	0·0386

The effect of cold-drawing of wire upon the density of the metal is clearly shown by the following data, obtained[4] with iron piano-wire. The density has been calculated for a vacuum at 4° C.

	Mean Density.
Piano-wire annealed . . .	7·7970
,, cold drawn . . .	7·7772
Decrease in density . . .	0·0198

Upon annealing the density tends to return to its original value.[5]

The density of solid iron near its melting-point is 6·95, whilst that of the liquid metal a few degrees higher in temperature is 6·88.[6]

Addition of carbon effects a reduction in the density of the metal.[7]

The *melting-point* of iron has frequently been determined; the most reliable results are as follow:—[8]

Melting-Point. °C.	Authority.
1505	Carpenter and Keeling, *J. Iron Steel Inst.*, 1904, I., 242.
1505	Carpenter, *J. Iron Steel Inst.*, 1908, III., 290.
1510	Saklatwalla, *ibid.*, 1908, II., 92.
1533±1	Burgess and Waltenberg, *J. Washington Acad. Sci.*, 1913, 88, 361; *Zeitsch. anorg. Chem.*, 1913, 88, 361.

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[1] Dewar and Hadfield, *Proc. Roy. Soc*, 1905, 74, 326.

[2] Landolt, *Physikalisch-chemische Tabellen*, p. 163 (Berlin, 1912).

[3] Lowry and Parker, *Trans. Chem. Soc*, 1915, 107, 1005.

[4] Kahlbaum and Sturm, *Zeitsch. anorg. Chem.*, 1905, 46, 217.

[5] Further data are given by Chappell and Levin, *Ferrum*, 1913, 10, 271.

[6] W. C. Roberts and Wrightson, *Ann. Chim. Phys.*, 1883, (5), 30, 274.

[7] See this volume, Part III.

[8] The earlier values of Pouillet (*Traité de physique*, 1836, 3, 789), Pictet (*Compt. rend.*, 1879, 88. 1315), etc., are now of historical interest only.

According to Knocke,[1] the *volatilisation* of iron *in vacuo* is sufficiently great to be detected at 755° C.[2] The metal boils[3] at 2450° C. ±50° C. at 36 mm. pressure.

Moissan succeeded in volatilising iron in his electric furnace with a current of 350 amperes at 70 volts. In a few minutes a sublimate or distillate of iron was obtained on a water-cooled tube[4] as a grey powder mixed with some brilliant and malleable scales, and possessed of the same chemical properties as the finely divided metal. The distillation of iron in this manner is difficult on account of the violent frothing caused by the boiling metal evolving occluded gases.[5]

The *specific heat* of iron rises with the temperature.

The following values for the specific heat of a sample of pure iron (Fe 99·87 per cent.)[6] for temperatures ranging from 0° to 100° C. are given by Griffiths,[7] the extreme temperature ranges being 1·4° C. :—

Temperature. °C.	Specific Heat
0	0·1045
10	0·1059
20·5	0·1078
50·3	0·1105
97·5	0·1137

For intermediate temperatures, the specific heat (S_t) may be calculated from the equation

$$S_t = 0{\cdot}1045\,(1 + 0{\cdot}001520t - 0{\cdot}00000617t^2).$$

Other recent results are :—

Temperature Interval. °C.	Specific Heat.	Authority.
17 to 100	0·10983	Tilden, *Phil. Trans.*, 1900, **A, 194**, 233.
17 to 100	0·1098	Schimpf, *Zeitsch. physikal. Chem.*, 1910, **71**, 257.
−188 to +20	0·0859	Richards and Jackson, *ibid.*, 1910, **70**, 414.
−185 to +20	0·095	Nordmeyer and Bernoulli, *Ber. deut. physikal. Ges.*, 1907, **5**, 175.

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[1] Knocke, *Ber.*, 1909, 42, 206.

[2] For the influence of iron, through supposed vaporisation at ordinary temperatures, on photographic plates, see Pellat, *Compt. rend.*, 1898, 126, 1338 ; 1896, 123, 104. Contrast Colson, *ibid*, 1896, 123, 49.

[3] Ruff and Bormann, *Zeitsch anorg. Chem*, 1914, 88, 259 ; Greenwood, *Proc. Roy. Soc.*, 1909, A, 82, 396 ; 1910, A, 83, 483.

[4] Moissan, *Compt. rend.*, 1893, 116, 1429 ; *Traité de Chimie Minérale*, 1905, IV. 307.

[5] Moissan, *Compt. rend.*, 1906, 142, 425.

[6] Obtained from the American Rolling Company. Density 7·858. Analysis showed it to contain the following percentages of impurity :—sulphur, 0 021 ; manganese, 0 036 ; oxygen, 0·015 ; phosphorus, 0·005 ; silicon, trace ; nitrogen, 0·0026 ; carbon, 0·012 ; copper, 0 040 ; hydrogen, 0·0005.

[7] E. H. Griffiths and E. Griffiths, *Proc. Roy. Soc.*, 1913, A, 88, 549.

The mean specific heats of pure iron [1] between 0° and t°, where t ranges from 200° to 1100° C., are given as follow :—[2]

Temperature Range °C.	Specific Heat.	Temperature Range °C	Specific Heat
0 to 200	0·1175	0 to 700	0·1487
0 ,, 300	0·1233	0 ,, 800	0 1597
0 ,, 400	0·1282	0 ,, 900	0·1644
0 ,, 500	0·1338	0 ,, 1000	0·1557
0 ,, 600	0·1396	0 ,, 1100	0·1534

There is marked discontinuity above 900° C.

The specific heat of iron appears to be very slightly increased by cold working.[3]

The coefficient of linear expansion of iron with rise of temperature has been determined [4] for a pure iron containing

Carbon . . .	0·057 per cent.
Manganese . . .	0·13 ,,
Silicon . . .	0·05 ,,

The results are as follow :—

Temperature Interval. °C.	Total Expansion per Unit Length	Coefficient of Expansion per 1° C.
0 to 100	0·0011	0·000011
0 ,, 200	0·0023	0·0000115
0 ,, 300	0·0036	0 000012
0 ,, 400	0·0050	0·0000125
0 ,, 500	0·0065	0·000013
0 ,, 600	0·0081	0·0000135
0 ,, 700	0 00975	0·000014
0 ,, 800	0 01125	0·000014

When heated to 950° C. in an inert atmosphere,[5] iron is disintegrated, emitting particles at right angles to its surface and assuming an etched appearance.

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[1] For a full discussion up to 1907 see Oberhoffer, *Metallurgie*, 1907, 4, 427, 447, 486. Other data are given by Brown, *Trans. Roy. Dublin Soc.*, 1907, (2), 9, 59 ; Behn, *Wied. Annalen*, 1898, 66, 237—for metals containing 0 5 per cent. carbon, Pirani (*Ber. deut. physikal. Ges.*, 1912, 14, 1037) between 110° and 970° C. Lecher (*ibid.*, 1907, 5, 647) gives relative values obtained by an electrical method. Schmitz, *Proc Roy. Soc*, 1903, 72, 177 ; Naccari, *Gazzetta*, 1888, 18, 13 ; Pionchon, *Ann. Chim. Phys.*, 1887, 11, 72 ; *Compt. rend.*, 1886, 103, 1122. Earlier data are those of Dulong and Petit (*Ann. Chim. Phys.*, 1818, (2), 7, 113) ; Regnault, *ibid.*, 1843, (3), 9, 322.

[2] Harker, *Phil. Mag*, 1905, (6), 10, 430. The composition of the iron was as follows :—carbon, 0 01 per cent.; silicon, 0·02 per cent.; sulphur, 0 03 per cent.; phosphorus, 0 04 per cent ; manganese, trace.

[3] Chappell and Levin, *Ferrum*, 1913, 10, 271.

Le Chatelier, *Compt. rend.*, 1899, 129, 331.

Kaye and Ewen, *Proc. Roy. Soc.*, 1913, A, 89, 58.

The *refractive index* of iron, for sodium light, is 1 85.[1]

The most intense lines in the spectrum of iron are as follow :—[2]

Arc[3] : 3020·75, 3021·19, 3047·72, 3440·77, 3441·13, 3466·02, 3490·73, 3565·54, 3570·24, 3570 29, 3581·34, 3581·38, 3609·01, 3618·91, 3631·60, 3648·00, 3705·74, 3708 06, 3709·39, 3720 09, 3722 73, 3735 02, 3737·30, 3745·70, 3748 40, 3749 62, 3763 92, 3763 99, 3816·00, 3820 61, 3824·60, 3826·07, 3828 00, 3834·40, 3860·03, 3886·45, 4045·99, 4063 74, 4063·77, 4071·92, 4260·68, 4271 95, 4308·09, 4325·97, 4383·71, 4404·95, 4415·31, 5167·67, 5233·15, 5269·70, 5324·38, 5365 00, 5367·61, 5370·13, 5383 58, 5404·34, 5411·15, 5415·40, 5424·30, 5429·94, 5445 28, 5447·15, 5455 81, 5573·09, 5586·98, 5615·89, 6400·25, 6495·25.

Spark: 2599·50, 2739·63, 2749·41, 2755·80, 4045·99, 4308·10, 4325·97, 4383·73, 4404·95.

Allotropy of Iron.—When a bar of pure iron is allowed to cool from its melting-point to 0° C., its time-temperature cooling curve exhibits three breaks,[4] or arrests, designated by the symbols Ar_4, Ar_3, and Ar_2 respectively.[5] These arrests are due to evolution of a small amount of heat consequent upon some internal alteration in the metal, whereby the rate of cooling is retarded. Indeed, the evolution of heat at the Ar_3 point is sufficient to raise the temperature of the iron by a very appreciable amount. The phenomenon is termed *recalescence*.[6] Similarly, on reheating the metal, three arrests, due to heat absorption, are observed at temperatures denoted by Ac_2, Ac_3, and Ac_4.[1] The points occur at approximately the following temperatures :—

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[1] Ross, *Physical Review*, 1911, 33, 549. See also Kundt, *Wied. Annalen*, 1888, 34, 469, from *Sitzungsber. K. Akad. Wiss Berlin*, 1888, p 255.

[2] Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911).

[3] For further researches on the arc and spark spectra of iron see Ainslie and Fuller, *Trans. Roy Soc Canada*, 1918, 12, (3), 65; Hoeltzenbein, *Zeitsch. wiss Photochem.*, 1917, 16, 225; Lang, *ibid.*, 1916, 15, 223; Janicki, *ibid.*, 1914, 13, 173; Viefhaus, *ibid.*, pp. 209, 245; Burns, *ibid.*, 235, also 1913, 12, 207; Goos, *ibid* , 1913, 12, 259; 1912, 11, 1, 305; Eversheim, *Ann Physik*, 1911, (4), 36, 1071; 1909, (4), 30, 815; Buisson and Fabry, *Ann. Physik*, 1912, (4), 38, 245; *Compt. rend* , 1908, 146, 751; 1906, 143, 165; Kayser, *Zeitsch. wiss. Photochem.*, 1911, 9, 173; Hartmann, *Physikal. Zeitsch* , 1909, 10, 121; Finger, *Ber. deut. physikal. Ges* , 1909, 11, 369; *Zeitsch. wiss. Photochem.*, 1909, 7, 329 , Pollok and Leonard, *Sci. Proc Roy. Dublin Soc* , 1907, (2), 11, 217; Keller, *Chem. Centr.*, 1906, II., 1231, from *Zeitsch. wiss Photochem.*, 1906, 4, 209; Lockyer and Baxandall, *Proc. Roy. Soc.*, 1904, 74, 255; Adeney, *Trans. Roy. Dublin Soc.*, 1901, (2), 7, 331; Crew, *Phil. Mag.*, 1901, (5), 50, 497; Lockyer, *Proc. Roy. Soc.*, 1897, 60, 475; 1893, 54, 359; Liveing and Dewar, *ibid* , 1881, 32, 225, 402. On the *flame spectrum* of iron see Hemsalech, *Phil. Mag* , 1918, 36, 209, 281; *Compt. rend* , 1916, 163, 757; Lockyer and Goodson, *Proc Roy. Soc.*, 1916, A, 92, 260; Hemsalech and de Watteville, *Compt. rend* , 1910, 150, 329; 1908, 146, 748, 859, 962; Auerbach, *Zeitsch wiss. Photochem.*, 1909, 7, 41; *Abstr. Chem. Soc* , 1909, ii. 279; de Watteville, *Phil Trans* , 1904, A, 204, 139; Perry, *Chem. News*, 1884, 49, 241; Lockyer, *Compt. rend.*, 1881, 92, 904. The *infra-red spectrum* of iron has been studied by Randall and Barker, *Astrophys. J.*, 1919, 49, 42; Lehmann, *Chem. Zentr.*, 1901, I., 81. The *vacuum tube spectrum* of iron . Pollok, *Sci. Proc. Roy. Dublin Soc* , 1912, 13, 253. The *furnace spectrum* of iron: King, *Ann. Physik*, 1905, (4), 16, 360. The spectrum of iron developed by exploding gases: Liveing and Dewar, *Phil. Mag* , 1884, (5), 18, 161. On the *magnetic resolution* of the iron spectrum, see Graftdyk, *Arch. Néerland*, 1912, (3A), 2, 192 , Luttig, Hartmann, and Peterke, *Ann. Physik*, 1912, (4), 38, 43.

[4] If the iron contains carbon—preferably about 0 25 per cent ,—a fourth arrest is observed, designated as Ar_1 on the cooling curve, and Ac_1 on the reheating curve Ar_1 occurs at approximately 690° C., and is generally recognised as due to a change in the condition of the carbon which, at higher temperatures, is held in solid solution, but at the Ar_1 point begins to separate out in combination with some iron as triferrocarbide or cementite (see p. 195).

[5] Symbols introduced by Osmond: A=arrêt, and r=refroidissement.

[6] Barrett, *Phil. Trans.*, 1873, (4), 46, 472.

Ac_2	770° C.	Ac_3	910° C.	Ac_4	1404° C.
Ar_2	760° C.	Ar_3	890° C.	Ar_4	1401° C.

The point now known as Ar_3 was the first to be discovered,[2] it being observed that, during the cooling of a piece of iron from a high temperature, on reaching " a very dull heat, a sudden accession of temperature occurred, so that it glowed once more with a bright heat."

It will be observed that the *Ac* points are slightly higher than the corresponding *Ar* points, but are indicative of the same phenomena. The divergence is explained by assuming that a certain amount of inertia or resistance to change exists, known as *lag*, which tends to lower the temperature of arrest during cooling, and probably to raise it slightly during heating.

When determinations are made of the variation of other physical properties of iron, with rise or fall of temperature, discontinuities or abrupt changes are usually observed at temperatures approximating to the various A points. The first of these to be observed was the sudden elongation manifested by iron wire, at a temperature not stated, when allowed to cool from red heat to about 15° C.[3] This peculiarity, announced by Gore in 1869, was confirmed by Barrett,[2] who also showed that during the heating of the wire an interruption of the expansion of the metal occurred at approximately the same temperature. The elongation of the metal on cooling was found to occur simultaneously with the recalescent point now known as the Ar_3 point.

The electric resistance of pure iron increases from 0° C. to a maximum at 757° C., corresponding to the A_2 point, and then falls to a minimum at 894° C.—the A_3 point. On cooling the reverse changes occur at practically the same temperatures.[4] The presence of hydrogen under atmospheric pressure does not materially affect the resistance of the metal up to 920° C.[5]

The thermo-electric potential differences between platinum and iron at various temperatures reach a maximum at 850° C.[6]—a temperature closely approximating to the A_3 point.

The magnetic susceptibility of iron rapidly increases at 1365° C., when the metal is raised to this temperature from a lower one, and the reverse change takes place at 1310° C. on cooling from a higher temperature. These points evidently correspond to the Ac_4 and Ar_4 points respectively.

The foregoing results are usually interpreted as indicating that iron is capable of existing in four allotropic modifications, designated respectively as α, β, γ, and δ ferrite, the points A_2, A_3, and A_4 representing their transition temperatures (that is, the temperatures at which the arrests, on cooling or reheating, would be observed were it not for the lagging). Thus α ferrite is the ordinary variety of pure iron, stable below A_2, at which point both α and β ferrite are in equilibrium. Between A_2 and A_3 the β ferrite constitutes the stable phase; between A_3 and A_4 γ ferrite is stable, whilst above A_4 δ ferrite exists. This may be represented diagrammatically as follows :—[1]

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[1] c = chauffage.

[2] Barrett, *Phil Trans.*, 1873, (4), 46, 472.

[3] Gore, *Proc. Roy. Soc.*, 1869, 17, 260.

[4] Burgess and Kellberg, *J. Washington Acad. Sci*, 1914, 4, 436. See also Honda and Ogura, *Science Reports Univ. Sendai*, 1914, 3, 113; Le Chatelier, *Compt. rend*, 1890, 110, 283. The resistance of iron at low temperatures has been determined by Schimank, *Ann. Physik*, 1914, (4), 45, 706.

[5] Sieverts, *Internat. Zeitsch. Metallographie*, 1912, 3, 36. See also Harding and D. P. Smith, *J. Amer. Chem. Soc*, 1918, 40, 1508

[6] Laschtschenko, Bykoff, and Efremoff, *J. Russ. Phys. Chem. Soc.*, 1916, 48, 279. See also Broniewski, *Compt. rend.*, 1913, 156, 699.

	A_2.	A_3.	A_4.	Melting-point.
0°	769°	906°	1404°	1505° C.
α	β	γ	δ	

Many metallurgists, however, incline to the view that β ferrite is really a solid solution of γ in α ferrite [2]; in other words, the assumption is made that when iron cools below A_3 the conversion of γ ferrite into α ferrite is not quite complete, a few γ molecules remaining dissolved in the α until the A_2 point is reached, at which point the transformation is completed, α ferrite alone remaining.[3]

Whether this view be accepted or not, it is convenient to retain the name β ferrite to indicate that particular phase of the metal between the A_2 and A_3 points.

α, β, and γ ferrite crystallise in the cubic system,[4] but present well-marked specific characters indicative of varying internal structures. It has been suggested [5] that δ ferrite is monatomic iron, Fe; γ ferrite is diatomic, Fe_2; and β ferrite is triatomic, Fe_3. At present, however, very little is known of the structure of the iron molecule.

Carbon readily dissolves in γ ferrite, is soluble to a slight extent in β ferrite, but is practically insoluble in α ferrite.

For a more detailed discussion of this subject and its bearing upon the metallurgy of iron and steel, see this volume, Part III.

Occlusion of Gases.—Iron readily absorbs or "occludes" gases,[6] and may contain from ten to twenty times its own volume of gas. Meteoric iron usually contains hydrogen, nitrogen, helium, and oxides of carbon. The gases are evolved on heating the metal *in vacuo*, the different gases being characterised by a definite temperature of evolution.[7] The gases most usually occluded by terrestrial iron are the oxides of carbon, nitrogen, and hydrogen, and sometimes the last traces of them are held very tenaciously by the metal, a third heating *in*

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[1] The mean temperatures given for the A_2, A_3, and A_4 points are those of Ruer and his co-workers, *Ferrum*, 1914, 11, 257; 1915, 13, 1.

[2] Benedicks, *J. Iron Steel Inst.*, 1912, II., 242; 1914, I., 407; Carpenter, *ibid.*, 1913, I., 315. Le Chatelier (*Rev. Metallographie*, 1904, I., 213) appears to have been the first to suggest that the A_2 point is not connected with allotropic change.

[3] See Carpenter, *J. Iron Steel Inst.*, 1913, I., 315, and the interesting discussion, pp 327–360.

[4] Osmond and Cartaud, *Compt. rend.*, 1906, 142, 1530; 1906 143, 44; *Ann. Mines*, 1900, (9), 18, 113.

[5] Weiss, *Trans. Faraday Soc.*, 1912, 8, 153. Contrast Honda and Takagi, *J. Iron Steel Inst.*, 1915, II., 181

[6] See Neumann and Streintz, *Monatsh.*, 1892, 12, 656. See also Deville and Troost, *Compt. rend.*, 1868, 66, 83; 1863, 57, 894, 965; Cailletet, *ibid.*, 1865, 60, 344; 1864, 58, 327, 1057; Deville, *ibid.*, 1864, 59, 102, 1864, 58, 328; Troost and Hautefeuille, *ibid.*, 1875, 80, 788; 1873, 76, 562; Graham, *Ber.*, 1879, 12, 93; *Compt. rend*, 1867, 64, 1067; Baxter, *Amer. Chem. J.*, 1899, 22, 362; Heyn, *Stahl und Eisen*, 1900, 20, 837, Richards and Behr, *Zeitsch. physikal. Chem.*, 1907, 58, 301. The absorption of hydrogen by thin films of iron on glass has been studied by Heald, *Physikal. Zeitsch.*, 1907, 8, 659.

[7] Belloc, *Compt. rend.*, 1907, 145, 1280.

vacuo to 1100° C. still yielding some gas.[1] Muller[2] showed that the gases occluded in iron are, for the most part, mechanically held in the pores of the metal, for they are liberated on boring, only a very little more gas being obtained when the borings are heated to redness *in vacuo*. Helium is absorbed by iron, but less readily than hydrogen.[3] Iron wire absorbs increasing quantities of hydrogen when heated in an atmosphere of that gas from 400° C. upwards, but on cooling the whole of the gas is evolved.[4] The solubility is independent of the superficial area of the metal,[5] so that the phenomenon is an example of true solution and not of adsorption, which is purely a superficial effect. At constant temperature the solubility of the gas is directly proportional to the square root of the pressure[6] in both the solid and the molten metal. At constant pressure the solubility of hydrogen increases with the temperature. The curve connecting the solubility with the temperature does not indicate any change in the neighbourhood of the A_2 point, but a rapid increase in solubility manifests itself in the neighbourhood of the A_3 point—that is, between 850° and 900° C. When the molten metal solidifies in an atmosphere of hydrogen, it exhibits the phenomenon of "spitting." The power to occlude gases is closely connected with the amorphous cement layers between the ferrite crystals (see p. 54).

Absorption of Nascent Hydrogen.—Iron readily absorbs nascent hydrogen.[7] When saturated with this gas, iron is characterised by unusual brittleness (see p. 54), but, on prolonged exposure to air, or more rapidly on heating, the hydrogen is evolved and the metal regains its usual physical properties.[8]

A ready method of studying these changes consists in immersing iron wires in very dilute sulphuric acid. Under these conditions the metal will absorb some twenty times its volume of hydrogen. The brittleness appears to be due to the adsorption of the gas by the thin intercrystalline cement joining the ferrite crystals together (see p. 54), the cement thus increasing in volume to such a degree as to force the crystals apart somewhat, thus reducing the intercrystalline cohesion.[9]

The property of absorbing nascent hydrogen is shared by steel and cast iron, but the purer forms of the metal are more readily affected. Cast iron was found by Ledebur[10] to require a very prolonged exposure to a relatively concentrated acid to produce a well-defined effect, possibly on account of its high silicon content. The general results obtained by Ledebur are given in the table on p. 45. Iron and steel wires were used, ranging in diameter from 0·065 to 0·140 inch. It will be observed that the hydrogenised wires possessed substantially the same tenacity, but their elongation decreased, whilst their brittleness showed a substantial increase. Exposure to air at the ordinary temperature gradually restored the wires to their normal state,—a change that was rapidly brought about by ignition to cherry-red heat in an inert atmosphere.

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[1] Boudouard, *Compt. rend.*, 1907, 145, 1283.

[2] Muller, *Ber.*, 1879, 12, 83; 1881, 14, 6.

[3] Tilden, *Proc. Roy. Soc.*, 1896, 59, 218.

[4] Sieverts, *Zeitsch. physikal. Chem.*, 1907, 60, 129

[5] Sieverts, *ibid.*, 1911, 77, 591.

[6] Sieverts, *loc. cit.*; Jurisch, *Stahl und Eisen*, 1914, 34, 252.

[7] See Thoma, *Zeitsch. physikal. Chem*, 1889, 3, 69.

[8] W. H. Johnson, *Proc. Roy. Soc.*, 1875, 23, 168; *Mem. Manchester Lit. Phil. Soc.*, 1872-3, 12, 74; 1873-4, 13, 100; Reynolds, *ibid.*, 1873-4, 13, 93.

[9] Andrew, *Trans. Faraday Soc.*, 1919, 14, 232.

[10] Ledebur, *Stahl und Eisen*, 1887, 7, 681.

LEDEBUR'S EXPERIMENTS WITH HYDROGENISED WIRES.

Series.	Treatment.	Tenacity in Tons per sq. inch.		Elongation. Per cent.		Number of times the metal could be bent.	
		Normal.	Hydrogenised.	Normal.	Hydrogenised	Normal.	Hydrogenised.
I.	Uncleaned wires immersed 24 hours in 1 per cent. sulphuric acid and examined after 3 days.	54·54	54·66	3·5	2·8	10·2	8·0
II.	Cleaned wires immersed 23 hours in 2·5 per cent. sulphuric acid and examined immediately.	54·09	56·00	3·4	2·7	7·4	3·0
III.	Wires connected with a block of zinc and immersed in 2·5 per cent. sulphuric acid for 3 hours. Examined immediately.	52·76	52·19	2·0	2·2	10·0	3·9
IV.	Similar to Series III. Wires examined 4 days later.	51·11	51·17	3·0	2·2	10·1	7·2
V.	Similar to Series III. Wires heated to cherry red for 15 minutes in an inert atmosphere.	27·24	28·51	17·9	16·9	16·2	14·6

Permeability to Gases.—Closely connected with the power to occlude gases is the property of transfusion, by virtue of which gases are able to pass through iron. In 1863 Cailletet [1] showed that nascent hydrogen could pass through an iron vessel immersed in sulphuric acid at the ordinary temperature, and this has been confirmed by numerous later investigators.[2]

This diffusion of nascent hydrogen is not inhibited even by a pressure of 14 atmospheres. Molecular hydrogen only passes through iron at a measurable velocity when the temperature is raised. Below 325° C. the velocity is inappreciable, at 350° C. it becomes perceptible, and at 850° C. the velocity is some forty times as great.[3]

Iron is softened by prolonged exposure at 500° to 1000° C. to the transfusion of hydrogen, for the gas reduces and removes the small quantities of non-metallic impurities usually existing in the metal. Thus, for example, sulphur, phosphorus, and carbon are reduced and escape as volatile hydrides, the metal being purified to a corresponding extent.[4]

The optimum temperature-range for this purpose lies between 950° and 1000° C., hydrogen containing small quantities of water vapour proving most efficient. The time of decarburisation is necessarily somewhat lengthy, and averages not less than some 4 or 5 days. The following results [5] may be regarded as typical:—

Time of Decarburisation. Days.	Carbon. Per cent.		Sulphur. Per cent.	
	Before.	After.	Before.	After.
4	0·094	0·076	0·025	0·017
5	0·182	0·015	0·030	0·017
4	0·326	0·027	0·026	0·018
5	0·683	0·026	0·016	0·006
5	1·05	0·035	0·011	0·003
12	1·67	0·220	0·042	0·008

No doubt if the decarburisation process were very greatly prolonged, the carbon and sulphur would be reduced to infinitesimal quantities. Analogous reactions take place between hydrogen and molten iron.[6]

Chemical Properties of Pure Compact Iron.—When exposed to dry air at ordinary temperatures, iron retains its silver-white appearance. If the air, however, is moist, and the temperature fluctuating so that liquid water collects on the surface of the metal, oxidation or rusting occurs (see Chap. IV.).

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[1] Cailletet, *Compt. rend.*, 1863, 66, 847.

[2] See Reynolds, *Mem. Manchester Lit Phil Soc.*, 1873–4, 13, 93; Winkelmann, *Ann. Physik*, 1905, (4), 17, 590; Charpy and Bonnerot, *Compt. rend*, 1912, 154, 592.

[3] Charpy and Bonnerot, *loc. cit.*

[4] Charpy and Bonnerot, *Compt. rend.*, 1913, 156, 394.

[5] Campbell, *J. Iron Steel Inst.*, 1919, II., 407.

[6] Schmitz, *Stahl und Eisen*, 1919, 39, 373, 406.

When heated in air or oxygen a piece of polished iron undergoes no apparent change below a temperature of about 150° C. Further heating results in tarnishing. As this is merely slight superficial oxidation, the temperature at which it becomes distinctly visible depends upon the duration of the experiment. Thus, for example, prolonged heating at 170° C. may result in the production of a pale straw colour, although for short periods of time a temperature of 220° C. is normally required to produce the same effect.[1] Given reasonably uniform conditions, however, the extent of the oxidation, which may be judged by the characteristic hues imparted to the iron, is a fairly accurate indication of the temperature. Workmen avail themselves of this with remarkable skill in tempering steels, the data usually accepted [2] being as follows :—

Colour.	Temperature. °C.	Colour.	Temperature. °C.
Pale yellow	220	Purple	277
Straw	230	Bright blue	288
Golden yellow	243	Full blue	293
Brown	255	Dark blue	316
Brown purple	265		

These tempering colours are obtained even in the presence of such dry air as that obtained by continued exposure to phosphorus pentoxide,[3] clearly proving that the reaction is one of direct oxidation of the metal, and therefore entirely distinct from ordinary rusting which involves a preliminary solution of the metal (see p. 67). The oxide produced is usually believed to have the composition represented by the formula Fe_3O_4. According to Mosander,[4] this is correct in so far as the extreme outer layers of oxide are concerned, those occurring nearer the metal itself having some such formula as $Fe_2O_3.6FeO$, or $Fe_3O_4.5FeO$. This does not necessarily imply the existence of a definite compound, however; it is more reasonable to assume that ferrous oxide is first formed, and this is relatively slowly converted into ferroso-ferric oxide on account of the difficulty experienced by the oxygen in penetrating the outer layers. Hence the above substance is really a mixture of Fe_3O_4 and FeO.

When iron wire is strongly heated in an atmosphere of oxygen it burns with a brilliant flame. A pleasing lecture experiment consists in holding a bunch of fine iron wire in the upper part of a Bunsen flame and allowing a jet of oxygen from a gas cylinder to impinge upon the whole.

A modification of this experiment consists in placing [5] a small piece of glowing wood charcoal on a heap of purified iron filings and a stream of oxygen directed upon it. Vigorous combustion ensues, the whole fusing to a white-hot mass of ferroso-ferric oxide, Fe_3O_4.

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[1] T. Turner, *Proc. Birm. Phil. Soc*, 1889, vi., part ii.; Guillet and Portevin, *Revue Métallurgie*: *Mémoires*, vi. p. 102; Loewenherz, *Zeitsch. Instrumentenkunde*, 9, 316. Roberts showed that these colours are due to the formation of oxide, as they are not produced by heating iron *in vacuo* (*Trans. Inst. Mech. Eng*, 1881, p. 710).

[2] Howe, *The Metallurgy of Steel*, 2nd ed., 1891, I., 23.

[3] Friend, *J. Iron Steel Inst.*, 1909, II., 172.

[4] Mosander, *Pogg. Annalen*, 1826, 6, 35.

[5] Kuspert, *Chem. Zentr.*, 1906, II., 87, from *Zeitsch. phys.-chem. Unterr.*, 19, 166.

According to Charpy, when iron is heated in contact with carbon (graphite) it does not become carburised even at 950° C. unless at least traces of oxygen or an oxide of carbon are present,[1] but this is disputed.[2]

Iron absorbs silicon, when heated with that element, at temperatures considerably below 950° C.[3]

When heated in steam electrolytic iron undergoes no change until about 330° C., when tarnishing begins to take place. At 400° C. a small but measurable quantity of hydrogen is formed, and the velocity of the reaction increases rapidly with further rise of temperature. The reaction appears to take place in three stages, involving [4]

1. Dissociation of the steam,

$$H_2O \rightleftharpoons H_2 + O.$$

2. Formation of ferrous oxide,

$$Fe + O \rightleftharpoons FeO.$$

3. Oxidation to ferroso-ferric oxide,

$$3FeO + O \rightleftharpoons Fe_3O_4.$$

For ordinary iron shavings, the lowest temperature at which hydrogen is evolved is about 300° C., and the optimum yield is obtained at 800° C.[5]

If the reaction is allowed to take place in an enclosed space, it does not proceed to completion. Equilibrium is set up, and the reaction obeys the law of Mass Action.[6] The initial and final stages of the equilibrium may be represented as follows :—

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

Designating the pressure of water vapour as p_1 when equilibrium has been reached, and the hydrogen pressure as p_2, Preuner obtained the following mean values for the ratio p_1/p_2 :—

Temperature. °C.	p_1/p_2.
900	0·69
1025	0·78
1150	0·86

When magnetic oxide of iron is heated in a current of hydrogen gas, one of the gaseous phases, namely steam, is swept away, with the result that the oxide is readily reduced to the metal. The same is true for the other oxides of iron, and the reduction has been observed to commence at relatively low temperatures, namely at about 305° C. with magnetic oxide and 370° C. with ferrous oxide.[1] Hilpert [2] finds that if the ferrous oxide has not previously been heated above 400° C., it can be reduced at 280° C. in hydrogen; but if previously heated to 1200° C., reduction is not apparent below 330° C. This shows that the physical condition of the oxide has an important influence upon its dissociation pressure.[3]

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[1] Charpy and Bonnerot, *Compt. rend.*, 1911, 153, 671 ; 1910, 150, 173 ; Guillet and Griffiths, *ibid.*, 1909, 149, 125.

[2] See Giolitti and Astorri, *Gazzetta*, 1910, 40, i. 1 ; Giolitti and Carnevali, *Atti R. Accad. Sci. Torinò*, 1910, 45, 337.

[3] Lebeau, *Bull. Soc. chim.*, 1902, (3), 27, 44.

[4] Friend, *J. West Scotland Iron Steel Inst.*, 1910, 17, 66 ; *J. Iron Steel Inst.*, 1909, II., 172.

[5] Lettermann, *Chem. Zentr.*, 1896, I., 952.

[6] This was first proved by Deville (*Annalen*, 1871, 157, 71 ; *Compt. rend.*, 1870, 70, 1105, 1201 ; 1870, 71, 30) and Chaudron (*Compt. rend.*, 1914, 159, 237), and subsequently confirmed by Preuner (*Zeitsch. physikal. Chem.*, 1904, 47, 385)

The oxidation of iron with steam is used technically as a means of protecting the metal against corrosion. This is the principle of the Bower-Barff process.

With nitrous oxide at 200° C. ferrous oxide is produced.[4] Nitrogen is absorbed by the heated metal to a slight extent, particularly when melted under a high pressure of the gas, yielding the nitride.[5] The nitride is also produced by heating the metal to 800° C. in an atmosphere of ammonia, the physical properties of the metal undergoing considerable alteration.

When iron is heated in contact with carbon and its oxides, many interesting reactions occur. At 900° C. in a current of carbon dioxide iron yields ferrous oxide, whilst at 1200° C. magnetite is produced, which is both magnetic and crystalline. Ignition in carbon monoxide at 1000° C. yields ferrous oxide.[6]

The reaction between carbon monoxide and iron at 650° C. involves the deposition of carbon in those cases where the gas is allowed to pass over the metal in a continuous stream. If, however, the gas and metal are allowed to remain in contact in a closed vessel at 650° C., no carbon is deposited; but a carbide, most probably cementite, Fe_3C, is formed, and an oxide. The iron may be dissolved in acid without leaving any carbonaceous residue. What the precise nature of the reactions may be is not certain.[7] The products appear to be the result of many balanced reactions which may be represented by the following equations :—

$$\begin{aligned}&\text{(i.)} && 3Fe+2CO \rightleftharpoons Fe_3C+CO_2.\\ &\text{(ii.)} && 2CO \rightleftharpoons C+CO_2.\\ &\text{(iii.)} && Fe_3C+4CO_2 \rightleftharpoons 3FeO+5CO.\end{aligned}$$

The carbide content falls with increase of pressure of carbon dioxide, becoming nil with a partial pressure of 43 per cent. of carbon dioxide, the remaining gas being carbon monoxide. At 850° C., iron decomposes carbon monoxide, yielding triferro carbide (cementite) and carbon dioxide ; thus

$$3Fe+2CO=Fe_3C+CO_2.$$

The iron carbide now decomposes more carbon monoxide, yielding the dioxide and unstable higher carbides of iron, which latter dissociate into free carbon and cementite.[1]

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[1] Glaser, *Zeitsch. anorg. Chem*, 1903, 36, 1.

[2] Hilpert, *Ber*, 1909, 42, 4575.

[3] Somewhat analogous conclusions have been drawn from the behaviour of cupric oxide (Allmand, *Trans. Chem. Soc.*, 1910, 97, 603).

[4] Sabatier and Senderens, *Compt. rend.*, 1892, 114, 1429.

[5] Andrews, *J. Iron Steel Inst.*, 1912, II, 210; Rogstadius, *J. prakt. Chem*, 1862, 86, 307.

[6] Tissandier, *Compt. rend*, 1872, 74, 531.

[7] Carpenter and C C Smith, *J Iron Steel Inst*, 1918, II, 139; Falcke, *Ber.*, 1913, 46, 743.

When carbon monoxide and hydrogen saturated with water vapour is passed over iron at 250° to 300° C., several interesting changes may take place. Formaldehyde may be detected in the distillate and a fatty substance, m.pt. 35° to 36° C., isolated by extraction with ether.[2] These reactions recall the behaviour of nickel under analogous conditions.[3]

Iron is readily corroded by moist chlorine at atmospheric temperatures, and when strongly heated in a current of the dry gas yields ferric chloride, which volatilises and condenses on a cooler part of the apparatus in a beautifully crystalline form.

A small ball of steel wool, if sprinkled with antimony, will ignite in chlorine at the ordinary temperature.[4] Iron is not attacked by anhydrous liquid chlorine.[5]

When heated in hydrogen chloride, iron yields ferrous chloride, free hydrogen being evolved.[6]

Heated to dull redness in bromine vapour, iron yields a yellow crystalline dibromide, $FeBr_2$, or the dark red ferric salt, $FeBr_3$, according to circumstances, excess of bromine vapour being essential to produce the latter compound.

Heated with excess of iodine, iron yields a grey mass of ferrous iodide; the same salt is formed when iron filings are triturated with iodine (see below).

When heated together, iron and sulphur readily unite to yield non-magnetic ferrous sulphide.

Sulphur dioxide, when dry, has no action on iron, even at 100° C., but the metal is slightly attacked by the moist gas.[7] Liquid sulphur dioxide has likewise but little action under atmospheric pressure, but in refrigerators, where the temperature is liable to rise somewhat during compression of the gas, corrosion of the iron is appreciable.

When heated to 150° to 200° C. in sealed tubes with thionyl chloride,[8] ferric chloride is obtained in accordance with the equation

$$2Fe+4SOCl_2=2FeCl_3+2SO_2+S_2Cl_2.$$

If, however, the metal is present in excess, ferrous sulphide and chloride result. Thus:

$$3Fe+2SOCl_2=2FeCl_2+FeS+SO_2.$$

Nickel is not attacked under these conditions.

When heated with sulphuryl chloride, SO_2Cl_2, anhydrous ferric chloride is obtained, large crystals being formed in favourable circumstances.[9] Sulphuryl fluoride, SO_2F_2, is without action on iron, even at red heat.[10]

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[1] Hilpert and Dieckmann, *Ber.*, 1915, 48, 1281. Compare Gautier and Clausmann, *Compt. rend.*, 1910, 151, 16.

[2] Gautier and Clausmann, *ibid.*, p. 355.

[3] See this volume, Part I., p. 93.

[4] Ohmann, *Chem. Zentr.*, 1914, I., 331.

[5] See this series, Vol VIII. (1915), p. 63.

[6] See Isambert, *Compt. rend.*, 1886, 102, 423.

[7] Lange, *Zeitsch. angew. Chem.*, 1899, 12, 275, 303, 595; Harpf, *ibid*, p. 495.

[8] North and Hageman, *J. Amer. Chem Soc*, 1912, 34, 890.

[9] North, *Bull. Soc. chim*, 1911, (4), 9, 646

[10] Moissan and Lebeau, *Compt. rend.*, 1901, 132, 374.

Silicon tetrachloride vapour is decomposed by iron at high temperatures, yielding diferrosilicide and ferrous chloride,[1]

$$SiCl_4+4Fe=Fe_2Si+2FeCl_2.$$

Nitric oxide is reduced by moist iron over mercury, yielding a mixture of nitrous oxide and nitrogen.[2] The nitrous oxide is slowly reduced to nitrogen.[3]

Iron precipitates copper, silver, antimony, lead, and tin from solutions of their salts. In the case of tin the deposit may be exceedingly small, as it forms a thin protecting layer on the surface of the iron. For this reason iron dissolves much less rapidly in an acid if a tin salt is present. A pretty experiment consists in immersing a strip of iron in a tube containing a solution, the bottom half of which consists of a concentrated electrolyte in which some tin salt is dissolved, and the upper half a dilute solution of the electrolyte without any tin. The lower portion of the iron strip becomes covered with crystals of tin, whilst the upper portion is quite free, although if completely immersed in the lower portion no tin deposit would be visible.[4]

In the precipitation of silver from dilute solutions of silver nitrate, unworked iron is found to be more active than the worked or strained metal.[5]

The precipitation of copper from solution by means of iron is used commercially as a wet method of extracting copper from pyrites.[6] The kind of scrap iron used appears to influence very markedly the physical condition in which the copper is precipitated. The mud which collects when neutral copper sulphate solutions are reduced in this manner contains a basic ferric sulphate, $Fe_2(OH)_4.SO_4$,[7] but addition of a little dilute sulphuric acid prevents this, and enables a clean deposit of copper to be obtained.

Iron dissolves in ammonium persulphate solution, yielding ferrous sulphate, a portion of which undergoes further oxidation.[8]

A solution of bleaching powder rapidly attacks iron, with evolution of oxygen.[9] A concentrated solution of ferric chloride has little action on iron, but the metal readily dissolves in a dilute solution.[10]

Iron has been recommended [11] as an electrode, together with carbon in a galvanic cell, the electrolyte being a concentrated solution of ferric chloride. The iron dissolves, yielding ferrous chloride,

$$2FeCl_3+Fe=3FeCl_2,$$

which is converted into the ferric state again by passage of chlorine gas. The generated current, of course, passes in the direction from the carbon to the iron through the connecting wire. The cell may be varied by immersing the carbon in ferric chloride solution in a porous cell, surrounded by a solution of sodium chloride into which the iron electrode is made to dip.[1]

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[1] Vigouroux, *Compt. rend*, 1905, **141**, 828.

[2] Sabatier and Senderens, *ibid*, 1895, **120**, 1158.

[3] Sabatier and Senderens, *ibid.*, p. 1212.

[4] Thiel and Keller, *Zeitsch anorg. Chem.*, 1910, 68, 220.

[5] Senderens, *Bull. Soc. chim*, 1897, (3), **15**, 691.

[6] See this series, Volume II.

[7] Essner, *Bull. Soc. chim.*, 1891, (3), 6, 147.

[8] Turrentine, *J. Physical Chem.*, 1907, **11**, 623. See also Levi, Migliorini, and Ercolini, *Gazzetta*, 1908, **38**, i. 583.

[9] White, *J Soc. Chem. Ind.*, 1903, **22**, 132.

[10] Spring, *Rec. Trav. Chim.*, 1897, **16**, 237.

[11] Pauling, *Zeitsch. Elektrochem.*, 1897, **3**, 332.

Iron and iodine interact in the presence of water, evolving heat, ferrous iodide passing into solution. The reaction appears to take place in stages involving the formation of ferric iodide, which decomposes into ferric oxide and hydrogen iodide, the last-named attacking the free iron with the formation of ferrous iodide.[2]

The Action of Acids upon Iron.—As a general rule, when acids act upon iron hydrogen gas is evolved and the metal passes into solution in the form of a ferrous salt. Thus, for example, dilute sulphuric acid solution reacts as follows :—

$$Fe+H_2SO_4=FeSO_4+H_2.$$

Prolonged exposure of such solutions to the air results in the more or less complete conversion of the ferrous salt to the ferric condition, which may either remain in solution or be precipitated as a basic salt according to circumstances. After exposure to acid attack, the undissolved pieces of iron very frequently exhibit a peculiar brittleness, but revert to their original condition if kept for one or two days at ordinary temperatures, or in the course of a few hours if gently warmed. This phenomenon was first observed by Johnson in 1873, and the following year was proved by Reynolds to be entirely due to the occlusion of hydrogen within the pores of the metal (see p. 54).

The purer forms of iron (wrought iron and steel) appear to be much more susceptible to this kind of reaction than cast iron.[3] If the attacking acid is readily reducible by hydrogen, many secondary reactions may take place. Thus with nitric acid, oxides of nitrogen and ammonia may be evolved ; whilst with selenic acid a deposit of elementary selenium is obtained (see below). When iron is exposed to the action of acids that are also powerful oxidisers—such as, for example, fairly concentrated solutions of nitric and chromic acids,—it is frequently rendered inert or passive.[4] Its surface may remain perfectly bright, but the metal does not show any appreciable solution in the acid, and if removed and immersed in dilute solutions of such salts as copper and silver sulphates, no reaction takes place, although ordinary active iron would cause an immediate precipitation of the more electronegative metal.

Sulphuric acid, in all stages of dilution, attacks iron. Hydrogen is evolved in the case of the diluted acid, both in the cold and on warming. The concentrated acid yields hydrogen in the cold, but sulphur dioxide is the main gaseous product at 160° C.[5] There is no hydrogen sulphide evolved.

Hydrochloric acid readily dissolves iron, hydrogen being evolved, ferrous chloride passing into solution. The rate of solution appears to be doubled for each rise of 10° C. in temperature for concentrations of acid ranging from 25 to 216 grams per litre. Increase in concentration of the acid likewise accelerates the rate of solution, the velocity being doubled for each increase of 30 grams of hydrogen chloride per litre. The presence of arsenious oxide exerts a remarkably retarding effect upon the activity of the acid.[1]

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[1] Küster, *Zeitsch. Elektrochem.*, 1897, 3, 383.

[2] Fleury, *J. Pharm.*, 1887, (5), 16, 529.

[3] Ledebur, *Stahl und Eisen*, 1887, 7, 681.

[4] Keir, *Phil. Trans*, 1790, 80, 359 ; Wetzlar, *Schweigger's J.*, 1827, 49, 470. For an account of passivity, see p. 55

[5] Berthelot, *Ann. Chim. Phys.*, 1898, (7), 14, 176 ; Adie, *Proc. Chem. Soc.*, 1899, 15, 132.

The action of nitric acid upon iron is both interesting and involved.[2]

When iron is dissolved in acid of density 1 40, both nitrogen peroxide and nitric oxide are obtained in proportions varying with the amount of solvent. It is believed that the nitric oxide is not a primary product of the reaction, but a secondary product formed by reduction of the peroxide.[3]

On reducing the density of the acid to 1·30, nitrous oxide is formed in amount equivalent to 7 per cent. of the iron dissolved. With acid of density 1 25, the reaction is further complicated, nitrogen and ammonia being produced: the former gas reaches a maximum in the case of acid of density 1·15, and then falling, whilst the ammonia reaches a maximum with acid of density 1·05.[3]

In the case of the very dilute acid of density less than 1·034, solution is not accompanied by evolution of gas, but with the formation of ferrous nitrate and ammonium nitrate.[2] If acid of density ranging from 1·034 upwards to 1·115 be employed, the resulting solution consists of a mixture of ferrous nitrate and ferric nitrate, the proportion of the latter increasing with the density of the acid. With acid of greater density than 1·115, ferric nitrate is the main product, and acid of density 1·33 is therefore recommended for the preparation of this salt.[2]

The pure, anhydrous acid, free from nitrous acid and dissolved oxides of nitrogen, is without action on pure qualities of iron [4] even at the boiling-point.

In nitric acid of density 1·45 iron remains bright and refuses to dissolve.[5] When removed and immersed in solutions of copper sulphate, no change takes place. In other words, the metal has been rendered "noble" or "passive."

Carbonic acid acts on iron, yielding ferrous carbonate or soluble ferrous hydrogen carbonate, and evolving hydrogen,

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

This reaction proceeds slowly but steadily in the cold, and is accelerated by vigorous shaking and the employment of iron filings.[6]

Selenic acid dissolves iron with the production of ferrous selenate, $FeSeO_4$, and a deposit of selenium which collects on the surface of the undissolved metal, thereby greatly retarding the reaction. No hydrogen is evolved, and the selenium is presumably obtained by the action of nascent hydrogen upon the excess of selenic acid. Thus :—

$$6H+H_2SeO_4=4H_2O+Se.$$

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[1] Conroy, *J. Soc. Chem. Ind.*, 1901, 20, 316.

[2] Scheurer-Kestner, *Ann. Chim. Phys.*, 1859, (3), 55, 330; Acworth and Armstrong, *J. Chem. Soc.*, 1877, 32, 54. See also Montemartini, *Gazzetta*, 1892, 22, 250.

[3] Freer and Higley, *Amer. Chem. J.*, 1899, 21, 377.

[4] Veley and Manley, *Proc. Roy Soc.*, 1897, 62, 223.

[5] Keir, *Phil Trans*, 1790, 80, 359; Wetzlar, *Schweigger's J.*, 1827, 49, 470. For an account of passivity, see p 55

[6] See Bruno, *Bull. Soc chim.*, 1907, (4), 1, 661; Petit, *Compt rend.*, 1896, 123, 1278; also this volume, p. 68.

The net result of the reaction may be represented by the equation

$$3Fe + 4H_2SeO_4 = 3FeSeO_4 + Se + 4H_2O.$$

Chloric acid, both dilute and in concentrated solution, attacks iron, the metal dissolving without evolution of hydrogen, the chloric acid being reduced.[1]

Aqueous hypochlorous acid slowly attacks iron, both hydrogen and chlorine being evolved.[2]

The Action of Alkalies upon Iron.—Dilute[3] solutions of the hydroxides of the alkali and alkaline earth metals are capable of preserving iron for an indefinite period from corrosion, provided they are kept out of contact with carbon dioxide, etc. When exposed to the open air, the alkali is readily neutralised by absorption of carbon dioxide, and the iron begins to corrode. Concentrated solutions of caustic soda or potash exert a slight solvent action upon iron, but they inhibit corrosion even when continuously exposed to the air, because solutions of their carbonates at similar concentrations likewise inhibit corrosion, so that the absorption of carbon dioxide from the air is immaterial. By continued immersion in a saturated solution of sodium hydroxide at 100° C., wrought iron is rendered brittle owing to the absorption of hydrogen. If, however, the immersion is still further prolonged, the metal loses its brittleness. It has been suggested that the initial brittleness[4] is due to the more rapid absorption of hydrogen by the amorphous layers between the crystals of the metal than by the crystals themselves, whereby a certain amount of expansion occurs, forcing the crystals apart and weakening their cohesion. After prolonged immersion, however, the hydrogen has had time to diffuse into the crystals themselves, and thus to reduce the intercrystalline strain so that the brittleness disappears.

When iron is made the anode in a concentrated solution of caustic soda or potash, a low current density (about 0·001 ampere per sq. centimetre) being employed, the metal is oxidised to the alkali ferrate[5] and passes into solution. Sodium hydroxide acts more rapidly than potassium hydroxide, probably on account of the superior solubility of sodium ferrate.

When electrolytic iron foil is immersed in concentrated solutions of sodium or potassium hydroxide for several weeks, and, after thorough cleaning, allowed to corrode in distilled water, the latter gradually becomes contaminated with traces of sodium or potassium salts, the presence of which can be detected by the spectroscope or by the usual Bunsen flame test.[6] Similar results have been obtained with lithium hydroxide, barium hydroxide, and with ammonia.[7] It appears probable that the alkali penetrates in minute quantities into the metal between the ferrite crystals, possibly in consequence of a certain amount of porosity in the intercrystalline cement. This theory is supported by the fact that iron which has been soaked in alkali invariably "pits" badly when allowed to corrode; and pitting is usually associated with electro-chemical activity between the boundaries of the crystals.[1]

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[1] Hendrixson, *J. Amer. Chem. Soc.*, 1904, 26, 747.

[2] White, *J. Soc. Chem. Ind*, 1903, 22, 132.

[3] Of the order of 0·1 per cent

[4] J. H. Andrew, *Trans. Faraday Soc.*, 1919, 14, 232; 1914, 9, 316.

[5] Haber, *Zeitsch. Elektrochem*, 1901, 7, 215, 724; Pick, *ibid.*, p 713.

[6] Friend, *Trans. Chem. Soc.*, 1912, 101, 50.

[7] Perkins, *ibid.*, 1914, 105, 102.

On boiling pure iron gently in concentrated sodium hydroxide solution, ferrous oxide passes into solution, and upon exposure to air oxidation to ferric oxide takes place.[2]

Fused caustic soda and potash, particularly under the influence of pressure, attack iron readily.[3]

Between 550° and 660° C. fused caustic potash attacks iron appreciably, but the liberation of hydrogen or potassium or the formation of water has not been demonstrated. What, therefore, the precise action is, remains uncertain.[4]

In the case of fused caustic soda between 400° and 720° C. the evolution of hydrogen and the formation of water have both been observed, indicative of the production of a compound $Fe(ONa)_x$.[5] Since caustic soda can be thoroughly dehydrated at 400° C. and undergoes no further loss on heating to 720° C., the formation of water on heating with iron cannot be due to simple decomposition according to the equation

$$2NaOH = Na_2O + H_2O.$$

At white heat, according to Deville,[6] metallic sodium is obtained.

When fused with sodium peroxide, iron yields dark red tabular crystals of the monohydrate, $Fe_2O_3.H_2O$. Density 3·8.[7]

Passivity of Iron.—In 1790 Keir [8] drew attention to the fact that a piece of iron, when placed in contact with nitric acid of density 1·45, is rendered inactive or *passive*. It does not *appear* to dissolve in the acid [9]; when placed in a dilute solution of copper sulphate it does not effect the deposition of copper; and when immersed in ordinary water it exhibits remarkable resistance to corrosion. And this, in many cases, to quote the words of Keir "without the least diminution of metallic splendour or change of colour" (see p. 57).

Nitric acid is not the only medium which may be employed for the passivification of iron. Other acids such as chromic,[10] iodic,[11] arsenic,[12] chloric,[12] hydronitric,[13] etc., exert a similar action, as also do mixtures of two or more acids or acids and certain salts, such, for example, as sulphuric and nitrous acids, or a mixture of these with potassium iodate, etc.[14] Iron may also be rendered passive by immersion in aqueous solutions of many oxidising metallic salts such as silver nitrate,[1] lead nitrate, potassium permanganate, soluble bichromates, etc. Hydrogen peroxide passivifies the metal, and a piece of cleaned electrolytic foil may be immersed in a warm, dilute solution of perhydrol without evincing any sign of corrosion, even although its surface is continuously swept with bubbles of oxygen due to the catalytic decomposition of the peroxide. Similarly iron may be rendered passive by making it the anode in an electrolyte containing water.[2]

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[1] See Aitchison's theory of the mechanism of corrosion, p. 71.

[2] Haber, *loc. cit*

[3] See Kestner, *Bull. Soc. chim*, 1897, 15, (3), 1250; Groves, *Proc. Chem. Soc*, 1903, 19, 158; Venator, *Chem. Zeit.*, 1886, 10, 319, 380.

[4] Le Blanc and Weyl, *Ber.*, 1912, 45, 2300.

[5] Le Blanc and Bergmann, *Ber.*, 1909, 42, 4728.

[6] Deville, *Ann. Chim. Phys.*, 1855, (3), 43, 5.

[7] Dudley, *Amer. Chem. J.*, 1902, 28, 59.

[8] Keir, *Phil. Trans.*, 1790, 80, 359.

[9] Although originally thought to be insoluble in nitric acid, this is not actually the case (Faraday, *Experimental Researches*, series viii, §§ 947, 996; Belck, *Dissertation*, Halle a/S., 1888).

[10] Beetz, *Pogg. Annalen*, 1844, 62, 234; 1844, 63, 420; 1846, 67, 186, 286, 365.

[11] Phillips, *Phil. Mag.*, 1848, (3), 33, 509.

[12] Boutmy and Chateau, "*Cosmos*," *Revue des Sciences*, 1861, 19, 117; Phillips, *loc. cit.*

[13] When stirred (Turrentine, *J. Amer. Chem. Soc.*, 1911, 33, 803).

[14] Schonbein, *Pogg. Annalen*, 1838, 41, 42; Daniell, *Phil. Trans.*, 1836, 126, 114.

Gases, also, may cause iron to assume the passive state. Compressed nitric oxide is a case in point.[3] The vapours of concentrated nitric acid have for many years been known to act similarly.[4]

Dry nitrogen peroxide induces a more intense passivity than nitric acid when allowed to come into contact with iron—an observation which suggests an explanation for the fact that iron is only rendered passive by nitric acid which is either yellow or red, whilst passive iron is actually rendered active by immersion in colourless nitric acid solutions. Apparently only acids of such concentrations as are capable of yielding nitrogen peroxide in contact with the metal are able to exert a passivifying action. This is further supported by the fact that by passing nitrogen peroxide into those concentrations of nitric acid in which iron is normally active, the metal becomes passive.[5]

Testing for Passivity. — According to Heathcote,[6] iron may be regarded as passive when no chemical action can be detected by the unaided eye after immersing, shaking, and finally holding motionless a piece of the metal in nitric acid of density 1·20, at the room temperature (15° to 17° C.). This is a preferable method to that of Schönbein,[7] who employed nitric acid of density 1·35 in a similar manner, because this latter concentration of acid is sufficient to render active iron passive,[8] whereas acid of density 1·20 does not do so, *at the room temperature.*

It is important to note this temperature restriction, however, for whereas nitric acid of density 1·250 does not render iron passive at 0° C., yet if the temperature is raised to 10° C. or above, the metal is readily passivified [9] by it.

Dunstan [10] recommends as a convenient test for passivity the employment of a 0·5 per cent. solution of copper sulphate. This solution at once deposits a film of copper on active iron, whilst the passive metal will remain, ofttimes for hours, bright and apparently entirely unaffected.

The action of distilled water on iron may also be used as a test for passivity.[11] Active iron immersed in it usually shows visible signs of corrosion in from 8 to 10 minutes, whilst the passive metal may remain perfectly bright for an hour or more. When, in this latter case, corrosion begins, the action is very local for a considerable time.

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[1] Bergmann (*Opuscula Chimica et Physica,* 1779–88, 3, 140. See also de Benneville, *J. Iron Steel Inst*, 1897, II., 40. Senderens (*Bull Soc. chim.*, 1896, 15, 691; 1897, 17, 279) had already observed, prior to the discovery by Keir of the passivity of iron, that this metal does not precipitate silver from concentrated aqueous solutions of silver nitrate.

[2] Ramann, *Ber*, 1881, 14, 1430.

[3] Varenne, *Compt. rend*, 1879, 89, 783; 1880, 90, 998.

[4] Renard, *ibid.*, 1874, 79, 159.

[5] Young and Hogg, *J. Physical Chem.*, 1915, 19, 617.

[6] Heathcote, *J. Soc. Chem. Ind.*, 1907, 26, 899

[7] Schönbein, *Pogg. Annalen*, 1836, 37, 390, 590. Compare Noad, *Phil. Mag.*, 1837, (3), 10, 276; 1838, (3), 11, 48.

[8] Faraday and Schönbein, *Phil. Mag*, 1836, 9, 53, 122.

[9] Young and Hogg, *loc. cit*

[10] Dunstan, *Trans. Chem Soc.*, 1911, 99, 1835.

[11] Dunstan, *loc. cit.*

Passivity is also readily detected electrically by the difference in potential between passive and active iron,[1] the former having a lower potential. This is a particularly convenient method of detecting passivity caused by anodic polarisation.

Cause of Passivity.—Several theories have been suggested to account for passivity, but no one theory suffices to explain every case. The probability is that several kinds of passivity exist and that not a few of the different theories are correct in certain cases.

(1) *The oxide theory*, apparently the first to be suggested,[2] postulates the formation of a thin layer of oxide upon the surface of the metal, thereby protecting the underlying portions from reacting. Such an action is not at all uncommon. Thus ordinary lead is well known to resist atmospheric corrosion by reason of the thin protective film of suboxide formed on its surface. Aluminium behaves similarly, and the difficulty of finding a suitable solder for the metal is connected with this oxide layer. The theory receives substantial support from the fact that most passivifying agents are oxidisers, and is in entire harmony with the fact that passivity is a surface phenomenon and can be removed by mechanical processes or by heating in a reducing atmosphere.

The action of 3 per cent. ozone in the cold is a sensitive method of detecting a film of oxide on a metallic surface, inasmuch as a visible deposit of oxide is immediately produced. Iron which has been passivified by immersion in nitric acid or anodically in dilute sulphuric acid instantly reacts with ozone, showing that its surface is coated with oxide.[3] Active iron, on the other hand, exhibits no such sensitiveness towards ozone. The nature of the oxide is uncertain. It has been suggested[4] that it is not likely to be higher than FeO_3, but may be FeO_2.

Exception to this oxide theory, however, has been taken by Muller and Konigsberger,[5] on the ground that the reflecting power of iron, rendered passive anodically when immersed in alkaline solution, remains undimmed, whereas if a layer of oxide were formed an alteration would be expected. But it is not necessary to postulate the formation of a *thick* layer of oxide. If of merely molecular dimensions, it would still preserve the underlying metal from attack, whilst a thickness comparable with that of the length of a light wave would be necessary to affect the reflecting power.[6]

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[1] See Flade, *Zeitsch physikal Chem.*, 1911, 76, 513, etc.

[2] See Schonbein and Faraday, *Phil. Mag*, 1836, (3), 9, 53, 122, 1837, (3), 10, 175; *Pogg Annalen*, 1836, 39, 342; Schonbein, *ibid.*, 1836, 37, 393; 1836, 38, 444; 1838, 41, 42; 1838, 43, 1; 1843, 59, 149, 421; Beetz, *loc. cit*; von Martens, *Pogg. Annalen*, 1844, 61, 121; Wetzlar, *Schweigger's J*, 1827, 49, 470; 1827, 50, 88, 129; Schonbein, *Das Verhalten des Eisens zum Sauerstoff* (Basel, 1837).

[3] Manchot, *Ber.*, 1909, 42, 3942.

[4] Bennett and Burnham, *Trans. Amer. Electrochem. Soc.*, 1916, 29, 217. See also Haber and Goldschmidt, *Zeitsch. Elektrochem*, 1906, 12, 49.

[5] W. J. Muller and Konigsberger, *Zeitsch. Elektrochem*, 1907, 13, 659; 1909, 15, 742; *Physikal. Zeitsch*, 1904, 5, 415, 797; 1905, 6, 847, 849; 1906, 7, 796; Muller, *Zeitsch. Elektrochem.*, 1905, 11, 823.

[6] See Findlay, *Ann Reports Chem. Soc.*, 1907, 4, 28; also Krassa, *Zeitsch. Elektrochem.*, 1909, 15, 490, 981, with the reply of Müller and Konigsberger, *ibid.*, p. 742.

On the other hand, when highly polished iron rods are immersed in concentrated nitric acid a visible dulling usually ensues.[1] This is exactly what might be anticipated in accordance with the oxide theory, inasmuch as such a powerful oxidiser might easily induce the formation of a sufficient thickness of oxide to be visible.

(2) *Gaseous Film Theory.*—It is well known that gases frequently adhere with extraordinary tenacity in the form of thin films to solid surfaces, and it has been suggested that some such gaseous film is the cause of the passivity assumed by iron in certain circumstances. The film need not necessarily be one of oxygen, although in perhaps the majority of cases this may be the predominant gas.[2] Nitric oxide [3] or nitrogen [4] gas may likewise induce passivity in this manner.

It may be presumed that whilst gaseous films of widely differing gases may in the main behave alike, they will yet show minor differences or eccentricities in their behaviour. An explanation is thus forthcoming for the differences in the behaviour of irons passivified in various ways. Thus, for example, iron that has been rendered passive by anodic polarisation in sulphuric acid differs slightly from that passivified by immersion in concentrated nitric acid. In the former case it is therefore presumed that the metal is covered with a film of gaseous oxygen, but in the latter with a film of some oxide of nitrogen.[5]

This, like the oxide theory, has much to recommend it. An explanation is afforded for the superficial nature of passivity, and the theory also offers an explanation for the passivity induced in certain cases where oxygen cannot be the cause.

A close connection has been found to exist between passivity and photo-electric behaviour. Thus dry, active iron is found to exhibit a considerably higher photo-electric activity than the metal rendered passive by immersion in concentrated nitric acid or by anodic polarisation in dilute sulphuric acid; and this is regarded as supporting the gaseous film theory.[6]

(3) *Physical Theories.*—Several theories have been put forward according to which the phenomena of passivity are due to a physical change in the superficial layers of the iron. What the precise nature of that change may be remains a matter of controversy.

According to some authorities,[7] passivity is the normal state of pure iron, the metal only being rendered active by the presence of some catalyst, such as hydrogen or hydrogen ions, which increases its solution pressure. This view receives powerful support from the experiments of Lambert and Thomson,[8] who prepared specimens of exceptionally

[1] Heathcote, *J. Soc. Chem. Ind.*, 1907, 26, 899.

[2] See Osann, *Pogg. Annalen*, 1855, 96, 498; de Regnon, *Compt. rend.*, 1874, 79, 299; Mulhmann and Frauenberger, *Zeitsch. Elektrochem.*, 1904, 10, 929.

[3] Mousson, *Pogg. Annalen*, 1836, 39, 330; Varenne, *Compt. rend.*, 1879, 89, 783; 1880, 90, 998; *Ann. Chim. Phys.*, 1880, (5), 19, 251; 1880, 20, 240; Fredenhagen, *Zeitsch. physikal. Chem.*, 1903, 43, 1; 1908, 63, 1; *Zeitsch. Elektrochem.*, 1905, 11, 857; 1906, 12, 797.

[4] St Edmé, *Compt. rend.*, 1861, 52, 930; 1888, 106, 1079.

[5] Fredenhagen, *loc. cit.*

[6] H. S. Allen, *Proc. Roy. Soc.*, 1913, A, 88, 70.

[7] Foerster, *Abhandlungen der Bunsen Gesellschaft*, 1909, No. 2; Grave, *Zeitsch. physikal. Chem.*, 1911, 77, 513. See also Ader, *ibid.*, 1912, 80, 385; and Le Blanc, *Boltzmann Festschrift*, 1904, p. 183.

[8] Lambert and Thomson, *Trans Chem. Soc.*, 1910, 97, 2426.

pure iron by methods already indicated (see p. 34) and found them to be remarkably inert or passive.

Other investigators[1] have suggested allotropy as a possible cause, a layer of passive, allotropic metal being formed in contact with the passivifying reagent. This, however, is simply substituting another name for passivity inasmuch as no explanation of this type of allotropy is forthcoming. If this allotropy is due to a rearrangement of the atoms in consequence of change of valency, this theory is equivalent to that of Kruger and Finkelstein,[2] who regard ordinary active iron as the ferrous or divalent variety, the passive metal being ferric or trivalent. Since valency is an electrical phenomenon, the valency hypothesis is equivalent to assuming an electrical difference between the active and passive metal. This is the basis of Muller's theory.[3]

An attractive hypothesis is that of Smits,[4] who inclines to the view that iron contains, in addition to uncharged atoms and free electrons, two kinds of ions, α and β, which differ in their reactivity, and which are in equilibrium with one another. Thus :—

$$\alpha \rightleftharpoons \beta.$$

The production of the passive state is attributed to a disturbance of this equilibrium. During anodic polarisation of iron the more reactive or α ions dissolve with greater rapidity than equilibrium can be established, with the result that an excess of "noble," inert, or passive β ions collects on the surface of the metal, tending to render it passive. This explains why passivity is purely a surface phenomenon. Hydrogen ions, like halogens, are assumed to catalytically accelerate the conversion of α into β ions until equilibrium is re-established.

When iron is immersed in a passivifying reagent such as nitric acid, not only do the α ions dissolve with great rapidity ; but the acid, being a powerful oxidiser, quickly removes any hydrogen ions from the surface of the metal and thus reduces the tendency for equilibrium to be re-established, and the metal again becomes thoroughly passive.

If, now, the current density is increased to such an extent that oxygen begins to be evolved at the anode, all the hydrogen ions, normally present in ordinary iron, will be completely expelled from the surface of the metal, the tendency for reversion to equilibrium of the α and β ions being reduced to a minimum. In other words, the metal is rendered thoroughly passive.

If, on the other hand, iron is immersed in a solution of ferrous chloride, although the α ions rapidly dissolve passivity is not induced because the chlorine and halogen ions rapidly readjust the equilibrium, and the β ions never accumulate in sufficient excess on the metallic surface to produce passivity.

Iron which has been passivified anodically can be rendered active by the introduction of halogen ions; by the electrolysis of a mixed solution of ferrous sulphate and chloride passivity can be made a *periodic* phenomenon.[1]

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[1] See especially Keir, *loc. cit.*, Senderens, *Bull. Soc. chim.*, 1896, (3), 15, 691 ; 1897, (3), 17, 279 ; de Benneville, *J. Iron Steel Inst.*, 1897, II., 40 ; Hittorf, *Zeitsch. physikal. Chem.*, 1898, 25, 729 ; 1899, 30, 481 ; 1900, 34, 385 ; *Zeitsch. Elektrochem.*, 1898, 4, 482 ; 1899, 6, 6 ; 1900, 7, 168.

[2] Finkelstein, *Zeitsch. physikal. Chem.*, 1901, 39, 91.

[3] W. J. Muller, *Zeitsch. physikal. Chem.*, 1904, 48, 577 ; *Zeitsch. Elektrochem.*, 1905, 11, 755, 823 ; Fredenhagen, *Zeitsch physikal. Chem.*, 1908, 63, 4

[4] Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 191. See also Smits and Lobry de Bruyn, *ibid*, 1917, 19, 880 ; Smits, *J. Soc. Chem. Ind*, 1916, 35, 928 , Smits and Aten, *Zeitsch. physikal. Chem.*, 1915, 90, 723 ; *De Ingenieur*, 1915, p. 357.

From the foregoing it is evident that widely divergent views are held as to the cause of passivity. For further particulars the reader is referred to the subjoined references.[2]

An instructive series of papers on passivity was read at the general discussion on the subject held by the Faraday Society, November 12, 1913. The papers are printed in the *Transactions* of the Society for 1914, vol. ix.

Properties of Iron Powder.—Iron powder, as obtained by the reduction of ferrous or ferric salts, is considerably more chemically reactive than the compact metal. Thus, the powder obtained by reduction of iron oxide, carbonate, or oxalate in a current of hydrogen at 440° C. is pyrophoric, becoming incandescent upon exposure to moist air. It decomposes acetylene with incandescence, depositing free carbon and yielding small quantities of benzene.[3] Reduced iron absorbs some 2 per cent. of nitrogen at atmospheric temperature, the solubility of the gas being proportional to the square root of the pressure.[4] According to Sieverts, Kahlbaum's reduced iron absorbs nitrogen at 900° C., and this is quantitatively released on cooling.[5]

When maintained at 310° to 320° C. for about forty-eight hours, pyrophoric iron is transformed into the non-pyrophoric form, the change being accompanied by an increase in volume.[6] Probably the pyrophoric form consists of a mixture of molecules of different kinds which are not in a state of equilibrium.

Nitrogen peroxide is decomposed by reduced iron at the ordinary temperature, the metal becoming incandescent and yielding a mass of ferric oxide, Fe_2O_3.[1] Nitrous oxide is reduced at 170° C., and nitric oxide at 200° C., ferrous oxide resulting.

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[1] Smits and Lobry de Bruyn, *Proc. K. Akad Wetensch. Amsterdam*, 1919, 21, 382: 1916, 18, 807.

[2] Fechner, *Schweigger's J.*, 1828, 53, 129; 1830, 59, 113; *Pogg. Annalen*, 1839, 47, 1; Braconnot, *Ann. Chim Phys.*, 1833, (2), 52, 286, *Pogg Annalen*, 1833, 29, 174, Herschel, *Ann. Chim. Phys.*, 1833, (2), 54, 87; *Pogg. Annalen*, 1834, 32, 211; Andrews, *Phil Mag*, 1838, 11, 305, *Proc Roy Soc*, 1890, 49, 481; von Martens, *Pogg. Annalen*, 1842, 55, 437, 612, 1844, 61, 127; Scheurer-Kestner, *Ann. Chim. Phys.*, 1859, (3), 55, 330; Heldt, *J. prakt. Chem.*, 1863, 90, 167, 257; Ordway, *Amer J. Sci.*, 1865, (2), 40, 316; Thomlinson, *J. Chem. Soc*, 1869, 22, 125; le Blanc, *Zeitsch Elektrochem.*, 1900, 6, 472; 1905, 11, 705; Ostwald, *ibid.*, 1901, 7, 635; *Zeitsch physikal. Chem*, 1900, 35, 33, 211, Heathcote, *Zeitsch. physikal. Chem.*, 1901, 37, 368, Mugdan, *Zeitsch. Elektrochem*, 1903, 9, 442; Sackur, *ibid.*, 1904, 10, 841; 1906, 54, 641; 1908, 14, 607; E. Müller and Spitzer, *Zeitsch. anorg. Chem*, 1906, 50, 321; Gordon and Clark, *J. Amer. Chem. Soc.*, 1906, 28, 1534; *Zeitsch. Elektrochem.*, 1906, 12, 769; Haber and Maitland, *ibid.*, 1907, 13, 309; Faust, *ibid.*, p. 161; Byers, *J. Amer. Chem. Soc*, 1908, 30, 1718; Kistiakowsky, *Seventh Internat. Cong. Applied Chem*, 1909, Sect. X. 56; Alvarez, *Zeitsch. Elektrochem*, 1909, 15, 142 Byers and Darrin, *J. Amer Chem. Soc*, 1910, 32, 750; Schoch and Randolph, *J. Physical Chem.*, 1910, 14, 719; Flade and Koch, *Zeitsch. Elektrochem*, 1911, 18, 335; *Zeitsch. physikal. Chem.*, 1914, 88, 307, 569; Turrentine, *J. Amer. Chem. Soc.*, 1911, 33, 803; Byers and Morgan, *ibid.*, p. 1757; Grube, *Zeitsch. Elektrochem*, 1912, 18, 189; Byers and Langdon, *J. Amer. Soc.*, 1913, 35, 759, 2004; 1916, 38, 362; M'Leod-Brown, *Chem. News*, 1913, 107, 15; Hanaman, *Dissertation*, Tech. Hochschule, Berlin, 1913; Rathert, *Zeitsch. physikal. Chem.*, 1914, 86, 567; Foerster and co-workers, *Zeitsch. Elektrochem.*, 1916, 22, 85; Stapenhorst, *Zeitsch physikal. Chem.*, 1917, 92, 238.

[3] Moissan and Moureu, *Bull. Soc. chim*, 1896, 15, 1296.

[4] Jurisch, *Stahl und Eisen*, 1914, 34, 252

[5] Sieverts, *Zeitsch. physikal. Chem.*, 1907, 60, 129.

[6] Smits, Kettner, and de Gee, *Proc. K. Akad Wetensch Amsterdam*, 1914, 16, 999. See also Smits, *ibid.*, 1913, 16, 699.

Nitric oxide is almost quantitatively converted into ammonia when mixed with hydrogen and passed over the warmed metal.[2] The reaction begins at about 300° C., and is very rapid at 350° C.

When heated in a continuous current of carbon monoxide at 650° C., a considerable quantity of carbon is deposited. If, however, the carbon monoxide is admitted to a closed vessel containing the heated metal, absorption of the gas takes place, possibly with the formation of cementite—that is, iron carbide, Fe_3C.

In contact with air and water iron powder readily rusts at ordinary temperature. When warmed with water, hydrogen gas is evolved.[3] Dilute solutions of sodium and potassium hydroxides are decomposed at their boiling-points in a similar manner. Under the influence of gentle heat iron powder decomposes steam—a reaction that has been recommended as a most convenient one for rapidly obtaining small quantities of pure hydrogen.[4] The gas is evolved at considerably lower temperatures than when compact iron is used, decomposition proceeding slowly, in the presence of Kahlbaum's reduced iron, at about 250° C.[5]

Finely divided iron decomposes sulphuric acid of density 1·75 at 200° C., yielding sulphur dioxide.[6]

It is spontaneously inflammable in sulphur vapour, the ignition temperature lying below 448° C.[7]

The exceptionally pure reduced metal obtained by Lambert [8] and Thomson possessed several unusual properties. Thus, it exhibited remarkable inertness or "passivity," remaining free from rust upon prolonged exposure to air and tapwater.[9]

Cold, dilute sulphuric and nitric acids had very little action on the metal, but on warming the iron readily dissolved. Aqueous hydrogen chloride attacked the metal even in the cold. Saturated solutions of the sulphate or nitrate of copper exerted no action at ordinary temperatures; even after an exposure of several months to copper sulphate solution, no change could be detected in the iron when examined under the microscope. On raising to 100° C., however, the iron gradually dissolved, copper being simultaneously deposited.

Solutions of copper chloride, when concentrated, immediately attacked the metal, depositing copper. Even dilute solutions (less than one per cent.) attacked the iron, although slowly.

Copper was also deposited on the metal if the latter was subjected to pressure in an agate mortar prior to being placed in the copper sulphate solution. Pressure with a quartz rod whilst immersed in the solution had a like effect.

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[1] Sabatier and Senderens, *Compt. rend*, 1892, 114, 1429; 1892, 115, 237; 1895, 120, 618.

[2] Adhikary, *Chem. News*, 1915, 112, 163.

[3] Hall and Guibourt, *Gmelin-Kraut*, iii. 300; Ramann, *Ber.*, 1881, 14, 1433; Birnie, *Chem. Weekblad*, 1907, 4, 291; Friend, *J. Iron Steel Inst.*, 1908, II., 5.

[4] Birnie, *Chem. Zentr.*, 1907, I., 1771.

[5] Friend, *J. West Scotland Iron Steel Inst.*, 1910, 17, 66.

[6] Hart, *English Patent*, 13950 (1885).

[7] Ohmann, *Chem. Zentr*, 1911, I, 458.

[8] Lambert and Thomson, *Trans. Chem. Soc.*, 1910, 97, 2426.

[9] Lambert, *ibid.*, 1912, 101, 2056.

These remarkable results might be attributed to a film of hydrogen protecting the metal in the first experiments from attack in copper sulphate solution, the film being disrupted in the later experiments by the pressure; but specimens of the metal which had been heated for several hours at 1000° C. in a vacuum, until spectroscopic tests showed that all hydrogen had been removed, behaved in precisely the same manner.

When the pure metal was treated with ferroxyl (see p. 72), unlike ordinary iron, it remained quite bright for an indefinite time, manifesting no tendency to corrode. On applying pressure locally, however, corrosion set in, a pink colour developing round the pressed portion, and Turnbull's blue appearing round the unpressed parts, indicating solution of the metal.

Iron sponge is produced commercially, notably in Sweden, whence it was, prior to the Great European War, exported to Germany for use in open-hearth steel manufacture. The process consists in heating iron ore and coal placed in alternate layers in a vessel sealed against the entrance of air. The source of heat is producer gas made from an inferior type of coal, and the vessel is successively heated and cooled for from five to seven days. The maximum temperature attained during the heatings ranges from 1050° to 1200° C. The resulting spongy iron consists of approximately [1]

Iron	96 to 97	per cent.
Sulphur	0·01 to 0·02	,,
Phosphorus . . .	0·012	,,
Silica	1·4	,,

Spongy iron acts as a powerful reducer towards organic matter dissolved in water.[2] In some cases marsh gas is produced. The organic nitrogen is in nearly all cases reduced to nitrogen.[3]

Iron amalgam cannot be obtained by direct union of the elements. By introduction of a 1 per cent. sodium amalgam into a concentrated solution of ferrous sulphate an iron amalgam is obtained as a viscid mass, which is attracted by a magnet in small pellets. It may also be prepared by triturating powdered iron, mercuric chloride, and water. A more convenient method, perhaps, consists in electrolysing with a very weak current a saturated solution of ferrous sulphate. A bundle of iron wire serves as anode, whilst the cathode consists of platinum foil dipping into a small dish of mercury. The iron amalgamates with the mercury, and at the conclusion of the process excess of the latter element is squeezed out, leaving an amalgam of buttery consistency and containing from 10 to 12 per cent of iron.[4]

Ramann [5] recommends addition of a small quantity of water to a mixture of sodium amalgam and finely divided iron. The product is squeezed to remove excess of mercury, a crystalline amalgam being left which contains 15·75 per cent. of iron and corresponds to the formula Fe_2Hg_3. Iron amalgam blackens both upon exposure to air and water.

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[1] Handy, *Proc. Eng. Soc. Western Pennsylvania*, 1913, 29, 1. See also *Stahl und Eisen*, 1912, 32, 830.

[2] See experiments by Hatton, *Trans. Chem. Soc.*, 1881, 39, 258.

[3] See this series, Volume VII.

[4] Joule, *Mem. Manchester Lit. Phil. Soc.*, 1865, (3), 2, 115; Fowler, *Trans Chem. Soc.*, 1901, 79, 290

[5] Ramann, *Ber.*, 1881, 14, 1433.

When heated, mercury is expelled, and a porous iron left behind. Upon slow oxidation in air ferrous oxide is produced.[1]

Colloidal iron, together with a small quantity of ferrous hydroxide and a ferrous salt, is obtained by electrolysing a solution of pure gelatin and a dilute solution of an alkali chloride or sulphate between iron electrodes.[2] The sol resembles those of lead and bismuth in that it bears a positive charge. The majority of metallic sols, on the other hand, are negative.

Colloidal solutions of iron in ether have been obtained [3] by allowing sparks to pass between iron wire clippings immersed in that liquid and connected up with an induction coil.

Pyrophoric Iron.—Mention has already been made of the fact that reduction of iron oxide, carbonate,[4] or oxalate [5] in a current of hydrogen or carbon monoxide results in the formation of a very pure iron in the form of a black powder. If the temperature is kept low throughout the experiment—namely at about 435° C.,—the resulting iron powder, usually contaminated with more or less ferrous oxide,[6] is pyrophoric, becoming incandescent when exposed to the air in consequence of the heat set free by the rapid oxidation of the metal.[7] Complete reduction to metallic iron at this temperature, however, is exceedingly slow in taking place. Ferrous oxide is first formed, and it was not until the passage of hydrogen had been continued for ninety-six hours that Moissan [6] was, in his experiments, able to obtain the iron entirely free from oxide. At 600° C. the reaction proceeds fairly rapidly, but the reduced iron is not pyrophoric.

Pyrophoric iron decomposes water rapidly at 50° to 60° C., and its action is perceptible even below 10° C. Its reactivity appears to be independent of the presence of occluded gases or the presence of carbon, and to be solely dependent upon its fine state of division.[5]

Iron as a Catalyst.—Metallic iron can, in certain circumstances, act as a catalyst, in this respect resembling, albeit feebly, the more noble elements of Group VIII. of the Periodic Table. Thus, for example, iron assists the production of ammonia from a mixture of nitrogen and hydrogen at 800° to 1000° C. under a pressure of 100 atmospheres. No ammonia is obtained under these conditions in a porcelain vessel if iron or any other catalyst be excluded.[8]

When reduced iron is heated with certain nitrogenous organic substances and metallic sodium, a cyanide is formed, the iron apparently acting as catalyser, being alternately oxidised and reduced.[9] The presence of potassium cyanide in blast furnaces is thus readily accounted for.

Metallic iron sometimes behaves as a *negative catalyst.* Thus, for example, the activity of palladium as a hydrogen carrier is reduced by contact with iron, whereas cobalt and nickel exert no such influence.[10]

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[1] Férée, *Bull. Soc. chim*, 1901, (3), 25, 615.

[2] Serono, *Arch. Farm. sperim*, 1910, 9, 152.

[3] Svedberg, *Ber.*, 1905, 38, 3616.

[4] Zangerle, *Rep. Pharm*, 1857, 6, 27.

[5] Birnie, *Chem. Zentr.*, 1884, p 85; Moissan, *vide infra.*

[6] Moissan, *Traité de Chimie Minérale*, 1905, vol. iv.; *Ann. Chim. Phys*, 1880, (5), 21, 199.

[7] This is made the basis of an effective lecture experiment. See Newth, *Chemical Lecture Experiments* (Longmans), 1910, No. 380.

[8] Jellinek, *Zeitsch. anorg Chem*, 1911, 71, 121.

[9] Remsen, *Amer Chem. J.*, 1881, 3, 134.

[10] Paal, *Ber.*, 1911, 44, 1013.

Iron Ions.—The transport numbers and mobilities for iron ions at infinite dilution in solutions of ferrous and ferric chlorides respectively are as follow:—

	Transport Number.	Mobility.
Ferrous ion [1] . .	0·414	46
Ferric ion [2] . .	0·396	43

The ferric ion appears to be less hydrated than the ferrous ion, which is associated with 60 molecules of water.

Atomic Weight.—*Approximate Atomic Weight.*—That the atomic weight of iron is approximately 56, and not a multiple or submultiple of this amount, is indicated by various considerations.

1. The mean specific heat of iron is approximately 0·110. Assuming a mean atomic heat of 6·4, the atomic weight of iron, according to Dulong and Petit's Law, is approximately 58.

2. As already indicated,[3] iron closely resembles manganese in many of its chemical properties, and the three elements iron, cobalt, and nickel constitute very fitting intermediaries between manganese and copper. Reference to the Periodic Table [4] shows that the only manner in which this relationship can be harmonised with the Periodic Law is to assume that the atomic weights of these three metals lie between 54·93 (the atomic weight of manganese) on the one hand and 63·57 (the atomic weight of copper) on the other.

3. Ferric sulphate yields, with the sulphates of the alkali metals, a series of well-defined crystalline salts which are isomorphous with similar series yielded by aluminium sulphate. By the application of Mitscherlich's Law, therefore, analogous formulæ are to be anticipated, so that the general formula for these iron alums is

$$M_2SO_4.Fe_2(SO_4)_3.24H_2O.$$

Analyses of these compounds indicate that the atomic weight of iron is 56.

Exact Combining Weight and Atomic Weight.—The early determinations of the atomic weight of iron are of no present value, and little need be said concerning them. Most investigators chose to determine the composition of ferric oxide; Wackenroder,[5] Svanberg and Norlin,[6] Erdmann and Marchand,[7] and Rivot [8] worked by reducing the weighed oxide to metal in a stream of hydrogen, while Berzelius,[9] Maumené,[10] and also Svanberg and Norlin [6] converted a known weight of iron into ferric oxide by oxidation. Their results are summarised in the following table :—

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[1] Marinković, *Monatsh.*, 1915, 36, 831.
[2] Hopfgartner, *ibid.*, p 751.
[3] See this volume, Part I., Chapter I.
[4] See Frontispiece.
[5] Wackenroder, *Arch. Pharm.*, 1843, 35, 279; 36, 22.
[6] Svanberg and Norlin, *Annalen*, 1844, 50, 432.
[7] Erdmann and Marchand, *Annalen*, 1844, 52, 212; *J prakt. Chem.*, 1844, 33, 1.
[8] Rivot, *Annalen*, 1851, 78, 214.
[9] Berzelius, *Berzelius' Jahresber.*, 1844, 25, 43.
[10] Maumené, *Ann. Chim. Phys.*, 1850, (3), 30, 380.

Date.	Experimenter	Method.	Per cent. of Iron in Ferric Oxide.	Atomic Wt. of Iron ($O=16$).
1843	Wackenroder . . .	Reduction	69·988	*55·97*
1844	Berzelius	Oxidation	70·020	*56·05*
,,	Svanberg and Norlin .	,,	69·953	*55·88*
,,	,, ,, . .	Reduction	70·035	*56·09*
,,	Erdmann and Marchand .	,,	70·009	*56·03*
1850	Maumené . . .	Oxidation	70·001	*56·00*
1851	Rivot	Reduction	69·330	*54·25*

The only other early determinations to be mentioned are Dumas' analyses of anhydrous ferrous and ferric chloride, in which the amount of silver required to combine with the chlorine was determined,[1] and a few experiments by Winkler,[2] in which a weighed amount of iron was dissolved in a solution of iodine in potassium iodide, the excess of iodine being determined by titration with sodium thiosulphate. The results were as follow ($Cl=35·457$, $I=126·92$, $Ag=107·880$) :—

2 expts. Dumas. $2Ag : FeCl_2 :: 100·000 : 58·866$ *Fe=56·09*
2 ,, ,, $3Ag : FeCl_3 :: 100·000 : 50·244$ *Fe=56·23*
6 ,, Winkler. $I_2 : Fe :: 100·000 : 22·145$ *Fe=56·21*

Modern work on the atomic weight of iron begins in 1900 with Richards and Baxter's analyses of ferric oxide[3] by reduction to the metal in a stream of hydrogen. Richards and Baxter found that the exact determination of this ratio is a matter of extreme difficulty, and regarded their experiments as preliminary in character. The mean result was as follows ($O=16·000$) :—

7 expts. $Fe_2O_3 : 2Fe :: 100·000 : 69·9576$ *Fe=55·887*

Three years later Baxter[4] made another determination of the atomic weight of iron, analysing anhydrous ferrous bromide for the purpose. The salt was sublimed in a porcelain tube, which introduced a little sodium bromide into it ; due allowance was made for this source of error, and the following results obtained ($Ag=107·880$, $Br=79·916$):—

4 expts. $FeBr_2 : 2AgBr :: 57·4195 : 100·000$ *Fe=55·833*
2 ,, $FeBr_2 : 2Ag :: 99·960 : 100·000$ *Fe=55·842*

At the time these experiments were made an erroneous value for the atomic weight of silver was in use, in consequence of which the value *Fe=55·87*, in confirmation of that deduced from the oxide analyses, was deduced from the bromide analyses. With the establishment of the modern value for the atomic weight of silver, it accordingly became desirable to repeat the preceding work in order to determine the source and magnitude of the errors involved in it. Hence, in 1911, Baxter, Thorvaldson, and Cobb[1] repeated the analyses of ferrous bromide, which they were able to obtain quite free from sodium bromide by utilising fused quartz apparatus in its preparation. Their preliminary analyses gave the following results (Ag=107·880, Br=79 916):—

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[1] Dumas, *Ann. Chim. Phys.*, 1859, (3), 55, 157.
[2] Winkler, *Zeitsch. anorg. Chem.*, 1895, 8, 291.
[3] Richards and Baxter, *Proc. Amer. Acad.*, 1900, 35, 253.
[4] Baxter, *ibid.*, 1903, 39, 245.

7 expts. $FeBr_2$: 2Ag : : 99·9593 : 100·0000 *Fe=55·840*
4 „ $FeBr_2$: 2AgBr : : 57·4221 : 100·0000 *Fe=55·840*

and the final experiments gave almost identical results :—

11 expts. $FeBr_2$: 2Ag : : 99·9583 : 100·0000 *Fe=55·838*
11 „ $FeBr_2$: 2AgBr : : 57·4214 : 100·0000 *Fe=55·838*

The essential accuracy of Baxter's earlier work on the bromide was thus confirmed.

Baxter and Thorvaldson[2] extended the preceding investigation by making a number of analyses of ferrous bromide prepared from meteoric iron. The results were as follow :—

5 expts. $FeBr_2$: 2Ag : : 99 9561 : 100·0000 *Fe=55·834*
5 „ $FeBr_2$: 2AgBr : : 57·4191 : 100·0000 *Fe=55·829*

These results are a trifle lower than the preceding, but in each series of five experiments two are of doubtful value as the result of a modification of the method of analysis ; excluding the doubtful analyses, the above two results become *Fe=55·837* and *Fe=55·835* respectively.

The preceding results leaving little doubt that Richards and Baxter's analyses of ferric oxide are affected by a slight, but, nevertheless, appreciable error, Baxter and Hoover[3] undertook a thorough revision of this process. For full details of their work, which, though apparently quite simple, was, in reality, extremely difficult, the reader must be referred to the original memoir. The result was as follows (O=16·000):—

12 expts. Fe_2O_3 : 2Fe : : 100·0000 : 69·9427 *Fe=55·847*

The preceding result requires slight correction. Baxter and Hoover found that at 1050° to 1100° C., the temperature at which they prepared and reduced their ferric oxide, there was a slight doubt as to the stability of the ferric oxide. Five grams of the oxide when ignited to constant weight in oxygen, lost in weight when ignited in air, the loss being one-fifth of a milligram. The subsequent researches of Sosman and Hostetter[4] have shown that this loss in weight is due to the dissociation of ferric oxide into magnetic oxide and oxygen. Thus the higher weight is the correct weight of ferric oxide. Baxter and Hoover, however, chose the lower, regarding the higher weight as due to occluded oxygen. The necessary correction to the atomic weight of iron is −0·007, and so the corrected value is *Fe=58·840*. Of the twelve analyses on which this result is based, seven were made with terrestrial and five with meteoric iron, and no difference in the results was observed.

The International Committee for 1920 give the value

Fe=55·84.

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[1] Baxter, Thorvaldson, and Cobb, *J. Amer. Chem. Soc.*, 1911, 33, 319.
[2] Baxter and Thorvaldson, *ibid*, 1911, 33, 337.
[3] Baxter and Hoover, *ibid.*, 1912, 34, 1657.
[4] Sosman and Hostetter, *ibid.*, 1916, 38, 1188. See this volume, p. 117.

CHAPTER IV.

THE CORROSION OF IRON.[1]

The Chemistry of Corrosion.—When exposed to the combined action of air and liquid water iron readily oxidises or "corrodes," being converted into a brown, porous mass of ferric oxide in various stages of hydration. This oxide is popularly termed "rust." Any attempt to explain the changes taking place during the corrosion of iron must take into account the following facts :—

1. *Dry air or oxygen has no effect upon iron at the ordinary temperature.* If, however, the metal is heated in either of the gases, superficial oxidation takes place, the action being visible at about 220° C., when the metal acquires a pale yellow tint. This, as the temperature rises, gives place to a straw colour, and ultimately to purple and blue ; but no rust is formed.

2. *Liquid water alone, at ordinary temperatures, has no appreciable action on iron.* A piece of polished iron may be kept for an indefinite time in a hermetically sealed tube in contact with air-free distilled water without undergoing any appreciable change.

Pure Swedish iron has been kept by the author under these conditions for twelve years, during which time, apart from the merest trace of tarnishing, which could only be detected under a bright light, the metal appeared to undergo no change whatever. Even at its boiling-point water appears to have no action on compact iron, although the finely divided metal decomposes it with evolution of hydrogen gas.

3. *A mixture of air or oxygen and water vapour has no action on iron,* provided the temperature is not allowed to fall to that at which liquid water begins to be deposited.[2]

On allowing the temperature to fluctuate, however, so that liquid water forms upon the iron, corrosion readily takes place. This disposes of the possibility that rusting is a simple case of direct oxidation, such as occurs when the metal is heated in air.

The fact thus established that the presence of liquid water is essential to corrosion points to the conclusion that before iron can rust it must pass into solution, presumably first in the ferrous state from which it is then precipitated by atmospheric oxygen in the form of hydrated ferric oxide or rust. In other words, the reaction is essentially ionic.

In the majority of cases of aerial and aqueous rusting there can be little doubt that one of the most active and important agents is carbonic acid. This unites with the iron, forming ferrous carbonate, $FeCO_3$, or perhaps the soluble bicarbonate, $FeH_2(CO_3)_2$, according to the equation :—

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[1] For a detailed account of this subject with full references up to 1911, see Friend, *The Corrosion of Iron and Steel* (Longmans, 1911).

[2] Dunstan, Jowett, and Goulding, *Trans Chem. Soc.*, 1905, 87, 1557.

$$Fe+2CO_2+2H_2O=FeH_2(CO_3)_2+2H,$$

the nascent hydrogen uniting with any dissolved oxygen to form water. The ferrous carbonate thus produced is next converted into rust by the oxygen of the air with the simultaneous liberation of carbon dioxide, which is now free to attack more iron. Thus a small quantity of carbon dioxide is able to assist catalytically the conversion of an infinite quantity of iron into rust.

In the presence of excess of carbon dioxide *free* oxygen is not, according to Paul,[1] essential to corrosion. As the result of several series of experiments carried out with iron in contact with air-free water and carbon dioxide, this investigator concludes that under these special conditions the reactions involved are as follow :—

1. Solution of some iron and evolution of hydrogen gas :—

$$Fe+CO_2+H_2O=FeCO_3+2H.$$

2. The ferrous carbonate is decomposed by water into ferric oxide, carbonic acid, and formic acid :—

$$2FeCO_3+2H_2O=Fe_2O_3+H.COOH+H_2CO_3.$$

The carbonic acid is then free to dissolve more iron, but after each neutralisation its amount is reduced by some 50 per cent., in consequence of the formation of formic acid.

3. The formic acid attacks the free metal, yielding ferrous formate :—

$$Fe+2H.COOH=Fe(CHO_2)_2+2H.$$

4. A portion of the formate is reduced by nascent hydrogen, yielding some formaldehyde and ferric oxide :—

$$2Fe(CHO_2)_2+4H=Fe_2O_3+3H.CHO+H.COOH.$$

The formaldehyde, being inert, passes out of the system, whilst the liberated formic acid is free to attack more metal.

From the foregoing it is evident that the ultimate fate of the carbon dioxide is conversion into formaldehyde, so that a trace of carbon dioxide cannot be expected to catalytically assist the oxidation of an infinite quantity of iron, as, theoretically, it should be capable of doing according to the simple cycle first described as occurring in the presence of air. Paul suggests that these reactions probably take place during the ordinary atmospheric corrosion of iron. Very possibly such is the case to a minute extent, but a great deal more evidence would be required before accepting these complicated cycles as representing the main course of corrosion. In any case, however, the theory is very suggestive, and is worthy of further investigation, for reduction of carbon dioxide in aqueous solution to formaldehyde is *not* an entirely new idea, Fenton[2] having effected it by the nascent hydrogen generated from amalgamated magnesium, and observed that the presence of ferric hydroxide assists the reaction.

The problem as to whether or not a pure iron will rust in the presence of pure water and pure oxygen alone is one which has been the subject of considerable discussion. It is well known that many reactions which take place readily when the reagents are of mere commercial purity proceed only with diffidence when the substances are carefully purified. Thus, for example, commercial zinc dissolves with great rapidity in dilute sulphuric acid, whilst the pure metal is highly resistant to solution. Again, commercial hydrogen peroxide, which usually contains small quantities of dissolved salts, readily attacks iron, yielding a voluminous precipitate of rust. But the metal remains untarnished in a solution of Merck's pure hydrogen peroxide in pure distilled water, despite the fact that its surface is swept by a continuous stream of oxygen bubbles from the peroxide which it is catalytically assisting to decompose.

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[1] Paul, *Boiler Chemistry and Feed Water Supplies* (Longmans, 1919), chapter x.

[2] Fenton, *Trans. Chem. Soc.*, 1907, 91, 687.

The question, therefore, as to whether or not pure liquid water and pure oxygen are alone sufficient to induce corrosion is one of considerable theoretical interest; and opinions are divided.

Berzelius was aware that iron does not rust when immersed in aqueous solutions of alkali hydroxides, and during the greater part of last century this fact was regarded as definitely proving that the presence of an acid or negative radicle is essential to corrosion. In 1903, however, Whitney[1] suggested that, water being an electrolyte and split up, albeit to only a minute extent, into hydrogen and hydroxyl ions, renders it unnecessary to assume that any substance other than oxygen is required to effect the corrosion of iron in water. The condition of equilibrium between the whole and the ionised molecules of water may be represented as follows :—

$$nH_2O \rightleftharpoons (n-1)H_2O + H^{\cdot} + OH',$$

where n represents a large whole number, the precise value for which is uncertain. If, now, a piece of iron is placed in the water, a minute portion will pass into solution in the ionic condition, free, gaseous, molecular hydrogen being deposited upon the surface of the undissolved metal. Thus :—

$$Fe + 2H^{\cdot} + 2OH' \rightleftharpoons Fe^{\cdot\cdot} + H_2 + 2OH'.$$

Some of the ferrous and hydroxyl ions unite to form un-ionised ferrous hydroxide, until equilibrium is attained, according to the equation :—

$$Fe^{\cdot\cdot} + 2OH' \rightleftharpoons Fe(OH)_2.$$

The admission of oxygen to the system serves the double purpose of oxidising the liberated molecular hydrogen and converting the ferrous hydroxide into the basic ferric derivative, popularly known as rust. These two changes disturb the equilibrium, more iron passing into solution to be converted, in turn, into a further quantity of rust.

According to this theory, therefore, the presence of an acid is unnecessary; and the inhibiting power of alkalies is attributed to the suppression of aqueous ionisation by the presence of so many additional hydroxyl ions in accordance with the law of Mass Action.

Theoretically, it should be a simple matter to decide whether or not pure water, pure oxygen, and pure iron are alone sufficient to induce corrosion. In practice, however, the problem is one of extreme difficulty, owing to the elaborate precautions that must be taken to obtain each of the three substances in a pure condition, for any small trace of impurity, acting as a catalyst, may be sufficient to effect the oxidation of an indefinitely large quantity of the metal.

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[1] Whitney, *J. Amer. Chem. Soc.*, 1903, 25, 394.

The extreme difficulty of removing traces of carbon dioxide from the walls of any apparatus was probably first realised by Moody.[1] This investigator placed a piece of pure Swedish iron (99·8 per cent. Fe) in a tube containing a 1 per cent. solution of chromic acid to clean its surface, and a current of pure carbon dioxide-free air was passed through the apparatus for several weeks in order to remove all traces of foreign gases. Water was now distilled on to the metal, washing the chromic acid away, and the passage of air continued. The metal did not rust.

Similar results may be obtained in a much simpler manner [2] by means of the apparatus shown in fig. 1. A is a small iron cylinder closed at one end, the other end being fitted with a stopper and tubes so arranged as to allow a constant stream of water to circulate through the cylinder to keep it cool. The whole is inserted in a flask containing a twice-normal solution of alkali hydroxide, and well shaken to remove all traces of carbon dioxide. Upon inserting in a water bath pure carbon dioxide-free water condenses on A in a continuous stream, washing away the alkali. The metal may be kept for an indefinitely long time in contact with the air and pure condensed water without corroding.

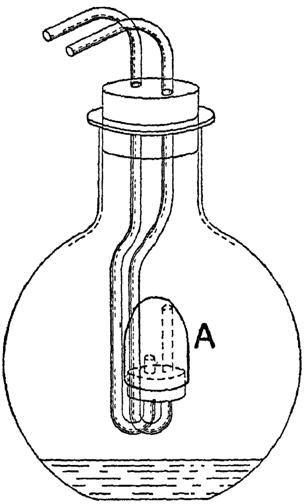

FIG. 1.

These experiments appear to prove fairly conclusively that pure oxygen and pure water are not sufficient to effect the corrosion of the purer forms of iron.

Unless the surface of the iron is cleaned and freed from condensed or occluded gases by a preliminary washing with chromic acid or alkali hydroxide, as in the experiments described, contact with pure water and oxygen invariably leads to corrosion,[3] as is to be expected. It has therefore been urged that the cleansing reagents referred to above render the iron passive (see p. 57), so that the results are misleading. In 1910, however, Lambert and Thomson [4] described their experiments with iron of an exceptionally pure character (see p. 34), prepared by reduction of highly purified ferric nitrate. The metal was found to be remarkably inert or passive, and could be exposed to the combined action of water and oxygen for several months without undergoing any visible oxidation. Passivity is thus one of the characteristic properties of pure iron, and it is very justly claimed that any passivity induced in the metals used by Moody and by Friend is simply due to the thorough cleansing of the metallic surfaces, and is, to that extent, an indication of their purity.[1]

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[1] Moody, *Trans. Chem. Soc.*, 1906, 89, 720.

[2] Friend, *Proc. Chem. Soc.*, 1910, 26, 179.

[3] See the experiments of Whitney, *loc. cit.*; Dunstan, Jowett, and Goulding, *Trans. Chem. Soc.*, 1905, 87, 1548; Cushman, *U.S. Dept Agriculture*, Bulletin No. 30, Washington, 1907; Walker, Cederholm, and Bent, *J. Amer. Chem. Soc.*, 1907, 29, 1251; Tilden, *Trans. Chem. Soc.*, 1908, 93, 1358; Heyn and Bauer, *Mitt. königl. Material-prufungsamt*, 1908, 26, 2.

[4] Lambert and Thomson, *Trans. Chem. Soc.*, 1910, 97, 2426.

The Mechanism of Corrosion.—An attractive theory of the mechanism of corrosion has been outlined by Aitchison.[2] Compact iron, when examined under the microscope (see Part III.), is seen to consist of crystals of ferrite separated from each other by an amorphous cement. It is reasonable to suppose that the solution pressure of this cement differs from that of the ferrite, for differences of this kind invariably occur between amorphous and crystalline varieties of substances. Upon immersion in an electrolyte, therefore, such as ordinary tap water or aqueous solutions of inorganic salts, a difference of potential exists leading to corrosion. If the cement is positive to the ferrite, it is the cement that will oxidise away ; and vice versa. In a perfectly annealed specimen, in which there is but little mechanical strain, the action will, in the main, be confined to that between the cement and ferrite. If, however, there is any appreciable potential difference between the crystals of ferrite themselves, this will increase the effect, the total observed corrosion being the sum of the two actions.

The solution pressure of the cement might, conceivably, lie between that of the more positive and the more negative ferrite crystals, in which case the cement would function cathodically towards the one and anodically towards the other.

Taking the simplest case, however, in which the ferrite is at practically the same potential throughout, the corrosion will proceed at the junctions of the crystals and the cement. The action will not of necessity be confined to one face of contact, but may be expected to proceed at a maximum rate on that plane, resulting in the formation of a pit.

Corrosion is further accelerated by the presence of impurities such as oxides, sulphides, carbides, phosphides, and silicates, since these are invariably at a lower potential than the ferrite.[3] The influence of alloying elements[4] is particularly interesting. With carbon, for example, cementite or iron carbide, Fe_3C, is formed, and as this is electro-negative to ferrite, the latter corrodes at the points of contact. Addition of carbon, therefore, to iron tends to enhance its corrodibility. If a third element is added to the system, its influence upon corrosion is determined largely by the manner in which it distributes itself.[5] If it dissolves in the ferrite, reducing its solution pressure, it reduces the potential difference between the ferrite and cementite, and thus enhances the resistance of the whole to corrosion. Nickel behaves in this manner, the whole of the metal passing into solid solution with the ferrite until the steel contains more than 8 per cent. of nickel. Such steels, therefore, do not readily corrode.

If, on the other hand, the third element is associated entirely with the carbon and forms part of the carbide, the corrodibility of the alloy will not be appreciably affected. Vanadium, tungsten, and molybdenum are cases in point, their saturation percentages in the carbide being approximately as follows :—

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[1] Compare Moody, *Proc. Chem. Soc.*, 1909, 25, 34.

[2] Aitchison, *J. Iron Steel Inst.*, 1916, I , 77.

[3] See Cobb, *ibid.*, 1911, I , 170.

[4] The corrodibilities of steels and other alloys of iron are discussed in Part III. of this volume

[5] Aitchison, *loc. cit.* See also *Trans. Chem. Soc.*, 1915, 107, 1531 ; 1916, 109, 288, Arnold and Read, *J. Iron Steel Inst.*, 1910, I., 169 ; 1911, I., 249 ; 1912, I., 215 ; *J. Inst. Mech. Eng.*, 1914, I., 233 ; 1915, I., 247.

Vanadium . . .	5·4 per cent.
Tungsten . . .	11·7 „
Molybdenum . .	19·0 „

Below these concentrations the metals do not pass into solid solution, but remain entirely associated with the carbide.

The behaviour of chromium is interesting, for this metal distributes itself between the ferrite and carbide, and tends to reduce the corrodibility of the alloy to an extent determined by the portion that passes into solid solution.

Ferroxyl.—An effective method of showing that differences of potential exist between different parts of a piece of iron consists in utilising the ferroxyl indicator devised jointly by Cushman[1] and Walker.[2] A 1·5 per cent. solution of agar-agar jelly is prepared, a few drops of phenolphthalein added, and the whole rendered perfectly neutral whilst hot by titration either with alkali or acid as occasion requires. A small quantity of potassium ferricyanide solution is now added, and the solution poured into a shallow dish to cool. A clean sample of iron is placed on the solidified jelly and covered with a layer of warm solution, and the whole allowed to cool. After a few hours some very beautiful colour effects will have developed, and may be preserved for several months by keeping the surface of the agar covered with alcohol.

Where the iron remains bright the agar assumes a pink colour indicative of the presence of hydroxyl ions. At those points where the iron passes into solution the familiar colour of Turnbull's blue compound (see p. 227) makes its appearance.

The Influence of Dissolved Salts upon Corrosion.—The presence of salts dissolved in water may greatly influence the manner in which the iron is attacked. Many salts exert a distinct chemical action on the metal. Thus, for example, when immersed in solutions of copper sulphate, iron readily dissolves, an equivalent amount of copper being precipitated in accordance with the equation :—

$$Fe+CuSO_4=FeSO_4+Cu.$$

On the other hand, iron remains perfectly bright and free from all traces of corrosion when immersed in solutions of the chromates or bichromates of the alkali metals, unless, indeed, the solutions are excessively dilute. This is generally attributed to the formation of a thin film of oxide on the surface of the metal which shields the underlying portions from attack, but this is not the only explanation, as has been seen (p. 71).

Ammonium salts are very corrosive, particularly in warm or hot solutions, probably on account of the ease with which they undergo hydrolysis. For example, a saturated solution of ammonium sulphate is less corrosive than distilled water at 6° C., but at 18° C. it is much more corrosive.[1] Again, on boiling iron drillings in a concentrated solution of ammonium chloride, hydrogen and ammonia are evolved, ferrous chloride passing into solution. Thus :—[2]

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[1] Cushman, *U.S. Dept. Agriculture*, Bulletin No. 30, Washington, 1907 ; *J. Iron Steel Inst.*, 1909, I., 33.

[2] Walker, *J. Amer. Chem. Soc.*, 1907, 29, 1257.

$$Fe+2NH_4Cl=FeCl_2+2NH_3+H_2.$$

When ammonium nitrate solutions are heated in contact with iron, an analogous reaction occurs; ammonia is evolved, whilst the iron suffers appreciable corrosion under the action of the liberated nitric acid.[3]

It is instructive to examine the effect of exposing iron plates to the action of salt solutions of varying concentrations by determining the losses in weight consequent upon corrosion. Curve ACLS (fig. 2) shows diagrammatically the usual type of results obtained. The point A indicates the loss in weight of the plate immersed in distilled water to which no salt has been added.

The presence of small quantities of the dissolved salt effects an increase in the corrosion of the iron, a maximum being reached at C, known as the *critical* concentration. Further increase in the quantity of the salt reduces the corrosion to nil at L, which point is termed the *limiting* concentration, and from this point onwards, until saturation is reached, the liquid is non-corrosive.

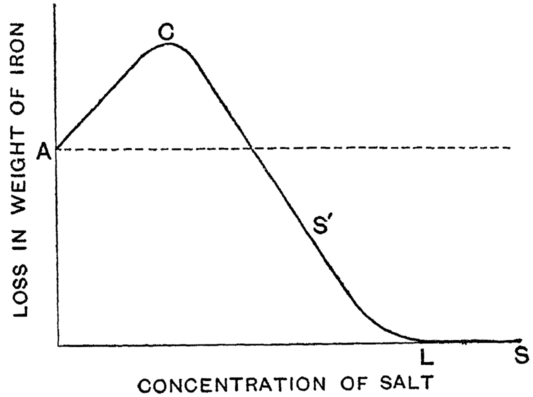

FIG. 2.

There are several salts that behave in this way at atmospheric temperatures, the more important being ammonium acetate; potassium bromate, carbonate, cyanide, ferricyanide, ferrocyanide, iodate, and permanganate; disodium hydrogen phosphate; and sodium borate and carbonate.[4] In the case of potassium chlorate the points L and S appear to be practically coincident, whilst for the majority of salts the point S lies somewhere to the left of L, namely at S′—that is to say, saturation occurs before the limiting concentration is reached. Generally speaking, at the ordinary temperature, concentrated solutions of salts are less corrosive than distilled water—that is, the point S′ lies below the level of A, exceptions being[5] ammonium sulphate, aluminium sulphate, ferrous sulphate, and (at temperatures in the neighbourhood of 6° C.) sodium sulphate, potassium nitrate, and barium chloride.

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[1] Friend and Barnet, *J. Iron Steel Inst.*, 1915, I., 336.
[2] Santi, *Chem. Zentr.*, 1904, II, 1625.
[3] See Prideaux and Caven, *J. Soc. Chem. Ind.*, 1919, 38, 353T.
[4] Heyn and Bauer, *Mitt. königl. Material-prufungsamt*, 1908, 26, 2.
[5] Friend and Barnet, *J. Iron Steel Inst.*, 1915, I., 336.

Sufficient data have not as yet been accumulated to allow of a complete explanation of the form of the curve ACLS. The initial rise from A to C is probably connected with the number of ions introduced into the solution with rise of salt concentration. As the latter increases, however, another factor begins to make itself felt, namely, the decreased solubility of oxygen in the solution. This acts in the opposite direction by retarding corrosion. This is shown in fig. 3, where the relative corrodibilities of Kahlbaum's pure iron foil in various concentrations of sodium chloride solution are depicted at 10° C. and 23·5° C., the relative solubility curve for oxygen being represented by the broken line.[1]

On raising the temperature above that of the atmosphere, the tendency is for the critical concentration to fall—in other words, the point C (fig. 2) is pushed towards the left. Hence a solution that is more corrosive than fresh water at the ordinary temperature may prove to be less corrosive than fresh water at higher temperatures.

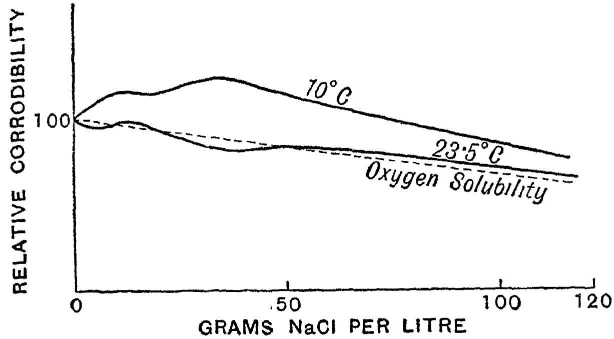

FIG. 3.

For example, a 3 per cent. solution of common salt at 10° C. is much more corrosive than tap water at the same temperature; but as the temperature rises the relative corrosivity falls, so much so that at 21° C. the salt solution is the less corrosive of the two. Since sea water contains some 3 per cent. of sodium chloride, it is of interest to inquire into the effect of temperature upon its corrosive powers. The few laboratory tests that have been carried out on the subject[2] indicate that at temperatures below 13° C. sea water is more corrosive than tap water, whilst at all higher temperatures it is less so. Now, in the western part of the tropical Pacific Ocean a temperature of 32° C. is sometimes attained, and in the Red Sea and Persian Gulf temperatures of 34·4° C. and 35·5° C. respectively have been registered. Such waters should therefore prove less corrosive than river waters at the same temperatures.

In the Arctic Ocean, on the other hand, where the temperature lies in the neighbourhood of 0° C., the sea water is more corrosive than fresh.

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[1] The solubility of oxygen in distilled water at either temperature is taken as 100° C., and the corrodibilities of iron in distilled water, as measured by loss in weight, are likewise taken as 100 (see Friend and Barnet, *loc. cit.*).

[2] Friend and Brown, *Trans. Chem. Soc.*, 1911, 99, 1302.

The foregoing observations are of great importance to marine engineers, and further research on the subject is eminently desirable.

Mention has already been made of the fact (see pp. 54, 69) that iron may be preserved from corrosion by immersion in dilute solutions of the alkali hydroxides.

An interesting case arises when iron is immersed in alkaline solutions containing inorganic salts. For example, iron will remain bright in a 1 per cent. solution of caustic potash for an indefinite time, but upon addition of potassium chloride corrosion readily takes place. It is possible, however, to increase the alkali to such an extent that corrosion is entirely prevented, no matter how concentrated the solution of chloride. The minimum amount of alkali required rises with the percentage of chloride until saturation of the latter is arrived at. This is indicated in fig. 4. AK represents the solubility curve of potassium chloride in aqueous solutions of potassium hydroxide, and CE the maximum concentration of the chloride that may be present in the corresponding alkali solution without causing corrosion. Within the area CEA, therefore, corrosion readily takes place, but outside this area corrosion is impossible.

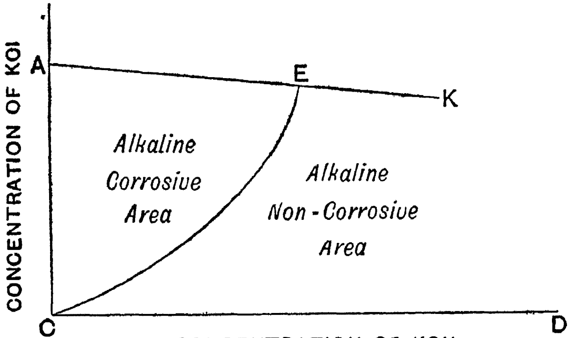

FIG. 4.

A characteristic feature of the corrosion under these conditions, however, is the tendency to "pit." This is a form of localised corrosion, the rust eating deeply into the metal at small isolated areas. Undoubtedly the rusting is originated by some irregularity—chemical or physical—in the metal, each pit being started at some point between the crystal grains. Even Kahlbaum's pure electrolytic foil readily pits in this manner, although when immersed in neutral solutions it usually corrodes fairly uniformly over its entire surface. The masses of rust formed during pitting are rich in ferrous oxide. Sometimes filaments of rust spread out in hair-like growths, brown in colour, which float or sink according to the density of the solution in which they are produced.

In practice such corrosion may prove disastrous. For example, an iron boiler might lose several pounds in weight through uniform superficial corrosion and yet not be much the worse. But a single ounce removed through pitting might be sufficient to perforate the metal and lead to serious consequences. The employment of weakly alkaline feed waters containing dissolved salts in ordinary boilers is a dangerous procedure, for the foregoing reason. The remedy would appear to lie in the addition of sufficient alkali to render the liquid non-corrosive.

Corrosion and Ionisation.—Iron will remain untarnished for indefinite periods in the presence of concentrated solutions of the carbonates of the alkali metals, even in the presence of small quantities of other salts. If, however, the alkali carbonate is very dilute, it cannot entirely inhibit corrosion. Now, the minimum quantities of alkali carbonate required to inhibit the corrosive actions of a given concentration of various other salts of the same alkali metal have been determined.[1] The results show that, if the added salts are arranged in order according to the amount of alkali carbonate required to inhibit corrosion, they are also not merely in the order of the relative strengths of their acid radicles, but the relative quantities of carbonate bear a general relationship to the numerical values found for the strengths of the acids by electrical conductivity methods. This is well illustrated in the following table :—

Sodium Salts (Concentration N/20).	Relative Concentrations of Na_2CO_3 inhibiting Corrosion	Relative Strengths of the Free Acids [2]
Chloride	100	100
Iodide	89	98
Bromide	72	98
Nitrate	54	98
Sulphate	52	70
Fluoride	39	10·5
Acetate	9	2

The close connection between ionisation and corrosion in dilute solution thus receives interesting confirmation.

The Chemical Nature of Rust.—Both the physical condition and chemical composition of rust vary considerably according to the conditions under which corrosion has taken place. Dunstan[3] gives the result of analysing (A) rust collected from iron apparatus rusted in the laboratory, and (B) rust from an iron railing exposed for thirty years to the air within twenty yards of the sea. His data are as follow :—

	A.	B.	Calculated for $Fe_2O_3.H_2O$.
Ferrous iron . . .	0·13	3·25	. .
Ferric iron . . .	60·93	59·25	62·8
Hydrogen	1·01	1·17	1·3
Oxygen	34·35	35·70	35·9
Carbon dioxide . . .	0·15	. .	. .
Ammonia	0·006	. .	. .
Insoluble matter . .	3·20	0·60	. .

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[1] Friend and Marshall, *Trans Chem. Soc.*, 1914, 105, 2776.

[2] Calculated from electric conductivities.

[3] Dunstan, Jowett, and Goulding, *Trans. Chem. Soc.*, 1905, 87, 1564.

From this it is evident that ordinary rust produced by exposure of iron to air corresponds very closely to the formula $Fe_2O_3.H_2O$.[1]

When iron is completely immersed in distilled water there is usually no pitting, and the metal becomes covered with a loosely adherent cover of brown oxide, in which there may or may not be a trace of greenish ferrous oxide. When the metal is only partially immersed in water, a particularly vigorous oxidation takes place at the surface of the liquid, for at this point the latter is relatively rich in dissolved oxygen. The resulting mass of rust is frequently high in ferrous oxide. A somewhat similar result obtains when iron is exposed alternately to the action of water and air, the proportion of ferrous oxide in the mass depending upon the difficulty experienced by the atmospheric oxygen in penetrating its surface. This is clearly shown[2] by the following analyses of samples of rust obtained from the unpainted interiors of iron flushing tanks in constant use. Several of the tanks had been unscraped for years, and the sides were blistered with masses of rust, brown without but black within. Every sample when placed in dilute aqueous hydrogen chloride effervesced briskly, evolving carbon dioxide. The analyses were as follows :—

No. of Sample . . .	1.	2.	3.	4.	5.	6.
Percentage of iron as ferric oxide . .	55·73	51·12	64·60	65·13	68·89	67·46
Percentage of iron as ferrous oxide . .	32·86	36·57	25·74	25 66	23·18	24·40
Percentage of iron as ferrous carbonate .	11·40	12·31	9·66	9·21	7·93	8·14

The Corrosion of Wrought Iron, Cast Iron, and Steel.—This subject is discussed in Part III. of this volume, together with the influence of various impurities and alloying elements.

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[1] Other analyses of rust are given by Calvert, *Chem. News*, 1871, 23, 98 ; Jamieson, *Min. Proc. Inst. Civil Engineers*, 1881, 65, 323 ; Weinwurm, *Chem Zeit.*, 1893, 17, 101 ; Gaines, *Chem. News*, 1910, 101, 205 ; T. Steel, *J. Soc. Chem. Ind.*, 1910, 29, 1141 ; Donath and Indra, *Chem Zeit.*, 1911, 35, 773 ; Moody, *vide infra* ; J. H. Paul, *Boiler Chemistry and Feed Water Supplies* (Longmans, 1919), pp. 126–129.

[2] Moody, *Trans. Chem. Soc.*, 1906, 89, 726.

CHAPTER V.

GENERAL PROPERTIES OF IRON SALTS.

Salts of Iron may be roughly divided into two groups, according as the iron behaves as a divalent or trivalent atom. Salts of divalent iron are termed *ferrous*, and in neutral or faintly alkaline solution are readily oxidised to *ferric* compounds, in which the iron has a valency of three. Ferrous salts, when hydrated, are usually greenish in colour, copperas or ferrous sulphate being typical. Anhydrous ferrous salts are white or pale yellow in colour, as witness ferrous chloride and bromide. Ferric salts, when crystalline, are also white and opaque (ferric sulphate), colourless (ferric nitrate), or yellow (ferric chloride), although many basic compounds are brown. When in combination with other salts, various colours may appear—as, for example, in the case of iron alum, the delicate violet hue of which is well known. Iron salts impart a distinct and bitter taste to water, one part of iron per million of water being distinctly perceptible to the average individual.[1]

A peculiar property of ferrous salts consists in their power, when in solution,[2] of uniting with nitric oxide, the limit of combination being reached with one molecule of NO to one atom of iron. The substances thereby produced are very unstable, partaking of the nature of additive or associated compounds. Two of these compounds have been isolated, namely, $FeSO_4.NO$[3] and $FeHPO_4.NO$[4]; and several other salts, such as $FeCl_2.NO$ and $FeBr_2.NO$, have been shown to exist in solution. In this respect ferrous salts closely resemble salts of divalent copper, which yield, with nitric oxide, additive compounds of the type $CuX_2.NO$.[5] Ferric salts—for example, ferric chloride—also combine with nitric oxide to yield unstable compounds. Both ferrous and ferric salts readily decompose barium peroxide, the former after being first oxidised to ferric. The reaction, in the case of ferric chloride, takes place according to the equation :—[6]

$$6BaO_2+4FeCl_3+6H_2O=3O_2+4Fe(OH)_3+6BaCl_2.$$

Iron Salts as Catalysts.—Schönbein, in 1857, drew attention to the fact that ferrous salts are capable of acting as oxygen-carriers in certain circumstances,[7] but it was not until thirty-seven years had elapsed that attention was again drawn to the subject by the observation of Fenton [1] that hydrogen peroxide oxidises tartaric acid to dihydroxymaleic acid in the presence of a ferrous salt—in particular, ferrous sulphate. He explained this on the assumption that the divalent iron replaces the two non-hydroxylic hydrogen atoms of tartaric acid, and, upon oxidation by the peroxide to the trivalent condition, breaks away from them. Thus

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[1] See Rideal, *Water Supplies* (Crosby Lockwood, 1914).

[2] Whether aqueous, alcoholic, ethereal, or in acetic acid (Thomas, *Bull. Soc. chim.*, 1898, (3), 19, 419.

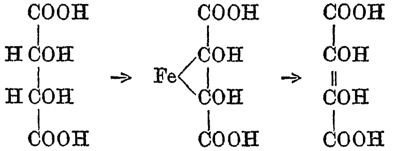
[3] See p. 153.

[4] See p. 185.

[5] See Manchot, *Ber.*, 1914, 47, 1601.

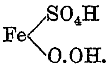
[6] Kwasnik, *ibid.*, 1892, 25, 67.

[7] Schonbein, "Ueber die Gleichheit des Einflusses welchen in gewissen Fallen die Blutkörperchen und Eisenoxydulsalze auf die chemische Thatigkeit des gebundenen Sauerstoffes ausuben," *Verhand. Naturf. Gesell. Basel*, 1860, II., p. 9.



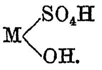
(tartaric acid). (dihydroxymaleic acid).

Suggestive as this theory is, there are other reactions in which ferrous sulphate acts as a catalyser, in which the above explanation cannot possibly hold, and several other theories have been offered. Manchot and Wilhelms [2] believe that a highly oxidised compound of iron, such as Fe_2O_5 or $Fe_2O_3.2H_2O_2$, is formed by contact of the ferrous salt and peroxide, and that this is reduced by the oxidisable substance. Brode [3] reached a somewhat similar conclusion, suggesting that the peroxide and ferrous salt unite to form an intermediate, highly oxidised compound, whilst Mummery [4] combines the essential features of these two theories into a very attractive hypothesis, according to which ferrous sulphate and hydrogen peroxide unite to form ferrous sulphate perhydrol,



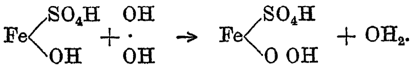
$$\text{Fe}\left\langle\begin{matrix}SO_4H\\ O.OH.\end{matrix}\right.$$

He arrives at this in the following manner. In view of the retention of a molecule of water by the isomorphous members of the ferrous sulphate series, they may be regarded as hemisulphate hemihydrols of the type



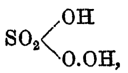
$$\text{M}\left\langle\begin{matrix}SO_4H\\ OH.\end{matrix}\right.$$

With hydrogen peroxide, therefore, ferrous sulphate reacts as follows :—



$$\text{Fe}\left\langle\begin{matrix}SO_4H\\ OH\end{matrix}\right. + \begin{matrix}OH\\ \cdot\\ OH\end{matrix} \rightarrow \text{Fe}\left\langle\begin{matrix}SO_4H\\ O\ OH\end{matrix}\right. + OH_2.$$

This perhydrol bears a resemblance in constitution to Caro's permonosulphuric acid, H_2SO_5, or



$$SO_2\left\langle\begin{matrix}OH\\ O.OH,\end{matrix}\right.$$

and may be expected to possess the properties of a powerful oxidiser. The reason why such a compound acts more powerfully than hydrogen peroxide itself is attributed to the fact that it is an electrolyte, whereas hydrogen peroxide, for all practical purposes, is not. This perhydrol is alternately produced from, and reconverted into, ferrous sulphate, when an oxidisable substance is present, together with hydrogen peroxide.

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[1] Fenton, *Trans. Chem. Soc.*, 1894, 65, 899 ; *Proc. Chem. Soc.*, 1898, 14, 119.

[2] Manchot and Wilhelms, *Ber.*, 1901, 34, 2479.

[3] Brode, *Zeitsch. physikal. Chem.*, 1901, 37, 257.

[4] Mummery, *J. Soc. Chem. Ind.*, 1913, 32, 889.

Methyl, ethyl, and propyl alcohols are oxidised by permanganate or hydrogen peroxide in the presence of ferrous salts. If ferrous sulphate is employed, the ethyl alcohol is, in dilute solution, oxidised by the permanganate to aldehyde; but in the presence of ferrous oxalate the oxidation proceeds further, acetic acid resulting. Thus

$$CH_3.CH_2OH \rightarrow CH_3.CHO \rightarrow CH_3.COOH.$$

These reactions proceed so regularly that they may be followed up quantitatively. Ferric salts have no catalytic influence upon these reactions.[1] Iron salts, however, can act as oxygen-carriers in the absence of such powerful oxidisers as hydrogen peroxide and potassium permanganate. Thus, for example, it is well known that, upon exposure to sunlight, iodine is ordinarily liberated from a solution of mercuric iodide in potassium iodide. Curiously enough, if traces of iron salts are rigidly excluded, the liberation of iodine does not take place.[2]

Ferrous salts accelerate the oxidation of sulphurous acid to sulphuric acid in the presence of oxygen.[3]

Ferrous chloride accelerates the oxidation of stannous chloride solution in air, the maximum effect being obtained with one molecule of $FeCl_2$ to 100 molecules of $SnCl_2$.[4]

Ferrous salts accelerate markedly the reaction between persulphates and iodides, as represented, in the case of the potassium salts, by the equation

$$K_2S_2O_8+2KI=2K_2SO_4+I_2.^5$$

In acid solution chlorates are reduced to chlorides by soluble iodides. For example, in the case of the potassium salts the reaction proceeds as follows:—

$$KClO_3+6KI+3H_2SO_4=KCl+3K_2SO_4+3I_2+3H_2O.$$

Addition of a small quantity of a ferric or ferrous salt greatly accelerates the reaction,[6] due to the alternate formation of ferric iodide and reduction to the ferrous salt as follows:—

$$KClO_3+6FeI_2+6KI+3H_2SO_4=KCl+3K_2SO_4+6FeI_3+3H_2O,$$
$$6FeI_3=6FeI_2+3I_2.$$

It is well known that a mixed solution of ordinary mercuric chloride and ammonium oxalate undergoes decomposition when exposed to light, mercurous chloride being precipitated and carbon dioxide evolved. The reaction may be represented by the equation

$$2HgCl_2+(NH_4)_2C_2O_4=2HgCl+2NH_4Cl+2CO_2.$$

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[1] Doroschevski and Bardt, *J. Russ. Phys Chem. Soc.*, 1914, 46, 754, 1669.

[2] H. S. Hatfield, *Zeitsch. Elektrochem.*, 1913, 19, 617.

[3] Meyer, *Ber.*, 1887, 20, 3058.

[4] Warynski and Towtkiewicz, *Ann. Chim. anal.*, 1913, 18, 130. See Noyes, *Zeitsch. physikal. Chem*, 1896, 21, 16.

[5] Price, *Zeitsch. physikal. Chem.*, 1898, 27, 474.

[6] Green, *J. Physical Chem.*, 1908, 12, 389; Pisarshevski and Averkiev, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 2057.

This change, which proceeds at a measurable rate, has been utilised in quantitative determinations of the intensity of light—so-called *actinometric* measurements. The sensitiveness of the reaction, however, is largely dependent upon the purity of the salts, traces of iron salts increasing the sensitiveness in proportion to the amount of iron—provided the amount is very small. Indeed, there is reason to believe that if the solution were entirely free from iron no photochemical effect would be observed.[1]

Hydrochloric acid is without action on gold, but addition of a small quantity of ferric chloride causes the gold to dissolve, the ferric salt presumably acting as a chlorine-carrier [2] in the presence of hydrochloric acid and oxygen. Salts of iron are frequently used in organic chemical processes as halogen-carriers.[3]

Iron Salts as Negative Catalysts.—In certain cases small quantities of ferrous salts act as retarding agents in chemical reactions, and may therefore be termed negative catalysts. For example, ferrous sulphate has long been known [4] to hinder the action of nitric acid on metals.

Traces of ferric salts retard the dissolution of mercury in nitric acid, a phenomenon which is attributed [5] to decomposition of the nitrous acid by the catalytic alternate reduction and oxidation of the iron radicle.

Oxidation of Ferrous Salts.—Ferrous salts are readily converted into ferric derivatives in a variety of ways. Thus their solutions are gradually oxidised upon exposure to air, with the deposition of basic ferric salts. The rate of oxidation by air in the presence of free acids is, in the case of ferrous sulphate, proportional to the partial pressure of the oxygen.[6] Hence the addition of inert soluble salts, such as the chlorides and sulphates of sodium, potassium, or magnesium, to the solution reduces the rate of oxidation in proportion as they decrease the solubility of the oxygen.[7]

At 60° C. the relative rates of oxidation of ferrous chloride, sulphate, and acetate, are as follow:—1 : 10 : 100. The oxidation appears to depend upon the un-ionised portion of the dissolved salt.[6]

In alkaline solution oxidation of ferrous iron is fairly rapid,[8] but certain acids retard the reaction. Ferrous sulphate, for example, in the presence of free sulphuric acid, is very stable in air. Concentrated hydrochloric acid assists the oxidation, as also do traces of certain substances, such as platinic and cupric chlorides, palladium nitrate, etc.[9]

The aerial oxidation of solutions of ferrous salts may be accelerated by certain micro-organisms, known as iron bacteria. Mumford [10] describes an organism through the agency of which a dilute solution of ferrous ammonium sulphate was completely oxidised to ferric hydroxide in fewer than thirty-six hours at 37° C., no iron remaining in solution. There can be no doubt that the natural deposits of bog iron ore, occurring in Sweden and elsewhere, owe their existence to the action of these lowly organisms.[1]

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[1] Winther, *Zeitsch. wiss. Photochem.*, 1910, 8, 197, 237; 1909, 7, 409.

[2] M'Ilhiney, *Amer. J. Sci.*, 1896, (4), 2, 293.

[3] See, for example, L. Meyer, *Annalen*, 1885, 231, 195; Scheufelen, *ibid.*, p 152; Meyer and Scheufelen, *Ber.*, 1885, 18, 2017; Willgerodt, *J. prakt. Chem.*, 1885, (2), 31, 539; Page, *Annalen*, 1884, 225, 196; Aronheim, *Ber.*, 1875, 8, 1400; 1876, 9, 1788.

[4] Millon, *Compt. rend.*, 1842, 19, 904; Veley, *Phil. Trans*, 1891, A, 182, 279.

[5] Ray, *Trans. Chem. Soc.*, 1911, 99, 1012.

[6] M'Bain, *J. Physical Chem*, 1901, 5, 623; Ennos, *Proc. Camb. Phil. Soc.*, 1913, 17, 182. Compare Baskerville and Stevenson, *J. Amer Chem. Soc.*, 1911, 33, 1104.

[7] MacArthur, *J. Physical Chem.*, 1916, 20, 545. See p. 152.

[8] See Muller and Kapeller, *Zeitsch. Elektrochem.*, 1908, 14, 76.

[9] Warynski, *Ann. Chim. anal*, 1909, 14, 45.

[10] Mumford, *Trans. Chem. Soc*, 1913, 103, 645.

The presence of platinum also appears to accelerate the oxidation of solutions of ferrous salts.[2]

The action of hydrogen peroxide upon ferrous salts is interesting in view of the possible connection between ferrous salts acting as oxygen-carriers in the blood. The decomposition of the peroxide is hindered or " poisoned " by the presence of arsenious oxide, hydrogen sulphide, carbon monoxide, and other well-known poisons, and the subject is worthy of careful consideration.[3]

The usual oxidising media, such as permanganates, bichromates, etc.,[4] react instantaneously with ferrous salts, yielding in acid solution the normal ferric salts. Many methods for the quantitative determination of iron are based on these reactions. Thus, for example, with potassium permanganate the oxidation of ferrous sulphate proceeds as follows :—

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

The persistence of the pink colour of the permanganate indicates with great accuracy when sufficient of this reagent has been added. With potassium bichromate the reaction proceeds according to the equation

$$6FeSO_4+K_2Cr_2O_7+7H_2SO_4=K_2SO_4+3Fe_2(SO_4)_3+Cr_2(SO_4)_3+7H_2O,$$

the end point of the reaction being determined by removing a drop of the mixture and testing with a solution of potassium ferricyanide, which remains colourless if no ferrous salt is present, but otherwise yields a deep blue colour (see p. 242).

The mechanism of the oxidation of ferrous salts in the various ways mentioned above has been studied by Manchot,[5] who concludes that the first action is to produce a high and generally unstable oxide, termed a *primary* oxide, which then decomposes into the final oxidation product (that is, the ferric compound) and active oxygen, which latter then oxidises a further portion of the ferrous salt to ferric.

Ferrous Salts as Reducing Agents.—Owing to their ready oxidisability, ferrous salts are frequently employed as mild reducing agents. Thus ferricyanides are reduced to ferrocyanides by ferrous sulphate in alkaline solution (see p. 224).

In photography ferrous sulphate is used for the reduction of auric chloride, metallic gold being precipitated. Thus

$$AuCl_3+3FeSO_4=Au+FeCl_3+Fe_2(SO_4)_3.$$

On adding a solution of a ferrous salt to an ammoniacal solution of a cupric salt, ferric hydroxide is precipitated, the cupric salt being reduced to cuprous and remaining in solution. This affords a convenient method of preparing ammoniacal cuprous solutions for the absorption of carbon monoxide in gas analysis.[1]

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[1] See also Ellis, *Iron Bacteria* (Methuen, 1920).

[2] Jordis and Vierling, *ibid.*, 1904, 10, 679 Warynski, *loc. cit.*

[3] Fischer and Brieger, *Zeitsch. physikal. Chem.*, 1912, 80, 412; 1912, 78, 582; Rocchi, *Chem. Zentr.*, 1911, II., 1870.

[4] The rate of oxidation of ferrous salts with chromic acid has been studied by Benson, *J. Physical Chem.*, 1903, 7, 1.

[5] Manchot, *Annalen*, 1902, 325, 93, 105; *Zeitsch. anorg. Chem.*, 1901, 27, 379, 420.

Ferrous salts reduce nitrites to nitric oxide. On addition, for example, of barium nitrite to ferrous sulphate, barium sulphate is precipitated, and the liquid turns brown. Ferric hydroxide and a basic ferric nitrate are next precipitated, nitric oxide being evolved. Apparently the first product of the reaction is ferrous nitrite, which then spontaneously decomposes in accordance with the equation [2]

$$6Fe(NO_2)_2 = 10NO + Fe_2O_3 + 2Fe_2O_3.N_2O_5.$$

Photochemical Oxidation.—Mercuric chloride solution is reduced by ferrous chloride under the influence of light, mercurous chloride being precipitated.

$$HgCl_2 + FeCl_2 = FeCl_3 + HgCl.$$

If the relative proportion of mercuric chloride is small, the rate of reduction is almost independent of the concentration of the ferrous salt, and the sensitiveness to light increases with dilution.[3] Equimolecular solutions, however, do not vary to the same extent, but their maximum sensitiveness occurs at a concentration of 3 gram-molecules of each salt per litre. The presence of oxygen is without appreciable influence on the equimolecular solutions.

Reduction of Ferric Salts.—The reverse reactions, namely conversion of ferric salts into ferrous, are likewise easily effected by means of the usual reducing agents, such as nascent hydrogen, sulphur dioxide, etc. By the introduction of zinc into an acidified solution of a ferric salt, reduction is rapidly caused. Excess of acid slightly retards the reaction.[4] This affords a convenient method of volumetrically determining the presence of ferric iron, the solution after reduction being titrated with permanganate.

Zinc dust is particularly rapid in its action, even in neutral solution. In this latter case, however, the iron is partially precipitated as ferric hydroxide. The reduction takes place with ease in absolute alcohol, and is entirely independent of the presence of occluded hydrogen in the zinc. It would appear, therefore, that the zinc acts directly as a dechlorinator, and that the reduction is not effected by nascent hydrogen.[5] Thus :—

$$2FeCl_3 + Zn = 2FeCl_2 + ZnCl_2.$$

Sulphur dioxide may be passed into a solution of a ferric salt for a similar purpose, or it may be generated in the solution by addition of an alkali sulphite and a little dilute mineral acid.[6] Thus, ferric sulphate is reduced in accordance with the equation

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4.$$

The reducing action of thiosulphates on ferric salts is interesting, ranking as one of the few tetramolecular reactions that have been studied. The reduction proceeds[1] in accordance with the ionic equation

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[1] Frischer, *Chem. Zeit.*, 1908, 32, 1005 ; Herrmann, *Chem. Zentr.*, 1907, I., 1394, from *Chem. Ind*, 1907, 30, 152 ; Biddle, *Amer. Chem. J.*, 1901, 26, 377.

[2] Piccini and Zuco, *Gazzetta*, 1885, 15, 475.

[3] Winther, *Zeitsch. wiss. Photochem.*, 1912, 11, 60.

[4] Carnegie, *Trans. Chem. Soc*, 1888, 53, 468 ; Cumming and H. Smith, *Proc. Roy. Soc. Edin*, 1912, 32, 12.

[5] Carnegie, *loc. cit.*

[6] Cumming and Smith, *loc. cit.* ; Austen and Hurff, *Chem. News*, 1882, 46, 287

$$2Fe^{\cdot\cdot\cdot}+2S_2O_3''=2Fe^{\cdot\cdot}+S_4O_6''.$$

Reduction of ferric salts with potassium iodide is usually regarded as taking place as follows,[2] in the case of ferric chloride :—[3]

$$2FeCl_3+2KI\rightleftharpoons 2FeCl_2+2KCl+I_2;$$

or with ferric sulphate :—[4]

$$Fe_2(SO_4)_3+2KI\rightleftharpoons 2FeSO_4+K_2SO_4+I_2.$$

It is quite possible, however, that intermediate iodo-compounds are first formed, and, being unstable, rapidly decompose, liberating iodine.[5] Thus :

$$2FeCl_2.Cl+2KI=2FeCl_2I+2KCl,$$
$$2FeCl_2I=2FeCl_2+I_2,$$

and

$$\begin{matrix}FeSO_4\\FeSO_4\end{matrix}.SO_4+2KI=2FeSO_4I+K_2SO_4,$$
$$2FeSO_4I=2FeSO_4+I_2.$$

A useful reducing agent is stannous chloride, which reacts with ferric chloride as follows :—

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4,$$

the reaction being one of the third order or trimolecular[6] and not bimolecular, as Kahlenberg suggested,[7] in neutral solution. In the presence of acid the reaction apparently approximates to one of the second order, but the rôle played by the acid is not clear.

Photochemical Reduction.—Ferric salts are reduced by organic substances under the influence of light. Thus an alcoholic solution of ferric chloride, when exposed to sunlight, is converted into ferrous chloride, the alcohol being oxidised to aldehyde. For example, in the case of methyl[8] and ethyl alcohols :—

$$2FeCl_3+CH_3OH=2FeCl_2+H.CHO+2HCl,$$
$$2FeCl_3+CH_3.CH_2OH=2FeCl_2+CH_3.CHO+2HCl.$$

In this reaction the light acts, not as a catalyst, but as a source of energy. The quotient

$$\frac{\text{Time required for decolorisation}}{\text{Concentration of ferric chloride}}$$

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[1] In such few cases as it has proved possible to determine. Hewitt and Mann, *Trans. Chem. Soc.*, 1913, 103, 324.

[2] The reaction is reversible, for under certain conditions ferrous salts reduce iodine to hydrogen iodide (see p. 152).

[3] Seubert and Gaab, *Zeitsch. anorg. Chem.*, 1895, 9, 212 ; Seubert, *ibid.*, 1894, 5, 334 ; Seubert and Dorrer, *ibid.*, p. 339 ; Carnegie, *Chem. News*, 1889, 60, 87.

[4] Seubert and Rohrer, *Zeitsch. anorg. Chem.*, 1894, 7, 137.

[5] Seubert and Dorrer, *ibid.*, 1894, 5, 411 ; Orlov, *J. Russ. Phys. Chem. Soc.*, 1913, 45, 489.

[6] Noyes, *Zeitsch. physikal. Chem*, 1895, 16, 546 ; 1895, 18, 118.

[7] Kahlenberg, *J. Amer. Chem. Soc.*, 1894, 16, 314.

[8] Benrath, *J. prakt. Chem.*, 1909, (2), 80, 283.

is nearly constant, from which it is concluded that the amount of light energy required to reduce a definite quantity of ferric chloride is nearly constant and independent of the concentration.

Similarly a ferric salt of an organic acid is reduced by sunlight, ferric oxalate being a well-known example.[1]

$$Fe_2(C_2O_4)_3=2FeC_2O_4+2CO_2.$$

In this case the progress of the reaction may be followed by noting the rate of evolution of carbon dioxide. The blue prints used by engineers are prepared by exposing to light, under a drawing which serves as negative, sheets of paper previously soaked in a solution of an organic ferric salt. After a suitable exposure the paper is washed with a solution of potassium ferricyanide, which gives the characteristic Turnbull's blue colour where the light has effected the reduction of the ferric salt.[2]

Ultraviolet light, such as that, for example, emitted by an electric spark passing between aluminium terminals, is very active in reducing ferric salts, its activity being greatly increased by the presence of sugar. Alteration of temperature appears to exert only a small influence.[3]

It is interesting to note that ferric salts of organic acids such as citric, tartaric, etc., are not as a rule ferric salts in the ordinary acceptation of the term. The iron has entered into the electro-negative radicle in an analogous manner to copper in the organic copper derivatives.[4] In ferric oxalate and in the ferricyanides, which latter do not contain hydroxylic or carboxylic groups, the iron is similarly in the negative radicle.

Ferrous oxalate is only slightly soluble in water, but the double salt $K_2Fe(C_2O_4)_2.2H_2O$ dissolves more readily. The iron is mainly present in solution as the complex anion $Fe(C_2O_4)_2''$, but this is not very stable, owing to dissociation, which takes place as follows:—

$$Fe(C_2O_4)_2'' \rightleftharpoons \underset{\text{(solid)}}{FeC_2O_4}+C_2O_4'',$$

unless an excess of alkali oxalate is present, ferrous oxalate being precipitated.[5]

The **magnetic properties of iron salts** have been the subject of a considerable amount of investigation.[6]

Reduction of Iron Salts to Metallic Iron.—Both ferrous and ferric salts can be reduced to the metal in a variety of ways. In solution many of them are reduced by the introduction of more electro-positive metals such as magnesium, zinc, or aluminium, as also by electrolysis. In the dry way they are reduced by heating in a current of hydrogen or carbon monoxide, or with zinc dust or by ignition with carbon in an air blast (see Chapter III.).

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[1] See Baur, *Zeitsch. physikal. Chem.*, 1908, 63, 683; Jodlbauer, *ibid.*, 1907, 59, 513; Lemoine, *Compt rend.*, 1895, 121, 817; 1895, 120, 441; 1883, 97, 1208; Roloff, *Zeitsch. physikal. Chem.*, 1894, 13, 327; Jodin, *Compt. rend.*, 1882, 94, 1315; Eder, *J. Chem. Soc. Abstr.*, 1881, p. 670. The reaction was known and made use of in actinometry long before these dates, however.

[2] The photochemical sensitiveness of various organic salts has been examined by Winther and Howe, *Zeitsch. wiss. Photochem.*, 1914, 14, 196; Jodlbauer, *loc. cit.*

[3] Ross, *J. Amer. Chem. Soc.*, 1906, 28, 786.

[4] Pickering, *Trans. Chem. Soc.*, 1913, 103, 1358.

[5] Sheppard and Mees, *Trans. Chem. Soc.*, 1905, 87, 189.

[6] Pascal, *Compt. rend.*, 1908, 147, 56, etc.

When ferric acetate solution is exposed to hydrogen gas at 350° C. and under 230 atmospheres' pressure, ferric oxide is precipitated as an anhydrous red mass, insoluble in water but soluble in hydrochloric acid. At 400° C. and under a pressure of 420 atmospheres, metallic iron is obtained.[1]

Alloys of Iron.—These are dealt with in Part III. of this volume.

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[1] Ipatieff and Werchowsky, *Ber.*, 1909, 42, 2078.

CHAPTER VI.

COMPOUNDS OF IRON WITH HYDROGEN AND THE HALOGENS.

Iron Hydride.—It is a moot point as to whether or not a hydride of iron is capable of existence. It has been suggested that ferrous hydride results on treating ferrous iodide with zinc ethyl. Thus

$$FeI_2+ZnEt_2=ZnI_2+FeH_2+2C_2H_4,$$

but the evidence is not conclusive.[1]

IRON AND FLUORINE.

Ferrous fluoride, FeF_2, may be obtained as colourless monoclinic crystals of density 4.09 by heating reduced iron or anhydrous ferrous chloride to redness in a current of dry hydrogen fluoride.[2] In the amorphous condition it results on passing hydrogen fluoride over ferrous chloride in the cold.

It volatilises at 1100° C., and is reduced by hydrogen at high temperatures to metallic iron. It dissolves slowly in water, and the solution gradually deposits hydrated ferric oxide.

The *tetrahydrate*, $FeF_2.4H_2O$, results in the form of white or faintly green prisms when iron is dissolved in aqueous hydrogen fluoride and the solution allowed to crystallise at the ordinary temperature. On warming gently the crystals lose their combined water, and the anhydrous salt is left. The crystals are more soluble in hydrogen fluoride solution than in pure water. The solution decolorises permanganate, the ferric salt being obtained, and the same result accrues, albeit more slowly, by simply exposing the aqueous solution to the atmosphere.

The mineral acids dissolve the crystals completely. When ignited in air, ferric oxide is obtained, as also when the crystals are fused with an alkali carbonate. Double salts formed by union with the fluorides of the alkali and certain other metals have been described.[3] These may be termed

Ferrofluorides or *Fluoferrites.*

Thus, for example, with ammonium fluoride two salts have been obtained—namely **ammonium trifluoferrite,** $NH_4FeF_3.2H_2O$ or

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[1] Wanklyn and Carius, *Annalen*, 1861, 120, 69. See also Dupasquier, *Compt. rend.*, 1842, 14, 511 ; Fresenius and Schlossberger, *Annalen*, 1844, 51, 413.

[2] Poulenc, *Compt. rend.*, 1892, 115, 941 ; *Ann. Chim. Phys.*, 1894, (7), 2, 5.

[3] Marignac, *Ann. Chim. Phys.*, 1860, (3), 60, 306 ; 1873, (4), 30, 45 ; R. Wagner, *Ber.*, 1886, 19, 897 ; Barteczko, *Dissertation*, Bern, 1900 ; Weinland and Koppen, *Zeitsch. anorg. Chem.*, 1900, 22, 266.

$FeF_2.NH_4F.2H_2O$ (green); and the **tetrafluoferrite,** $(NH_4)_2FeF_4$ or $FeF_2.2NH_4F$ (brown). With potassium fluoride the flesh-coloured **trifluoferrite,** $KFeF_3.2H_2O$ or $FeF_2.KF.2H_2O$, is formed. The **tetrafluoferrite,** K_2FeF_4, is also known.[1]

Aluminium pentafluoferrite, $AlFeF_5.7H_2O$ or $FeF_2.AlF_3.7H_2O$, is obtained as small, greenish-white crystals on mixing a solution of ferrous carbonate in dilute hydrofluoric acid with one of aluminium hydroxide in the same acid and concentrating over lime at the ordinary temperature.[2]

The **ferric** analogue, $FeF_2.FeF_3.7H_2O$, has also been obtained (see p. 89).

Silicon hexafluoferrite, $SiFeF_6.6H_2O$, is more generally known as **ferrous fluosilicate,** $FeSiF_6.6H_2O$ (see p. 240).

Ferric fluoride may be obtained in the hydrated condition by dissolving ferric hydroxide in aqueous hydrogen fluoride,[3] or by oxidation of ferrous fluoride with nitric acid in the presence of hydrofluoric acid. Upon evaporation crystals of the *nonahydrate,* $2FeF_3.9H_2O$, separate out, which, at 100° C., yield the *hexahydrate,* $2FeF_3.6H_2O$, and when gently heated in gaseous hydrogen fluoride, evolve water yielding the *anhydrous* salt, FeF_3.

The last-named is also obtained when hydrogen fluoride is passed over red-hot iron, ferric oxide, or ferric chloride;[4] or by heating the double salt, ferric ammonium fluoride, $FeF_3.3NH_4F$, in an inert gas.

At 1000° C. ferric fluoride partially volatilises and partially crystallises to small green crystals, possibly triclinic,[4] of density 3·18. When fused with alkali carbonates it yields ferric oxide, as also when ignited in air or steam. Hydrogen reduces the salt at dull red heat. Boiling water dissolves only traces of the anhydrous salt. Aqueous solutions of ferric fluoride are colourless, and their electric conductivity very small, so that but little ionisation takes place. Determinations of the freezing-points of dilute solutions[5] indicate a molecular weight corresponding to the simple formula FeF_3. Addition of ammonium hydroxide causes the precipitation of a yellow basic fluoride.[6]

It has been suggested that the formula for the hexahydrate would be more correctly[7] represented as $Fe_2F_4(OH)_2(HF)_2.4H_2O$, since only two atoms of fluorine enter into double decomposition with barium chloride solution, although the reaction is complicated by the precipitation of barium ferrifluoride, $Ba_3(FeF_6)_2$. Again, on boiling the salt with alcohol, two molecules of hydrogen fluoride are readily evolved, whilst the remaining fluorine is expelled very slowly. On prolonged heating at 95° C. an oxyfluoride, Fe_2OF_4, is produced:—[7]

$$Fe_2F_4(OH)_2(HF)_2.4H_2O = Fe_2OF_4 + 5H_2O + 2HF.$$

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[1] Wagner, *loc. cit.*

[2] Weinland and Koppen, *Zeitsch. anorg. Chem*, 1900, 22, 266.

[3] The heat of neutralisation, $Fe(OH)_3.3HF.Aq.$, is 23,745 calories (Petersen, *Zeitsch. physikal. Chem.*, 1889, 4, 384; *Ber*, 1888, 21, 3257).

[4] Poulenc, *Compt. rend.*, 1892, 115, 941; *Ann. Chim. Phys.*, 1894, (7), 2, 5.

[5] Speransky, *J. Russ. Chem. Soc.*, 1892, 24, 304.

[6] Scheurer-Kestner, *Ann. Chim. Phys*, 1863, (3), 68, 471.

[7] Recoura, *Compt. rend.*, 1912, 154, 655.

These reactions appear to indicate that four of the fluorine atoms are attached to the iron considerably more firmly than the remaining two atoms.

Some double salts have been described,[1] and those of general formula

$$FeF_3.3MF, \text{ or } M_3FeF_6,$$

are known as *ferrifluorides* or *hexafluoferrates*. They form an isomorphous series, likewise isomorphous with corresponding double fluorides of aluminium and chromium.[2]

Ferrifluorides or *Fluoferrates*, M_3FeF_6.

These salts are usually known as ferrifluorides.

Ammonium ferrifluoride, $(NH_4)_3FeF_6$, is prepared by nearly neutralising a solution of ferric fluoride in hydrofluoric acid with ammonia, and evaporating.[3]

Barium ferrifluoride, $Ba_3(FeF_6)_2$, is obtained as a precipitate when barium chloride is added to an aqueous solution of ferric fluoride.[4]

Potassium ferrifluoride, K_3FeF_6, may be obtained in a similar manner to the sodium salt, which it closely resembles.[5]

Sodium ferrifluoride, Na_3FeF_6, is obtained on adding ferric chloride or fluoride to a neutral solution of sodium fluoride.[5] It is formed as a white, crystalline precipitate, which is only sparingly soluble in water. It does not give a red colour with thiocyanates, thus indicating that the iron atom is part of the negative radicle.[6]

The *subhydrate*, $2Na_3FeF_6.H_2O$, has also been obtained.[7]

Sodium fluoride and ferric fluoride yield a eutectic mixture, melting at 892° C. and corresponding in composition to the formula $65\ NaF.35FeF_3$.[8]

Thallous ferrifluoride, $3TlF.2FeF_3$, is obtained as pink crystals on evaporating a solution of thallous fluoride and excess of ferric fluoride.[9]

Ferrous diferrifluoride, $FeFe_2F_8.10H_2O$, or $FeF_2.2FeF_3.10H_2O$, obtained by the action of hydrogen fluoride on iron in the presence of nitric acid, crystallises in colourless octahedra, which appear flesh-coloured in thick layers. It gives the ordinary ferrous and ferric reactions only after addition of an acid.[10]

Ferrous monoferrifluoride, $FeF_2.FeF_3.7H_2O$, is obtained as yellow crystals on mixing a solution of ferric hydroxide in dilute hydrofluoric acid with a solution of ferrous carbonate in the same acid and concentrating at the ordinary temperature over lime.[1]

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[1] See Recoura, *Compt. rend*, 1913, 156, 1618; 1912, 154, 655; Ephraim and Barteczko, *Zeitsch. anorg. Chem.*, 1909, 61, 238; Christensen, *J. prakt. Chem*, 1887, (2), 35, 161; Guyot, *Compt. rend.*, 1870, 71, 274; Nicklès, *J. Pharm. Chim*, 1869, (4), 10, 14; 1868, (4), 7, 15; Marignac, *loc. cit.*; Berzelius, *Pogg. Annalen*, 1825, 4, 129.

[2] Helmolt, *Zeitsch. anorg. Chem.*, 1893, 3, 115.

[3] Marignac, *Ann. Chim. Phys.*, 1860, (3), 60, 306; 1873, (4), 30, 45; Wagner, *Ber.*, 1886, 19, 896.

[4] Recoura, *Compt. rend.*, 1912, 154, 655.

[5] Wagner, *loc. cit.*

[6] Greeff, *Ber.*, 1913, 46, 2511.

[7] Peters, *Zeitsch. physikal. Chem.*, 1898, 26, 193.

[8] Baskov, *J. Russ. Phys. Chem. Soc.*, 1913, 45, 82.

[9] Ephraim and Barteczko, *Zeitsch. anorg. Chem.*, 1909, 61, 238.

[10] Deussen, *Monatsh.*, 1907, 28, 163.

Cobalt ferrifluoride, $CoF_2.FeF_3.7H_2O$ (rose-coloured), **nickel ferrifluoride**, $NiF_2.FeF_3.7H_2O$ (green crystals), and **zinc ferrifluoride**, $ZnF_2.FeF_3.7H_2O$ (faintly red crystals), have been obtained in an analogous manner.

IRON AND CHLORINE.

Ferrous chloride, $FeCl_2$, may be obtained in the anhydrous condition in a variety of ways. A convenient method consists in heating to dull red heat excess of iron filings in a current of chlorine, of ammonium chloride,[2] or of gaseous hydrogen chloride, the latter methods being preferable, as the first-named generally yields small quantities of the ferric salt. Ferrous chloride also results when ferric chloride is heated in a current of pure hydrogen [3]; but care must be taken that the temperature does not rise too high, or the ferrous chloride will itself be reduced.

When a current of low density is passed through dilute ethereal solutions of ferric chloride, reduction to ferrous chloride takes place at the cathode.[4]

If the hydrated salt, $FeCl_2.4H_2O$, is dissolved in ammonium chloride solution, evaporated to dryness, and subsequently heated in the absence of air, the water and ammonium chloride escape, leaving the anhydrous ferrous chloride behind.[5]

Anhydrous ferrous chloride as obtained by these methods is a white scaly crystalline substance when pure,[6] but usually it possesses a yellow colour in consequence of the presence of traces of the ferric salt. Its density is 2·53. It readily dissolves in alcohol and in water, with the latter yielding a colourless solution which turns green upon exposure to air.

When heated strongly in air ferric chloride and oxide are produced, the former volatilising. Thus:—

$$12FeCl_2+3O_2=8FeCl_3+2Fe_2O_3.$$

When heated in steam, ferrous chloride yields hydrogen chloride and ferroso-ferric oxide:—

$$3FeCl_2+4H_2O=Fe_3O_4+6HCl+H_2.$$

In the absence of air, ferrous chloride fuses at red heat and volatilises at yellow heat.[7] Its vapour density has been determined under various conditions, both in an atmosphere of nitrogen and of gaseous hydrogen chloride.[7] At bright yellow heat in the latter gas the densities obtained in two experiments corresponded to molecular weights of 192·1 and 183·8 respectively—values that lie midway between those for the simple molecule $FeCl_2$ (namely 126·8) and the double molecule Fe_2Cl_4 (namely 253·6), respectively. This suggests that the vapour consists of a mixture of double and single molecules in equilibrium with each other, as represented by the equation

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[1] Weinland and Koppen, *Zeitsch. anorg. Chem.*, 1900, 22, 266.
[2] Geuther and Forsberg, *Annalen*, 1861, 120, 273.
[3] Wohler, *Annalen*, Suppl., 1865–66, 4, 255.
[4] H. E. Williams, *J. Amer. Chem. Soc*, 1912, 34, 1014.
[5] See Geuther and Forsberg, *Annalen*, 1861, 120, 273.
[6] Wohler and Liebig, *Pogg. Annalen*, 1831, 21, 582.
[7] Meyer, *Ber.*, 1879, 12, 1193; 1884, 17, 1335.

$$Fe_2Cl_4 \rightleftharpoons 2FeCl_2.$$

At 1300° to 1500° C. dissociation into single molecules of $FeCl_2$ is complete.[1]

In boiling solutions of organic liquids such as pyridine, ferrous chloride appears to have the simple formula $FeCl_2$.[2]

An ethereal solution of ferrous chloride heated in a sealed tube with ethylene absorbs the gas, yielding a compound, $FeCl_2.C_2H_4.2H_2O$, in the form of colourless, needle-shaped crystals, readily soluble in water.[3]

Ferrous chloride unites with bromine to yield an unstable chlorobromide, $FeCl_2Br$ (see p. 106).

Ferrous chloride readily absorbs ammonia, yielding a voluminous white mass, which on warming evolves some of the gas again, whilst on heating to above 350° C. reduction takes place, iron nitride being produced. Two definite compounds have been obtained, namely the *diammoniate*, $FeCl_2.2NH_3$, and the *hexammoniate*, $FeCl_2.6NH_3$; whilst the existence of the *monammoniate*, $FeCl_2.NH_3$, has been detected. Between the temperatures of −18° and 350° C. the reaction is reversible, the equilibrium being represented as follows :—[4]

$$xNH_3 + FeCl_2 \rightleftharpoons FeCl_2.xNH_3.$$

The hexammoniate is formed at the ordinary temperature, and the diammoniate by heating the hexammoniate to 100° C. in hydrogen.[5]

The dissociation pressures and heats of dissociation of these compounds have been determined as follow :—[6]

	Temperature. °C.	Dissociation Pressure. mm.	Heat of Dissociation. Cals
$FeCl_2.6NH_3$ . . .	90	270	13·65
$FeCl_2.2NH_3$ . . .	230	121	20·3
,, ,, . . .	277	555	20·7
$FeCl_2.NH_3$ . . .	214·5	5·8	22·5
,, ,, . . .	277	54·4	23·1

With methylamine, ferrous chloride yields two compounds: namely, a white voluminous compound containing six molecules of methylamine, $FeCl_2.6CH_3NH_2$; and a grey compound, $FeCl_2.2CH_3NH_2$.

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[1] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 828.

[2] Werner, *Zeitsch. anorg. Chem.*, 1897, **15**, 1.

[3] Kachler, *J. prakt. Chem.*, 1869, **106**, 254.

[4] Girardet, *Bull. Soc. chim.*, 1910, (4), **7**, 1028; Fowler, *Trans. Chem. Soc.*, 1901, **79**, 285; Miller, *Amer. Chem. J.*, 1895, **17**, 570.

[5] Miller, *loc. cit.*

[6] Biltz and Huttig, *Zeitsch. anorg. Chem.*, 1919, **109**, 89.

The hydrazinate, $FeCl_2.2N_2H_4$, has also been prepared.[1]

A study of the vapour tensions of hydrated ferrous chloride indicates the existence of four hydrates—namely the hexahydrate, $FeCl_2.6H_2O$; tetrahydrate, $FeCl_2.4H_2O$; dihydrate, $FeCl_2.2H_2O$; and monohydrate, $FeCl_2.H_2O$.[2] Of these, the best known are the tetra- and di-hydrates, the former being the usual hydrate under normal conditions.

The *tetrahydrate*, $FeCl_2.4H_2O$, is readily obtained in the form of bluish monoclinic crystals when iron is dissolved in aqueous hydrogen chloride and the solution evaporated out of contact with air.[3] The density of the crystals is 1·937. They deliquesce upon exposure to air, acquiring a greenish colour consequent upon slight oxidation.

The tetrahydrate is converted into the *dihydrate*, $FeCl_2.2H_2O$, on gentle heating, the transition temperature for the phases

$$FeCl_2.4H_2O \rightleftharpoons FeCl_2.2H_2O + 2H_2O$$

being 65·2° C.[4] From a saturated solution it separates out at 72·6° C.[5] In a saturated solution of ferrous magnesium chloride the dihydrate forms at 43·2° C.[6] The dihydrate is also formed by allowing the tetrahydrate to effloresce at the ordinary temperature in a vacuum[7]; and by passing a current of dry hydrogen chloride through a saturated solution of ferrous chloride,[8] when it is obtained as fine, transparent pale-green needles, which do not alter in a vacuum. The heats of formation of the anhydrous and hydrated salts are given as follow :—

$[Fe]+(Cl_2)+Aq.=FeCl_2.Aq.+99{,}950$ calories,[9]
$[Fe]+(Cl_2)=[FeCl_2]+82{,}050$ calories,[9]
whence $[FeCl_2]+Aq.=FeCl_2.Aq.+17{,}900$ calories.

$[Fe]+2(HCl)=[FeCl_2]+(H_2)+60{,}000$ calories,[9]
$[Fe]+2HCl.Aq.=FeCl_2Aq.+H_2+21{,}320$ calories,[9]
$[FeCl_2]+2H_2O=[FeCl_2.2H_2O]+6920$ calories,[10]
$[FeCl_2.2H_2O]+2H_2O=[FeCl_2.4H_2O]+2520$ calories,[10]
$[FeCl_2]+\underset{\text{(solid)}}{2[H_2O]}=[FeCl_2.2H_2O]+6400$ calories,[11]
$[FeCl_22H_2O]+\underset{\text{(solid)}}{2[H_2O]}=[FeCl_2.4H_2O]+2600$ calories.[11]

The heat of solution of the dihydrate at 20° C. is 8700 calories.[11]

A *monohydrate*, $FeCl_2.H_2O$, has been described by Lescœur.[12]

The solubility of ferrous chloride in water is as follows :—[13]

Temperature, °C. .	16	18	25	28	43	50	53	72	89	96	118
Grams $FeCl_2$ per 100 grams solution .	40·5	40·9	41·0	42·5	44·4	45·0	45·9	49·2	51·3	51·0	51·7

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[1] Franzen and O. von Mayer, *Zeitsch. anorg Chem.*, 1905, 60, 247.

[2] Lescœur, *Ann. Chim. Phys.*, 1894, (7), 2, 78.

[3] Lescœur (*loc. cit.*; *Bull. Soc. chim.*, 1894, (3), 11, 853) states that by the same method he obtained the *hexahydrate*, $FeCl_2.6H_2O$.

[4] Kremann and Noss, *Monatsh.*, 1912, 33, 1205.

[5] Boeke, *Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 24, 632.

[6] Boeke, *Jahrb. Min.*, 1911, I., 48.

[7] Sabatier, *Compt. rend.*, 1881, 93, 56; *Bull. Soc. chim.*, 1889, (3), 1, 88.

[8] Sabatier, *Bull. Soc. chim.*, 1894, (3), 11, 546.

[9] Thomsen, *Thermochemistry*, translated by Burke (Longmans, 1908), p. 264.

[10] Sabatier, *Bull. Soc. chim.*, 1881, (2), 36, 197.

[11] Sabatier, *ibid.*, 1889, (3), 1, 90.

[12] Lescœur, *loc. cit.*

[13] Etard, *Ann. Chim. Phys.*, 1894, (7), 2, 503.

The specific gravities of solutions of ferrous chloride at 15 5° C. at various concentrations are as follow :—[1]

Grams of $FeCl_2$ in 100 c c. of Solution.	Specific Gravity at 15 5° C.
5·19	1·0459
10·27	1 0892
19·73	1·1688
30·16	1·2528
44·65	1·3674
54·20	1·4439

Ferrous chloride in acid solution is partially oxidised by sulphur dioxide to the ferric salt, sulphur being deposited.[2] Solutions of ferrous chloride in various solvents such as water, alcohol, ethylacetate, pyridine, etc., absorb nitric oxide, the extent of absorption depending upon the concentration of the iron salt, the temperature, gaseous pressure, and the nature of the solvent. The limit of absorption is reached with one molecule of NO to one atom of iron. Presumably the compound $FeCl_2.NO$ exists in solution, most probably combined with the solvent.[3] It has not as yet been isolated.[4]

Dry ferrous chloride also absorbs nitrogen peroxide, yielding a fairly stable compound $4FeCl_2.NO_2$, which does not lose its nitrogen peroxide content even *in vacuo*.[5] In the presence of moisture more of the gas is absorbed, but the reaction is complicated.

Ferrochlorides or *Chlorferrites*.

Ferrous chloride readily unites with other metallic chlorides to form double salts, a considerable variety of which is known. Those of formula M_2FeCl_4 recall the chlor-ruthenites, M_2RuCl_4, already discussed.[6] The best-known double salts are as follow :—

Ammonium tetrachlorferrite, $(NH_4)_2FeCl_4$ or $FeCl_2.2NH_4Cl$, is readily obtained by concentrating a mixed solution of the constituent salts.[1] It is slowly soluble in water. The solution is reduced by zinc at the boiling-point, depositing metallic iron.

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[1] Dunn, *J. Soc. Chem. Ind.*, 1902, 21, 390.

[2] Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1913–14, 5, 187.

[3] See Graham, *Phil. Mag.*, 1828, 4, 265, 331 ; Gay, *Ann. Chim. Phys.*, 1885, (6), 5, 145 ; Thomas, *Bull. Soc. chim.*, 1898, (3), 19, 343, 419 ; Manchot and Zechentmayer, *Annalen*, 1906, 350, 368 ; Manchot and Huttner, *ibid.*, 1910, 372, 153.

[4] By passing nitric oxide into a saturated ethereal solution of ferric chloride until no more gas is absorbed, and subsequently concentrating the solution over sulphuric acid, Thomas (*Compt. rend.*, 1895, 120, 447; the result is disputed by Bellucci, *Gazzetta*, 1914, 44, ii. 384) isolated a substance in the form of black needles to which he ascribed the composition represented by the formula, $FeCl_2.NO+2H_2O$. At 60° small yellow crystals of an anhydrous compound were obtained, to which the formula, $FeCl_2.NO$, was given. The substance proved to be readily soluble in water without gaseous evolution, yielding a yellow solution the colour of which deepened on warming, and from which caustic alkalies precipitated ferrous hydroxide.

A second solid substance, brownish yellow in colour, is described (Thomas, *Compt. rend.*, 1895, 121, 128) as resulting on heating ferric chloride in a current of nitric oxide. Partial reduction takes place, leaving a residue of composition corresponding to the formula, $2FeCl_2.NO$. A red hygroscopic and unstable compound, $10FeCl_2.NO$, is also described.

[5] Thomas, *Compt. rend.*, 1897, 124, 366.

[6] This volume, Part I.

Cæsium tetrachlorferrite,[2] $Cs_2FeCl_4.2H_2O$.

Cæsium trichlorferrite,[2] $CsFeCl_3.2H_2O$.

Magnesium tetrachlorferrite,[3] $MgFeCl_4.8H_2O$.

Potassium tetrachlorferrite, $K_2FeCl_4.2H_2O$ or $2KCl.FeCl_2.2H_2O$.—This salt occurs in nature as *Douglasite* (see p. 29) and is formed by mixing solutions of ferrous chloride and potassium chloride at the boiling-point and concentrating in the warm.[4] It is stable up to 85° C. The *monohydrate*, $K_2FeCl_4.H_2O$, is described [5] as forming red, hygroscopic prisms.

Potassium trichlorferrite,[6] $KFeCl_3.2H_2O$.

Rubidium tetrachlorferrite,[7] $Rb_2FeCl_4.2H_2O$.

Rubidium trichlorferrite,[7] $RbFeCl_3.2H_2O$.

Sodium chloride does not appear to yield double salts of this type, but the double sodium-potassium salt, $FeCl_2.3KCl.NaCl$, occurs in nature as *rinneite* (see p. 29).

When ferroboron is heated in chlorine, iridescent green crystals of $3FeCl_2.BCl_3$ are obtained.[9]

With stannic chloride, *ferrous stannichloride*, $FeSnCl_6.6H_2O$, is obtained.[10]

Ferric chloride, $FeCl_3$, occurs in nature in the lava of Vesuvius, as the mineral *molysite*. In the laboratory it is prepared in the anhydrous condition by passing a rapid current of dry chlorine through a retort over heated iron wire, advantageously cut into pieces some 6 mm. in length. The ferric chloride volatilises and condenses as beautiful crystals on the upper, cooler portions of the retort.

At the end of the operation the heating is discontinued and the chlorine expelled from the apparatus by a rapid current of carbon dioxide. The salt is now rapidly transferred to a tube and hermetically sealed.

Ferric chloride may also be obtained by passing a current of dry, gaseous hydrogen chloride over heated amorphous ferric oxide; by passing chlorine over heated ferrous chloride; and by heating together ferrous sulphate and calcium chloride.[11]

As prepared by any of these methods ferric chloride consists of dark, iridescent, hexagonal scales, which appear red by transmitted light, but exhibit a green lustre when viewed by reflected light. It melts under pressure at 301° C., but volatilises at 280° to 285° C., at atmospheric pressure, its real melting-point at 760 mm. being 303° C.[1] Between 321° and 442° C. its vapour density in an atmosphere of chlorine is practically constant, and corresponds to the double formula Fe_2Cl_6.[2]

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[1] Winkler, *Rep Pharm*, 1836, 59, 171. See also Hisinger and Berzelius, *Gilbert's Annalen*, 1807, 27, 273; Vogel, *J. prakt. Chem*, 1834, 2, 192; Chassevant, *Ann. Chim. Phys*, 1893, (6), 30, 5.

[2] Wilke-Dorfurt and Heyne, *Ber.*, 1912, 45, 1012.

[3] Boeke, *Jahrb. Min.*, 1911, I., 48.

[4] Schabus, *Sitzungsber. K. Akad Wiss. Wien*, 1850, 4, 456.

[5] Fritzsche, *J. prakt. Chem.*, 1839, 18, 483.

[6] Boeke, *Jahrb. Min.*, 1911, I., 48.

[7] Wilke-Dorfurt and Heyne, *Ber.*, 1912, 45, 1012.

[8] Boeke, *Chem. Zeit.*, 1908, 32, 1228.

[9] J. Hoffmann, *Zeitsch. anorg. Chem.*, 1910, 66, 361.

[10] Biron, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 489.

[11] Deville and Troost, *Compt. rend.*, 1861, 52, 920

At temperatures above 500° C. anhydrous ferric chloride dissociates into the ferrous salt and free chlorine, the equilibrium being represented by the equation :—

$$Fe_2Cl_6 \rightleftharpoons Fe_2Cl_4 + Cl_2.$$

The dissociation is already perceptible at 122° C.,[3] but is very small, becoming appreciable only at temperatures in the neighbourhood of 500° C.

At higher temperatures still, the ferrous chloride dissociates into simple molecules of $FeCl_2$. These facts probably suffice to account for the low results obtained for the density of ferric chloride in an inert atmosphere, such as nitrogen,[4] since under these conditions dissociation might well be expected to proceed to a greater extent at any given temperature than in an atmosphere of chlorine, by the law of Mass Action.

In boiling solutions of alcohol, ether, pyridine, and other organic solvents, ferric chloride appears to exist as simple molecules [5] of $FeCl_3$, if the interpretation usually placed upon the results that have been obtained is regarded as correct.[6]

When heated in a current of hydrogen, ferric chloride is reduced to the ferrous salt,[7] provided the temperature is not allowed to rise too high; otherwise further reduction ensues. Traces of reduction can be detected after several hours at temperatures as low as 100° C.[8] Heated in oxygen, chlorine is evolved, leaving a residue of ferric oxide; and, when heated in steam, gaseous hydrogen chloride and ferric oxide are produced. Anhydrous ferric chloride absorbs nitric oxide at ordinary temperatures, yielding a brown mass having the composition $2FeCl_3.NO$. On raising the temperature to 60° C., the proportion of nitric oxide is reduced to one half, a red powder, of composition corresponding to $4FeCl_3.NO$, being obtained. At temperatures at which ferric chloride begins to volatilise reduction takes place, ferrous chloride being produced.[9] In ethereal solution ferric chloride is reduced by nitric oxide at the ordinary temperature to the ferrous salt, which latter absorbs excess nitric oxide yielding a compound to which the formula $FeCl_2.NO + 2H_2O$ (*vide supra*, p. 93, footnote 4) has been given, which crystallises out at the ordinary temperature. If, however, the temperature is first raised to approximately 60° C., small yellow crystals of the anhydrous compound, $FeCl_2.NO$, are stated to result; but this is disputed, as has been already mentioned (see footnote, p. 93). With nitrogen peroxide in the cold, ferric chloride yields a brownish-yellow, deliquescent powder, of composition represented by the formula $FeCl_3.NO_2$. This substance is stable in air as also in a vacuum, but is decomposed by water, yielding nitrous acid.[1]

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[1] Hachmeister, *Zeitsch. anorg. Chem.*, 1919, 109, 145; Carnelley, *Trans. Chem. Soc.*, 1880, 37, 125.

[2] Friedel and Crafts, *Compt. rend.*, 1888, 107, 301; Biltz, *Zeitsch. physikal. Chem.*, 1902, 40, 185, 211. The results support the earlier work of Deville and Troost, *Ann. Chim. Phys.*, 1860, (3), 58, 280.

[3] Fireman and Portner, *J. Physical Chem.*, 1904, 8, 500.

[4] Grunewald and Meyer, *Ber.*, 1888, 21, 687.

[5] Muller, *Compt. rend.*, 1894, 118, 641; Werner, *Zeitsch anorg. Chem.*, 1897, 15, 1.

[6] See Turner, *Molecular Association* (Longmans, 1915), chapter ix.

[7] Wohler, *Annalen*, Suppl, 1865–66, 4, 255.

[8] Phillips, *Amer. Chem. J.*, 1894, 16, 255.

[9] Thomas, *Compt. rend.*, 1895, 120, 447; Besson, *ibid.*, 1889, 108, 1012.

$FeCl_3.NOCl$ is obtained as a black, crystalline substance when ferric chloride is heated in the dried vapours from aqua regia.[2] It is very hygroscopic and dissolves in water, evolving oxides of nitrogen. When heated it readily fuses and volatilises without decomposition. In a sealed tube it melts at 116° C.[3]

Anhydrous ferric chloride readily absorbs ammonia at the ordinary temperature, yielding the *hexammoniate*, $FeCl_3.6NH_3$. This decomposes upon exposure to air, yielding the *pentammoniate*, $FeCl_3.5NH_3$, which is stable in a dry atmosphere. When heated to 100° C. the *tetrammoniate*, $FeCl_3.4NH_3$, results.[4]

The anhydrous salt when heated to dull redness with metallic calcium is reduced to iron.[5]

Ferric chloride combines with ether[6] to form a dark red, highly deliquescent solid of composition $FeCl_3.(C_2H_5)_2O$. It is soluble in water and alcohol, and at 100° C. decomposes quantitatively, yielding the oxychloride FeOCl:—

$$FeCl_3.(C_2H_5)_2O = 2C_2H_5Cl + FeOCl.$$

The heats of formation of anhydrous ferric chloride and of its hydrates are as follow:—

$$2[Fe] + 2(Cl_2) + Aq. = 2FeCl_2.Aq. + 199{,}900 \text{ calories,}^7$$
$$2FeCl_2.Aq. + (Cl_2) = 2FeCl_3.Aq. + 55{,}540 \text{ calories,}^8$$

whence

$$2[Fe] + 3(Cl_2) + Aq. = 2FeCl_3.Aq. + 255{,}440 \text{ calories;}$$

again,

$$2[FeCl_3] + Aq. = 2FeCl_3.Aq. + 63{,}360 \text{ calories,}^9$$

whence, by subtraction,

$$2[Fe] + 3(Cl_2) = 2[FeCl_3] + 192{,}080 \text{ calories,}$$

$$2[FeCl_3] + 5[H_2O] = [2FeCl_3.5H_2O] + 14{,}400 \text{ calories,}^{10}$$
$$[2FeCl_3.5H_2O] + Aq. = 2FeCl_3.Aq. + 42{,}000 \text{ calories }^{10} \text{ at } 20° \text{ C.}$$

Anhydrous ferric chloride is very deliquescent, and the study of its solubility in water is interesting, there being four distinct curves corresponding to the appearance of four hydrated salts, namely, $2FeCl_3.4H_2O$

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[1] Thomas, *Bull. Soc. chim.*, 1896, (3), 15, 1001.
[2] Weber, *Pogg. Annalen*, 1863, 118, 481
[3] van Heteren, *Zeitsch. anorg. Chem.*, 1899, 22, 277.
[4] Miller, *Amer. Chem. J.*, 1895, 17, 570.
[5] Hackspill, *Bull. Soc. chim.*, 1907, (4), 1, 895.
[6] Forster, Cooper, and Yarrow, *Trans. Chem. Soc*, 1917, 111, 809.
[7] See p. 92.
[8] Thomsen, *Thermochemistry*, translated by K. A. Burke (Longmans, 1908), p. 264.
[9] Thomsen, *loc. cit*; Sabatier (*Compt. rend.*, 1881, 93, 56; *Bull. Soc. chim.*, 1881, (2), 36, 197) obtained a closely similar value, namely, 63,400 calories.
[10] Sabatier, *Bull. Soc. chim.*, 1889, (3), 1, 90.

(m. pt. 73·5° C.), $2FeCl_3.5H_2O$ (m. pt. 56° C.), $2FeCl_3.7H_2O$ (m. pt. 32 5° C.), and $2FeCl_3.12H_2O$ (m. pt. 37° C.) respectively. From the last point of discontinuity, namely F in figure 5 (66° C.), onwards the salt is anhydrous and is deposited from solution in that condition.[1]

SOLUBILITY OF FERRIC CHLORIDE IN WATER.

(The melting-points are given in bold type.)

Solid phase $2FeCl_3$ $12H_2O$.

Temperature, °C.	−55	0	20	30	**37**	30	27·4	20	8
Grams $FeCl_3$ in 100 grams H_2O	49 52	74 39	91·85	106 8	**150 0**	201·7	219 0	231·1	246 7

Solid phase $2FeCl_3$ $7H_2O$.

Temperature, °C.	20	32	**32·5**	30	25
Grams $FeCl_3$ in 100 grams H_2O	204 4	244 0	**257·6**	272 4	280·0

Solid phase $2FeCl_3$ $5H_2O$.

Temperature, °C.	12	27	35	50	55	**56**	55
Grams $FeCl_3$ in 100 grams H_2O	231·8	267·5	281·6	315 2	344·8	**360 4**	365·9

Solid phase $2FeCl_3$ $4H_2O$.

Temperature, °C.	50	55	60	69	**73·5**	70	66
Grams $FeCl_3$ in 100 grams H_2O	359 3	365 9	372 8	387 7	**450 2**	502·4	525 9

Solid phase $FeCl_3$.

Temperature, °C.	66	75	80	100
Grams $FeCl_3$ in 100 grams H_2O	525 9	511·4	525·9	535 8

A study of the curves in fig. 5 is particularly interesting from the point of view of the Phase Rule. AB represents the various states of equilibrium between ice and ferric chloride solutions, a minimum temperature being reached at the cryohydric point B, which is −55° C. At this point ice, solution, and the dodecahydrate of ferric chloride are in equilibrium. The number of degrees of freedom is nil—in other words, the system is invariant, and if heat be subtracted the liquid phase will solidify without change of temperature until the whole has become a solid mass of ice and dodecahydrate. Further abstraction of heat merely lowers the temperature of the system as a whole.

If, starting at the point B, heat be added to the system, ice will melt, and more of the dodecahydrate will dissolve in accordance with the equilibrium curve BCH, which is the solubility curve of this hydrate in water. At 37° C. the dodecahydrate melts, and if anhydrous ferric chloride be added to the system, the temperature at which the dodecahydrate remains in equilibrium with the solution is lowered until the eutectic point C is reached at 27·4° C. At this point the whole solidifies to a solid mixture of the dodecahydrate and heptahydrate.

The curve has been followed in the direction of the broken line CH to +8° C., the solution being supersaturated with respect to the dodecahydrate. Similarly the curve ED has been continued backwards until it intersects CH at H at 15° C. This is a metastable triple point or eutectic, and is capable of realisation experimentally on account of the fact that the heptahydrate is not so readily formed.

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[1] See Roozeboom, *Zeitsch. physikal. Chem.*, 1892, 10, 477.

Curves EF and FG represent the solubilities of the tetrahydrate and the anhydrous salt respectively.

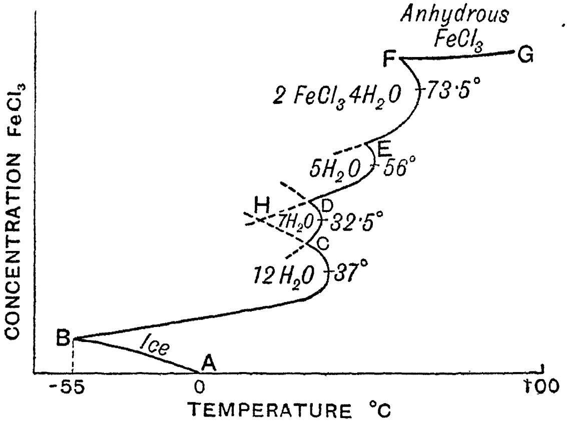

Fig. 5.

The following are the transition temperatures or eutectic points corresponding to the points B, C, H, D, E, and F in fig. 5 :—

B.	Ice $-2FeCl_3.12H_2O$	$-55°$ C.
C.	$2FeCl_3.12H_2O-2FeCl_3.7H_2O$	$+27·4°$
H.	$2FeCl_3.12H_2O-2FeCl_3.5H_2O$	15°
D.	$2FeCl_3.7H_2O-2FeCl_3.5H_2O$	30°
E.	$2FeCl_3.5H_2O-2FeCl_3.4H_2O$	55°
F.	$2FeCl_3.4H_2O-FeCl_3$	66°

The *dodecahydrate*,[1] $2FeCl_3.12H_2O$, is obtained as deliquescent crystals by treating solid commercial ferric chloride with a current of hydrogen chloride, filtering the resulting liquid, and concentrating over potash *in vacuo*.[2]

The same hydrate is obtained on allowing a concentrated solution of ferric chloride to evaporate slowly in the cold. It separates out as reniform masses of lemon-yellow crystals, or in opaque, yellow rhombic prisms,[3] according to circumstances.[4] This hydrate melts at 37° C.[5]

The *heptahydrate*, $2FeCl_3.7H_2O$, first obtained by Roozeboom, yields monoclinic crystals, somewhat darker than the preceding hydrate, but readily distinguished by their dichroism, the colours ranging from yellow to blue. When exposed to the air at room temperature, the crystals become coated with the yellow dodecahydrate. They melt at 32·5° C.

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[1] Known to, and described by, Mohr (*Annalen Pharm.*, 1839, 29, 173), and Fritzsche (*J. prakt. Chem.*, 1839, 18, 479).

[2] Engel, *Compt. rend.*, 1887, 104, 1708.

[3] Roozeboom states them to be monoclinic.

[4] Sabatier, *ibid.*, 1881, 93, 56.

[5] Roozeboom, *loc. cit.*

The *pentahydrate*,[1] $2FeCl_3.5H_2O$, may be prepared by heating the preceding hydrate to 100° C. for several hours, when hydrogen chloride is evolved. Upon slowly cooling deep red crystals of the pentahydrate are deposited.[2] It also results on keeping crystals of the dodecahydrate *in vacuo* over sulphuric acid. Liquefaction to a brown solution at first takes place, but finally deep red, deliquescent crystals of the pentahydrate separate out.[3] These melt at 56° C.[4] and deliquesce upon exposure to air.

When treated with a current of dry hydrogen chloride, the pentahydrate readily liquefies, and if saturated with the gas at 25° C. and then cooled to 0° C. it deposits yellow lamellæ of the acid salt $FeCl_3.HCl.2H_2O$.[5]

The *tetrahydrate*, $2FeCl_3.4H_2O$, first obtained by Roozeboom, crystallises in the rhombic system. The crystals appear pleochroic in polarised light, the colours ranging from yellow to brown. They melt at 73·5° C.

Aqueous solutions of ferric chloride are conveniently prepared by dissolving iron in hydrochloric acid and subsequently saturating the solution with chlorine to oxidise the ferrous salt to the ferric condition. After standing, the solution should still smell of chlorine, otherwise sufficient of the gas has not been added. Excess may now be removed by bubbling carbon dioxide through the warm solution. Other methods of preparation consist in dissolving ferric hydroxide in aqueous hydrochloric acid; and by oxidation of ferrous chloride in the presence of hydrochloric acid by some oxidiser such as nitric acid.

In concentrated solution ferric chloride is somewhat oily in appearance, and dark brown in colour.[6] When such a solution is diluted with water, a considerable amount of heat is liberated in consequence of hydrolysis[7]; thus

$$FeCl_3+3H_2O \rightleftharpoons Fe(OH)_3+3HCl.$$

Very dilute solutions of ferric chloride are practically colourless when freshly prepared, but become brownish yellow on keeping, owing to the separation of ferric hydroxide in accordance with the above equation.

For example, fresh solutions containing less than 1·1 per cent. of ferric chloride appear colourless in a 40-cm. tube, but after several hours become yellow, the colour intensifying during forty-eight hours after preparation.[8]

Excessively dilute solutions of ferric chloride[9] give no coloration with potassium ferrocyanide, the salt being completely hydrolysed and converted into colloidal ferric hydroxide (see p. 125).

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[1] Believed to contain six molecules of water by Wittstein (*Repertorium Pharm.*, 1844, (2), 36, 30) and Ordway (*J. Pharm. Chim.*, 1844, (3), 5, 301), but shown by Fritzsche and Gobley (*J. Pharm. Chim.*, 1854, (3), 25, 259) to be the pentahydrate.

[2] Engel, *Compt. rend.*, 1887, 104, 1708.

[3] Sabatier, *loc. cit.*; *Bull. Soc. chim.*, 1889, (3), 1, 88.

[4] Roozeboom, *loc. cit.*

[5] Sabatier, *Bull. Soc. chim.*, 1881, (2), 36, 197; Engel, *loc. cit.*

[6] Ditz, *Chem. Zeit.*, 1901, 25, 109. For a comparison of the colours of ferric, cupric, and cobalt chlorides in solution under various conditions, see Donnan and Bassett, *Trans. Chem. Soc.*, 1902, 81, 955. Other notes on the colours of ferric chloride solutions are given by Schaer, *Arch. Pharm.*, 1901, 239, 257, 340.

[7] Lemoine, *Compt. rend.*, 1893, 116, 880.

[8] Antony and Giglio, *Gazzetta*, 1895, 25, ii. 1.

[9] Of the order of 0·00083 per cent.

The hydrolysis of ferric chloride may be illustrated for lecture purposes by filling a tube to about three-fourths of its height with a 5 to 10 per cent. solution of gelatin rendered pink with faintly alkaline phenolphthalein. When the gelatin has solidified, a 10 per cent. solution of ferric chloride is added. As diffusion proceeds downwards, two layers become increasingly distinct—namely, the lower, colourless layer, due to the more rapid diffusion of the acid liberated by hydrolysis; and the upper, opaque layer of brown ferric hydroxide.[1]

An interesting lecture experiment to illustrate suppression of hydrolysis of ferric chloride under certain conditions consists in diluting a solution of the salt until it is practically colourless. Concentrated hydrochloric acid is now added, and the solution assumes a yellow colour, characteristic of the un-ionised $FeCl_3$-molecule.[2] The addition of glycerol to a solution likewise intensifies the colour, and this is attributed to diminished dissociation consequent upon the introduction of a substance possessing a lower dielectric constant.

Measurement of the electric resistance of aqueous solutions of ferric chloride indicates a gradual increase in conductivity after dilution, a definite maximum value ultimately being reached for each concentration of the salt. The time required to reach a final stage of equilibrium varies with the concentration of the salt. For a 0·0001-normal solution some three hours are required, whilst a week is usual for a 0·0006-normal solution.[3] This increase in conductivity is usually attributed to the gradual liberation of hydrochloric acid in accordance with the equation

$$FeCl_3+3H_2O \rightarrow Fe(OH)_3+3HCl.$$

The difficulty, however, is to understand the extreme slowness with which equilibrium is attained, for the hydrolysis should take place with great rapidity. In order to account for this, the change has been regarded as taking place in stages as follows :—[4]

$$FeCl_3 \rightarrow FeCl_2(OH) \rightarrow FeCl(OH)_2 \rightarrow Fe(OH)_3.$$

This theory, however, cannot be regarded as altogether satisfactory.

Spring,[5] on the other hand, holds that ferric chloride in solution dissociates into ferrous chloride and chlorine, in the same manner as when heated in the gaseous state:—

$$FeCl_3 \rightleftharpoons FeCl_2+Cl.$$

The chlorine then reacts with water, yielding hydrogen chloride and oxygen, which latter combines with the ferrous chloride to yield the oxychloride, Fe_2Cl_4O, until the equilibrium represented by the following equation is attained :—

$$2FeCl_2+H_2O+2Cl \rightleftharpoons Fe_2Cl_4O+2HCl.$$

A suggestive theory, supported by ultra-microscopic examination of dilute ferric chloride solutions has been advanced by Wagner,[6] according to which hydrolysis is instantaneous, but the gradual change in electric conductivity is due to changes in the superficial magnitude of the colloid particles. At first the colloid particles are small, and thus present *in toto* an enormous surface which adsorbs practically the whole of the liberated acid. Gradually the particles increase in size, becoming less numerous, so that the total superficial area falls, liberating proportional amounts of the adsorbed acid. Wagner's theory appears to the present author to be the most satisfactory that has as yet been advanced.

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[1] Vanzetti, *Gazzetta*, 1908, 38, ii. 98.

[2] See Byk and Jaffe, *Zeitsch. physikal. Chem*, 1909, 68, 323.

[3] Goodwin, *Zeitsch. physikal. Chem.*, 1896, 21, 1.

[4] Antony and Giglio, *Gazzetta*, 1895, 25, ii. 1.

[5] Spring, *Rec. Trav. Chim.*, 1897, 16, 237. Supported by Jufereff, *Zeitsch. anorg. Chem.*, 1908, 59, 82

[6] Wagner, *Monatsh.*, 1913, 34, 95, 931.

Ferric chloride decomposes sodium nitrite in aqueous solution with evolution of oxides of nitrogen. The reaction is believed[1] to take place in two stages, namely:—

$$2FeCl_3+6NaNO_2=2Fe(NO_2)_3+6NaCl,$$
$$2Fe(NO_2)_3+3H_2O=2Fe(OH)_3+3NO_2+3NO.$$

A solution of ferric chloride decomposes lead sulphide or powdered galena with ease on warming, the products being ferrous chloride, lead chloride, and sulphur.[2]

$$2FeCl_3+PbS=2FeCl_2+PbCl_2+S.$$

A similar reaction takes place with copper pyrites or with copper sulphides. Thus:—

$$2FeCl_3+CuS=2FeCl_2+CuCl_2+S,$$
and
$$2FeCl_3+Cu_2S=2FeCl_2+2CuCl+S.$$

This reaction has been utilised in the separation of copper from pyrites, a solution of ferric chloride being allowed to slowly percolate through the ore raised in heaps, the residual ferrous chloride being oxidised to ferric and used over again.[3]

Ferric chloride is readily reduced by suitable reagents to the ferrous salt. Metallic zinc or iron, or even nascent hydrogen, effects the reduction in aqueous solution. Alkali sulphides reduce it with deposition of sulphur, and alkali iodides[4] with liberation of iodine, thus:—

$$2FeCl_3+2KI=2FeCl_2+2KCl+I_2.$$

Alcoholic solutions of ferric chloride are reduced by light,[5] which acts, not as a catalyst, but as a generator of the necessary chemical energy. Ferrous chloride, hydrogen chloride, and formaldehyde are the primary products of the reaction.[6]

Dilute solutions of ferric chloride in pure anhydrous ether are rapidly reduced to ferrous chloride upon exposure to direct sunlight. The chlorine is used up, partly in chlorinating the ether and partly in oxidation processes, so that the reaction is not reversible in the dark. More concentrated solutions yield ferrous chloride and a black organic compound containing iron.[7]

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[1] Matuschek, *Chem. Zeit.*, 1905, 29, 31. See also Pesci, *Chem. Zentr.*, 1888, p. 1023

[2] Gabba, *Chem. Zentr*, 1889, p. 667.

[3] See *J. Chem. Soc., Abstr.*, 1884, p. 516.

[4] See Carnegie, *Chem. News*, 1889, 60, 87; also this volume, p. 134.

[5] See p. 84.

[6] See Benrath, *J. prakt. Chem.*, 1905, (2), 72, 220; 1909, (2), 80, 283.

[7] Puxeddu, *Gazzetta*, 1920, 50, i. 154.

Ferric chloride is reduced by aqueous stannous chloride solution in accordance with the following equation (see p. 84):—

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4.$$

Acid Chlorides.—Several acid salts of ferric chloride have been described. On saturating the pentahydrate, $2FeCl_3.5H_2O$, with hydrogen chloride at 25° C. and cooling the liquid so obtained to 0° C., the compound, $FeCl_3.HCl.2H_2O$, is obtained in the form of yellow, crystalline lamellæ.[1] The compounds, $FeCl_3.HCl.4H_2O$ and $FeCl_3.HCl.6H_2O$, have been obtained respectively as greenish crystals, melting at −3° C., and yellow crystals, melting at −6° C.[2]

Ferric chloride unites with chlorides of other metals to yield several series of double salts, resembling in composition the double chlorides of certain of the platinum metals. These are conveniently grouped as follows:—

Tetrachlorferrates, $MFeCl_4$.

Ammonium tetrachlorferrate, NH_4FeCl_4, or $FeCl_3.NH_4Cl$, obtained by heating the two substances together, is interesting as possessing a definite boiling-point, namely 386° C.[3] A salt of similar empirical composition has been obtained [4] by crystallisation from mixed solutions of ferric chloride and ammonium chloride in the form of olive-brown needles, which, however, are unstable.

Cæsium tetrachlorferrate, $2CsFeCl_4.H_2O$, or possibly anhydrous, is extremely hygroscopic.[5]

Cuprous tetrachlorferrate, $CuFeCl_4$, melts at 320° C. If crystallised from an aqueous solution, the *tetrahydrate*, $CuFeCl_4.4H_2O$, is obtained.[6]

Pentachlorferrates, M_2FeCl_5.

Ammonium pentachlorferrate, $(NH_4)_2FeCl_5.H_2O$, associated with varying quantities of ammonium chloride, is known popularly as ammonio-chloride of iron. It is used medicinally, and is obtained as garnet cubes by crystallising from a solution of the mixed chlorides.[7]

Cæsium pentachlorferrate,[7, 9] $Cs_2FeCl_5.H_2O$, has been obtained as a red salt.

Glucinum pentachlorferrate,[8] $GlFeCl_5.H_2O$.

Magnesium pentachlorferrate,[8] $MgFeCl_5$.

Potassium pentachlorferrate,[7, 8, 9] $K_2FeCl_5.H_2O$, is obtained by dissolving ferric chloride in concentrated hydrochloric acid, adding potassium chloride, and allowing to crystallise. It is a red, deliquescent salt, decomposed by water.

Rubidium pentachlorferrate,[8] $Rb_2FeCl_5.H_2O$.

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[1] Sabatier, *Bull. Soc. chim.*, 1881, (2), 36, 197; *Compt rend*, 1887, 104, 1849.

[2] Roozeboom and Schreinemakers, *Zeitsch. physikal. Chem.*, 1894, 15, 588.

[3] Hachmeister, *Zeitsch. anorg. Chem.*, 1919, 109, 145.

[4] Mohr, *Zeitsch. physikal. Chem.*, 1898, 27, 193.

[5] Walden, *Amer. J. Sci.*, 1894, (3), 48, 283.

[6] Herrmann, *Zeitsch. anorg. Chem.*, 1911, 71, 257.

[7] Fritzsche, *J. prakt. Chem.*, 1839, 18, 483; Mohr, *Zeitsch. physikal. Chem.*, 1898, 27, 193

[8] Neumann, *Annalen*, 1888, 244, 328; *Ber.*, 1885, 18, 2890.

[9] Walden, *Amer. J. Sci.*, 1894, (3), 48, 283; *Zeitsch. anorg. Chem.*, 1894, 7, 331.

Thallium pentachlorferrate,[1] Tl_2FeCl_5.

Apparently no double salts with sodium exist, at any rate between 0° and 60° C.[2]

Hexachlorferrates, M_3FeCl_6.

Cæsium hexachlorferrate,[3] $Cs_3FeCl_6.H_2O$.

Miscellaneous Double Salts.

From solutions of ferric and ammonium chlorides, cubic crystals of $2FeCl_3.NH_4Cl.4H_2O$ have been isolated [4] similarly.

Ferric chloride yields solid solutions with zinc chloride and with lead chloride, but no compounds appear to be formed.[5] The existence of the double salt $FeCl_3.2KF$ [6] has not been confirmed.[7]

Ferric ammonium antimony chloride, $2FeCl_3.9NH_4Cl.3SbCl_4$, crystallises in black octahedra from solutions of the constituent chlorides in concentrated hydrochloric acid.[8]

With sulphur tetrachloride the double compound $SCl_4.FeCl_3$ is obtained as a yellow, crystalline precipitate; with phosphorus oxychloride, the compound $2FeCl_3.POCl_3$ separates on warming.[9]

A double chloride of phosphorus and iron, $FeCl_3.PCl_5$, has been isolated [10] by acting on ferric oxide with phosphorus pentachloride. It also results on direct union of the two chlorides.

With alkaloids ferric chloride yields complexes, many of which are characterised by definite melting-points.[11]

Ferroso-ferric chloride, $Fe_3Cl_8.18H_2O$, or $FeCl_2.2FeCl_3.18H_2O$, results when the corresponding oxide, Fe_3O_4, is dissolved in concentrated aqueous hydrogen chloride and evaporated over sulphuric acid. The salt separates out as a yellow crystalline mass, which readily deliquesces.[12]

Ferrous perchlorate, $Fe(ClO_4)_2.6H_2O$, may be prepared either by the solution of iron in perchloric acid [13] or by the interaction of solutions of ferrous sulphate and barium perchlorate.[14]

On evaporation light green crystals are produced which evolve water at 100° C. and decompose completely at higher temperatures.

Ferric perchlorate, $Fe(ClO_4)_3$, results on dissolving hydrated ferric oxide in perchloric acid. It has not been obtained in crystalline form.

Ferrous chlorate, $Fe(ClO_3)_2$, is probably formed in solution when ferrous sulphate and barium chlorate solutions are allowed to react. It is very unstable, however.[15]

Ferric chlorate, $Fe(ClO_3)_3$, is obtained when chlorine is passed through water containing hydrated ferric oxide in suspension. Its heat of formation is given by Thomsen[1] as follows :—

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[1] Scarpa, *Atti R. Accad. Lincei*, 1912, (5), 21, ii. 719.

[2] Hinrichsen and Sachsel, *Zeitsch. physikal. Chem.*, 1904, 50, 81.

[3] Walden, *loc cit*

[4] Mohr, *Zeitsch. physikal. Chem.*, 1898, 27, 193.

[5] Herrmann, *loc. cit.*

[6] Guyot, *J Chem. Soc.*, 1871, 24, 854.

[7] Greeff, *Ber.*, 1913, 46, 2511.

[8] Ephraim and Weinberg, *Ber*, 1909, 42, 4447.

[9] Ruff and Einbeck, *Ber*, 1904, 37, 4513.

[10] Weber, *J. prakt. Chem.*, 1859, 76, 410.

[11] See Scholtz, *Ber. deut. pharm. Ges.*, 1908, 18, 44.

[12] Lefort, *J. Pharm. Chim*, 1869, (4), 10, 81.

[13] Roscoe, *Annalen*, 1862, 121, 355.

[14] Serullas, *Ann. Chim. Phys*, 1831, (2), 46, 305.

[15] Wächter, *J. prakt. Chem.*, 1843, 30, 321.

$$2[Fe(OH)_3]+6HClO_3.Aq.+Aq.=2Fe(ClO_3)_3.Aq.+32,340 \text{ calories.}$$

Oxychlorides.—Numerous basic- or oxy-chlorides of iron have been described at various times, but it is very doubtful if the chemist is justified in regarding these as separate chemical entities.[2] For example, Béchamp found that, on oxidising ferrous chloride with nitric acid in the presence of a small quantity of hydrochloric acid, an insoluble, yellow residue was obtained, of composition corresponding to the formula $FeCl_3.6Fe_2O_3$. On treatment with water a product, $2FeCl_3.17Fe_2O_3$, resulted, whilst addition of ammonium hydroxide induced the formation of a still more basic residue, namely $FeCl_3.72Fe_2O_3$. Such precipitates are of little theoretical interest.

A crystalline oxychloride is obtained[3] when solutions of ferric chloride containing not less than 80 per cent. of the salt are heated in sealed tubes to 150°–160° C. in the presence of a few fragments of magnesium carbonate to neutralise the liberated hydrochloric acid. The crystals consist of lustrous rhombic prisms, reddish brown in colour, and of composition corresponding to the formula $2FeCl_3.Fe_2O_3.2Fe(OH)_3$. These, on contact with hot water, retain their crystalline form, although they lose their chlorine as hydrogen chloride, being converted completely into oxide corresponding in composition to Goethite.

If, in the foregoing method of preparation, an 85 to 90 per cent. solution of ferric chloride is maintained at 225° to 280° C. for some time, an oxychloride of composition $FeCl_3.Fe_2O_3$ is obtained as reddish brown lamellæ, whilst between 300° and 340° C. large plates of brownish black $2FeCl_3.3Fe_2O_3$ result.

Upon heating anhydrous ferric chloride in a slow current of carbon dioxide saturated with water vapour, the oxychloride $FeCl_3.Fe_2O_3$ is produced at 275° to 300° C. in the form of reddish brown needles, whilst larger and darker needle-shaped crystals of $2FeCl_3.3Fe_2O_3$ result if the temperature is raised to between 350° and 400° C.

IRON AND BROMINE.

Ferrous bromide, $FeBr_2$, may be prepared in the anhydrous form as a yellow crystalline mass by heating iron to dull redness in an atmosphere of bromine vapour.[4] When the reaction is complete, the bromine is replaced by carbon dioxide or air, heating being discontinued. The dry salt is rapidly transferred to a glass tube and hermetically sealed. It readily absorbs ammonia at the ordinary temperature, yielding a white *hexammoniate*,[5] $FeBr_2.6NH_3$. This dissociates on heating, yielding a darker salt, the *diammoniate*, $FeBr_2.2NH_3$; whilst at higher temperatures the *monammoniate*, $FeBr_2.NH_3$, is obtained as a dark grey mass.

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[1] Thomsen, *Thermochemistry*, translated by Burke (Longmans, 1908), p. 123.

[2] See Pettenkofer, *Repertorium Pharm*, 1892, (2), 41, 289 ; Béchamp, *Ann. Chim. Phys*, 1859, (3), 57, 296 ; Ordway, *Amer J. Sci.*, 1858, (2), 26, 197 ; Phillips, *Phil. Mag*, 1833, (3), 2, 75.

[3] Rousseau, *Compt rend.*, 1890, 110, 1032 ; 1891, 113, 542 ; 1893, 116, 188.

[4] Berthemot, *Ann. Chim Phys*, 1830, (2), 44, 391 ; Scheufelen, *Annalen*, 1885, 231 152.

[5] Ephraim, *Ber*, 1912, 45, 1322.

The following data have been obtained [1] for these compounds :—

	Temperature. °C.	Dissociation Pressure mm.	Heat of Dissociation Cals.
$FeBr_2.6NH_3$ . . .	107	126	14·9
$FeBr_2.2NH_3$ . . .	215	11·5	21·9
,, ,, . . .	230	23·5	21 9
,, ,, . . .	277	126	22 3
$FeBr_2.NH_3$ . . .	215	5·7	22·6
,, ,, . . .	230	9·7	22·8
,, ,, . . .	277	61·5	23·1

On dissolving in water and subsequent crystallisation in the cold, the *hexahydrate*, $FeBr_2.6H_2O$, is obtained in bluish green, rhombic prisms. The same salt may be more readily prepared by dissolving iron in hydrobromic acid.

At 50° C. the salt loses two molecules of water, yielding green crystals of the *tetrahydrate*, $FeBr_2.4H_2O$. Upon further heating more water is expelled.

Both the aqueous and alcoholic solutions of ferrous bromide absorb nitric oxide,[2] the limit of absorption being reached with one molecule of NO to each atom of iron. The compound $FeBr_2.NO$ has not been isolated.

Anhydrous ferrous bromide absorbs dry nitrogen peroxide, yielding a stable compound, $4FeBr_2.NO_2$, which retains its nitrogen peroxide even *in vacuo*. In the presence of moisture more peroxide is absorbed, but the reaction is complex, bromine being evolved.[3]

Ferrous bromide unites with ethylene [4] and acetylene.

The solubility of ferrous bromide in water is given as follows :—[5]

Temperature, °C. .	−21	−7	+10	21	37	50	65	95
Grams $FeBr_2$ in 100 grams solution .	47·0	48 3	52·3	53·7	56·0	58 0	59 4	63·3

The heat of formation is

$$[Fe]+(Br_2)+Aq.=FeBr_2.Aq.+78,070 \text{ calories.}^6$$

A few double salts with the bromides of the alkali metals have been prepared.[7]

Ferric bromide, $FeBr_3$, results when iron is heated in excess of bromine vapour, when ferrous bromide is heated from 170° to 200° C. with twice its weight of bromine,[1] and when sulphur monobromide, S_2Br_2, is passed over ferric oxide [2] at 450° to 650° C. It is a dark red, crystalline but deliquescent substance, yielding a red solution in water. At boiling-point the solution dissociates to ferrous bromide and free bromine.[3] On heating away from air ferric bromide partly sublimes and partly dissociates. When dry the salt is reduced by nitric oxide with the formation of ferrous and nitrosyl bromides.[4]

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[1] Biltz and Huttig, *Zeitsch anorg. Chem.*, 1919, 109, 89.

[2] Thomas, *Compt. rend.*, 1896, 123, 943; *Bull. Soc. chim.*, 1898, (3), 19, 343, 419: Manchot, *Ber.*, 1914, 47, 1601.

[3] Thomas, *Compt. rend*, 1897, 124, 366.

[4] Chofnacki, *Zeitsch. Chem*, 1863, 6, 419.

[5] Etard, *Ann. Chim. Phys.*, 1894, (7), 2, 503.

[6] Thomsen, *Thermochemistry*, translated by Burke (Longmans, 1908), p. 318.

[7] Walden, *Zeitsch. anorg. Chem*, 1894, 7, 331.

The aqueous solution upon concentration in the ordinary way decomposes with the precipitation of insoluble basic bromides.

The *hexahydrate*, $FeBr_3.6H_2O$, separates as dark green needles when the dark brown solution obtained by the action of bromine under water is slightly evaporated and concentrated in a desiccator over sulphuric acid. It is soluble in alcohol and ether, and melts at 27° C. without decomposition.[5]

The heat of formation [6] is

$$[Fe]+(Br_3)+Aq.=FeBr_3.Aq.+106{,}050 \text{ calories.}$$

Double salts with the bromides of ammonium and the alkali metals have been obtained.[7] These may be grouped into two classes, namely:—

Tetrabromferrates, $MFeBr_4$.

Ammonium tetrabromferrate, $NH_4FeBr_4.2H_2O$, and **Cæsium tetrabromferrate,** $CsFeBr_4$, being the best-known salts;

Pentabromferrates, M_2FeBr_5.

Cæsium pentabromferrate, $Cs_2FeBr_5.H_2O$.
Rubidium pentabromferrate, $Rb_2FeBr_5.H_2O$.

Ferric chloro-bromide,[8] $FeCl_2Br$, is obtained as an unstable crystalline substance by heating ferrous chloride and excess bromine in sealed tubes at 100° C. The crystals are dark coloured and lustrous, appearing green by reflected light and quite opaque, even in thin sections. Although insoluble in bromine, they readily dissolve in water, ether, or alcohol, their solubility in ether rendering easy their separation from ferrous chloride. The crystals readily decompose on warming, but sublime unchanged if heated in a tube containing a slight excess of bromine.

Ferrous bromate, $Fe(BrO_3)_2$, is obtained in regular octahedra on dissolving ferrous carbonate in bromic acid and concentrating *in vacuo*.

Ferric bromate results as a syrupy liquid on dissolving freshly precipitated ferric hydroxide in dilute bromic acid and concentrating *in vacuo*.

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[1] Scheufelen, *Annalen*, 1885, 231, 152.
[2] Barre, *Bull. Soc. chim.*, 1912, (4), 11, 433.
[3] de Koninck, *Zeitsch. angew. Chem.*, 1889, p 149.
[4] Thomas, *Compt. rend.*, 1897, 124, 366.
[5] Bolschakoff, *J. Russ. Chem. Soc.*, 1898, 30, 386; *Chem Zentr*, 1898, II., 660.
[6] Berthelot. See Moissan, *Traité de Chimie Minérale*, 1905, iv., p 338.
[7] Walden, *Zeitsch. anorg. Chem.*, 1894, 7, 331; *Amer. J. Sci.*, 1894, (3), 48, 283; Pfeiffer, *ibid.*, 1902, 31, 231.
[8] Lenormand, *Compt. rend.*, 1893, 116, 820.

Oxybromides are described by Béchamp[1] and Ordway,[2] but are probably not separate chemical entities.

IRON AND IODINE.

Ferrous iodide, FeI_2, is obtained when the constituent elements are allowed to react in the presence of water, heat being evolved[3] when iron filings are triturated with iodine; and by heating iron filings in a crucible to which small quantities of iodine are continually added. When the mass reaches a red heat, excess of iodine is added and the whole heated until iodine vapour ceases to escape. On cooling, a grey crystalline mass is obtained, which melts at 177° C.[4] Ferrous iodide also results when clean iron wire clippings are heated in nitrogen gas saturated with iodine vapour.[5] The salt is formed as deep red plates which appear almost black when thick. It is very deliquescent, but when kept in a desiccator turns white and subsequently evolves iodine, becoming grey or black. The white compound is believed to be the *dihydrate*,[6] $FeI_2.2H_2O$. The anhydrous salt readily absorbs ammonia, forming the hexammoniate, $FeI_2.6NH_3$, as a voluminous powder.[7] It is decomposed by water, and is converted by bromine vapour into ferric bromide, ammonium bromide, and ammonium bromo-iodobromide, $NH_4Br.IBr$.

When heated, the hexammoniate yields the *diammoniate*, $FeI_2.2NH_3$. No monammoniate has as yet been obtained. The dissociation pressures and heats of dissociation of the two compounds have been determined as follow :—[8]

	Temperature. °C.	Dissociation Pressure. mm.	Heat of Dissociation Cals.
$FeI_2.6NH_3$ . . .	153	206	16·5
$FeI_2.2NH_3$ . . .	215	6·1	22·5
,, ,, . . .	231	12·1	22·6
,, ,, . . .	278	85·4	22·8

An aqueous solution of ferrous iodide is readily prepared by warming iron filings and iodine together in water, when a colourless solution is obtained. This, however, is not stable in air, as it absorbs oxygen, liberating free iodine. If a little sugar be added to the clear solution, oxidation is retarded, and the crystalline *pentahydrate*, $FeI_2.5H_2O$, may be isolated.

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[1] Béchamp, *Ann. Chim. Phys.*, 1859, (3), 57, 296.

[2] Ordway, *Amer. J. Sci.*, 1859, (2), 26, 197.

[3] Fleury, *J. Pharm.*, 1887, (5), 16, 529; also this volume, p. 52.

[4] Carius and Wanklyn, *Annalen*, 1861, 120, 69. See also Thomson, *Compt. rend.*, 1862, 55, 615.

[5] C. L. Jackson and Derby, *Amer. Chem. J.*, 1900, 24, 15.

[6] A dihydrate was also mentioned by Lescœur, *Ann. Chim. Phys.*, 1894, (7), 2, 78.

[7] Compare ferrous chloride and bromide, pp. 91, 105.

[8] Biltz and Hüttig, *Zeitsch. anorg Chem*, 1919, 109, 89. Compare Ephraim, *Naturwiss.*, 1919, 7, 49; *Chem. Zentr.*, 1919, I., 409.

A solution containing ferrous iodide and water in the proportion of 1 to 8·5 molecules respectively, deposits a deliquescent *hexahydrate*, $FeI_2.6H_2O$, at −16° C. This, on warming to +8° C., yields the tetrahydrate, $FeI_2.4H_2O$. The *nonahydrate*,[1] $FeI_2.9H_2O$, and *monohydrate*,[2] $FeI_2.H_2O$, are also stated to exist.

Ferric iodide, FeI_3, has not as yet been prepared, but the possibility of its existence is perhaps indicated by the fact that hydrated ferric oxide dissolves in hydriodic acid, yielding a *brown* solution.

Two **ferrous per-iodates** are described by Kimmins,[3] namely $Fe_5(IO_6)_2$ and $FeH_3(IO_6)$. The former is a brick-red crystalline salt produced on adding ferrous sulphate to a solution of $K_4I_2O_9$. $FeH_3(IO_6)$ results as a light brown powder on adding a solution of $Na_2H_3IO_6$ to ferrous sulphate.

Two **ferric per-iodates** have been prepared,[3] namely $FeHI_2O_9$ and $Fe(IO_4)_3$. The former is obtained by drying at 100° C. the light brown precipitate resulting from the interaction of solutions of ferric chloride and $Na_2H_3IO_6$. It is also formed when $K_4I_2O_9$ is used instead of the sodium salt. It is a reddish-brown powder, stable towards boiling dilute nitric acid. With concentrated nitric acid, however, $Fe(IO_4)_3$ is formed as a bright yellow powder.

Ferrous iodate.—On addition of potassium iodate to ferrous sulphate solution, a pale yellow precipitate is obtained, consisting probably of ferrous iodate.[4]

Ferric iodate, $Fe_2O_3.I_2O_5$, is obtained as a brown precipitate[5] on mixing hot solutions of an alkali iodate and a ferric salt. Small crystals may be prepared by addition of an acid solution of iron in nitric acid to sodium iodate. The precipitate first formed readily dissolves, and upon concentration of the solution the salt crystallises out. It is stable in air at ordinary temperatures, but decomposes when heated.

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[1] Volkmann, *J. Russ. Phys. Chem. Soc*, 1894, 1, 239.

[2] Lescœur, *loc. cit.*

[3] Kimmins, *Trans. Chem Soc*, 1889, 55, 148.

[4] Rammelsberg, *Pogg. Annalen*, 1838, 44, 559.

[5] Ditte, *Ann. Chim. Phys.*, 1890, (6), 21, 157.

CHAPTER VII.

IRON AND THE ELEMENTS OF GROUP VI.

IRON AND OXYGEN.

Ferrous oxide, FeO, does not occur free in nature on account of the ease with which it absorbs oxygen, yielding ferric oxide. It is exceedingly difficult to prepare in a pure state. It results in a more or less impure condition when ferric oxide is heated to 300° C. in a current of hydrogen, and is then pyrophoric, becoming incandescent upon exposure to air, and reverting to its original ferric condition. After keeping in an atmosphere of hydrogen for some twelve hours, however, it loses this property. This method of preparation is not altogether satisfactory, however, since the product is liable to be contaminated with ferroso-ferric oxide, Fe_3O_4. Moissan [1] obtained a fairly pure product on heating ferric oxide in hydrogen for twenty minutes at about 500° C.

A better method consists in reducing ferric oxide in a current of pure, dry carbon monoxide at 500° C.,[1] or with a mixture of equal parts of carbon monoxide and dioxide at red heat.[2]

When hydrogen mixed with water vapour is passed over heated ferric oxide, ferrous oxide is formed in increasing amount with rise of temperature.[3] Thus at 700° C. the product contains 85 per cent. of FeO, and at 800° C. some 92 per cent. FeO. Perfectly pure ferrous oxide is not obtained, however, even at 1100° C. Neither does it seem possible to obtain the pure oxide from reduced iron by oxidation with a mixture of steam and hydrogen.

Ferrous oxide is also formed, together with metallic iron, when ferrous oxalate is heated to 150°–160° C., and allowed to cool in an atmosphere of carbon dioxide.[4] To avoid separation of carbon or the formation of iron carbide, it is advantageous to heat ferrous oxalate gradually up to 520° in a current of nitrogen.[5] The temperature is finally raised to about 900° C. The product is grey in colour, and dissolves completely in hydrochloric acid, evolving hydrogen, indicating the presence of some free iron. Metallic iron may be oxidised to ferrous oxide by ignition in carbon monoxide at 1000° C.[6]; or by heating with ferric oxide, according to the reaction :—[7]

$$Fe_2O_3+Fe=3FeO.$$

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[1] Moissan, *Compt. rend*, 1877, 84, 1296.
[2] Debray, *Compt. rend*, 1857, 45, 1018.
[3] Hilpert and Beyer, *Ber.*, 1911, 44, 1608.
[4] Liebig, *Annalen*, 1855, 95, 116 ; Moissan, *Ann. Chim. Phys.*, 1880, (5), 21, 199.
[5] Mixter, *Amer. J. Sci.*, 1913, (4), 36, 55.
[6] Tissandier, *Compt. rend.*, 1872, 74, 531.
[7] Mills, *Patentblatt*, 17, 362.

When nitrous oxide is passed over iron at 200° C. ferrous oxide is produced,[1] and also when iron is heated in steam to 350° C.[2]

Iron amalgam yields ferrous oxide upon slow oxidation by exposure to air.[3]

According to Moissan,[4] ferrous oxide can exist in two polymorphic modifications, according as it is produced at high or at lower temperatures. The variety obtained at the lower temperatures, namely below 600° C., is more chemically reactive, uniting with oxygen, upon exposure to air, with such rapidity that the whole mass becomes incandescent. It decomposes water, slowly in the cold but with considerable rapidity at the boiling-point. It is readily soluble even in dilute acids, such as acetic acid, and easily displaces ammonia from its salts.

When obtained at 1000° C., or if heated to this temperature after production at lower temperatures, ferrous oxide is no longer pyrophoric; it does not decompose water, neither is it soluble in dilute acetic acid.

Both varieties of ferrous oxide are reduced by hydrogen gas to the free metal. If the oxide has not previously been heated above 400° C., the reaction begins at about 280° C.; but if it has been previously heated to about 1200° C., it cannot be reduced by hydrogen below 330° C.[5]

The foregoing observations, however, do not necessarily prove that two polymorphic forms of ferrous oxide can exist. The observed chemical differences may well be due to the variation in the state of subdivision of the oxide, that produced at the lower temperatures being the more finely subdivided.

Ferrous oxide is reduced to metallic iron at 850° C. by a mixture of carbon monoxide and dioxide in the proportion of 10 parts CO to 4 parts CO_2.[6]

Chlorine, dissolved in carbon tetrachloride, reacts even at −18° C. with violence upon ferrous oxide, yielding ferric oxide and chloride.[7] Thus:—

$$6FeO+3Cl_2=2Fe_2O_3+2FeCl_3.$$

Ferrous oxide dissolves in acids to yield well-defined series of ferrous salts, which are pretty stable when dry or present in acid solution, but readily oxidise in moist air and in neutral or alkaline solution. They are usually colourless or pale green.

Ferrous oxide obtained by slow reduction of ferric oxide in hydrogen at 300° C. readily reacts with sulphur dioxide on warming, the mass becoming incandescent. Clouds of sulphur and sulphur dioxide are evolved, a solid residue of sulphide and oxide remaining.[8]

When ferrous oxide is heated with pure forms of carbon, no reaction takes place below 650° C. Above this temperature reduction occurs, but the rate of reaction depends greatly upon the mode of preparation of the carbon. Thus sugar charcoal is relatively inert, a vigorous reduction not taking place until about 800° C. Carbon obtained by burning acetylene in chlorine reacts vigorously at 650° C.[1]

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[1] Sabatier and Senderens, *Compt. rend.*, 1892, 114, 1429.

[2] Friend, *J. West Scotland Iron Steel Inst*, 1910, 17, 66.

[3] Férée, *Bull. Soc. chim*, 1900, (3), 25, 615.

[4] Moissan, *Ann. Chim. Phys.*, 1880, (5), 21, 199; *Traité de Chimie Minérale*, 1905, iv. 340.

[5] Hilpert, *Ber.*, 1909, 42, 4575. Compare Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 1.

[6] Akermann and Sarnstrom, *Dingl. Poly. J.*, 1883, 248, 291.

[7] Michael and Murphy, jun., *Amer. Chem J.*, 1910, 44, 365.

[8] Hammick, *Trans. Chem. Soc.*, 1917, 111, 379.

The heat of formation of ferrous oxide is as follows :—

$$[Fe]+(O)=[FeO]+64{,}600 \text{ calories},^{2}$$
$$[Fe]+(O)=[FeO]+64{,}300 \text{ calories},^{3}$$

and at 680° C. and under constant pressure,

$$[Fe]+(O)=[FeO]+67{,}350 \text{ calories}.^{4}$$

Ferrous hydroxide, $Fe(OH)_2$, may be obtained in the crystalline form as green hexagonal prisms by deposition from sodium hydroxide solution. Even after washing with alcohol and ether and drying out of contact with air, the prisms oxidise immediately they are brought into contact with oxygen, developing considerable heat and yielding a residue of ferric oxide.[5]

In the amorphous condition ferrous hydroxide is usually prepared as a white precipitate by addition of sodium or potassium hydroxide to a solution of a ferrous salt in the complete absence of air.[6] The precipitate is washed in an atmosphere of nitrogen and dried with ether. If air is present, the precipitate assumes a green colour which becomes greenish black in consequence of the formation of hydrated magnetic oxide, and ultimately turns brown owing to further oxidation to ferric hydroxide.

If, however, after precipitation, the supernatant mother liquor is poured off and solid potassium hydroxide is added to the residue, the ferrous hydroxide shrinks in volume to a greenish grey pulverulent precipitate which is considerably more stable, and oxidises in air direct to ferric hydroxide without the intermediate formation of magnetic oxide.[7]

Such ferrous hydroxide suspended in potassium hydroxide solution is slowly oxidised by nitric oxide to ferric hydroxide, the nitric oxide being largely converted into ammonia.[7]

Ferrous hydroxide is not completely precipitated from solutions of ferrous salts by ammonium hydroxide in the presence of ammonium chloride.

As ordinarily prepared, ferrous hydroxide undergoes oxidation upon exposure to moist air with such rapidity as to become incandescent. It readily dissolves in dilute acids yielding ferrous salts.

Towards iodic acid and the salts of such readily reducible metals as mercury and platinum, ferrous hydroxide acts as a reducing agent. It can even decompose water, slowly in the cold but more rapidly on boiling,[8] the solution becoming turbid in air,[9] and possessing a distinctly ferruginous taste. Solutions of the alkali hydroxides readily dissolve ferrous hydroxide ; even ammonium hydroxide acts similarly, and in the presence of air or oxygen the ferrous hydroxide is rapidly converted by this means into hydrated ferric oxide. The heat of formation of ferrous hydroxide is given as follows:—[1]

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[1] Falcke, *Zeitsch. Elektrochem.*, 1915, 21, 37 ; *Ber.*, 1913, 46, 743.

[2] Le Chatelier, *Compt. rend.*, 1895, 120, 624. See also Ruff and Gersten, *Ber.*, 1913, 46, 394.

[3] Mixter, *Amer. J. Sci.*, 1913, (4), 36, 55.

[4] Baur and Glaessner, *Zeitsch. physikal. Chem.*, 1903, 43, 354.

[5] de Schulten, *Compt. rend.*, 1889, 109, 266.

[6] Schmidt, *Annalen*, 1840, 36, 101.

[7] Divers and Haga, *Trans. Chem. Soc.*, 1885, 47, 364.

[8] Liebig and Wöhler, *Pogg. Annalen*, 1831, 21, 582.

[9] Bineau, *Compt. rend.*, 1855, 41, 509.

$$[Fe]+(O)+H_2O=[Fe(OH)_2]+68,280 \text{ calories.}$$

The *dihydrate*, $FeO.2H_2O$, has been found in clay near Cuxhaven, in a more or less impure form as hard, yellowish-brown lumps, which crumble upon exposure to air.[2]

Ferroso-ferric oxide, Triferric tetroxide, Magnetite, or Magnetic oxide of iron, Fe_3O_4, occurs in nature as the mineral *magnetite* (see p. 12) and may be regarded as a compound of ferrous oxide and ferric oxide, namely $FeO.Fe_2O_3$, or as the ferrous salt of hypothetical metaferrous acid, namely $FeFe_2O_4$. It has a black, metallic appearance, and crystallises in octahedra and dodecahedra, of hardness 5·5 to 6·5, and density approximately 4·9 to 5·2. It was first recognised as a definite oxide of iron by Gay-Lussac,[3] who obtained it by the action of steam on iron. As its name would appear to imply, magnetite possesses magnetic properties, being attracted by a magnet. It is quite possible, however, that the name of the ore does not really refer to the magnet, but to Magnesia, a town in Lydia, Asia Minor, where the ore was first found. In the laboratory the oxide may be obtained in a variety of ways. Thus, when iron is heated in steam to upwards of 820° C.,[4] it becomes covered with a skin of magnetic oxide, the layers underneath consisting of various amounts of ferrous oxide associated with magnetic oxide in solid solution. If the iron is in the form of very thin plates, these may, by prolonged heating in the steam, be converted completely into the higher oxide.

Magnetic oxide also occurs as a superficial layer when iron is heated to dull redness in air—that is, at a temperature of 625° to 650° C. The oxide beneath the outermost skin has the composition[5] represented by the formula $Fe_3O_4.xFeO$.

When ferric oxide is maintained at 1500° C. in nitrogen[6] or at very high temperatures in air, such as those obtaining in the electric furnace, it is reduced to magnetite, for which reason it is possible, though scarcely profitable, to apply magnetic concentration to hæmatites at high temperatures.[7] When iron burns in oxygen, the magnetic oxide is produced, and also when ferric oxide is heated to 400° C. in a current of hydrogen saturated with water vapour at 30° to 50° C.[8] At higher temperatures products increasingly rich in ferrous oxide are obtained. Thus:—

700° C.. . . .	85 per cent. FeO.
800° C.. . . .	92 „ „

On heating reduced iron in carbon dioxide at 440° C., and by reducing ferric oxide by hydrogen or carbon monoxide at 500° C., Moissan has been able to obtain the magnetic oxide.

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[1] Thomsen, *Thermochemistry*, translated by Burke (Longmans, 1908), p. 265.
[2] Hart, *Chem. Zeit.*, 1908, 32, 746.
[3] Gay Lussac, *Ann. Chim. Phys.*, 1811, (1), 80, 163; 1816, (2), 1, 33.
[4] Friend, Hull, and Brown, *Trans. Chem. Soc.*, 1911, 99, 969.
[5] See Mosander, *Pogg. Annalen*, 1826, 6, 35.
[6] Mugge, *Jahrb. Min. Beil.-Band*, 1911, 32, 491. See also Sidot, *Compt. rend.*, 1869, 69, 201.
[7] See this volume, Part III.
[8] Hilpert and Beyer, *Ber.*, 1911, 44, 1608.

Crystals of magnetic oxide have been obtained in a variety of ways, such as by calcination of sodium carbonate and ferrous chloride [1]; by fusion of potassium sulphate and iron phosphate [2]; by the action of hydrogen chloride upon heated ferrous oxide [3]; and by ignition of ferrous fluoride with boric anhydride.[4]

When strongly heated with excess of sodium chloride for several hours ferric oxide is converted into black crystals of magnetic oxide.[5] Pure iron wire, heated to 1200° C. in a current of carbon dioxide, yields crystalline magnetic oxide, the crystals frequently exhibiting magnetic polarity. The presence of moisture facilitates the formation of larger crystals.[6]

When iron wire is subjected to prolonged fusion with sodium sulphate, it is converted into magnetite, the sodium sulphate acting catalytically being first reduced to sulphite and re-oxidised to sulphate by the oxygen of the atmosphere.[7] Ferrous sulphide may be oxidised to magnetite in a similar manner. As obtained in this manner, the crystalline magnetic oxide closely resembles the natural product. Its crystals are opaque, magnetic octahedra, possessed of a metallic lustre. Hardness 6 to 6·5; density, 5·21 to 5·25. The crystals are not affected by steam or carbon dioxide at bright red heat, are not attacked by diluted mineral acids, and are but slowly dissolved by the concentrated acids or aqua regia.

Ordinary magnetic oxide of iron melts at 1527° C.[8] Its specific heat is 0·1655.[9] When heated with platinum to 1600° C. in contact with air, magnetic oxide is reduced to the metal, oxygen being evolved, the iron passing into solid solution in the platinum.[10] Under low oxygen pressures reduction in the above manner can take place at 1400° C. When heated in air for a prolonged period at 1300° C., the oxide is almost completely converted into ferric oxide.[11] According to the reversible reaction

$$4Fe_3O_4+O_2 \rightleftharpoons 6Fe_2O_3,$$

magnetic oxide has no perceptible dissociation pressure at 1350° C.[12]

It does not react appreciably with sulphur dioxide at dull redness.[13] Raised to white heat in a current of hydrogen sulphide, it yields ferrous sulphide, accompanied by the evolution of hydrogen, sulphur dioxide, and a little sulphur trioxide.[14]

When placed in freshly-fused potassium hydrogen sulphate, a crystal of magnetite is only slightly attacked; but at a higher temperature there is an energetic action.

Hydrogen reduces magnetic oxide to the metal, the reaction being perceptible at 305° C.[15]

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[1] Liebig and Wohler, *Pogg. Annalen*, 1831, 21, 582.

[2] Debray, *Compt rend.*, 1861, 52, 985.

[3] Debray, *ibid.*, 1861, 53, 199.

[4] Deville and Caron, *ibid.*, 1858, 46, 764.

[5] Thompson, *Trans. Ceramic Soc.*, 1918, 17, (2), 340.

[6] Donau, *Monatsh.*, 1904, 25, 181.

[7] Gorgeu, *Compt rend.*, 1887, 104, 1174.

[8] Hilpert and Kohlmeyer, *Ber.*, 1909, 42, 4581.

[9] Abt, *Wied. Annalen*, 1897, (2), 62, 474.

[10] Sosman and Hostetter, *J. Washington Acad Sci.*, 1915, 5, 293.

[11] Honda and Soné, *Sci. Rep. Tohoku Imp. Univ.*, 1914, 3, 223.

[12] Walden, *J. Amer. Chem. Soc.*, 1908, 30, 1350.

[13] Hammick, *Trans. Chem Soc.*, 1917, 111, 379.

[14] Gautier, *Compt. rend.*, 1906, 143, 7.

[15] Glaser, *Zeitsch anorg. Chem.*, 1903, 36, 1.

Magnetic oxide dissolves in hydrochloric acid. If the latter is not present in sufficient quantity to yield a complete solution of ferrous and ferric chlorides, ferric oxide and ferrous chloride are produced.

The heats of formation of magnetite are as follow :—

$$\underset{\text{(calcined)}}{3[Fe_2O_3]}=2[Fe_3O_4]+(O)-45{,}180\text{ calories.}^1$$
$$3[Fe]+4(O)=[Fe_3O_4]+265{,}200\text{ calories.}^2$$
$$3[Fe]+4(O)=[Fe_3O_4]+265{,}700\text{ calories.}^3$$
$$[FeO]+[Fe_2O_3]=[Fe_3O_4]+9200\text{ calories.}^3$$
$$3[FeO]+(O)=[Fe_3O_4]+85{,}800\text{ calories.}^4$$
$$3[FeO]+(O)=[Fe_3O_4]+75{,}600\text{ calories.}^1$$
$$3[FeCO_3]+(O)=[Fe_3O_4]+3CO_2+0\text{ calories.}^1$$

and at 490° C. under constant pressure,[5]

$$3[Fe]+4(O)=[Fe_3O_4]+267{,}380\text{ calories.}$$

According to Moissan,[6] magnetic oxide of iron exists in two polymorphic forms, according to its method of preparation. The one form, obtained by high temperature methods, such as the combustion of iron in oxygen, the action of steam on iron at red heat, and the calcination of ferric oxide at bright red heat, is characterised by its insolubility in concentrated boiling nitric acid, by its high density (5 to 5·09), and by its resistance to further oxidation when heated in air.

The second variety resembles the former in its black appearance and magnetic properties, but differs from it in density (4·86), in its solubility in nitric acid, and in its tendency to oxidise to ferric oxide when calcined in air. It is converted into the other variety when raised to white heat in nitrogen. As explained in the case of ferrous oxide, however, these differences may simply be due to variations in the states of aggregation of the oxide, according to its method of preparation.

Several substances, such as $4FeO.Fe_2O_3$,[7] $3FeO.Fe_2O_3$,[8] etc.,[9] have been described. It is highly probable, however, that these are not definite chemical entities.

When ferroso-ferric ammonium carbonate (see p. 202) is decomposed by a hot concentrated solution of potassium hydroxide in the absence of air, hydrated ferroso-ferric oxide separates out, which, when dried at 100° C., corresponds in composition to the formula $Fe_2O_3.4FeO.5H_2O$. It is readily acted on with air, yielding hydrated ferric oxide, $Fe_2O_3.H_2O$.[10]

A bluish black oxide, corresponding in composition to $2FeO.3Fe_2O_3$, is described [11] as resulting when potassium nitrate is added to a boiling solution of ferrous sulphate rendered alkaline with ammonia.

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[1] Le Chatelier, *Compt. rend.*, 1895, 120, 623

[2] Ruff and Gersten, *Ber.*, 1912, 45, 63.

[3] Mixter, *Amer. J. Sci.*, 1913, (4), 36, 55. Compare Berthelot, *Compt. rend.*, 1881, 92, 17.

[4] Ruff and Gersten, *Ber*, 1913, 46, 394.

[5] Baur and Glaessner, *Zeitsch. physikal Chem*, 1903, 43, 354

[6] Moissan, *opus cit.*, p. 342 ; *Ann. Chim Phys.*, 1880, (5), 21, 199.

[7] Berthier, *Ann. Chim Phys.*, 1824, (2), 27, 19

[8] Doebereiner, *Arch. Pharm.*, 1845, (2), 41, 29

[9] See Mosander, *loc. cit.* ; Laurent and Holms, *Ann Chim Phys.*, 1835, (2), 60, 330.

[10] Hauser, *Ber.*, 1907, 40, 1958

[11] Kaufmann, *Zeitsch. Elektrochem.*, 1901, 7, 733.

Hydrated Magnetic Oxide.—Magnetic oxide dissolves in hydrochloric acid, and the solution so obtained yields, on pouring into an excess of sodium hydroxide solution, a black precipitate which, on drying, is attracted by a magnet. It is the *monohydrate*, $Fe_3O_4.H_2O$.

The *sesqui-hydrate*, $2Fe_3O_4.3H_2O$, is obtained by precipitation in an analogous manner from mixed solutions of ferrous and ferric salts in the proportions theoretically required.[1] The precipitate is dark green to black in colour, and strongly magnetic.[2] It may be washed in the presence of air without oxidising, and loses water only, on heating.

Ferric oxide, Iron sesqui-oxide, Fe_2O_3, occurs in abundant quantities in nature, both in the massive and crystalline forms, the former being known as *red hæmatites*, whilst the latter are termed *specular iron* (see p. 16) when the crystals are rhombohedra and scalenohedra, or *micaceous iron* when in thin translucent scales.

In the laboratory ferric oxide may be obtained in a variety of ways. Thus when ferric hydroxide or sulphate is strongly heated ferric oxide remains behind, and the same applies if ferric chloride or sulphide, ferrous oxide or carbonate, or indeed the majority of ferrous salts,[3] are heated in contact with air. Several of these methods are adopted on a manufacturing scale. For example, in the manufacture of sulphuric acid [4] iron pyrites is roasted in air, leaving a residue of ferric oxide. Thus:—

$$2FeS_2+11O=4SO_2+Fe_2O_3.$$

Ferric oxide is manufactured in large quantities for use as a pigment by roasting ferrous sulphate obtained by weathering iron pyrites, as described on page 147.

Ferric oxide is also prepared from liquors containing ferric salts in solution, and which are otherwise waste products in many manufacturing processes. If ferrous salts are present, they are first oxidised by addition of nitric acid or bleaching powder. The acid is neutralised by addition of soda or lime, ferric hydroxide being precipitated. The washed product is finally dehydrated by heat, becoming perfectly anhydrous at 500° C. upwards.[5]

Ferric oxide, in a more or less impure condition, is manufactured for pigmentary purposes by the ignition of natural ferric hydroxides such as *ochres* (see p. 18). The colour of the final product depends largely upon the completeness with which the water has been expelled.[6] Thus *Venetian reds* are produced after ignition at dull red heat for some eight hours; ten hours' heating yields *light reds*; twelve hours' the so-called *Indian reds*; and so on.[7]

Crystalline Ferric Oxide.—Small crystals of ferric oxide may be obtained by fusing amorphous ferric oxide with sodium borate (borax), and extracting them from the cooled mass with the aid of dilute aqueous nitric or hydrochloric acid.[1] Passage of gaseous hydrogen chloride over the ferric oxide[2] at red heat; of steam containing some ammonium fluoride over the oxide at 600° C.[3]; of ammonium chloride over ferric oxide at 700° C.[4]; or of vaporised ferric chloride over heated lime, results in the formation of small crystals of ferric oxide. Crystals have been found, produced by the first of these methods, in iron pipes which have for many years conducted alternately hydrogen chloride and air in a plant connected with Deacon's process for the manufacture of chlorine.[5] Crystals have also been found as products of smelting operations, whilst crystals having the form of specular iron have been found in iron rust from a building seven hundred to eight hundred years old.[6] By heating mixed solutions of the sulphates of copper and iron (ferrous) in sealed tubes to 210° C. for ten hours, crystals resembling those of micaceous iron are produced.[7] When ferric sulphate is heated, it decomposes, yielding hexagonal lamellæ of ferric oxide, having a density of 4·95 at 14° C.[8]

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[1] Liebig and Wohler, *Pogg Annalen*, 1831, 21, 583; Lefort, *Compt. rend.*, 1852, 34, 488.

[2] See Preuss, *Annalen*, 1838, 26, 96; Wohler, *ibid.*, 1838, 28, 92.

[3] *i.e.* salts whose acids are volatile at high temperatures.

[4] See this series, Volume VII.

[5] Carnelley and J Walker, *Trans. Chem. Soc.*, 1888, 53, 89.

[6] The action of heat on ochres and the production of allotropic forms has been studied by Bouchonnet, *Bull. Soc chim*, 1912, (4), 11, 6; 1911, (4), 9, 345.

[7] See *A Treatise on Colour Manufacture*, by Zerr and Rubenkamp. Translated by C. Mayer (Chas. Griffin & Co., 1908); also Bradford, *Proc Paint Varnish Soc*, 1920, No 3, p. 135.

Ferric oxide, pseudomorphous with magnetite, may be obtained by heating magnetite crystals in the blow-pipe flame for several hours; oxidation takes place, the crystals retaining their original form almost unaltered, but losing their magnetic properties.[9]

Ferric oxide may be obtained in an exceptionally pure condition,[10] very useful for analytical purposes, by dissolving a piece of metallic iron, preferably of high purity, in hydrochloric acid, diluting, and precipitating as sulphide by passage of hydrogen sulphide, any copper, etc., with which the metal is contaminated. The clear filtrate is evaporated to small bulk, oxidised with nitric acid, evaporated to dryness with hydrochloric acid, taken up with water, and extracted with ether. The ethereal solution is distilled, and the residual ferrous and ferric chlorides dissolved in diluted hydrochloric acid, reduced with sulphur dioxide and precipitated as ferrous oxalate with the ammonium salt. After thorough washing the oxalate is ignited to ferric oxide.

Pure ferric oxide is recommended for the standardising of permanganate solutions for volumetric analysis. It is dissolved in hydrochloric acid, reduced with stannous chloride, and titrated with permanganate.[11]

As obtained by any of the foregoing methods, ferric oxide is an extremely stable substance, soluble in acids only with difficulty. It melts at 1565° C.,[12] and freezes at 1562° to 1565° C.[13]

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[1] Hauer, *Sitzungsber. K. Akad. Wiss Wien*, 1854, 13, 456.

[2] Deville, *Compt. rend.*, 1861, 52, 1264.

[3] Bruhns, *Chem. Zentr*, 1889, II., 886; Arctowski, *Zeitsch. anorg. Chem*, 1894, 6, 377.

[4] Arctowski, *Bull. Acad. roy. Belg.*, 1894, (3), 27, 933; *Zeitsch. anorg Chem.*, 1894, 6, 377.

[5] Munroe, *Amer. J. Sci*, 1907, (4), 24, 485.

[6] Roscoe and Schorlemmer, *Treatise on Chemistry*, vol. ii. (Macmillan & Co., 1907).

[7] de Senarmont, *Ann. Chim. Phys.*, 1851, (3), 32, 144.

[8] Lachaud and Lepierre, *Compt. rend.*, 1892, 114, 915.

[9] Friedel, *Bull. Soc. franç. Min.*, 1894, 17, 150.

[10] Brandt, *Chem. Zeit.*, 1916, 40, 605, 631.

[11] Brandt, *ibid.*, 1908, 32, 812, 830, 840, 851.

[12] Hilpert and Kohlmeyer, *Ber*, 1909, 42, 4581.

[13] Kohlmeyer, *Metallurgie*, 1909, 6, 323.

Its cubical coefficient of expansion with rise of temperature is 0 00004.[1]

Its specific heats for various temperature intervals are as follow :—[2]

Temperature Interval. °C.	Specific Heat.	Molecular Heat.
−191·9 to −81·6	0·0728	11·59
−191·9 ,, −80·4	0·0724	
− 73·6 ,, 0	0·1318	21 05
− 73·8 ,, 0	0·1318	
3·9 ,, 43·8	0·1604	25 53
3·2 ,, 44·3	0·1596	

At about 2500° to 3000° C. it shows signs of volatilising.[3]

It crystallises in tabular hexagonal scales belonging to the hexagonal system, and possesses a steel-like lustre. The edges are ruby-red in colour, and give a red streak. Density, 5·187 to 5·193.[4]

At 640° C. ferric oxide appears to undergo a polymorphic change.[5] The magnetic properties of ferric oxide are ordinarily very feeble,[6] but when heated to a very high temperature, as, for example, in the electric furnace,[7] or oxy-hydrogen flame,[8] it becomes magnetic, owing to conversion into the magnetic oxide, Fe_3O_4. It is not reducible by solid carbon, in the absence of gases, below 950° C.[9] When heated with platinum to 1600° C. in the air, ferric oxide is reduced to the metal, oxygen being evolved and the iron passing into solid solution in the platinum.[10] Under low oxygen pressures the temperature of reduction may be as low as 1200° C.

When heated to 480° C., under a pressure of twelve atmospheres of oxygen, ferric oxide undergoes no chemical change, a higher oxide not being formed.[11]

With magnetic oxide ferric oxide yields a continuous series of solid solutions, ranging from Fe_2O_3 down to practically Fe_3O_4 itself. No intermediate oxides have been detected.[12]

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[1] Fizeau, *Ann. Chim. Phys.*, 1866, (4), 8, 335.

[2] Russell, *Physikal. Zeitsch.*, 1912, 13, 59. Other data are given by Abt, *Wied Annalen*, 1897, 62, 474. Compare also Lallemand, *Ann. Chim. Phys.*, 1863, (3), 69, 223 ; Malagutti and Lallemand, *ibid*, 1862, (3), 64, 214.

[3] Elsner, *J. prakt. Chem.*, 1866, 99, 257.

[4] Kohlmeyer, *Metallurgie*, 1909, 6, 323.

[5] Keppeler and d'Ans, *Zeitsch. physikal. Chem.*, 1908, 62, 89.

[6] See Malagutti, *Ann. Chim Phys.*, 1863, (3), 69, 214 ; Lallemand, *ibid*, p. 223 ; de Luca, *Compt. rend.*, 1862, 55, 615 ; Smith, *Ann. Chim. Phys.*, 1844, (3), 10, 120 ; Plucker, *Pogg. Annalen*, 1848, 74, 321.

[7] Moissan, *Compt rend.*, 1892, 115, 1034.

[8] Read, *Trans. Chem. Soc.*, 1894, 65, 314

[9] Charpy and Bonnerot, *Compt rend.*, 1910, 151, 644.

[10] Sosman and Hostetter, *J. Washington Acad. Sci.*, 1915, 5, 293.

[11] Milbauer, *Eighth Inter. Cong. App. Chem.*, 1912, 2, 183

[12] Sosman and Hostetter, *J. Amer. Chem. Soc.*, 1916, 38, 807.

The dissociation pressures of ferric oxide between 1100° and 1400° C. are as follow :—[1]

Temperature. °C.	Pressure (mm. mercury).
1100	5·0
1150	7·0
1200	9·0
1250	20·0
1300	59·5
1350	166 0
1400	454 0

Ferric oxide is reduced to ferrous oxide or the metal, according to circumstances, by carbon monoxide. At temperatures below 1000° C. the dry gas is more effective than the moist, but at 1050° C. both moist and dry gases behave alike.[2] At and below 850° C. the iron is converted into carbide.[3] At 700° C. the reaction

$$3Fe_2O_3+CO=2Fe_3O_4+CO_2$$

also takes place.[4]

Ferric oxide is reduced to metallic iron when strongly heated in a current of hydrogen, the water vapour formed during the reduction being rapidly carried away in the current of gas.

The temperature at which reduction begins depends on the temperature to which the oxide has previously been heated.[5]

In the case of hydrogen gas the reaction usually begins at about 330° C. with the formation of magnetic oxide. Thus :—

$$3Fe_2O_3+H_2=2Fe_3O_4+H_2O.$$

Carbon monoxide is active even at 240° C.[5] At 500° C. ferrous oxide is formed :—

$$Fe_3O_4+H_2=3FeO+H_2O\,;$$

and at 600° C. complete reduction to metallic iron is effected :—

$$FeO+H_2=Fe+H_2O.$$

The metal obtained at this temperature, however, is not pyrophoric.[6]

It must be remembered that the foregoing temperatures are only approximations, and refer to experiments of ordinary duration. For example, the last reaction, stated to begin at about 600° C., will take place, albeit very slowly, at considerably lower temperatures. Thus, after ninety-six hours of treatment, Moissan was able to reduce the oxide to metallic iron at 440° C., and the metal was then pyrophoric.

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[1] Walden, *J. Amer. Chem. Soc.*, 1908, 30, 1350. Slightly different data are given: Treadwell, *Zeitsch Elektrochem.*, 1916, 22, 414. See also Hostetter and Sosman, *J. Amer. Chem. Soc*, 1916, 38, 1188.

[2] Boudouard, *Compt. rend.*, 1905, 140, 40.

[3] Hilpert and Dieckmann, *Ber.*, 1915, 48, 1281.

[4] See Braithwaite, *Chem. News*, 1895, 72, 211; Baur and Glaessner, *Zeitsch. physikal. Chem*, 1903, 43, 354.

[5] Hilpert, *Ber.*, 1909, 42, 4575 Compare Glaser (*Zeitsch. anorg. Chem*, 1903, 36, 1), who gives 287° C. as the commencing temperature.

[6] Moissan, *opus cit.*, p. 347.

If, however, the reduction is made to take place in a more or less confined area, various equilibria are set up, according to circumstances. Thus :—

$$Fe_2O_3+3H_2 \rightleftharpoons 2Fe+3H_2O,$$
$$Fe_2O_3+3CO \rightleftharpoons 2Fe+3CO_2,$$

and these reactions are still further complicated by the formation of ferrous oxide and magnetic oxide.[1]

Ferric oxide is rapidly reduced by nascent hydrogen. If added to hydrochloric acid in which metallic iron is dissolving, it is reduced and quickly dissolved, yielding ferrous chloride.[2]

Ferric oxide is not attacked by thionyl chloride, $SOCl_2$, at the ordinary temperature. At 150° C. the following reaction readily takes place :—

$$Fe_2O_3+3SOCl_2=2FeCl_3+3SO_2,$$

the ferric chloride crystallising out in green hexagonal plates.[3]

Heated with sulphur, ferric oxide yields ferrous sulphide and sulphur dioxide. With hydrogen sulphide at white heat hydrogen and sulphur dioxide are evolved :—[4]

$$2Fe_2O_3+7H_2S=4FeS+3SO_2+7H_2.$$

Ferric oxide reacts slowly at 700° to 800° C. with sulphur dioxide, yielding sulphur trioxide and magnetic oxide :—

$$3Fe_2O_3+SO_2=2Fe_3O_4+SO_3.^5$$

Below 600° C. there is no action.

Ferric oxide is attacked by chlorine at high temperatures, yielding a sublimate of ferric chloride,[6] the same salt being also produced upon ignition of the oxide in hydrogen chloride.[7] Ammonia, under similar conditions, is oxidised to water, a nitride of iron being produced.

Ferric oxide is dissolved by hydrochloric acid. Nitric acid does not attack the ignited oxide. Sulphuric acid, particularly a mixture of 8 parts of acid with 3 parts of water, effects its solution.[8]

When heated with calcium sulphate, ferric oxide causes the expulsion of sulphur trioxide, and a similar reaction takes place with lead and magnesium sulphates.[9]

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[1] See this volume, Part III, where the reactions taking place in the blast furnace are discussed.

[2] Borntrager, *Zeitsch anal. Chem.*, 1896, 35, 170.

[3] North and Hagemann, *J. Amer. Chem. Soc*, 1913, 35, 352.

[4] Gautier, *Compt. rend*, 1906, 143, 7.

[5] Keppeler, *Zeitsch. angew. Chem*, 1908, 21, 579 ; Hammick, *Trans. Chem. Soc.*, 1917, 111, 379.

[6] Weber, *Pogg. Annalen*, 1861, 112, 619 ; *Jahresber*, 1861, 14, 148.

[7] Deville, *Compt. rend*, 1861, 52, 1264

[8] Mitscherlich, *J prakt. Chem.*, 1860, 81, 110 ; Siewert, *Jahresber*, 1864, 17, 266.

[9] Scheurer-Kestner, *Compt. rend.*, 1884, 99, 876.

The heats of formation of anhydrous ferric oxide below 400° C. are given as follow :—

$$2[\mathrm{Fe}]+3(\mathrm{O})=[\mathrm{Fe_2O_3}]+194{,}400 \text{ calories.}^1$$
$$2[\mathrm{Fe}]+3(\mathrm{O})=[\mathrm{Fe_2O_3}]+192{,}200 \text{ calories.}^2$$
$$2[\mathrm{FeO}]+(\mathrm{O})=[\mathrm{Fe_2O_3}]+65{,}200 \text{ calories.}^1$$
$$2[\mathrm{FeO}]+(\mathrm{O})=[\mathrm{Fe_2O_3}]+63{,}700 \text{ calories.}^2$$
$$2[\mathrm{Fe_3O_4}]+(\mathrm{O})=3[\mathrm{Fe_2O_3}]+54{,}500 \text{ calories.}^2$$

Ferric Oxide as a Catalyst.—Ferric oxide possesses the power of catalytically promoting the combination of sulphur dioxide and oxygen at red heat. The action is perceptible at temperatures just above 400° C., attaining a maximum at 625° C. when 70 per cent. of the sulphur dioxide is converted into trioxide.[3] The origin of the ferric oxide is of considerable importance, that prepared from the hydroxide being particularly active. Admixture of copper oxide increases the efficiency, as does also the presence of arsenic at temperatures above 700° C.[4]

In commercial practice, the ferric oxide is obtained from pyrites cinder, and experience shows that its catalytic activity is greatest if the ferric oxide is used fresh and not first allowed to get cold.[5] It appears that if the air required for oxidation of the pyrites is dried previous to admission to the burners, the resulting mixture of sulphur dioxide and air is more sensitive to the action of the catalyst than is otherwise the case. Under highly favourable conditions 90 per cent. of the sulphur dioxide is converted into sulphur trioxide, and a conversion of 60 per cent. is quite readily obtained.

Owing to the high temperature required, however, there appears to be a loss of sulphur trioxide through dissociation when the process is carried out on a commercial scale. A process has therefore been patented according to which the conversion of the sulphur dioxide into trioxide is rendered practically complete by passing the partially converted gases emerging from the ferric oxide chamber through a second chamber containing platinum as catalyst.[6]

The manner in which the ferric oxide is able to function as a catalyst has been the subject of discussion. According to one theory, it is supposed to undergo alternate reduction to magnetic oxide and oxidation to ferric oxide ; thus :—

$$3\mathrm{Fe_2O_3}+\mathrm{SO_2}=2\mathrm{Fe_3O_4}+\mathrm{SO_3},$$
$$4\mathrm{Fe_3O_4}+\mathrm{O_2}=6\mathrm{Fe_2O_3}.$$

It has also been suggested that sulphur dioxide and oxygen combine with the ferric oxide to form ferric sulphate, which then dissociates into the trioxide, regenerating the ferric oxide. Thus :—

$$2\mathrm{Fe_2O_3}+6\mathrm{SO_2}+3\mathrm{O_2}=2\mathrm{Fe_2(SO_4)_3},$$
$$\mathrm{Fe_2(SO_4)_3}=\mathrm{Fe_2O_3}+3\mathrm{SO_3}.$$

A third theory[7] has been put forward by Keppeler, according to

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[1] Le Chatelier, *Compt. rend.*, 1895, 120, 623.
[2] Mixter, *Amer. J. Sci.*, 1913, (4), 36, 55.
[3] Lunge and Reinhardt, *Zeitsch. angew. Chem*, 1904, 17, 1041.
[4] Lunge and Pollitt, *ibid.*, 1902, 15, 1105.
[5] See *English Patents*, 17266 (1898), 24748 (1899).
[6] *English Patent*, 24748 (1899).
[7] Keppeler and his co-workers, *Zeitsch. angew. Chem.*, 1908, 21, 532, 577.

which the catalytic action is attributable to a physical cause, the gases being condensed on the surface of the ferric oxide and uniting under these conditions. This theory explains the similarity existing between the catalytic activities of ferric oxide and platinum, and harmonises very satisfactorily with the conclusions of Bone and Wheeler, relative to the catalytic activity of ferric oxide and other heated surfaces in the surface combustion of mixtures of hydrogen and oxygen.[1]

Many other reactions are known in which ferric oxide acts as a catalyser. Thus, it assists the decomposition of mercuric oxide at temperatures between 360° and 480° C.,[2] and the oxidation of carbon monoxide with steam, the reaction proceeding very slowly at 250° C. but rapidly at 400° C.[3]

It assists catalytically the conversion of sodium chloride into sodium sulphate when heated in a current of air along with finely divided pyrites.[4] It also accelerates the decomposition of potassium chlorate when heated with this salt, much in the same way as manganese dioxide has long been known to do. More chlorine is evolved during the decomposition, however, and under certain conditions the oxygen is evolved at an even lower temperature than when manganese dioxide is used.[5]

Polymorphism of Ferric oxide.—The yellow colour in certain bricks is stated to be due to a yellow modification of anhydrous ferric oxide rendered stable by alumina.[6]

It may well be, however, that the colour of ferric oxide is determined by the size of the grain rather than by any variation in molecular structure.[7] Thus, brown and violet samples of ferric oxide are converted into the yellowish red variety by alternate grinding and washing —processes which, in view of the chemical stability of ferric oxide, are hardly likely to effect a molecular transformation.

Hydrated ferric oxide, $Fe(OH)_3.Aq.$, occurs in nature in various stages of hydration, the best-known minerals being (see pp. 17–19) as follow :—

Turgite, $2Fe_2O_3.H_2O$.
Goethite, $Fe_2O_3.H_2O$.
Hydrogoethite, $3Fe_2O_3.4H_2O$.
Limonite, $2Fe_2O_3.3H_2O$.
Xanthosiderite, $Fe_2O_3.2H_2O$.
Limnite, $Fe_2O_3.3H_2O$.
Esmeraldaite, $Fe_2O_3.4H_2O$.

When heated with water under enormous pressures (some 5000 atmospheres) ferric oxide becomes hydrated.[8] At 42·5° C. it yields brown iron stone; at 42·5° to 62·5° C., Goethite, $Fe_2O_3.H_2O$, and at higher temperatures, a hydro-hæmatite, $2Fe_2O_3.H_2O$, resembling turgite in composition.[1]

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[1] See Bone and Wheeler, *Phil. Trans.*, 1906, A, 206, 1; also this series, Volume VII.

[2] Taylor and Hulett, *J. Physical Chem.*, 1913, 17, 565.

[3] Armstrong and Hilditch, *Proc. Roy. Soc*, 1920, A, 97, 265.

[4] Krutwig, *Rec. Trav. Chim.*, 1897, 16, 173.

[5] Hodgkinson and Lowndes, *Chem. News*, 1888, 58, 309; 1889, 59, 63; Mills and Donald, *Trans. Chem. Soc*, 1882, 41, 18; Fowler and Grant, *Trans. Chem. Soc.*, 1890, 57, 278. See also this series, Volume VII., Part I.

[6] Scheetz, *J. Physical Chem*, 1917, 21, 570; Tommasi, *Bull. Soc. chim*, 1882, (2), 38, 152.

[7] Wöhler and Condrea, *Zeitsch. angew. Chem.*, 1908, 21, 481.

[8] Ruff, *Ber.*, 1901, 34, 3417.

Ferric hydroxide, dried at 100° C., gradually becomes rehydrated upon prolonged exposure to a saturated atmosphere.[2] Although the above substances are usually described as hydrates of ferric oxide, it is by no means certain that all of them are to be regarded as definite chemical entities.[3] They are mostly hygroscopic substances, the amount of water they contain at any moment fluctuating with the temperature and humidity of the atmosphere. The task of determining precisely how much of the contained water is merely physically attached to the oxide, and how much is chemically combined with it, is not easy.

Precipitated ferric hydroxide becomes gradually dehydrated when its temperature is raised. At 55° C. it attains the composition $Fe_2O_3.3H_2O$, and with further rise in temperature, more water is gradually evolved until at about 385° C., a substance represented by the formula $10Fe_2O_3.H_2O$ is obtained, which remains constant in weight for several hours at 385° to 415° C. At 500° C. the oxide is perfectly dehydrated, and its weight remains constant.[4]

The *subhydrate*, $2Fe_2O_3.H_2O$, occurs in nature as the mineral turgite (see p. 17). It may be prepared in the laboratory[5] by boiling ferric hydroxide with distilled water for prolonged periods, when it becomes partially dehydrated and loses its gelatinous appearance. It still contains from 4 to 6 per cent. of water, approximating to a composition of $2Fe_2O_3.H_2O$. The same effect is produced by heating the hydroxide for 1000 to 2000 hours at 50° to 60° C., the resulting oxide having a brick-red appearance, and a density of 4·5, and generally resembling red hæmatite. It seems reasonable to suppose that the change may take place at still lower temperatures, given sufficient time, and it is thus unnecessary to postulate the need for high temperatures to account for the production of some of our deposits of red hæmatite.

The *monohydrate*, $Fe_2O_3.H_2O$, occurs in nature as the mineral Goethite (see p. 18), which is regarded as a definite crystalline hydroxide[6] and not as a colloid like limonite. The monohydrate may be prepared in the laboratory in the amorphous condition by the prolonged boiling of the brown precipitate resulting from the addition of alkali to ferric chloride solution.[7] The colour gradually changes from brown to brick-red, and the resulting hydrate is remarkably resistant to acid attack. Boiling concentrated nitric acid has but little effect, and even concentrated hydrochloric acid only attacks it after prolonged digestion at the boiling-point. After some hours of treatment with acetic acid at 100° C. a colourless colloidal solution is obtained, from which addition of a trace of sulphuric acid effects the precipitation of the insoluble monohydrate. If, however, the solution is prepared in the cold, it possesses a wine-red colour and reacts like a ferric salt.

[1] See Tommasi, *Ber.*, 1879, 12, 1929.

[2] Cross (*Chem. News*, 1883, 47, 239) continued his experiments for 192 days

[3] See Fischer, *Zeitsch. anorg. Chem.*, 1910, 66, 37 ; van Bemmelen, *Rec. Trav. Chim.*, 1899, 18, 86 ; van Bemmelen and Klobbie, *J. prakt. Chem.*, 1892, (2), 46, 497.

[4] Carnelley and Walker, *Trans. Chem. Soc.*, 1888, 53, 89 ; Ramsay, *J. Chem. Soc.*, 1877, 32, 395.

[5] Davies, *ibid.*, 1866, 19, 69.

[6] Fischer, *Zeitsch anorg. Chem.*, 1910, 66, 37, Posnjak and Merwin, *Amer. J. Sci.*, 1919, 47, 311.

[7] Saint Gilles, *Compt. rend.*, 1855, 40, 568, 1243 ; *Ann. Chim. Phys.*, 1856, (3), 46, 47. See also Bancroft. *J. Physical Chem.*, 1915, 19, 232.

When iron is exposed to moist air, it readily becomes coated with a light, friable, and porous mass of oxide, which is brown in colour, and is generally termed rust. Numerous analyses of rust have been published from time to time,[1] which prove that its composition varies according to the age and method of formation of the rust. When formed by exposure to ordinary air its composition corresponds fairly closely to the formula $Fe_2O_3.H_2O$.

The monohydrate has been obtained in crystalline form in several ways, such as, for example, by the action of concentrated potassium hydroxide solution upon potassium nitroprusside.[2]

When iron is attacked by fused sodium peroxide, dark red, tabular crystals of a monohydrate, $Fe_2O_3.H_2O$, are obtained, of density 3·8 at 27° C. The hydrate is magnetic, and when heated to low redness a magnetic form of anhydrous ferric oxide is obtained.[3]

Crystals of Goethite have been maintained under a pressure of 9500 atmospheres for 26 days at 15° C. without showing any loss of water, although almost all the water is expelled when the crystals are immersed in water for 7 days at 320° to 330° C. under a pressure of 135 atmospheres.[4]

An unstable variety of $Fe_2O_3.H_2O$ is obtained by partially dehydrating the dihydrate by exposure in a desiccator.

Ferrous acid, $Fe_2O_3.H_2O$, or $HFeO_2$, possesses the same empirical formula as the monohydrate, and is discussed on p. 129.

The *sesqui-hydrate*, $2Fe_2O_3.3H_2O$, is generally regarded as resulting when the normal trihydrate is allowed to dry in a vacuum. It occurs in nature as the mineral *limonite* (see p. 18), and is a valuable source of iron. It is probably not a chemical entity but a colloidal substance containing adsorbed water.[5]

A satisfactory explanation for the yellow colour of limonite has not as yet been offered. Possibly the colour is due to the adsorption of an iron salt, but this has not been proved.[6]

A substance having a composition corresponding to the *dihydrate*, $Fe_2O_3.2H_2O$, is obtained by dissolving reduced iron in hot, diluted sulphuric acid and heating until the acid begins to fume and the iron is transformed into a faintly red, crystalline powder. The acid is poured off and the precipitate shaken with sodium hydroxide solution and finally washed with water. The substance is formed as brownish plates of density 3·234 at 15° C.[7]

It is probably not a definite hydrate. It loses water when kept in a desiccator, yielding a substance corresponding in composition to the monohydrate, $Fe_2O_3.H_2O$, but which is not very stable, and is probably not the normal monohydrate.

The *trihydrate*, $Fe_2O_3.3H_2O$, or $Fe(OH)_3$, is the brown voluminous precipitate obtained on adding an alkali to a solution of a ferric salt. The reaction is delicate, 1 part of iron in 80,000 parts of water being detectable by the precipitate obtained if ammonia is the alkali employed.[1]

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[1] See p. 77, where analyses and references are given

[2] Roussin, *Ann. Chim. Phys.*, 1858, (3), 52, 285. See the criticism of van Bemmelen and Klobbie, *J. prakt. Chem*, 1892, (2), 46, 497.

[3] Dudley, *Amer. Chem. J.*, 1902, 28, 59. See also Brunck and Graebe, *Ber.*, 1880, 13, 725.

[4] Spezia, *Atti R Accad. Sci. Torino*, 1911, 46, 682.

[5] Fischer, *loc cit.*; Posnjak and Merwin, *Amer. J. Sci*, 1919, 47, 311.

[6] Bancroft, *J. Physical Chem.*, 1915, 19, 232

[7] Vesterberg, *Ber.*, 1906, 39, 2270. See also Weltzien, *Annalen*, 1866, 138, 129; Muck, *Jahresber.*, 1867, 20, 287.

A mixed solution of ferrous sulphate and hydrogen carbonate deposits ferric hydroxide upon standing, even in the dark.[2] Its heat of formation is

$$2[Fe]+3(O)+3H_2O=2[Fe(OH)_3]+191{,}150 \text{ calories.}^3$$

If the trihydrate is boiled with water for several hours it gradually assumes a brick-red colour, being converted into the monohydrate, $Fe_2O_3.H_2O$ (see p. 122). The trihydrate is readily soluble in acids yielding ferric salts. It also is slightly soluble in ordinary distilled water, namely, to the extent of 0·151 mgm. of $Fe(OH)_3$ per litre at 20° C.[4]

Freshly precipitated ferric hydroxide adsorbs arsenious acid from solution; the extent of adsorption is diminished by the presence of sodium hydroxide, but addition of sodium chloride appears to have no influence.[5] It has therefore been recommended as an antidote in cases of arsenic poisoning. The amount of adsorption is given by the expression

$$y=0{\cdot}631\times\sqrt[5]{x}$$

when y and x are the amounts of acid adsorbed and remaining in solution respectively. The following data illustrate the general agreement between the calculated and observed values of x:—

y	x (calculated)	x (observed)
0·251	0·010	0·010
0·415	0·123	0·107
0·549	0·498	0·495
0·712	1·826	1·898
0·824	3·740	3·875

Ferric hydroxide dissolves in fused sodium hydroxide,[6] and, if the latter is present in excess, lustrous needles and lamellæ of composition approximating to $20Fe_2O_3.32H_2O.3Na_2O$ are obtained. These dissolve readily in acids, and begin to lose water at 120° C., becoming anhydrous at dull red heat. The resulting product, $20Fe_2O_3.3Na_2O$, resembles specular hæmatite in appearance and is conceivably a solution of sodium ferrate in ferric oxide. By heating ferric hydroxide with sodium hydroxide to 110° C., a product resembling Goethite, $Fe_2O_3.H_2O$, is obtained, but again admixed with small quantities of sodium oxide.[6]

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[1] Curtman and St John, *J. Amer. Chem. Soc.*, 1912, 34, 1679; Hampe, *Chem. Zentr.*, 1889, 2, 906.

[2] Molisch, *Zeitsch. Kryst. Min.*, 1913, 53, 92.

[3] Thomsen, *Thermochemistry*, translated by Burke (Longmans, 1908), p. 265.

[4] Almkvist, *Zeitsch. anorg. Chem*, 1918, 103, 240.

[5] Biltz, *Ber*, 1904, 37, 3138. See Boswell and Dickson, *J. Amer. Chem. Soc.*, 1918, 40, 1793; Mecklenburg, *Zeitsch. physikal. Chem.*, 1913, 83, 609; Lockemann and Lucius, *ibid*, 1913, 83, 735; Lockemann, *Verh. Ges. deut. Naturforsch. Aertze*, 1911, 11, 25; Lockemann and Paucke, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 273; Taylor, *The Chemistry of Colloids* (Arnold, 1915).

[6] Rousseau and Bernheim, *Compt. rend.*, 1888, 106, 1530.

Ferric hydroxide dissolves in potassium hydroxide in the presence of ozone, yielding potassium perferrate.[1]

On passing a current of air into a hot, concentrated solution of sodium hydroxide containing ferric hydroxide in suspension, an appreciable quantity of iron passes into solution without colouring the liquid.[2] On standing for several days the liquid becomes turbid owing to separation of ferric hydroxide, but is readily clarified again by warming. Probably sodium ferrate is formed in solution.

Ferric hydroxide is readily soluble in mineral acids yielding the corresponding ferric salt, and in ferric chloride solution yielding oxy compounds which are acidic in their behaviour, decomposing carbonates, and can therefore hardly be termed *basic* chlorides.[3] It dissolves in aqueous oxalic acid to an extent directly proportional to the concentration of the acid, no definite basic oxalate being formed at 25° C. from solution.[4] It does not combine with carbon dioxide when freshly precipitated and suspended in water.[5]

It dissolves to a considerable extent in a concentrated solution of aluminium sulphate,[6] yielding a brown solution which may be evaporated to dryness without decomposition. Addition of water induces the formation of a basic salt, $3Fe_2O_3.SO_3.3H_2O$.

Inasmuch as the majority of ferric salts in the crystalline state are whitish, the question arises as to why ferric hydroxide should be brown.[7] Ferric hydroxide can be obtained as a white precipitate on adding a freshly prepared and concentrated solution of a ferric salt to cooled ammonium hydroxide solution, but it rapidly becomes brown—due, it has been suggested, to molecular condensation or aggregation. When kept under water for a year, ferric hydroxide changes in colour from brown to yellowish red, and about 30 per cent. becomes insoluble in dilute acids.[8] Possibly these changes are due to a similar cause.

A mineral having a composition corresponding to a *tetrahydrate*, $Fe_2O_3.4H_2O$, has been found as an inclusion in limonite in Esmeralda Country, Nevada, whence the name *Esmeraldaite* (see p. 19). It is glassy and brittle, but possesses a yellowish brown streak. Its density is 2·58. A substance of similar composition [9] is obtained when the voluminous precipitate of hydrated oxide, resulting from addition of ammonia to dilute ferric chloride solution, is allowed to dry in the air. It is vitreous in appearance, black in colour when viewed in mass, although thin sections appear red by transmitted light. Its density is 2·436 at 15° C. Pressure does not decompose it, but it loses water when placed in a desiccator.

Colloidal ferric hydroxide.—Ferric hydroxide may be obtained in colloidal solution [10] by adding 5 c.c. of 33 per cent. ferric chloride to a litre of boiling water and removing the chloride remaining, together with the hydrochloric acid, by dialysis.

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[1] Mailfert, *Compt. rend.*, 1882, 94, 860.

[2] Zirnité, *Chem. Zeit.*, 1888, 12, 355

[3] See p. 104; also Nicolardot, *Ann. Chim. Phys.*, 1905, 6, 334; Weyman, *J. Soc Chem. Ind.*, 1918, 37, 333T.

[4] Cameron and Robinson, *J. Physical Chem.*, 1909, 13, 157.

[5] Raikow, *Chem. Zeit.*, 1907, 31, 55, 87.

[6] Schneider, *Ber.*, 1890, 23, 1349; *Annalen*, 1890, 257, 359.

[7] Nicolardot, *Compt. rend.*, 1905, 140, 310.

[8] Tommasi and Pellizzari, *Bull Soc. chim.*, 1882, (2), 37, 196.

[9] Spring, *Rec Trav. Chim.*, 1898, 17, 222; *Bull. Soc. chim.*, 1899, (3), 21, 87.

[10] See this series, Volume I., pp. 78–86.

Another method consists in boiling a solution of ferric nitrate with copper filings or zinc dust. The ferric nitrate need not be specially isolated for the purpose, but may be made merely as an intermediate product during the course of the reaction—if, for example, iron filings containing copper are treated with concentrated nitric acid. After dilution and filtration, the solution is dialysed, whereby a deep red liquid is obtained, containing colloidal ferric hydroxide.[1]

By saturating a solution of ferric chloride with ammonium carbonate and purifying the solution thus obtained by dialysis, ferric hydroxide is readily obtained in the colloidal state,[2] or by dialysing the solution obtained by adding ammonia to a solution of ferric chloride in such small quantities at a time that the ferric hydroxide at first thrown out is completely dissolved on stirring. The clear, dark brown solution so obtained scarcely tastes of iron. The last traces of chlorine are not removed in this way, although the colloid is free from ammonium salts.[3]

When a 10 per cent. solution of ferric chloride is poured into excess of ammonia, the colloidal ferric hydroxide initially produced is coagulated by the ammonium chloride. On evaporating to dryness and washing with water, the ammonium salt washes out, and then the ferric hydroxide deflocculates, passing into subsequent wash waters as a red colloidal solution.[4]

On addition of a dilute solution of potassium permanganate to one of ferrous chloride, and subjecting to dialysis, the pure colloidal hydroxide is readily obtained.[5] The sol is also obtained by oxidising a solution of ferrous chloride containing one gram equivalent of $FeCl_2$ per litre with a 3 per cent. solution of hydrogen peroxide.[6]

The colloid, as usually prepared, is electro-positive in character, and may be precipitated from solution by electrolysis, by the addition of small quantities of electrolytes, or by the action of an oppositely charged colloid, such, for example, as (negative) arsenious sulphide, whereby the two electrical charges neutralise each other.[7] The smallest quantities of a few electrolytes required to precipitate colloidal ferric hydroxide from solution are given in the following table :—[8]

Electrolyte.	Concentration in Gram-molecules per Litre of Solution.	Electrolyte.	Concentration in Gram-molecules per Litre of Solution.
KNO_3 . .	0·0119	K_2SO_4 . .	0·00020
$\frac{1}{2}Ba(NO_3)_2$.	·0140	$MgSO_4$ . .	·00022
NaCl . .	·00925	$K_2Cr_2O_7$ . .	·00019
$\frac{1}{2}BaCl_2$ . .	·00964		

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[1] Cohen, *J. Amer. Chem. Soc.*, 1914, 36, 19.

[2] Dumansky, *J. Russ. Phys. Chem Soc.*, 1904, 36, 1067.

[3] Wobbe, *Chem. Zentr*, 1900, I., 165.

[4] Kratz, *J. Physical Chem.*, 1912, 16, 126. See Wright, *Trans. Chem. Soc.*, 1883, 43, 156.

[5] One gram equivalent of $KMnO_4$ in 600 c c., and one gram equivalent of $FeCl_2$ in 1000 c.c. Dilute to 2000 c c. Neidle and Crombie, *J. Amer. Chem. Soc*, 1916, 38, 2607.

[6] Neidle and Barab, *ibid.*, 1917, 39, 71.

[7] W. Biltz, *Ber.*, 1904, 37, 1095 Billiter, *Zeitsch physikal. Chem*, 1905, 51, 142.

[8] See Hardy, *Zeitsch physikal. Chem*, 1900, 33, 385; also Pappadà, *Zeitsch. Chem Ind. Kolloide*, 1911, 9, 233; Freundlich, *Zeitsch. physikal. Chem.*, 1903, 44, 129.

From the above it is clear that it is the negative ion which influences the precipitation most, the divalent ions being considerably more effective than the monovalent.

Non-electrolytes, even in concentrated solution, have usually no action on the colloid.

When the colloidal solution is boiled with Fehling's solution (made by mixing copper sulphate and alkaline sodium potassium tartrate solutions), the colloid is precipitated along with cuprous oxide.[1]

It is possible also to prepare colloidal ferric hydroxide with a negative charge. This may be done by adding slowly 100 c.c. of 0·01-normal ferric chloride solution to 150 c.c. of 0·01-normal sodium hydroxide, the mixture being continuously shaken during the process.[2]

Ferric hydroxide is not unique in this respect, for stannic hydroxide has likewise been prepared both as a positive [3] and a negative [4] colloid.

Negative colloidal ferric hydroxide may be converted into the positive colloid by adding it to a very dilute solution of sodium hydroxide (0 005-normal) with constant shaking. In order to account for this amphi-electrical behaviour, it is suggested that the potential difference at the surface of colloidal particles is due to adsorption of ions from the solution. Hence the sign depends upon whether cations or anions are in excess in the layers nearest the particles.[5]

The composition and nature of precipitated ferric hydroxide have been made the objects of considerable research. When precipitated from aqueous solutions the hydroxide contains very varying quantities of water, and the problem has been to determine in what manner that water is associated with the complex. This has been attempted in a variety of ways, such as by measuring the rate of dehydration at constant temperature [6]; by studying the dehydration at different temperatures [7]; by determining the vapour pressures during dehydration,[8] etc.[9] A particularly useful method is that of Foote and Saxton,[10] which consists in freezing the precipitate at low temperatures and calculating the quantity of water physically attached to it by observing dilatometrically the change in volume undergone in consequence of the expansion of this water in forming ice. If, in the case of ferric hydroxide, this amount is subtracted from the total amount, as determined by finally heating to redness and weighing the anhydrous ferric oxide, Fe_2O_3, the difference gives the weight of water chemically combined.

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[1] Dumansky, *loc cit.*

[2] Powis, *Trans. Chem. Soc*, 1915, 107, 818. See also Fischer, *Biochem. Zeitsch.*, 1910, 27, 223.

[3] Ghxelli, *Kolloid Zeitsch*, 1913, 13, 194.

[4] Biltz, *Ber.*, 1904, 37, 1095.

[5] Powis, *loc cit.* Compare Pauli and Matula, *Kolloid Zeitsch*, 1917, 21, 49.

[6] Ramsay, *J. Chem. Soc*, 1877, 32, 395; Tschermak, *Zeitsch. physikal Chem.*, 1905, 53, 349; *Zeitsch anorg. Chem.*, 1909, 63, 230; *Monatsh*, 1912, 33, 1151.

[7] Carnelley and Walker, *Trans Chem. Soc*, 1888, 53, 59; Baikow, *Kolloid Zeitsch*, 1907, 2, 374.

[8] van Bemmelen, *Zeitsch anorg. Chem.*, 1893, 5, 467; 1897, 13, 233; 1899, 20, 185; Zsigmondy, Bachmann, and Stevenson, *ibid.*, 1912, 75, 189; Bachmann, *ibid.*, 1913, 79, 202; Anderson, *Zeitsch. physikal. Chem*, 1914, 88, 191.

[9] See Foote, *J. Amer. Chem. Soc*, 1908, 30, 1388; Muller Thurgau, from Fischer, *Beitr. Biol. Pflanz*, 1911, 10, 200, 232; Fischer, *Biochem. Zeitsch*, 1909, 18, 58; 1909, 20, 143; *Kolloid Zeitsch.*, 1911, 8, 291; *Beitr Biol Pflanz*, 1911, 10, 133.

[10] Foote and Saxton, *J. Amer. Chem. Soc.*, 1916, 38, 588.

Application of certain of these methods, and particularly the last-named, to precipitated ferric hydroxide, indicates that its contained water is present in three ways, namely :—

(*a*) Very loosely attached, which readily freezes out at about −5° C.

(*b*) More intimately associated with the precipitate, and considerably more difficult to remove. It is known as *capillary water* and requires a temperature of the order of −30° C. to effect its complete removal by freezing.

(*c*) Chemically combined. This amount corresponds to the formula $Fe_2O_3.4{\cdot}25\ H_2O$ for the hydroxide.[1]

Attempts to determine the molecular weight of colloidal ferric hydroxide lead to very high values. Thus, a colloidal solution prepared by addition of ammonium carbonate to ferric chloride solution was purified by dialysis, and the freezing-point determined of that portion which would not pass through a collodion membrane. The point was only slightly lower than that of the filtrate, indicative of a molecular weight of 3120 for the colloid.[2]

A result of this kind is uncertain, however, owing to the exceedingly small difference in temperature to be registered. Thus Kraft [3] found a colloidal solution containing 3·38 per cent. of ferric hydroxide, and 0·098 per cent. of ferric chloride froze at a temperature within 0·001° C. of the freezing-point of pure water. Other investigators [4] have sometimes obtained negative and at other times positive differences in the freezing-points.

Similar difficulties are encountered when attempts are made to determine the molecular weight by means of measurements of the osmotic pressures of colloidal solutions,[5] the observed pressures being exceedingly small, thus indicating a high molecular weight, but one of uncertain value.

For particulars of further researches on colloidal ferric hydroxide the reader is referred to the subjoined references.[6]

The heat of coagulation of colloidal ferric hydroxide with potassium oxalate has been studied by Doerinckel.[7]

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[1] Foote and Saxton, *loc. cit.* This value is supported by the earlier results of Ruff (*Ber.*, 1901, 34, 3417), who found that ferric hydroxide, after freezing at −10° C. and −185° C., had the composition $Fe_2O_3.4{\cdot}2H_2O$.

[2] Dumansky, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 232; *J. Russ. Phys. Chem. Soc.*, 1911, 43, 546; Duclaux (*J. Chim. phys.*, 1909, 7, 405) found a molecular weight of 115,000.

[3] Kraft, *Ber.*, 1899, 32, 1608.

[4] Malfitano and Michel, *Compt rend*, 1906, 143, 1141.

[5] See van der Feen, *Chem. Weekblad*, 1916, 13, 453.

[6] Carli, *Zeitsch. physikal. Chem.*, 1913, 85, 263; Kuriloff, *Zeitsch. anorg. Chem.*, 1912, 79, 88; Michel, *Compt. rend.*, 1908, 147, 1052, 1288; Malfitano and Michel, *ibid.*, 1908, 147, 803; 1908, 146, 338; 1907, 145, 185, 1275; Giolitti, *Gazzetta*, 1908, 38, 11, 252; Foote, *J. Amer. Chem. Soc.*, 1908, 30, 1388; A. Muller, *Zeitsch. anorg. Chem*, 1908, 57, 311; Dumansky, *J. Russ. Phys. Chem. Soc.*, 1907, 39, 743; 1906, 38, 595; 1905, 37, 213, 502; Fischer, *Habilitations-schrift, Breslau*, 1907; Oechsner, *Bull. Acad. roy. Belg.*, 1907, p. 34; Giolitti, *Gazzetta*, 1906, 36, ii 157; Giolitti and Battisti, *ibid*, 1906, 36, ii 433; Duclaux, *Compt. rend.*, 1906, 143, 296; Malfitano, *Compt. rend.*, 1906, 142, 1277, 1418; 1906, 143, 171; 1905, 141, 660, 680, 1245; Tribot and Chrétien, *Compt. rend.*, 1905, 140, 144; Linder and Picton, *Trans. Chem. Soc.*, 1905, 87, 1918; van Bemmelen, *Zeitsch. anorg. Chem.*, 1899, 20, 185; *Rec. Trav. Chim.*, 1888, 7, 106; Ewan, *Proc Roy. Soc*, 1894, 56, 286, Schneider, *Annalen*, 1890, 257, 359; Sabanéeff, *J. Russ Phys. Chem. Soc*, 1889, 21, 515, Grimaux, *Compt. rend*, 1884, 98, 105, 1485, 1578; de la Source, *Compt. rend.*, 1880, 90, 1352.

[7] Doerinckel, *Zeitsch. anorg. Chem*, 1910, 66, 20

Ferrites, $MFeO_2$.

Ferric oxide unites with many bases to form *ferrites*, to which the general formula $M_2O.Fe_2O_3$, or $MFeO_2$, is given. The free acid $HFeO_2$ possesses the same empirical formula as the monohydrate of ferric oxide, $Fe_2O_3.H_2O$.

Ferrous acid, $HFeO_2$, is obtained[1] by the action of water on sodium ferrite, $NaFeO_2$. It has the same crystalline form and transparency as the sodium salt, but differs from Goethite in that it begins to lose water below 100° C., whereas Goethite is stable even at 300° C.

Calcium ferrite, $Ca(FeO_2)_2$, is formed as deep red or nearly black crystals[2] by heating together ferric oxide and calcium oxide.

It also results on adding limewater to a neutral solution of ferric chloride and igniting the resulting brown precipitate.[3] It appears to dissociate at its melting-point. A basic ferrite, $Ca(FeO_2)_2.CaO$, is produced as black crystals on heating finely powdered ferric oxide and calcium carbonate at temperatures considerably below 1385° C. Three other basic ferrites have been described,[4] namely $Ca(FeO_2)_2.2CaO$,[4] $2Ca(FeO_2)_2.CaO$,[4] and $3Ca(FeO_2)_2.2CaO$,[5] but the existence of these has been disputed.[2, 6]

Cobalt ferrite, $Co(FeO_2)_2$, is obtained by addition of normal sodium hydroxide solution to a mixed solution of cobalt nitrate and ferric chloride, and igniting. It is a black powder, magnetic when cold, but non-magnetic above 280° to 290° C.[7]

Cupric ferrite, $Cu(FeO_2)_2$ is obtained[8] by adding black copper oxide to neutral ferric chloride solution, and igniting. It also results[9] by heating copper oxide and ferric oxide to a high temperature, the ferrite being separated from uncombined oxide by making use of its density and magnetic properties. It is strongly magnetic.

Cuprous ferrite, $CuFeO_2$, occurs in nature as the mineral *delafossite* (see p. 20). It is not magnetic, is easily fusible, and readily soluble in hydrochloric or sulphuric acid. The crystals are tetragonal, possibly isomorphous with the sodium salt.[10] It is obtained artificially by melting together cuprous and ferric oxides in a current of nitrogen. It then results as a crystalline mass, faintly magnetic.[11]

Ferrous ferrite, $Fe(FeO_2)_2$, is more commonly known as magnetite, Fe_3O_4 (see p. 12).

Magnesium ferrite, $Mg(FeO_2)_2$. occurs in nature as *magnesio-ferrite* (see p. 15) and crystallises in the cubic system. It may be prepared in crystalline form by heating ferruginous magnesia to redness in a current of air and hydrogen chloride. It also results when sodium or potassium hydroxide is added to a solution of magnesium sulphate and ferric chloride, and the precipitate ignited.[1] It is then obtained as a brown magnetic powder.

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[1] van Bemmelen and Klobbie, *J. prakt. Chem.*, 1892, (2), 46, 497.
[2] Sosman and Merwin, *J. Washington Acad. Sci.*, 1916, 6, 532.
[3] List, *Ber.*, 1878, 11, 1512.
[4] Hilpert and Kohlmeyer, *Ber.*, 1909, 42, 4581.
[5] Campbell, *J. Ind. Eng. Chem.*, 1915, 7, 835.
[6] Campbell, *ibid.*, 1919, 11, 116.
[7] Elliot, *Magnetic Combinations* (Gottingen, 1862); Hilpert, *Ber.*, 1909, 42, 2248.
[8] List, *Ber.*, 1878, 11, 1512; Hilpert, *ibid.*, 1909, 42, 2248.
[9] Walden, *J. Amer. Chem. Soc.*, 1908, 30, 1350.
[10] Rogers, *Amer. J. Sci.*, 1913, (4), 35, 290.
[11] Hilpert, *Ber.*, 1909, 42, 2248.

Nickel ferrite, $Ni(FeO_2)_2$, is obtained on addition of potassium hydroxide to a mixed solution of a nickel salt and ferric chloride,[2] and igniting. It is a brown substance, strongly magnetic.

Potassium ferrite, $KFeO_2$, is prepared in an analogous manner to the sodium salt (*vide infra*), but crystallises in regular octahedra.[3]

Sodium ferrite, $NaFeO_2$, is obtained [4] by continued heating of ferric oxide in concentrated sodium hydroxide solution, and by heating ferric oxide with fused sodium carbonate or chloride. The salt crystallises in hexagonal plates, which, when treated with water, yield ferrous acid, $HFeO_2$.

Zinc ferrite, $Zn(FeO_2)_2$ or $ZnO.Fe_2O_3$, occurs in nature as *franklinite* (see p. 14) and may be artificially prepared in the laboratory in a variety of ways,[5] such as by fusing an intimate mixture of the sulphates of sodium, zinc, and ferric iron at cherry-red heat, and extracting the melt with boiling water. Any basic zinc sulphate is removed with dilute acetic acid. Crystalline zinc ferrite also results when zinc chloride is heated in moist air with ferric chloride or hæmatite. The zinc chloride may be replaced by the corresponding fluoride.[6]

As obtained by these methods crystalline zinc ferrite closely resembles the natural franklinite. It crystallises in regular octahedra, small crystals being reddish brown and translucent, whilst the larger ones are opaque. Their hardness is 6·5 and density 5·33, the corresponding values for the mineral being H=5·5 to 6·5 and D=5 to 5·2 respectively. The crystals are not magnetic, are resistant to heat, and are but slowly attacked by acids. The natural mineral is magnetic, but this is attributed to impurities.[6]

Ferrates, M_2FeO_3.

Although the dioxide FeO_2 has not been isolated,[7] certain compounds of it with basic metallic oxides are known, and designated as ferrates.

Barium ferrate, $BaFeO_3$, is best produced by heating a mixture of ferric and barium hydroxides to 600° C. in a current of oxygen.[8] It is a friable, black, amorphous substance, stable up to about 650° C. Cold water decomposes it slowly, warm water somewhat more rapidly, with evolution of oxygen. Acids readily effect its decomposition, yielding barium and ferric salts. If hydrochloric acid is used, free chlorine and oxygen are simultaneously liberated.

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[1] List, *Ber.*, 1878, 11, 1512.

[2] List, *loc. cit.*

[3] van Bemmelen and Klobbie, *loc. cit.*

[4] Schaffgotsch, *Pogg. Annalen*, 1837, 43. 117; Salm Horstmar, *J. prakt. Chem*, 1852, 55, 349; van Bemmelen and Klobbie, *J. prakt. Chem.*, 1892, (2), 46, 497.

[5] Ebelmen, *Ann. Chim. Phys.*, 1851, (3), 33, 47; Daubrée, *Compt. rend.*, 1854, 39, 135; List, *Ber.*, 1878, 11, 1512

[6] Gorgeu, *Compt rend.*, 1887, 104, 580.

[7] See Manchot and Wilhelms (*Ber.*, 1901, 34, 2479; *Annalen*, 1902, 325, 105), whose experiments suggest the formation of Fe_2O_5. The action of hydrogen peroxide on ferrous chloride, ferrous or ferric hydroxide, or ferric chloride results in the formation of a pale red substance which is very unstable—so much so that its composition cannot be established with certainty. It *may* be FeO_2 (Pellini and Meneghini, *Gazzetta*, 1909, 39, i. 381; *Zeitsch anorg. Chem.*, 1909, 62, 203).

[8] Moeser and Borck, *Ber.*, 1909, 42, 4279.

Strontium ferrate, $SrFeO_3$, is produced by evaporating to dryness a mixed solution of ferric and strontium nitrates, and heating in a current of oxygen to a temperature not exceeding 600° C. until no more oxides of nitrogen are evolved.[1] It is also produced by suspending freshly precipitated ferric hydroxide in a concentrated solution of strontium hydroxide, and heating the resulting brownish precipitate to 300° C. It resembles the barium salt.

Perferrates, M_2FeO_4.

Attempts to prepare iron trioxide have hitherto proved abortive, but compounds of this oxide with basic metallic oxides are known, and designated as perferrates.

Barium perferrate,[2] $BaFeO_4.H_2O$, is obtained as a purple precipitate on addition of barium chloride to a solution of the calcium salt [3] or of barium chromate to a solution of sodium perferrate.[4]

Barium perferrate is the most stable salt of the series. It is insoluble in water, and its suspension in water may be boiled without decomposition. It is practically unaffected by dilute sulphuric acid in the cold. Apart from this it is readily attacked by acids, even carbonic; dilute hydrochloric or nitric acid decomposes it instantly, yielding salts of barium and iron.[5] When treated in the cold with very dilute hydrochloric acid, chlorine is evolved and the solution assumes a red colour, probably due to the presence of the FeO_4'' ion.[6] Acetic acid reacts similarly. On boiling, the solution evolves oxygen, and becomes colourless.

The composition of barium perferrate is proved iodometrically by means of the reaction [5]

$$2BaFeO_4+8KI+16HCl=2BaCl_2+2FeCl_2+8KCl+8H_2O+4I_2.$$

Calcium perferrate, $CaFeO_4$, is obtained by adding ferric chloride solution to bleaching powder, and boiling.[3] It is soluble in water.[7]

Potassium perferrate, K_2FeO_4, may be prepared in a variety of ways. It results when chlorine acts on ferric hydroxide suspended in potassium hydroxide solution:—

$$2Fe(OH)_3+10KOH+3Cl_2=2K_2FeO_4+6KCl+8H_2O.$$

The chlorine in the above reaction may be replaced by ozone [8] or sodium hypochlorite.[9]

On adding a piece of potassium hydroxide to ferric chloride solution in a test-tube, together with a few drops of bromine, a brown mass is obtained which dissolves in water, yielding the intense red colour characteristic of potassium perferrate.[10]

Potassium perferrate crystallises from the warm solution in microscopic black prisms or sharp pyramids, and is isomorphous with potassium sulphate, selenate, and chromate.[1] The solution is stable, and may be kept for days without decomposition,[2] particularly if a small quantity of a mineral salt is present. Acids, ammoniacal salts, and reducing agents readily effect its decomposition.

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[1] Moeser and Borck, *Ber.*, 1909, 42, 4279.

[2] Rose, *Pogg. Annalen*, 1843, 59, 315.

[3] Bloxam, *Chem. News*, 1886, 54, 43.

[4] Rosell, *J. Amer. Chem. Soc*, 1895, 17, 760.

[5] de Mollins, *Ber*, 1871, 4, 626.

[6] Baschieri, *Gazzetta*, 1906, 36, ii. 282.

[7] Not *insoluble*, as stated by Frémy

[8] Mailfert, *Compt. rend.*, 1882, 94, 860.

[9] Forster, *Ber*, 1879, 12, 846.

[10] Bloxam, *Chem News*, 1886, 54, 43; Moeser, *Arch. Pharm*, 1895, 233, 521.

Sodium perferrate, Na_2FeO_4, may be prepared in an analogous manner to the potassium salt already described. It also results when ferric oxide is fused with sodium peroxide and the cooled mass treated with ice. Sodium perferrate then passes into solution.[3]

Strontium perferrate, $SrFeO_4$, is obtained [4] by double decomposition of the potassium salt and a saturated, neutral solution of strontium bromide. The precipitate is washed with alcohol and ether. Obtained in this manner, the strontium ferrate is not pure, but contains admixed ferric oxide. It is deep red in colour, slightly soluble in water, and readily decomposed by acids. It is useful for preparing aqueous solutions [4] of the perferrates of the less common alkali metals—lithium, rubidium, cæsium—of calcium and magnesium.

IRON AND SULPHUR.

Subsulphides.—Several supposedly subsulphides of iron have been described from time to time, namely Fe_8S,[5] Fe_2S,[6] and Fe_4S_3. The last-named is produced when iron is heated in an atmosphere of carbon disulphide vapour, at 1300° to 1400° C., and allowed to cool in the disulphide vapour.[7] It is a crystalline body of density 6·96, and soluble in dilute mineral acids evolving hydrogen sulphide and hydrogen. It does not alter when exposed to air, and is oxidised only with difficulty.

Ferrous sulphide, FeS, occurs in nature as the mineral *troilite* (see p. 23), which is found in nodules in the majority of meteorites containing iron. When crystalline it appears to belong to the hexagonal system, and has probably been formed in the presence of excess of iron.[8] It may be obtained by the direct union of iron and sulphur at red heat. If the iron is in the form of filings and is intimately mixed with the sulphur, the mass becomes incandescent when once the reaction has been started. Synthetic iron disulphide, heated above 700° C., is converted into ferrous sulphide.[9]

When iron pyrites, FeS_2, is heated to bright redness in the absence of air or in hydrogen, it yields ferrous sulphide.[10] In crystalline form ferrous sulphide is produced by passing hydrogen sulphide over ferrous oxide at high temperatures [11] or over metallic iron at dull red heat.[12]

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[1] Retgers, *Zeitsch. physikal. Chem.*, 1892, 10, 529.

[2] Denham Smith's statement (*Phil. Mag.*, 1843, (3), 23, 217) that it turns green on standing is incorrect (Rosell, *J. Amer. Chem. Soc.*, 1895, 17, 760). Smith was misled by his solution containing manganese as an impurity.

[3] Rosell, *loc. cit.*

[4] Eidmann and Moeser, *Ber.*, 1903, 26, 2290.

[5] Arvfedson, *Pogg. Annalen*, 1824, 1, 72.

[6] *Ibid.*, p. 806.

[7] Gautier and Hallopeau, *Compt. rend.*, 1889, 108, 806.

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

[9] Gedel, *Chem. Zentr.*, 1905, II., 445, from *J. Gasbeleuchtung*, 1905, 48, 400.

[10] See Rose, *Pogg. Annalen*, 1825, 5, 533; Plattner, *ibid.*, 1839, 47, 369; Schaffgotsch, *ibid.*, 1840, 50, 533; Loebe and Becker, *Zeitsch. anorg. Chem.*, 1912, 77, 301.

[11] Sidot, *Compt. rend.*, 1868, 66, 1257.

[12] Lorenz, *Ber.*, 1891, 24, 1504.

If iron wire is used exposed in a bundle to the hydrogen sulphide, it readily becomes encrusted with tiny crystals, silver-white in appearance when first prepared. The crystals[1] are regarded as belonging to the hexagonal system.

The same reaction appears to take place at the ordinary temperature when iron and sulphur are brought into contact under enormous pressures, namely of the order of 6500 atmospheres. The product resembles ordinary ferrous sulphide in that it is homogeneous under the microscope, and evolves a continuous stream of hydrogen sulphide when immersed in dilute sulphuric acid.[2]

Ferrous sulphide has a bluish black appearance, reminiscent of that of magnetic oxide, but it is not magnetic. Density 4·67. It is stable when heated in hydrogen or in the absence of air, but when heated in air it readily oxidises to ferrous sulphate, whilst at red heat all the sulphur is expelled, red ferric oxide remaining.

When exposed to steam at red heat ferrous sulphide is decomposed, yielding hydrogen, hydrogen sulphide, and ferroso-ferric oxide.[3] Thus :—

$$3FeS+4H_2O=Fe_3O_4+3H_2S+H_2.$$

At higher temperatures sulphur dioxide and sulphur are also formed.

When heated in a current of chlorine, ferric chloride and sulphur chloride distil over.[4]

When heated in a sealed tube at 150° to 200° C. with thionyl chloride, ferrous sulphide is oxidised to ferric chloride. Thus :—[5]

$$6FeS+16SOCl_2=6FeCl_3+8SO_2+7S_2Cl_2.$$

Ferrous sulphide is reduced when heated with manganese, yielding metallic iron :—

$$FeS+Mn=MnS+Fe,$$

the reaction being exothermic. This reaction is of great practical importance in connection with the desulphurisation of steel.[6] Liquid ferrous sulphide freezes at 1171° C.,[7] and melts at 1187° C.[8] The heat of formation of ferrous sulphide from iron and sulphur has been determined as :—

$$[Fe]+[S]=[FeS]+23,070 \text{ calories.}^9$$
$$[Fe]+[S]=[FeS]+18,800 \text{ calories.}^{10}$$

When heated to about 130° C., both ordinary commercial ferrous sulphide and meteoric troilite undergo a polymorphic change,[11] and, on cooling, a break in the cooling curve is observed at this point. Synthetic ferrous sulphide which does not contain any excess of free iron exhibits no such break, although with 7 per cent. of free iron the transition point is very marked at 138° C., and further addition of iron does not change it.[1] It appears, therefore, that the excess of iron catalytically assists the change in the case of synthetic ferrous sulphide. Troilite, on the other hand, does not contain excess of iron, but possibly its carbon content behaves catalytically in an analogous manner. Ferrous sulphide, stable at ordinary temperatures, is thus known as the α variety, that above 130° C. being termed the β variety. When heated to 298° C. a second polymorphic transformation occurs.[2]

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[1] Groth, see Lorenz, *loc. cit.*; Linck, *Ber.*, 1899, 32, 881.

[2] Spring, *Ber.*, 1883, 16, 999.

[3] Gautier, *Compt. rend.*, 1906, 142, 1465; 1901, 132, 189; Regnault, *Ann. Chim. Phys.*, 1836, (2), 62, 379.

[4] Rose, *Pogg. Annalen*, 1837, 42, 540.

[5] North and Conover, *J. Amer. Chem. Soc.*, 1915, 37, 2486.

[6] See this volume, Part III.

[7] Friedrich, *Metallurgie*, 1908, 5, 23, 50; 1907, 4, 479.

[8] Biltz (*Zeitsch. anorg. Chem.*, 1908, 59, 273) heated precipitated ferrous sulphide in nitrogen and obtained the value 1197°±2°.

[9] Parravano and de Cesaris, *Gazzetta*, 1917, 47, i. 144 (for reduced iron). Berthelot found, for the precipitated sulphide 24,000 calories, and Thomsen 23,780 calories.

[10] Mixter, *Amer. J. Sci.*, 1913, (4), 36, 55.

[11] Le Chatelier and Ziegler, *Bull. Soc. Encouragement Ind.*, 1902, p. 368; Treitschke and Tammann, *Zeitsch. anorg. Chem.*, 1906, 49, 320; Rinne and Boeke, *ibid.*, 1907, 53, 338.

As ordinarily prepared, ferrous sulphide readily dissolves in dilute sulphuric or hydrochloric acid, evolving hydrogen sulphide—a reaction that affords a convenient laboratory method of preparing the gas. When pure, however, ferrous sulphide dissolves extremely slowly in the cold acids. The presence of free iron acts as an accelerator of the reaction, the nascent hydrogen produced by its solution in acid effecting the reduction of the adjacent particles of ferrous sulphide to hydrogen sulphide and metallic iron.[3]

Hydrated ferrous sulphide, $FeS.Aq.$, is readily obtained as a bulky black precipitate on adding an alkali sulphide to a solution of a ferrous salt. If a ferric salt is employed, it is reduced to the ferrous condition with simultaneous precipitation of sulphur. Thus :—

$$FeCl_2+(NH_4)_2S=FeS+2NH_4Cl,$$
$$2FeCl_3+3(NH_4)_2S=2FeS+6NH_4Cl+S.$$

Hydrated ferrous sulphide is slightly soluble in water, yielding a greenish solution. From electric conductivity measurements its solubility has been calculated[4] as $70{\cdot}1\times10^{-6}$ gram-molecules per litre.

Ferrous sulphide is insoluble in aqueous caustic soda or potash, although the mixture of ferrous sulphide and sulphur formed on adding ammonium sulphide to ferric chloride yields a dark green solution.[5]

Addition of dilute acid causes the evolution of hydrogen sulphide, a ferrous salt passing into solution. For this reason ferrous sulphide cannot be completely precipitated by passage of hydrogen sulphide through a neutral solution of a ferrous salt of a mineral acid, as the reaction is reversible, according to the equation :—

$$FeX+H_2S\rightleftharpoons FeS+H_2X.$$

In acid solution—for example, sulphuric acid—no precipitate is obtained unless the pressure of the hydrogen sulphide is increased. The greater the concentration of the acid the higher must be the pressure of the hydrogen sulphide.[6]

Ferrous sulphide may, however, be precipitated from solutions of ferrous salts in the presence of sodium acetate—a fact that was known to Gay-Lussac—and even from ferrous acetate in the presence of acetic acid, and from solutions of iron in citric or succinic acids.[7]

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[1] Rinne and Boeke, *loc. cit.*

[2] Loebe and Becker, *Zeitsch anorg. Chem.*, 1912, 77, 301.

[3] Lipschitz and Hasslinger, *Monatsh* , 1905, 26, 217.

[4] Weigel, *Zeitsch. physikal. Chem.*, 1907, 58, 293.

[5] Konschegg and Malfatti, *Zeitsch. anal. Chem.*, 1906, 45, 747.

[6] Padoa and Cambi, *Atti R. Accad. Lincei*, 1906, (5), 15, ii. 787 ; Bruni and Padoa, *ibid.*, 1905, (5), 14, ii. 525.

[7] Winderlich, *Zeitsch. physikal. Chem. Unterr.*, 1917, 30, 254.

Ferrous sulphide is oxidised by acidulated hydrogen peroxide solution, yielding ferric sulphate or hydrolysed products of this salt.[1] With ammoniacal zinc chloride no reaction occurs at the ordinary temperature, but at 160° to 170° C. in a sealed tube ferrous hydroxide and zinc sulphide are produced.[2]

Ferrous sulphide unites with other metallic sulphides to form stable double compounds. Many of these occur in nature as minerals, a few of the more important being *pyrrhotite* or *magnetic pyrites*, $5FeS.Fe_2S_3$ (see p. 23); *Pentlandite*, $2FeS.NiS$; *marmatite*, $FeS.4ZnS$; and *Daubreelite*, $FeS.Cr_2S_3$.

These and other more or less stable sulphides have been prepared in the laboratory. Thus $3FeS.2MnS$ is formed when ferrous and manganous sulphides are fused together. It melts at 1362° C., and forms solid solutions in all proportions with manganous sulphide.[3]

$FeS.Cr_2S_3$ results[4] on heating a mixture of iron, chromium hydroxide, and sulphur, as a black insoluble compound.

$FeS.Al_2S_3$[5] results when ferrous sulphide or pyrites is reduced with metallic aluminium. Thus :—

$$4FeS+2Al=FeS.Al_2S_3+3Fe,$$

and

$$2FeS_2+2Al=FeS.Al_2S_3+Fe.$$

On melting gold and iron together in the presence of sulphur, $FeS.Au_2S$ is obtained.[6]

A study of the freezing-point curves for mixtures of ferrous and cuprous sulphides appears to indicate the existence of three compounds, namely :—

$2Cu_2S.FeS$, which is stable at all temperatures below the freezing-point ;

$3Cu_2S.2FeS$, which undergoes a change at 180° to 230° C., metallic copper being set free, and a product rich in sulphur remaining ;

$2Cu_2S.5FeS$, which breaks up into the first compound and free ferrous sulphide at temperatures between 500° and 600° C.[7]

On calcining sodium thiosulphate with ferrous oxalate, $Na_2S.2FeS$ is obtained as bronze-coloured prisms.[8] The corresponding potassium compound, $K_2S.2FeS$, is formed on reducing potassium ferric sulphide, $K_2S.Fe_2S_3$, with hydrogen ; or by heating iron (1 part) with sulphur (5 parts) and potassium carbonate (5 parts). It yields needle-shaped crystals or thick tablets, resembling potassium permanganate in appearance.[9]

Ferrous thio-antimonite, $3FeS.Sb_2S_3$, or $Fe_3Sb_2S_6$, is obtained on precipitation of a ferrous salt with potassium thio-antimonite (see p. 194).

Hydrated ferric sulphide,[10] $Fe_2S_3.Aq.$, is readily produced by treating moist ferric hydroxide (or the hydroxide suspended in water) with hydrogen sulphide :—[1]

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[1] Hernández, *Anal. Fis. Quim.*, 1908, 6, 476.

[2] Stokes, *J. Amer. Chem. Soc.*, 1907, 29, 304.

[3] Rohl, *Iron Steel Inst. Carnegie Mem*, 1912, 4, 28.

[4] Groger, *Sitzungsber. K. Akad. Wiss. Wien*, 1880, (2), 81, 531.

[5] Houdard, *Compt. rend.*, 1907, 144, 801; Ditz, *Metallurgie*, 1907, 4, 786.

[6] Maclaurin, *Trans. Chem Soc*, 1896, 69, 1269.

[7] Bornemann and Schreyer, *Metallurgie*, 1909, 6, 619.

[8] Brünner, *Arch. Sci. Phys. Nat*, 1865, 22, 68.

[9] Schneider, *Pogg. Annalen*, 1869, 136, 460; Preis, *J. prakt. Chem.*, 1869, 107, 10. See also Malfatti, *Zeitsch. anal. Chem*, 1909, 48, 352.

[10] The literature dealing with this substance contains many conflicting statements. The data here given appear to be well established, however.

$$2Fe(OH)_3+3H_2S=Fe_2S_3+3H_2O.$$

It is thus produced during the commercial purification of coal gas from sulphuretted hydrogen.[2] In the laboratory preparation of the pure substance the reaction should be continued for several hours in the absence of air, the precipitated sulphide being black when the reaction is complete.[3]

A precipitate of ferric sulphide is also obtained when ammonium sulphide is added to a solution of a ferric salt, the alkali remaining in excess.[4] If, however, the ferric salt is present in excess, the precipitate appears to consist of a mixture of ferrous sulphide and free sulphur. As obtained by either of the foregoing methods, the sulphide is hydrated and unstable in air. Dilute hydrochloric acid decomposes it completely into ferrous chloride, with evolution of hydrogen sulphide and a simultaneous deposition of sulphur. When boiled with water it yields ferric hydroxide and hydrogen sulphide.

In the moist condition in the absence of air, or in the presence of excess hydrogen sulphide, ferric sulphide is transformed into a mixture of disulphide and ferrous sulphide :—[3]

$$Fe_2S_3=FeS_2+FeS.$$

This transformation, which takes a week at the ordinary temperature, may be effected in a few hours at 60° C. Upon exposure to air in the presence of alkaline substances, ferric sulphide becomes light yellow in colour, and sulphur is deposited.

Anhydrous ferric sulphide, Fe_2S_3, is obtained by exposing the hydrated compound in a vacuum over phosphorus pentoxide. It is then pyrophoric if suddenly brought into the air; otherwise it is quite stable.

Anhydrous ferric sulphide is produced in massive form by gently heating iron and sulphur together. As obtained in this way it is a yellow, non-magnetic mass, soluble in dilute mineral acids, density 4·4.

Ferric sulphide yields stable compounds with the sulphides of certain other metals. Some of these occur free in nature. Thus *copper pyrites* is generally regarded as $Cu_2S.Fe_2S_3$ (see p. 23); *Barnhardtite*, $2Cu_2S.Fe_2S_3$ (see p. 23); *Cubanite*, $CuS.Fe_2S_3$ (see p. 24).

These are amongst the best known. Other more or less stable double sulphides have been prepared in the laboratory.

Potassium ferric sulphide, $K_2S.Fe_2S_3$ or $K_2Fe_2S_4$, may be obtained[5] by heating together iron and sulphur with potassium carbonate. The sulphide is extracted with water, and, upon concentration, purplish needle-shaped crystals are obtained, of density 2 86. These are combustible when heated in air, but are reduced to a black mass of $K_2S.2FeS$ or $K_2Fe_2S_3$ upon ignition in hydrogen.

Sodium ferric sulphide, $Na_2S.Fe_2S_3$, may be obtained in a similar manner to the potassium salt, or by heating four parts of sodium thiosulphate with one of iron.[1] As obtained in this way, sodium ferric sulphide forms dark green acicular crystals, which gradually disintegrate upon exposure to air, becoming voluminous, and finally a brownish black powder.

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[1] Wright, *Trans. Chem. Soc.*, 1883, 43, 156; Malfatti, *Zeitsch. anal. Chem.*, 1908, 47, 133.

[2] See this series, Volume V., p. 93; Gedel, *J. Gasbeleuchtung*, 1905, 48, 400; Stokes, *J. Amer. Chem. Soc.*, 1907, 29, 304.

[3] Rodt, *Zeitsch. angew. Chem*, 1916, 29, (1), 422; Mecklenburg and Rodt, *Zeitsch. anorg. Chem.*, 1918, 102, 130.

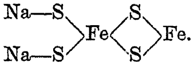
[4] Stokes, *loc cit.*

[5] Schneider, *Pogg. Annalen*, 1869, 136, 460; Brunner, *Chem. Zentr.*, 1889, II., 554.

When heated, sodium ferric sulphide is converted into oxide. With concentrated hydrochloric acid it yields hydrogen sulphide, free sulphur being deposited. It is insoluble in water; but, when boiled with an aqueous solution of potassium cyanide, it yields potassium ferrocyanide.

Sodium ferric sulphide occurs in the "black ash" liquors formed in the Leblanc Soda Process,[2] and a convenient wet method of producing it in the laboratory consists in adding a solution of a ferric salt to excess of sodium sulphide solution. It also results when excess of sodium polysulphide acts on a solution of a ferrous salt.[3]

The constitution assigned by Schneider [4] is :—



Cuprous ferric sulphide, $Cu_2S.Fe_2S_3$, occurs in nature as *copper pyrites, chalcopyrite,* or *towanite,* and is one of the commonest ores of copper (see p. 23). It is tetragonal, possessed of a brass-yellow colour, and exhibits a conchoidal fracture. It is decomposed by nitric acid, and tarnishes upon exposure to air, frequently yielding beautiful iridescent surfaces, a blue colour predominating. Masses of such tarnished ore are found in Cornwall, and are known as *peacock ore.* The blue colour is probably due to the formation of a surface layer of cupric sulphide or covellite, CuS.

Chalcopyrite may be distinguished from iron pyrites by its relative softness, and by the fact that with nitric acid it yields a green solution which becomes blue on addition of excess of ammonia—one of the characteristic reactions for copper. *Blistered copper ore* is a botryoidal or reniform variety, with a smooth brassy appearance.

Small crystals of artificial copper pyrites are obtained [5] by the action of hydrogen sulphide upon a mixture of copper oxide and ferric oxide gently warmed in a glass tube.

Copper pyrites may be obtained in the laboratory in the wet way by shaking a weakly ammoniacal solution of cuprous chloride with potassium ferric sulphide until the solution no longer contains copper :—[6]

$$K_2S.Fe_2S_3+2CuCl=2KCl+Cu_2S.Fe_2S_3.$$

The crystals obtained are practically identical with the natural copper pyrites.

Another method consists in heating copper carbonate and ferric sulphate with water containing hydrogen sulphide. The reaction is carried out in a closed tube, and the heating prolonged for several days.[7]

The internal structure of copper pyrites, $CuFeS_2$, has been studied by means of their X-ray interference phenomena.[8]

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[1] Faktor, *Chem. Zentr.*, 1905, II, 1218.

[2] See this series, Volume II.

[3] Mecklenburg and Rodt, *Zeitsch. anorg. Chem.*, 1918, 102, 130.

[4] Schneider, *loc. cit.*

[5] Doelter, *Zeitsch. Kryst. Min.*, 1886, 11, 29.

[6] Schneider, *J. prakt. Chem.*, 1888, (2), 38, 569.

[7] Doelter, *loc. cit.*

[8] Burdick and Ellis, *J. Amer. Chem. Soc.*, 1917, 39, 2518.

Iron disulphide, FeS_2, occurs in nature as the mineral *mundic* or *iron pyrites* belonging to the cubic system. When broken it exhibits a conchoidal fracture. It is pale brass-yellow in colour, and of hardness 6·5; by both of these features it is readily distinguishable from copper pyrites, which is darker in colour and softer (hardness 3·5–4).

The word pyrites (Greek πῦρ, fire) was used by the ancients to include a number of minerals which yield sparks when struck with a hammer. Iron pyrites is frequently found of botryoidal, spherical, or stalactitic form, having been deposited from solutions containing iron sulphate through the agency of organic matter. For this reason pyrites is frequently found in coal, and is known to miners as *brass* or *fools' gold.* Most probably its presence assists the spontaneous inflammability of coal, although it is not such an important factor as was at one time believed.[1]

Frequently fossils are found, particularly in London Clay, consisting of pyrites, the decaying organism having presumably reduced sulphates of iron present in the infiltrating waters.

When pure the density of iron pyrites is 5·027 at 25° C.[2] Nickel and cobalt are sometimes present, probably as isomorphous intermixtures of their corresponding sulphides; copper may also be present, perhaps as chalcopyrite. Thallium, silver, and even gold have been found in pyrites, the last-named in sufficient quantity to render the mineral a profitable source of that precious metal, as, for example, in British Columbia, where auriferous pyrites is largely worked.

From electric conductivity measurements the solubility of pyrites in water has been calculated as follows:—[3]

	Gram-molecules per Litre.
Pyrites from Freiberg . . .	$48{\cdot}9 \times 10^{-6}$,
Artificial pyrites	$40{\cdot}8 \times 10^{-6}$.

Aerated waters charged with calcium carbonate appear to decompose pyrites very slowly at the ordinary temperature, yielding limonite. Thus:—[4]

$$4FeS_2+15O_2+3H_2O+8CaCO_3=2Fe_2O_3.3H_2O+8CaSO_4+8CO_2.$$

Distilled water, in the presence of air, slowly oxidises pyrites to ferrous sulphate and sulphuric acid.

Sulphur monochloride has no action on pyrites in the cold, but effects its complete decomposition at 140° C.[5]

Another form of iron disulphide occurs in nature as the mineral *marcasite,*[6] which possesses a radiated structure and is frequently found as irregular balls on chalky downs. When broken open the fracture exhibits a fibrous crystalline structure radiating from the centre—whence the name *radiated pyrites.* The fresh fracture is almost white in colour, and if quite pure the marcasite would probably be quite tin-white in appearance.[7] When pure, its density at 25° C. is

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[1] See this series, Volume VII., where the subject is discussed at length

[2] Allen, Crenshaw, and Johnston, *Amer. J. Sci.*, 1912, (4), 33, 169.

[3] Weigel, *Zeitsch. physikal. Chem*, 1907, 58, 293. See also Doelter, *Monatsh.*, 1890, 11, 149.

[4] Evans, *Min. Mag.*, 1900, 12, 371.

[5] E. F. Smith, *J. Amer. Chem. Soc*, 1898, 20, 289.

[6] An Arabic or Moorish word.

[7] Stokes, *U.S. Geological Survey,* Bulletin 186, 1901.

4·887.[1] Marcasite has in general a density of 4·68 to 4·85. It oxidises more readily than pyrites, becoming covered, upon exposure to air, with white fungus-like growths of ferrous sulphate.

When heated to 450° C. and upwards, marcasite changes slowly into pyrites, but this change does not appear to be reversible.[2] It is not accelerated by pressures even of 10,000 atmospheres, but the change increases in rapidity with rise of temperature, being accompanied by an evolution of heat [1] and a decrease in the electrical resistance of the mineral.[3] A sample of marcasite on being heated to 610° C. increased in density from 4·887 to 4·911, changed in colour, and gave the chemical reactions characteristic of pyrites (see p. 140). The density (4·911) is too low for ordinary pyrites (5·02), but apparently that is due to the porosity of the product obtained under the experimental conditions.[1]

Sulphur monochloride has no action on marcasite in the cold, but decomposes it completely at 140° C.[4]

In order to facilitate a comparative study of the two sulphides, their more important chemical and physical properties are listed in the accompanying table :—

	Pyrites.	Marcasite.
Colour . . .	Brass-yellow	White.
Appearance . .	Striated cubes or pentagonal dodecahedra	Fibrous, radiating.
Crystal system . .	Cubic	Rhombic.
Streak . . .	Greenish to brownish black	Greyish to brownish black.
Density range . .	4·8 to 5·2	4·7 to 4·8.
Density at 25° C. when pure.	5·027	4·887.
Fracture . . .	Conchoidal	Uneven, radiating.
Hardness (Mohs' scale)	6 to 6 5	6 to 6·5. Frequently a trifle softer than pyrites.
Hardness relative to topaz (1000) [5]	182 to 199	134 to 140.
Specific heat . .	0·1306	0·1332.
Heat of combustion .	1550 calories	1550 calories.
Effect of heating to 450° C.	Stable	Converted into pyrites.
Action of air . .	More stable than marcasite	Readily oxidises.
Action of caustic soda solution	Less resistant than marcasite	Fairly resistant.
Action of nitric acid, density 1·4	Dissolves completely	Sulphur deposited.

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[1] Allen, Crenshaw, and Johnston, *Amer. J. Sci.*, 1912, (4), 33, 169.

[2] Allen, *J. Washington Acad. Sci*, 1911, 1, 170 ; Arbeiter, *Chem. Zentr.*, 1913, I., 1933.

[3] Konigsberger and Reichenheim, *Neues Jahrb.*, 1906, II, 36.

[4] Smith, *J. Amer. Chem. Soc*, 1898, 20, 289.

[5] Poschl, *Zeitsch. Kryst. Min*, 1911, 48, 572 Determined by the volume of material removed by a weighted diamond, the lower values being obtained when the diamond was weighted 20 grams, and the higher 50 grams, for each mineral.

When pyrites and marcasite are not distinctly crystallised it is frequently difficult to distinguish between them, as the foregoing characteristics are not clearly discernible. A convenient chemical method has been devised, however, which enables a discrimination to be made with certainty.[1] It consists in boiling the mineral with iron alum, containing 1 gram of ferric iron and 16 c.c. of 25 per cent. sulphuric acid per litre. The proportion of sulphur oxidised in the case of pyrites is 60·4 per cent. of the total sulphur contained in the mineral; in the case of marcasite it is only 18 per cent.[2] The reaction may be considered as taking place in two stages, namely :—

$$FeS_2+Fe_2(SO_4)_3=3FeSO_4+2S,$$
$$6Fe_2(SO_4)_3+2S+8H_2O=12FeSO_4+8H_2SO_4.$$

A labile phase of iron disulphide occurs in nature under the name *melnikovite.* It is a black, finely divided substance which impregnates certain miocene clays in Russia, and differs in many respects from the black hydrated sulphide of iron usually found in black muds of lakes. In composition it corresponds to the formula FeS_2. It is magnetic, and its true density is probably 4·2 to 4·3. Cold, dilute hydrochloric acid readily attacks it, evolving hydrogen sulphide. It has probably been derived from a colloidal deposit of an iron sulphide.[3]

Laboratory Preparation of Iron Disulphide.—In the laboratory iron disulphide may be prepared by several wet methods. Thus, it is formed when ferrous sulphide is boiled with flowers of sulphur; and when sodium trisulphide is added slowly to a boiling solution of ferrous sulphate, provided excess of the trisulphide is avoided. Sulphur is simultaneously precipitated.[4] It is obtained also by boiling the freshly precipitated monosulphide suspended in water with sulphur in the absence of alkalies[5]; by the action of sodium thiosulphate solution upon ferrous sulphate[6] in sealed tubes at temperatures even below 100° C.:—

$$4Na_2S_2O_3+FeSO_4=FeS_2+3S+4Na_2SO_4;$$

by the action of hydrogen sulphide upon ferrous thiosulphate,[7] or on ferric or ferrous sulphate[6]; by heating metallic iron with a solution of sulphur dioxide at about 200° C.,[8] or phosphorus penta-sulphide and ferric chloride[9]:—

$$6FeCl_3+2P_2S_5=3FeCl_2+3FeS_2+4PSCl_3.$$

As obtained by these methods, the iron disulphide is usually either amorphous or consists of a mixture of minute crystals of pyrites and marcasite. By prolonging the reactions crystals can be obtained of sufficient size to render possible an examination under the microscope. By heating an intimate mixture of ferric oxide, sulphur, and ammonium chloride, Wöhler[1] obtained small brass-yellow crystals, probably of pyrites.

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[1] Stokes, *loc. cit.*

[2] For other reactions see Stokes, *J. Amer. Chem. Soc*, 1907, 29, 307.

[3] Doss, *Jahrb. Min.*, 1912, 33, 662.

[4] Senarmont, *Ann. Chim. Phys.*, 1851, 32, 129; 1850, 30, 129; *Compt. rend.*, 1849, 28, 693; Rodt, *Zeitsch. angew. Chem.*, 1916, 29, (1), 422.

[5] Rodt, *Mitt. K. Materialprufungsamt*, 1918, 36, 93.

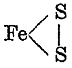
[6] Allen, Crenshaw, and Johnston, *Amer. J. Sci.*, 1912, (4), 33, 169. See p 166, where this reaction is explained.

[7] Feld, *Zeitsch. angew. Chem.*, 1911, 24, 290.

[8] Geitner, *Annalen*, 1864, 129, 350.

[9] Glatzel, *Ber.*, 1890, 23, 37.

Constitution of Pyrites and Marcasite.—When marcasite is heated to 200° C. in sealed tubes with copper sulphate solution, the product contains iron in the ferrous state only. Pyrites, under similar treatment, yields about 20 per cent. of its iron in the ferrous form, the remainder being ferric. It has therefore been suggested[2] that marcasite is represented by the formula[3]

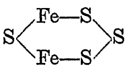


or a polymeride, whilst pyrites is $4\text{Fe}^{\cdots}\text{S}_2.\text{Fe}^{\cdot\cdot}\text{S}_2$.

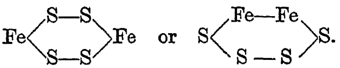
On the other hand, both marcasite and pyrites, when heated with excess of bismuth chloride in an atmosphere of dry carbon dioxide, yield only ferrous iron.[4]

Further, when heated to a red heat in an atmosphere of carbon dioxide, pyrites loses half its sulphur, and the residue consists of ferrous sulphide. A similar result is obtained when pyrites is heated at 300° to 400° C. in steam.[5]

From these experiments it would appear that the iron is present in *both* minerals in the ferrous state.[6] The evidence is thus seen to be conflicting and unreliable.[7] The heat of combustion of the two minerals is the same, namely 1550 calories,[8] which suggests a similar state of valency of the iron in both, and thus lends support to the latter view. The heat of formation is likewise the same,[9] assuming the iron to be in the ferrous state. Some difference in the molecular structure of the minerals is to be anticipated, and Arbeiter[10] suggests the following graphical formulæ:—



(Pyrites)



(Marcasite)

Formation of Pyrites and Marcasite in Nature.—As has already been mentioned, iron disulphide is obtained in both crystalline varieties —pyrites and marcasite—by the action of hydrogen sulphide upon a solution of ferric sulphate at the ordinary temperature. The reaction begins with the reduction of ferric sulphate to the ferrous salt with the deposition of sulphur:—

$$\text{Fe}_2(\text{SO}_4)_3+\text{H}_2\text{S}=2\text{FeSO}_4+\text{H}_2\text{SO}_4+\text{S}.$$

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[1] Wohler, *Annalen*, 1836, 17, 260.

[2] Brown, *Proc. Amer. Phil. Soc*, 1894, 33, 225; *Chem. News*, 1895, 71, 120, 131, 144, 155, 171, 179.

[3] This formula was suggested by Loczka for pyrites (*Zeitsch. Kryst. Min.*, 1894, 33, 501).

[4] Plummer, *J. Amer. Chem. Soc.*, 1911, 33, 1487.

[5] Benedek, *Zeitsch. Kryst. Min*, 1910, 48, 447.

[6] See also Morgan and E. F. Smith, *J. Amer. Chem. Soc.*, 1901, 23, 107.

[7] Stokes, *loc. cit.*

[8] Cavazzi, *Zeitsch. Kryst. Min*, 1900, 32, 515.

[9] Mixter, *Amer. J. Sci.*, 1913, (4), 36, 55.

[10] Arbeiter, *Chem. Zentr.*, 1913, I., 1933.

This is followed by the formation of the disulphides, if the reaction is carried out in a closed vessel where the hydrogen sulphide is prevented from oxidation or escape.

$$FeSO_4+H_2S+S=FeS_2+H_2SO_4.$$

At the ordinary temperature this reaction is very slow, but at 200° C. it is fairly rapid. The dark deposit is microcrystalline. On carrying out the reaction in a sealed tube at 100° C. with a solution containing 1 per cent. of free sulphuric acid, marcasite is the only product. Higher temperatures and reduction of acidity favour the production of pyrites, distinct crystals being produced at 200° C. Iron pyrites is formed in neutral or alkaline solutions, as, for example, by the action of sodium polysulphide on a ferrous salt. Marcasite is not produced under these conditions.[1] The foregoing results are in harmony with the observation that whilst iron pyrites in nature is usually formed in deep veins from hot alkaline solutions, marcasite is produced near the surface from acid solutions.[2]

Thus a recent formation of pyrites has been observed at Karlsbad, in the well-known springs, which have a temperature of about 55° C. The waters are faintly alkaline and contain dissolved sulphates and a trace of hydrogen sulphide.[3] Similarly the Tuscan lagoons are gradually depositing pyrites, whilst the hot vapours of the Icelandic fumaroles are slowly converting the ferrous silicate of the rocks into pyrites.[4]

Certain micro-organisms may indirectly facilitate the formation of natural pyrites and marcasite by evolving hydrogen sulphide as a product of reduction of sulphates. A considerable number of bacteria, algæ, flagellata, and infusoria exhibit this kind of activity.[5]

It is not probable, however, that they are directly responsible for any large quantity of pyrite or marcasite formation for several reasons.[6] Thus, for example, pyrites is usually formed at considerable depths, but micro-organisms are relatively superficial inhabitants of the soil. Again, pyrites is not infrequently associated with copper pyrites and analogous minerals, which indicates the presence of copper in the original solutions. Now, copper is exceedingly poisonous to most micro-organisms. Finally, marcasite could hardly be produced direct by micro-organisms, as the presence of free acid, which is a condition of its formation, is fatal to organisms.

It seems fairly well agreed amongst geologists that pyrites has also been formed in certain cases by direct crystallisation from rock magmas. This could never happen with marcasite, however, owing to its instability at temperatures above 450° C.

Artificial crystals of marcasite closely resemble the natural mineral in colour, lustre, and axial ratios. Thus :—

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[1] Allen, *J. Washington Acad Sci*, 1911, 1, 170; Stokes, *loc. cit.*; Allen, Crenshaw, and Johnston, *Amer. J. Sci*, 1912, (4), 33, 169.

[2] See Palla, *Jahrb. Min.*, 1887, II., Mem. 5.

[3] Daubrée, *Géologie expérimentale* (Paris, 1879), p. 93.

[4] Bunsen, *Pogg. Annalen*, 1851, 83, 259.

[5] Beyerinck, *Compt. rend.*, 1893, 116, 1494.

[6] Allen, Crenshaw, and Johnston, *loc. cit.*

Marcasite.	Axial Ratio. $a:b\cdot c$.
Natural	0·7662 : 1 : 1·2342 [1]
do.	0·7623 : 1 : 1·2167 [2]
do.	0·7580 : 1 : 1·2122 [3]
Artificial	0·7646 : 1 : 1·2176.[4]

The striations likewise agree with rhombic rather than with cubic symmetry.

The chief commercial use of pyrites (including marcasite) is in the manufacture of sulphuric acid.[5] The pyrites, on being roasted in air, yields sulphur dioxide and a residue of ferric oxide. Thus :—

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2.$$

A small quantity of sulphur trioxide is also formed, its proportion ranging from 0·1 to about 8·5 per cent.[6]

Magnetic pyrites or **pyrrhotite** is a mineral of somewhat variable composition ranging from $5FeS.Fe_2S_3$ to $9FeS.Fe_2S_3$, and is thus intermediate between ferrous sulphide (troilite) and iron pyrites. Some of the purest specimens yield an analysis closely approximating to that of ferrous sulphide. This is particularly the case with specimens derived from meteorites, the excess of sulphur having perhaps been lost during the heating of the meteorite.

Pyrrhotite has been prepared[7] artificially by heating ferrous chloride and sodium carbonate with water in a rifle-barrel at 200° C. for 16 days in an atmosphere of hydrogen sulphide and carbon dioxide. The reaction proceeds easily between 80° and 225° C.[8] at the lower temperature, yielding hexagonal crystals, and at the higher temperature rhombic ones.

In view of these experiments it seems probable that the natural mineral has been produced at a relatively low temperature from ferrous salts dissolved in water by the action of hydrogen sulphide on slightly acid solutions of a ferrous salt.

Artificial pyrrhotite has also been obtained by passing hydrogen sulphide over heated ferrous chloride, air having been previously expelled by passage of carbon dioxide[9]; and by decomposing marcasite or iron pyrites with hydrogen sulphide at temperatures above 575° C.[8] The reaction may be first detected at about this temperature and proceeds fairly rapidly at 665° C. The mineral is not a definite compound, but in all probability a solid solution of sulphur in iron sulphide.[10]

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[1] Prior, *Min. Mag.*, 1903, 13, 217.

[2] Gemacher, *Zeitsch. Kryst. Min.*, 1888, 13, 242.

[3] Goldschmidt, *Winkeltabellen* (Berlin, 1897).

[4] Larsen, *Amer. J. Sci.*, 1912, (4), 33, 218.

[5] See this series, Volume VII.

[6] Scheurer-Kestner, *Compt. rend.*, 1884, 99, 917 ; 1885, 100, 636.

[7] Doelter, *Zeitsch Kryst. Min*, 1888, 13, 624 ; Weinschenk, *ibid.*, 1890, 17, 499 ; Durocher, *Compt. rend.*, 1851, 32, 823.

[8] Allen, *J. Washington Acad. Sci.*, 1911, 1, 170 ; Allen, Crenshaw, and Johnston, *Amer. J. Sci.*, 1912, (4), 33, 169.

[9] Doelter, *loc. cit.*

[10] Allen, *J. Washington Acad. Sci.*, 1911, 1, 170 ; Arbeiter, *Chem. Zentr.*, 1913, I., 1933 ; Habermehl, *Jahrb. Min*, 1880, 2, Ref 303 ; Lindstrom, *Öfv. Akad. Stockholm*, 1875, 32, No. 2, 25.

The following data are interesting as illustrating the fall in density with rise of dissolved sulphur :—[1]

No.	Total Sulphur. Per cent	Calculated FeS. Per cent.	Calculated Dissolved Sulphur. Per cent	Density at 4° C.
1	36·72	99·59	0·41	4·755
3	37·71	98·04	1·96	4·677
5	38·54	96·73	3·27	4·632
7	38·84	96·26	3·74	4·619
9	39·49	95·23	4·77	4·585
10	40·30	93·96	6·04	4·520

The change from pyrite to pyrrhotite when heated in an atmosphere of hydrogen sulphide is represented by the reversible reaction :—

$$FeS_2 \rightleftharpoons FeS(S)_x + (1-x)S,$$

which is endothermic in the direction of left to right, a marked absorption of heat being evident at about 665° C., at which temperature pyrites is transformed into pyrrhotite. At 565° C. pyrrhotite is stable in an atmosphere of hydrogen sulphide, whilst at 550° C. it gradually passes over into pyrites. The transition temperature is thus approximately 565° C. Pyrrhotite melts at 1183° C. in a current of hydrogen sulphide.[2]

There has been considerable discussion as to the crystal system to which pyrrhotite belongs. It is generally regarded as hexagonal,[3] but several investigators have concluded that it is really rhombic,[4] and the suggestion has even been made that the mineral is monoclinic. It seems highly probable that the mineral occurs in two varieties—namely α pyrrhotite, which is rhombic ; and β pyrrhotite, which is hexagonal [5]; the α variety being produced from solution at a higher temperature (*circa* 225° C.) than the β (*circa* 80° C.).

The axial ratios for the rhombic variety vary between the limits

$$\begin{array}{c} a \cdot b : c \\ 0{\cdot}5793 : 1 : 0{\cdot}9267 \end{array}$$

and

$$0{\cdot}5793 : 1 : 0{\cdot}9927,$$

whilst for the hexagonal variety the value for c lies between 0·8632 and 0·8742.

Pyrrhotite is readily distinguished from ordinary pyrites by its softness, 3·5 to 4·5 (pyrites, 6 to 6·5), and by its crystal form and magnetic properties.[1] Its specific heat is 0 1539.[2]

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[1] These data refer to the artificial product (Allen, Crenshaw, and Johnston, *loc. cit.*).

[2] Allen, Crenshaw, and Johnston, *loc. cit.*

[3] See Dana, *A System of Mineralogy* (Wiley, 1889).

[4] Streng, *Jahrb. Min.*, 1878, p. 797 (contrast Streng, *ibid.*, 1882, I, 183); Vrba, *Zeitsch. Kryst. Min.*, 1879, 3, 190; Frenzel, *Min. Petr. Mitt.*, 1881, 3, 297; von Sachsen-Coburg, *ibid.*, 1888, 10, 451, Roth, *Zeitsch. Kryst. Min.*, 1884, 9, 309; Nicol, *ibid.*, 1899, 31, 53; Kaiser, *Centr. Min.*, 1906, p. 261.

[5] Larsen, *Amer. J. Sci.*, 1912, (4), 33, 218. See also Weiss, *Centr. Min.*, 1906, p. 338.

The solubility of pyrrhotite in water, as calculated from electric conductivity measurements,[3] is $53{\cdot}6 \times 10^{-6}$ gram-molecules per litre.

Oxysulphides of iron are not known in nature; but a substance, to which the formula $Fe_2O_3.3Fe_2S_3$ is given, has been obtained by the action of hydrogen sulphide on ferric oxide at temperatures below red heat.[4]

Ferrous sulphite, $FeSO_3.3H_2O$, is obtained by dissolving iron in aqueous sulphurous acid in the absence of air. Upon concentration the salt is deposited as colourless crystals. The reaction is somewhat complicated, for no hydrogen gas is liberated during the solution of the iron, the nascent hydrogen reducing some of the sulphurous acid (or ferrous sulphite) to thiosulphuric acid (or ferrous thiosulphate).[5] Thus :—

$$2Fe+3H_2SO_3=FeSO_3+FeS_2O_3+3H_2O.$$

The thiosulphate, being very soluble in water, remains in solution.

Ferrous sulphite also results when solutions of ferrous salts and sodium sulphite interact,[6] and when ferrous hydroxide is dissolved in aqueous sulphurous acid. In these circumstances a red solution is usually obtained, probably because of interaction with dissolved oxygen. The colour quickly disappears, however, particularly on warming. On concentration the salt crystallises out.

On passing a current of sulphur dioxide into an aqueous suspension of freshly precipitated ferrous sulphide, the latter passes into solution and ferrous sulphite is gradually deposited :—[7]

$$FeS+SO_2+H_2O=FeSO_3+H_2S.$$

On prolonging the passage of sulphur dioxide the salt dissolves and the *acid sulphite*, $Fe(HSO_3)_2$ is produced in solution. The normal salt is re-deposited on boiling, but the solution now contains ferrous thiosulphate in consequence of the reaction between a portion of the dissolved acid salt and sulphur produced by hydrogen sulphide and sulphur dioxide inter-reacting. Thus :—

$$Fe(HSO_3)_2+S=FeS_2O_3+H_2O+SO_2.$$

Ferrous sulphite solution readily oxidises in air, yielding a red solution.[6] From its colourless solutions alkalies precipitate ferrous hydroxide.

Ferric sulphite, $Fe_2(SO_3)_3$, has not been isolated. It is obtained in unstable solution on dissolving ferric hydroxide in sulphurous acid. If the ferric hydroxide is pure and well washed, it dissolves exceedingly slowly, yielding a yellow solution.[1] As ordinarily precipitated from solution, however, the hydroxide dissolves rapidly.[2] The solution is unstable, the yellow colour changing to green as the ferric salt undergoes reduction to ferrous dithionate in the course of a few hours :—[3]

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[1] For a discussion of its magnetic properties and crystal system see Kaiser, *Centr. Min.*, 1906, p. 261.

[2] Abt, *Wied Annalen*, 1897, (2), 62, 474.

[3] Weigel, *Zeitsch. physikal. Chem.*, 1907, 58, 293.

[4] See Rammelsberg, *Pogg. Annalen*, 1864, 121, 337.

[5] Berthollet, *Ann. Chim. Phys.*, 1830, (2), 2, 58; Fordos and Gélis, *J. Pharm. Chim.*, 1843, (3), 4, 333.

[6] Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 44. See also Muspratt, *Annalen*, 1847, 64, 240; *Phil. Mag.*, 1847, (3), 30, 414; Berthier, *Ann. Chim. Phys.*, 1832, (2), 50, 370.

[7] Henderson and Weiser, *J. Amer. Chem. Soc.*, 1913, 35, 239.

$$Fe_2(SO_3)_3 = FeS_2O_6 + FeSO_3.$$

Basic ferric sulphites, such as $Fe_2(SO_3)_3.7Fe(OH)_3$ and $Fe_2(SO_3)_3.6Fe(OH)_3$, have been prepared.[4]

Ferri-Sulphites.

A well-defined series of complex alkali salts of ferric sulphite has been prepared,[5] analogous to the ferri-sulphate derivatives of ferric sulphate (see p. 162), but containing one SO_4 radicle.

Potassium ferri-tetrasulphite, $K_2Fe_2(SO_3)_4.K_2SO_4$ or $K_4Fe_2(SO_3)_4.SO_4$, is obtained by adding sodium hydrogen sulphite solution to one of potassium ferro-heptanitroso sulphide, $KFe_4(NO)_7S_3$ (see p. 179), in alcohol and allowing to stand at the ordinary temperature for a couple of weeks. The salt separates as yellow, microscopic needles, insoluble in cold water. Acids dissolve the salt readily, and boiling with water effects the precipitation of ferric hydroxide.

Potassium ferri-disulphite, $K_3Fe(SO_3)_2SO_4$, results when a solution of potassium ferro-heptanitroso sulphide is digested at 4° C. with sodium hydrogen sulphite for about a month. It yields lustrous, dark yellow leaflets which are practically insoluble in cold water, but in boiling water are decomposed, yielding ferric hydroxide and a soluble ferric salt.

Potassium ferri-sulphite, $KFe(SO_3)SO_4$, is prepared by the action of potassium hydrogen sulphite upon ferric ammonium alum. It crystallises in slender needles, which are sparingly soluble in cold water. With hot water, ferrous and potassium sulphates pass into solution, leaving an insoluble yellow residue.

Ammonium ferri-sulphite, $NH_4.Fe(SO_3)SO_4.H_2O$, may be obtained by treating ferric ammonium alum with ammonium hydrogen sulphite. It crystallises in slender, yellow needles which are but slightly soluble in cold and hot water. Prolonged boiling decomposes the salt.

Sodium ferri-disulphite, $Na_3Fe(SO_3)_2SO_4.6H_2O$, may be prepared by digesting a solution of sodium ferro-heptanitroso sulphide with sodium hydrogen sulphite for several days. It crystallises in flat, yellow prisms, and closely resembles the corresponding potassium salt.

Sodium hydrogen ferri-tetrasulphite, $Na_2H_2Fe_2(SO_3)_4SO_4.2H_2O$, results on dissolving freshly precipitated ferric hydroxide in a concentrated solution of sodium hydrogen sulphite and sulphurous acid. On concentration over sulphuric acid a crystalline mixture of this salt with the preceding is obtained, and separation is effected by treating this mixture with a solution of sodium hydrogen sulphite. The salt crystallises out in bright, olive-green needles.

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[1] Carpenter, *Trans. Chem. Soc.*, 1902, 81, 1.

[2] Gélis, *Ann. Chim. Phys.*, 1862, (3), 65, 222.

[3] See p. 168. According to Buignet (*Compt. rend.*, 1859, 49, 587), the reaction is

$$Fe_2(SO_3)_3 = FeSO_4 + FeSO_3 + SO_2.$$

[4] Koene, *Pogg. Annalen*, 1844, 63, 444 ; Seubert and Elten, *loc. cit.*

[5] Hofmann, *Zeitsch. anorg. Chem.*, 1897, 14, 282.

Ferrous sulphate.—The usual form of this salt is the *heptahydrate*, $FeSO_4.7H_2O$, which is obtained when iron is dissolved in dilute sulphuric acid and the solution allowed to crystallise. The crystals belong to the monoclinic system, and owing to their green colour the salt has long been known as *green vitriol.* The density of the pure salt at 14·8° C. is 1·8987,[1] and at 15° C. 1·899 $\pm$·001,[2] and it is stable in contact with a saturated solution of ferrous sulphate up to 56·6° C. which is the transition point of the hepta- to the tetra-hydrate under these conditions.[3] It occurs native as the mineral *melanterite* or *copperas,* which may be crystalline, but is more usually massive. Mixed crystals of the heptahydrates of ferrous and cupric sulphates occur as *pisanite,* $(Fe, Cu)SO_4.7H_2O$, in the form of blue transparent crystals. Both these minerals are isomorphous with Boothite, $CuSO_4.7H_2O$.[4]

Drainage water from coal mines is frequently charged with ferrous sulphate consequent upon the oxidation of pyrites in the coal, and upon evaporation yields the impure salt. The salt is readily obtained in a pure state by dissolving electrolytic iron in dilute sulphuric acid and allowing to crystallise, preferably in an inert atmosphere. Commercially ferrous sulphate is obtained by exposing heaps of pyrites to the oxidising action of the air. Ferrous sulphate and free sulphuric acid drain off into tanks, the acid being neutralised with scrap iron :—

$$FeS_2+7O+H_2O=FeSO_4+H_2SO_4,$$
$$H_2SO_4+Fe=FeSO_4+H_2.$$

The salt obtained in this way is not pure, but contains small quantities of ferric sulphate and the sulphates of metals such as manganese naturally occurring in the pyrites. Copper sulphate is removed by allowing the liquors to remain a sufficient length of time in contact with the scrap iron, the copper being precipitated out :—

$$CuSO_4+Fe=FeSO_4+Cu.$$

Ferric sulphate is removed by re-crystallisation, but small quantities of the other salts remain.

When exposed to the air the ordinary commercial salt gradually oxidises, yielding a basic salt. It is easily dried, however, by powdering and repeatedly pressing between the folds of filter paper. It is then quite stable in air at 15° C. and neither oxidises, effloresces, nor deliquesces.[5] When heated in chloroform vapour a mixture of ferrous and ferric chlorides is produced.[6]

The salt melts at 64° C.[7] When heated *in vacuo,* ferrous sulphate heptahydrate undergoes dehydration, six molecules of water being removed at 140° C., complete dehydration being effected at a slightly higher temperature. When heated in a tube open at both ends, ferrous sulphate begins to decompose at 150° C., yielding ferric sulphate, $Fe_2(SO_4)_3$,[8] and at higher temperatures, in the presence of air, ferric oxide results. Its coefficient of expansion per degree C. rise in temperature[1] is $7\cdot 2 \times 10^{-5}$.

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[1] Andreae, *Zeitsch. physikal. Chem*, 1911, 76, 491.
[2] Retgers, *ibid*, 1889, 3, 289.
[3] Fraenckel, *Zeitsch. anorg. Chem*, 1907, 55, 223.
[4] For crystallographic data, see p. 25.
[5] de Forcrand, *Compt rend.*, 1914, 158, 20.
[6] Conduché, *ibid.*, 1914, 158, 1180.
[7] Tilden, *Trans. Chem. Soc.*, 1884, 45, 266.
[8] Hofmann and Wanjukow, *Met. Chem. Eng.*, 1912, 10, 172; *Bull. Amer. Inst. Min. Eng.*, 1912, p. 889.

Its specific heat is as follows :—

Temperature Range. °C.	Specific Heat of $FeSO_4.7H_2O$.
$-78\cdot 4$ to $+22$	$0\cdot 292 \pm 0\ 002$
$-190\cdot 0$ „ $+22$	$0\cdot 234 \pm 0\cdot 002$
$-190\cdot 0$ „ $-78\cdot 4$	$0\cdot 182 \pm 0\cdot 004$

and its molecular specific heat between 22° and 45° C. is 96·2 calories.[2] The heat of hydration of the heptahydrate is **1912** calories,[3] and its heat of solution is -4323 calories at 13·5° C.[4]

Crystals of the heptahydrate possess the same vapour tension at 44·01° C. as magnesium sulphate, $MgSO_4.7H_2O$. Below this temperature their dissociation pressure is greater, and above it is less, than that of the magnesium salt.[5] In the case of zinc sulphate, $ZnSO_4.7H_2O$, the equilibrium temperature between the two salts is 16·4° C.[6]

Examination of ferrous sulphate crystals by X-ray methods indicates that the seven molecules of water are not symmetrically disposed or equivalent in their structural relations to the other constituents.[7]

The heptahydrate is *dimorphous*, a rhombic variety occurring in nature as *tauriscite*[8] in a more or less impure condition. It has not been isolated in a pure condition in the laboratory, but Rammelsberg[9] obtained it in association with rhombic magnesium sulphate.

Experiment shows that crystals of magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, will hold up to 19 per cent. of ferrous sulphate, $FeSO_4.7H_2O$, in solid solution. Now, the pure magnesium salt is rhombic, and has a density of 1·677, whilst the usual form of ferrous sulphate is monoclinic, density 1·898. The mixed crystals, however, are rhombic. Determination of their density shows that it is not the mean value as calculated from the densities of the constituent salts, but is slightly less. In other words, it appears that the magnesium sulphate is mixed with a ferrous sulphate of density 1·875, rhombic in form, and too unstable to exist alone when quite pure under ordinary conditions. Similarly crystals of ferrous sulphate heptahydrate can hold 54 per cent. of magnesium sulphate in solid solution. The mixed crystals are, in this case, monoclinic, and their density is greater than the mean calculated from the densities of the constituents. It would thus appear that in this case the ferrous sulphate is associated with a monoclinic variety of magnesium sulphate heptahydrate, of density 1·691, but which is too unstable to exist alone in ordinary circumstances. Hence the two heptahydrates are isodimorphous.[1]

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[1] Andreae, *Zeitsch. physikal. Chem.*, 1911, 76, 491.

[2] Jackson, *J. Amer. Chem. Soc.*, 1912, 34, 1470. Rolla and Accame (*Atti R. Accad. Lincei*, 1913, (5), 22, ii. 109) give the molecular heat as 92·147.

[3] Cohen, *Zeitsch. physikal. Chem*, 1901, 36, 517.

[4] de Forcrand, *Compt. rend.*, 1914, 158, 20.

[5] Rolla, *Atti R. Accad. Lincei*, 1911, (5), 20, 112.

[6] Rolla and Ansaldo, *ibid.*, 1912, (5), 21, i. 272.

[7] Johnsen, *Physikal. Zeitsch.*, 1915, 16, 269. Compare p. 79.

[8] See p. 25; also Blaas, *Monatsh*, 1883, 4, 833.

[9] Rammelsberg, *Pogg. Annalen*, 1854, 91, 321; also Volger, *Jahrb Min*, 1855, p. 152.

The *hexahydrate*, $FeSO_4.6H_2O$, results on passing hydrogen chloride into a saturated solution of ferrous sulphate. Ferrous chloride separates first, and, concentrating the mother liquor, tabular crystals of ferrous sulphate hexahydrate separate out.[2]

When a crystal of copper sulphate, $CuSO_4.5H_2O$, is introduced into a supersaturated solution of ferrous sulphate, triclinic crystals of the *pentahydrate*,[3] $FeSO_4.5H_2O$, separate out, isomorphous with the copper salt, and of density 1·89.

The pentahydrate may also be obtained by allowing an acidified solution of ferrous sulphate to concentrate *in vacuo*. The heptahydrate crystallises first, next the pentahydrate, and finally the *tetrahydrate*,[4] $FeSO_4.4H_2O$, the relative proportions of these hydrates depending upon the amount of free sulphuric acid in solution.

The tetrahydrate is also formed when the heptahydrate is kept for several days over concentrated sulphuric acid.[5] It is monoclinic, and isomorphous with the corresponding hydrate of manganous sulphate, $MnSO_4.4H_2O$. Its limits of stability in contact with a saturated solution of ferrous sulphate are 56 6° C. to 64·4° C.[6] Its heat of solution at 13·5° C. is 1599 calories,[7] and its molecular heat is 63·587 calories.[8]

The *trihydrate*, $FeSO_4.3H_2O$,[9] and *dihydrate*, $FeSO_4.2H_2O$,[10] have also been obtained—the former, by solution of the heptahydrate in concentrated hydrochloric acid; the latter by separation from a concentrated solution of ferrous sulphate on addition of sulphuric acid in small quantities at a time. The existence of this latter hydrate is clearly indicated by a break in the time-dehydration curve at 100° C.[11]

The *monohydrate*, $FeSO_4.H_2O$, occurs in nature as the mineral *ferro-palladite*, in Chili,[12] and results when the heptahydrate is heated to 140° C. *in vacuo*, or is allowed to effloresce for prolonged periods in dry air,[13] and by passing air, dried over sulphuric acid, over the heptahydrate at 100° C.[14] It also results by bringing the heptahydrate into contact with sulphuric acid of concentration not less than 12·5 normal,[1] and by addition of concentrated sulphuric acid to saturated aqueous solutions of ferrous sulphate.[2] This is conveniently effected by dissolving 400 grams of the pure heptahydrate in 200 c.c. of 50 per cent. sulphuric acid on the water-bath. Almost immediately after solution is complete, the monohydrate separates out as a white, crystalline powder. It is dried with alcohol and ether, and finally over sulphuric acid.[3] The salt is permanent in air, and is not hygroscopic. It is useful, therefore, for standardising permanganate solutions for volumetric analysis. It clings most tenaciously to its combined water, but may be made to part with it to a small extent by heating to 100° C. in a current of air dried over phosphorus pentoxide.[4] The suggestion has therefore been made (see p. 79) that the salt is a hemihydrol of the formula

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[1] See Miers, *Mineralogy* (Macmillan, 1902), p. 230; also Retgers, *Zeitsch. physikal Chem.*, 1889, 3, 497; Blaas, *loc. cit.*

[2] Hensgen, *Ber.*, 1878, 11, 1775; also de Boisbaudran, *Ann. Chim. Phys.*, 1869, (4), 18, 255.

[3] Marignac, *Ann. Mines*, 1856, (5), 9, 11; Liebig and Kopp, *Jahresber.*, 1867, p. 152.

[4] Marignac, *loc. cit.*

[5] Scharizer, *Zeitsch. Kryst. Min.*, 1898, 30, 209; de Forcrand, *Compt. rend.*, 1914, 158, 20.

[6] Fraenckel, *Zeitsch. anorg. Chem.*, 1907, 55, 223. Compare Regnault, *Ann. Chim. Phys.*, 1841, 1, 201.

[7] de Forcrand, *loc. cit*

[8] Rolla and Accame, *Atti R. Accad. Lincei*, 1913, (5), 22, ii. 109.

[9] Kane, *Annalen*, 1836, 19, 7; Kühne, *Schweigger's J.*, 1831, 61, 235.

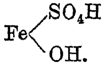
[10] Bonsdorff, *Bericht Versamml. deut. Naturforsch. Aerzte, Prag*, 1837, p. 124; *Pogg. Annalen*, 1834, 31, 81.

[11] Hannay, *J. Chem. Soc.*, 1877, 32, 381.

[12] Scharizer, *Zeit. Kryst. Min.*, 1903, 37, 529.

[13] Scharizer, *loc. cit.*

[14] Hannay, *J. Chem. Soc.*, 1877, 32, 390.



$$Fe\begin{cases}SO_4H\\OH.\end{cases}$$

It is stable in contact with ferrous sulphate solution at temperatures above 64·4° C., which point is the transition temperature in these circumstances between the mono- and tetra-hydrates.[5] Its heat of solution[6] in water at 13·5° C. is 7538 calories. It absorbs ammonia vapour, yielding the *pentammoniate*, $FeSO_4.5NH_3.H_2O$.[7]

The *anhydrous* salt, $FeSO_4$, is extremely difficult to prepare in a state of purity. It results, more or less contaminated with a basic salt,[6] when any hydrate is heated *in vacuo* to a temperature somewhat above 140° C. It is stated also to result when the heptahydrate is dissolved in concentrated sulphuric acid.[8] It then separates as microscopic prisms. It is white in appearance, insoluble both in alcohol and in concentrated sulphuric acid. Its heat of solution[6] in water is 14,901 calories at 13·5° C. Density 2·841. At dull red heat it decomposes, yielding first a basic sulphate and finally ferric oxide. Thus :—

$$2FeSO_4=Fe_2O_3+SO_3+SO_2.$$

Ferrous sulphate readily dissolves in water, and if acidified with dilute sulphuric acid the solution is fairly stable in the cold.[9] Exposure to light accelerates its rate of oxidation. The solubility of ferrous sulphate in water has been determined at different temperatures by many investigators,[10] the most recent and reliable work being that of Fraenckel,[5] who gives the following data :—

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[1] Wirth, *Zeitsch. anorg. Chem*., 1913, 79, 360.

[2] Etard, *Compt. rend.*, 1878, 87, 502, Eremin, *J. Russ. Chem. Soc.*, 1888, 20, 468; Lescœur, *Ann. Chim. Phys.*, 1896, (7), 19, 213, 416, 537; Scott, *Trans. Chem. Soc.*, 1897, 71, 564; Florentin, *Bull. Soc. chim.*, 1913, (4), 13, 362.

[3] Florentin, *loc. cit.*

[4] Hannay, *J. Chem. Soc.*, 1877, 32, 390.

[5] Fraenckel, *Zeitsch. anorg. Chem.*, 1907, 55, 223.

[6] de Forcrand, *Compt. rend.*, 1914, 158, 20.

[7] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[8] Bolas, *Annalen*, 1874, 172, 106, *J. Chem Soc*, 1874, 21, 266.

[9] Warynski, *Ann. Chim. anal*, 1909, 14, 45.

[10] See Etard, *Compt. rend.*, 1888, 106, 740; *Ann. Chim. Phys.*, 1894, (7), 2, 503; Mulder, *Scheikundige Verhandl.*, 1864, III., (3), 141; Tobler, *Annalen*, 1855, 95, 193.

Temperature. °C.	Grams $FeSO_4$ in 100 Grams of Water.	Solid Phase.	Transition Temperature. °C.
0·00	15·65	$FeSO_4.7H_2O$	..
10·00	20·51		..
15·25	23·86		..
20·13	26·56		..
25·02	29·60		..
30·03	32·93		..
35·07	36·87		..
40·05	40·20		..
45·18	44·32		..
50·21	48·60		..
52 00	50 20		..
54·03	52·07		56·6
60·01	54 95	$FeSO_4.4H_2O$	64·4
65·00	55·59	$FeSO_4.H_2O$	..
68·02	52·31		..
70·04	56 08		..
77·00	45·90		..
80·41	43·58		..
85·02	40·46		..
90·13	37·27		..

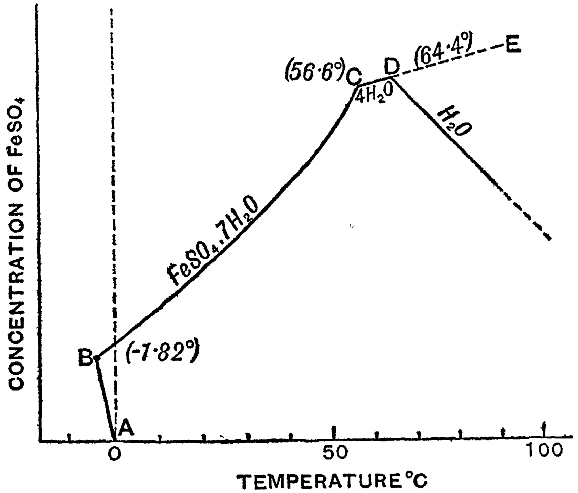

FIG. 6.

These results are shown graphically in fig. 6. At 25° C. 100 grams of saturated solution contain 22·98 grams (0·1503 mol.) of $FeSO_4$.[1]

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[1] Wirth, *Zeitsch. angew. Chem*, 1913, 26, 81.

The density of a solution of ferrous sulphate, saturated and in contact with crystals of the salt, at 8·9° C. is 1·1949.[1]

The rate of oxidation of ferrous sulphate solution upon exposure to air is proportional to the partial pressure of the oxygen.[2] Hence it is reduced by addition of concentrated solutions of inert soluble salts, such as chlorides and sulphates of sodium, potassium, and magnesium, owing to their presence causing a decrease in the solubility of the oxygen.[3] The oxidation depends upon the un-ionised portion of the dissolved salt.

Ferrous sulphate undergoes hydrolysis when its solution is boiled with potassium iodide and iodate. Thus:—

$$3FeSO_4+5KI+KIO_3+3H_2O=3Fe(OH)_2+3K_2SO_4+3I_2.$$

The excess of iodate then oxidises the ferrous hydroxide to the ferric condition.[4]

$$6Fe(OH)_2+KIO_3+3H_2O=KI+6Fe(OH)_3.$$

Ferrous Sulphate as a Reducing Agent.—Ferrous sulphate is frequently used as a mild reducing agent. Thus, auric chloride is reduced to the metal in aqueous solution—a reaction made use of in photographic toning:—

$$AuCl_3+3FeSO_4=Au+FeCl_3+Fe_2(SO_4)_3.$$

Silver salts are similarly reduced to the metal; thus:—

$$Ag_2SO_4+2FeSO_4=2Ag+Fe_2(SO_4)_3$$

and

$$3AgNO_3+3FeSO_4=3Ag+Fe_2(SO_4)_3+Fe(NO_3)_3.$$

These reactions with silver are particularly interesting inasmuch as Landolt[5] finds that they are accompanied by a loss in weight greater than that attributable to experimental error, and suggests that the atoms lose a small portion of their mass in the reaction, the detached particles passing through the walls of the containing vessel.[6]

Under the influence of light, potassium ferricyanide is reduced to ferrocyanide by ferrous sulphate in alkaline solution (see p. 224).

Potassium permanganate is instantaneously decolorised by ferrous sulphate in acid solution, being reduced to manganous sulphate. Thus:—

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

Similarly potassium bichromate is reduced to chromic sulphate in accordance with the equation:—

$$6FeSO_4+K_2Cr_2O_7+7H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+3Fe_2(SO_4)_3+7H_2O.$$

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[1] Sonstadt, *Trans. Chem. Soc.*, 1906, 89, 343.

[2] Ennos, *Proc. Camb. Phil. Soc.*, 1913, 17, 182.

[3] MacArthur, *J. Physical Chem*, 1916, 20, 545

[4] S. E. Moody, *Amer. J. Sci.*, 1906, (4), 22, 176.

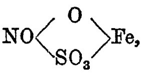
[5] Landolt, *Zeitsch. physikal. Chem.*, 1906, 55, 589.

[6] See Surdo, *Nuovo Cimento*, 1904, (5), 8, 45; Landolt, *Ber.*, 1893, 26, 1820; *Zeitsch. physikal. Chem*, 1893, 12, 1; Heydweiller, *Ann. Physik*, 1901, 5, 394; Rayleigh, *Nature*, 1901, 64, 181; Joly, *Trans. Roy. Dublin Soc.*, 1903, 8, 23.

Aqueous solutions of ferrous sulphate readily absorb nitric oxide,[1] the extent of absorption depending upon the concentration of the iron, the temperature, and the pressure. The limit of absorption is reached when one molecule of NO is present to each atom of iron and the brown solution undoubtedly contains the compound $FeSO_4.NO$, probably more or less combined with the solvent.[2] The addition of small quantities of sulphuric acid to the solution of ferrous sulphate tends to diminish the absorption of nitric oxide, the equilibrium represented by the equation

$$FeSO_4+NO \rightleftharpoons FeSO_4.NO$$

being pushed towards the left. Further increase of the acid, however, assists absorption, a maximum being reached in the presence of 82 per cent. of acid. Under these conditions the solution is cherry-red in colour. The colour is not due to the formation of ferrous nitroso sulphonate,[3]



$$\mathrm{NO}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{SO_3}}{>}\mathrm{Fe},$$

as assumed by Raschig.[4] The complex salt $FeSO_4.NO$ may be isolated by adding a concentrated aqueous solution of nitric oxide in ferrous sulphate to ice-cold sulphuric acid in an atmosphere of nitric oxide; the compound crystallises in small red leaflets, but is very unstable.[5] A second complex salt of the formula $FeSO_4NO.FeSO_4.13H_2O$ has also been obtained [6] by addition of ethyl alcohol to aqueous ferrous sulphate in an atmosphere of nitric oxide. It crystallises in small rectangular plates brown in colour and which slowly decompose on exposure to air.

On addition of nitric acid to a solution of ferrous sulphate acidified with sulphuric acid, nitric oxide is formed, a portion of the ferrous salt being oxidised to ferric. Thus :—

$$6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+4H_2O+2NO.$$

This is the basis of the "ring test" for nitric acid or nitrates, which usually consists in pouring a cold solution of ferrous sulphate gently down the sides of an inclined test-tube on to a layer of concentrated sulphuric acid, containing the nitrate. Since ferric sulphate yields a red compound, possibly $Fe_2(SO_4)_3.4NO$, with nitric oxide in the presence of concentrated sulphuric acid (see p. 161), the colour of the ring formed at the junction of the two liquids will depend upon whether the nitric oxide compound is formed in the concentrated acid or in the aqueous layer, being brown in the latter, but ruddy in the former.

The dark colour of the nitric oxide derivative may be utilised in the volumetric estimation of nitric acid, as its appearance depends upon the presence of excess ferrous sulphate in solution. Further addition of nitric acid oxidises this remaining ferrous sulphate and, when oxidation is complete, the colour disappears. The discharge of the colour is found to be sufficiently definite to enable the end point to be determined with reasonable accuracy.[1]

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[1] Gay, *Compt. rend.*, 1879, 89, 410; *Ann. Chim. Phys.*, 1885, (6), 5, 145.

[2] Manchot and Zechentmayer, *Annalen*, 1906, 350, 368; Usher, *Zeitsch. physikal. Chem.*, 1908, 62, 622; Hüfner, *ibid.*, 1907, 59, 416.

[3] Manchot, *Zeitsch. angew. Chem.*, 1910, 23, 2113.

[4] Raschig, *ibid*, 1905, 18, 1281.

[5] Manchot and Huttner, *Annalen*, 1910, 372, 153.

[6] Manchot and Huttner, *loc. cit.*

The formation of this brown compound can advantageously be utilised as a method of detecting ferrous salts in the presence of other metals that would obscure the more usual ferricyanide reaction.[2] The solution to be tested is mixed with an equal volume of concentrated sulphuric acid, and a crystal of potassium nitrate added. The last-named becomes surrounded with red-brown streaks of the nitroso compound.

A mixed solution of ferrous sulphate and catechol in the presence of an alkali readily absorbs oxygen, giving a deep red colour. The reaction is exceedingly sensitive, and is recommended as a delicate test for oxygen.[3]

Ferrous sulphate has been used as a dressing for crops, but apparently it is beneficial only when the soil contains an excess of lime, which is thereby converted into gypsum. It is this last-named salt which really benefits the soil.[4] Ferrous salts in general are toxic and are usually regarded as one cause of sterility of badly aerated soils.

The **double sulphate** with sodium, $FeSO_4.Na_2SO_4.4H_2O$, has been prepared [5] by crystallisation of the mixed solutions above 45° C.

Double Sulphates of the Type $(M'', N'')SO_4.xH_2O$, or $M''SO_4.N''SO_4.xH_2O$.

Ferrous sulphate yields, with the sulphates of certain divalent metals, mixed salts of the general type $(M'', N'')SO_1.H_2O$. They are prepared by mixing solutions of the constituent sulphates, and then adding concentrated sulphuric acid, when the mixed sulphates separate out on cooling.

Ferrous copper sulphate, $(Fe, Cu)SO_4.H_2O$, or $CuSO_4.2FeSO_4.3H_2O$, occurs in yellowish brown crystals which are not hygroscopic in ordinary air, but take up water in a warm atmosphere saturated with moisture.[6]

The brown colour increases in depth from both ends of the series, the maximum being reached with 18 per cent. of iron and 16 per cent. of copper. The crystals are perfectly homogeneous under the microscope. When gently heated they become chocolate-brown and finally mauve, but the original colour is restored upon exposure to air.

The origin of the brown colour has been a matter of discussion. The monohydrates of ferrous sulphate and copper sulphate are white and pale blue respectively, so cannot be the direct cause of the colour. Neither is the brown due to ferric salts or to cuprous oxide. The suggestion has been made [7] that it is the result of an oscillation of electrons due to the presence of metals in different stages of oxidation, the copper being saturated whilst the iron is not.

---

[1] Mangé, *Chem. Zentr.*, 1919, II., 720, from *L'Ind. chimique*, 1918, 8, 255. See also Bowman and W. W. Scott, *J. Ind. Eng. Chem.*, 1915, 7, 766; Bellucci, *Ann. Chim. Applicata*, 1914, 1, 549.

[2] Blum, *Zeitsch. anal. Chem.*, 1905, 44, 10.

[3] Binder and Weinland, *Ber.*, 1913, 46, 255.

[4] See Boiret and Paturel, *Ann. Agron.*, 1892, 18, 418; Delacharbonny and Destremx, *Bied. Centr.*, 1889, p. 9; Griffiths, *Trans. Chem. Soc*, 1887, 51, 215; 1886, 49, 114; 1885, 47, 46; 1884, 45, 71; Russell, *Soil Conditions and Plant Growth* (Longmans, 1912).

[5] Mohr, *Zeitsch. anal. Chem.*, 1873, 12, 373; Biltz, *ibid.*, 1874, 13, 126.

[6] Scott, *Trans. Chem. Soc.*, 1897, 71, 564.

[7] Allmand, *Zeitsch. anorg. Chem.*, 1909, 61, 202.

Ferrous cadmium sulphate,[1]
Ferrous chromous sulphate[2] (pale, yellowish green).
Ferrous magnesium sulphate,[3]
Ferrous manganese sulphate[2] (very faint pink), and
Ferrous zinc sulphate[2, 4] (white, well crystallised) have also been prepared.

Double Sulphates of the Type, $M'_2RO_4.M''RO_4.6H_2O$.

Ferrous sulphate readily combines with sulphates of the alkali metals and of ammonium to form well-defined crystalline salts of the type

$$M'_2SO_4.FeSO_4.6H_2O.$$

They are all monoclinic in structure and belong to an extensive class of isomorphous salts of the general formula :—

$$M'_2RO_4.M''RO_4.6H_2O,$$

where M' stands for ammonium or an alkali metal, M'' for (ferrous) iron, cobalt, nickel, manganese, copper, cadmium, magnesium, or zinc ; and R for sulphur, selenium, tellurium, or chromium.

These salts have been carefully studied by Tutton,[5] who gives their axial angles and ratios as follow :—

Sulphate.	$a : b : c$	β
Ferrous ammonium[6] .	0·7377 : 1 : 0·4960	106° 50′
,, potassium .	0·7377 : 1 : 0 5020	104° 32′
,, rubidium .	0·7377 : 1 : 0·5004	105° 44′
,, cæsium . .	0·7261 : 1 : 0·4953	106° 52′

It will be observed that if the ammonium salt be excepted, the axial angle steadily increases with the molecular weight. On the other hand, the axial ratios of the first three salts are very close, the cæsium salt here proving exceptional.

In the following table are given the densities and molecular volumes of the salts :—[7]

Sulphate.	Molecular Weight.	Density at 20° C.	Molecular Volume
Ferrous ammonium . .	389·32	1·864	208·86
,, potassium . .	431·16	2·177	198·05
,, rubidium . .	523·26	2·518	207·81
,, cæsium . .	617·26	2·796	220·77

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[1] Retgers, *Zeitsch. physikal. Chem.*, 1895, 16, 595 ; Stortenbeker, *ibid.*, 1900, 34, 108.
[2] Scott, *Trans. Chem Soc*, 1897, 71, 564.
[3] See Moissan, *Traité de Chimie Minérale* (Paris, 1905), vol. iv.
[4] Murmann, *Sitzungsber. K Akad. Wiss. Wien*, 1858, 27, 172.
[5] Tutton, *Proc. Roy. Soc.*, 1913, A, 88, 361 ; *Trans. Chem. Soc*, 1896, 69, 344; 1893, 63, 337.
[6] The values found by Murmann and Rotter (*Sitzungsber. K. Akad. Wiss. Wien*, 1859, 34, 153) were $a : b : c$=0 7466 : 1 : 0·4950. β=106° 48′.
[7] Tutton, *loc. cit.*

It is interesting to note that by interchanging rubidium for ammonium very little alteration is effected in the molecular volume, despite the fact that two atoms (Rb_2) now take the place of ten ($2NH_4$). The densities steadily rise with the molecular weight, and the same is true for the molecular volume if the ammonium salt be excepted.

The solubilities of the salts in water at 25° C. are as follow :—[1]

Sulphate.	Gram-molecules per Litre of Water.	Grams of Anhydrous Salt per Litre of Water.
Ferrous ammonium . .	1·044	351
,, potassium . .	. .	365[2]
,, rubidium . .	0·579	242
,, cæsium . .	1·967	1011

The high solubility of the cæsium salt is interesting in view of the low solubility of ferric cæsium alum (see p. 164).

Ferrous ammonium sulphate or **Mohr's salt,** $FeSO_4.(NH_4)_2SO_4.6H_2O$, may be prepared by adding a saturated solution of ammonium sulphate at 40° C. to the requisite quantity of ferrous sulphate dissolved also at 40° C. in the smallest amount of water. The solution, on cooling, deposits an abundant crop of pale green crystals, monoclinic,[3] and of density 1·864 at 20° C. The salt is kept dry by pressure between filter papers.

Ferrous ammonium sulphate is a stable salt at ordinary temperatures, and its solutions in the cold do not readily oxidise. Hence it is largely used in the laboratory for standardising solutions of potassium permanganate for volumetric analysis. Its solubility in water is as follows :—[4]

Temperature, °C.	0	15	40	50	70
Grams $FeSO_4.(NH_4)_2SO_4$ in 100 grams H_2O	12·5	20 0	33·0	40	52

According to Locke,[5] 351 grams of the anhydrous salt dissolve in one litre of water at 25° C.

These solutions readily absorb nitric oxide in a precisely similar manner to those of pure ferrous sulphate.

Ferrous potassium sulphate, $FeSO_4.K_2SO_4.6H_2O$, may be prepared in a similar manner to the ammonium salt. It yields monoclinic crystals of density 2·189. Its solubility in water is given[6] as follows :—

Temperature, °C. . . .	0	10	16	25	35	40	55	70
Grams $FeSO_4.K_2SO_4$ in 100 grams water . .	19·6	24·5	30·9	36·5	41	45	56	64·2

---

[1] Locke, *Amer. Chem. J.*, 1902, 27, 455.

[2] Tobler, *Annalen*, 1855, 95, 193. This figure is of doubtful accuracy.

[3] Class No. 5 holohedral-prismatic (Baumhauer, *Pogg. Annalen*, 1873, 150, 619; confirmed by Tutton, *loc. cit.*).

[4] Tobler, *loc. cit.* These data are of doubtful accuracy.

[5] Locke, *Amer. Chem. J.*, 1902, 27, 459.

[6] Tobler, *loc. cit.*

These data, however, are only approximately correct. From the solution of this salt in water three definite hydrates can be obtained according to the temperature of crystallisation. This is well illustrated by fig. 7, where the vertical column gives the solubility of the salt (expressed in the original memoir as c.c. of $KMnO_4$).[1]

The *dihydrate* is colourless, the *tetrahydrate* faintly green, and the *hexahydrate* distinctly green. The transition temperatures are as follow:—

$$FeSO_4.K_2SO_4.6H_2O \rightleftharpoons FeSO_4.K_2SO_4.4H_2O + 2H_2O \text{ at } 30^\circ \text{ C.}$$
$$FeSO_4.K_2SO_4.4H_2O \rightleftharpoons FeSO_4.K_2SO_4.2H_2O + 2H_2O \text{ at } 87^\circ \text{ C.}$$
$$FeSO_4.K_2SO_4.6H_2O \rightleftharpoons FeSO_4.K_2SO_4.2H_2O + 4H_2O \text{ at } 54^\circ \text{ C.}$$

The tetra- and di-hydrates may also be obtained by crystallisation from solutions containing varying quantities of sulphuric acid.[2]

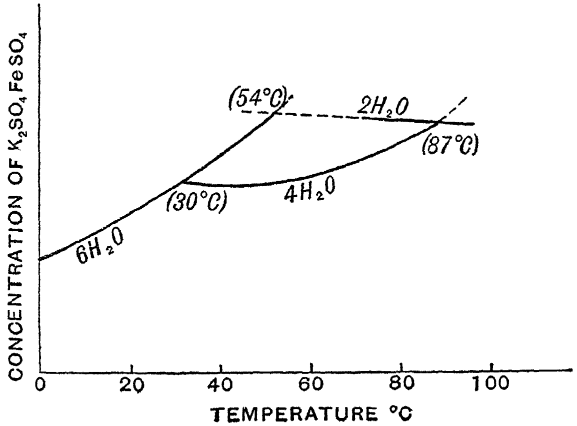

FIG. 7.

Ferrous aluminium sulphate, $FeSO_4.Al_2(SO_4)_3.24H_2O$, occurs in nature as *halotrichite* (see p. 25), and may be prepared in the laboratory by concentration of a solution containing ferrous and aluminium sulphates in equimolecular proportions. At first ferrous sulphate crystallises out, but this is followed by the double salt.[3]

The salt is washed with alcohol and ether. It is white in colour, but exhibits a green fluorescence. It melts on warming, and decomposes to oxides at high temperatures.

The salt has also been found as an efflorescence on bricks which have been continuously exposed to sulphur dioxide in bleaching chambers.[4] When the efflorescent mass is broken up it exhibits a silken or fibrous mass of white crystals not unlike asbestos in texture, whence the popular names of *hair salt* and *feather alum.*

Basic ferrous sulphate, $FeSO_4.FeO$, is apparently obtained in solution when a 30 per cent. solution of ferrous sulphate is electrolysed between iron electrodes by a very weak current in the dark. After a few weeks the liquid becomes dark green in colour, but upon exposure to light it decomposes, depositing ferrous hydroxide in the absence of air.[1]

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[1] Kuster and Thiel, *Zeitsch. anorg. Chem.*, 1899, 21, 116.

[2] See Mitscherlich and Brewster, *Schweigger's J.*, 1820, 33, 344; de Senarmont, *Ann. Chim. Phys.*, 1851, 33, 391; Marignac, *Ann. Min.*, 1856, (5), 9, 19; Linck, *Crell. Annalen*, 1796, 1, 30.

[3] Wirth, *Zeitsch. anorg. Chem.*, 1913, 26, 81.

[4] Paterson, *Trans. Chem. Soc.*, 1896, 69, 66.

The **acid sulphate**, $FeSO_4.5H_2SO_4.5H_2O$,[2] is obtained when excess of sulphuric acid is added to a concentrated solution of ferrous sulphate. It yields iridescent crystals, with a brilliant lustre, but which are unstable, decomposing at 95° to 97° C. into the monohydrate. Thus :—

$$FeSO_4.5H_2SO_4.5H_2O = FeSO_4.H_2O + 5H_2SO_4.4H_2O.$$

Other acid sulphates, namely $2FeO.3SO_3.2H_2O$, $FeO.2SO_3.H_2O$, and $FeO.4SO_3.3H_2O$, have been described.[3]

The following **acid double sulphates** have been prepared :—[4]

$2FeSO_4.Cr_2(SO_4)_3.H_2SO_4.2H_2O$,
$2FeSO_4.Al_2(SO_4)_3.H_2SO_4$,
$2FeSO_4.2ZnSO_4.H_2SO_4$,
$2FeSO_4.2ZnSO_4.H_2SO_4$, and
$FeSO_4.NiSO_4.H_2SO_4$.

Ferric sulphate, $Fe_2(SO_4)_3$, is readily obtained in the anhydrous condition by heating the nonahydrate to about 175° C.,[5] or by heating ferrous or any of the ferric ammonium sulphates (see p. 162) for prolonged periods in the presence of ammonium sulphate.

A convenient method of preparing anhydrous ferric sulphate consists in boiling 10 grams of ferrous sulphate with 100 c.c. of concentrated sulphuric acid for about an hour. When cold the bulk of the acid is poured off, the remainder being washed away with alcohol and finally with anhydrous ether. The salt is dried in an oven till constant weight is attained.[6] Pickering[7] found that it was necessary, in order to effect the complete removal of excess of sulphuric acid, to heat until the product assumes a light brown colour while hot, becoming pink on cooling, the colour being due to the presence of traces of ferric oxide.

It is, when pure, a white powder, slowly soluble in water, yielding a deep brown solution.

When heated, ferric sulphate dissociates into ferric oxide, sulphur trioxide, sulphur dioxide, and oxygen, equilibrium being established if the operation is carried out in a closed vessel.[8]

The equilibrium between ferric sulphate and its decomposition products is given by the equation :—

$$Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_3,$$

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[1] Tichvinsky, *J. Russ. Chem. Soc*, 1893, 25, 311 ; *Bull. Soc. chim.*, 1894, (3), 12, 851.

[2] Eremin, *J. Russ. Chem. Soc.*, 1888, 20, 468.

[3] Kenrick, *J. Physical Chem.*, 1908, 12, 693.

[4] Etard, *Compt. rend.*, 1878, 87, 602

[5] See Recoura, *ibid*, 1907, 144, 1427 ; Wirth and Bakke, *Zeitsch. anorg. Chem.*, 1914, 87, 13. The temperatures at which the natural mineral *coquimbite*, $Fe_2(SO_4)_3.9H_2O$, loses its water varies somewhat with the particular specimens tested.

[6] Milbauer and Quadrat, *Zeitsch. anal. Chem*, 1911, 50, 601.

[7] Pickering, *Trans. Chem. Soc.*, 1880, 37, 807.

[8] Bodenstein and Suzuki, *Zeitsch. Elektrochem.*, 1910, 16, 912.

and the variation of the gaseous pressure with temperature is given by the expression :—[1]

$$\log p = 11{\cdot}8626 - 44720/4{\cdot}584T.$$

The SO_3 itself, of course, partly dissociates, equilibrium being established according to the equation :—

$$2SO_3 \rightleftharpoons 2SO_2 + O_2.$$

p therefore represents the total pressure of all three gases, and T lies between 638° and 721° C.

At lower temperatures the pressures are as follow :—[2]

Temperature. °C.	Pressure. mm.
599	53
630	102·5

When heated to 530° C. in open air, ferric sulphate decomposes completely, leaving a residue of ferric oxide.[3] Several hydrates are known.

The *trihydrate*, $Fe_2(SO_4)_3.3H_2O$, is obtained as a yellow mass on dehydrating the nonahydrate at about 100° C. In alcohol it dissolves readily, yielding a solution from which barium chloride is unable to precipitate the SO_4 as barium sulphate. It is believed, therefore, that the composition of the salt is more correctly represented by the formula $Fe_2(SO_3)_3.(OH)_6$, analogous in constitution to the green chromium sulphate pentahydrate,[4] $Cr_2(SO_4)_3.5H_2O$.[5] It combines with two molecules of ethyl alcohol to form the compound $Fe_2(SO_4)_3.(OH)_4.(OC_2H_5)_2$, the ethoxy groups replacing two hydroxyl groups.

The *nonahydrate*, $Fe_2(SO_4)_3.9H_2O$, occurs in nature as *coquimbite* (see p. 25) in hexagonal prisms, and as rhombic crystalline plates under the name of *Janosite*. It may be prepared in the laboratory by evaporating a solution of ferric hydroxide in excess of sulphuric acid,[6] and taking to dryness, when a mixture of normal and acid sulphates is produced. Upon exposure to moist air, and subsequent washing with alcohol, the nonahydrate, $Fe_2(SO_4)_3.9H_2O$, is obtained as violet hexagonal plates, density 2·116. Recoura describes a second variety of this salt, which results on allowing the above yellow salt to stand in a moist atmosphere for several days. Its empirical composition appears to be the same.[7]

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[1] Keppeler and d'Ans, *Zeitsch. physikal. Chem.*, 1908, 62, 89; Keppeler, d'Ans, Sundell, and Kaiser, *Zeitsch. angew. Chem*, 1908, 532, 577.

[2] Wohler, Pluddemann, and P. Wohler, *Ber.*, 1908, 41, 703.

[3] Hofmann and Wanjukow, *Met. Chem. Eng.*, 1912, 10, 172. Friedrich (*Centr. Min.*, 1912, pp. 174, 207) gives 705° C.

[4] Recoura, *Compt. rend*, 1911, 153, 1223, 1907, 144, 1427.

[5] See this series, Volume VII

[6] Scharizer, *Zeitsch. Kryst. Min*, 1907, 43, 113. The ratio SO_3/Fe_2O_3 should lie between 3 and 4. If more sulphuric acid is present, the acid sulphate alone is produced.

[7] Recoura, *Compt. rend.*, 1907, 144, 1427.

The *decahydrate*, $Fe_2(SO_4)_3.10H_2O$, occurs in nature as *quenstedtite*, in monoclinic crystals, the crystallographic elements being :—[1]

$$a : b : c = 0{\cdot}3940 : 1 : 0{\cdot}4058. \qquad \beta = 78^\circ\ 7{\cdot}5'.$$

It is obtained as the stable solid in contact with acidified solutions of ferric sulphate containing from 25 to 28 per cent. of SO_3,[2] or by the combined action of nitric and sulphuric acids on ferrous sulphate.[3]

Ferric sulphate is slowly soluble in water, and dissolves more readily in the presence of ferrous sulphate,[4] but its solubility is lowered by addition of aluminium sulphate.[5]

The densities of various concentrations of the salt in water at 17·5° C. are given[6] as follow :—

$Fe_2(SO_4)_3$ (per cent.) .	10	20	30	40	60
Density . . .	1·0854	1·1825	1·3090	1·4506	1·8006

A neutral solution of ferric sulphate upon concentration does not deposit crystals of the nonahydrate, but a mixture of yellowish green copiapite (see p. 161), and the white acid sulphate, $Fe_2(SO_4)_3.H_2SO_4.8H_2O$ (see p. 161).

Upon dilution, ferric sulphate solutions readily undergo hydrolysis, precipitates being obtained which, however, have no well-defined composition.[7]

A study of the electric conductivities of aqueous solutions of the salt indicates that the hydrolysis proceeds in two stages, embodying (1) a rapid change unaccompanied by precipitation, and (2) a slower change, progressing at a measurable rate, and accompanied by the production of a so-called basic salt.[8] Colloidal ferric hydroxide does not appear to be formed during hydrolysis,[9] the salt thus differing from ferric chloride and nitrate.

Ferric sulphate also undergoes hydrolysis when its solution is boiled with potassium iodate and iodide.[10] Thus :—

$$Fe_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Fe(OH)_3 + 3K_2SO_4 + 3I_2.$$

In dilute solution ferric sulphate is reduced by metallic iron to ferrous sulphate.[11] In contact with platinum the velocity of the reaction is increased, but rise of temperature has the reverse effect.

Copper is readily dissolved by ferric sulphate solution, and the action is not affected by light. The reaction is practically instantaneous on the surface of the metal, so that the observed velocity in the solution is governed by the rate of stirring.[12]

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[1] Linck, *Jahrb. Min.*, 1888, 1, 213.

[2] Cameron and Robinson, *J. Physical Chem.*, 1907, 111, 641.

[3] Bertels, *Jahresber.*, 1874, 27, 268.

[4] Nilson and Pettersson, *Ber.*, 1880, 13, 1450.

[5] Wirth and Bakke, *Zeitsch. anorg. Chem.*, 1914, 87, 47.

[6] Franz, *J. prakt Chem.*, 1872, (2), 5, 274.

[7] Cameron and Robinson, *J. Physical Chem.*, 1907, 111, 641; Recoura, *Compt. rend.*, 1905, 141, 108; 1905, 140, 1634, 1685.

[8] Wells, *J. Amer. Chem. Soc.*, 1909, 31, 1027.

[9] Antony and Gigli, *Gazzetta*, 1896, 26, i. 293.

[10] S. E. Moody, *Amer. J. Sci.*, 1906, (4), 22, 176.

[11] Essner, *Bull. Soc. chim.*, 1891, (3), 6, 147; Thorpe, *Trans. Chem. Soc.*, 1882, 41, 287.

[12] Schluederberg, *J. Physical Chem.*, 1908, 12, 574.

Ferric sulphate is insoluble in concentrated sulphuric acid and in concentrated hydrochloric acid.

A solution of ferric sulphate in 90 per cent. sulphuric acid forms an intense red solution with nitric oxide, probably due to formation of a complex salt of formula $Fe_2(SO_4)_3.4NO$, which, however, has not been isolated.[1]

Ferric sulphate in solution possesses a remarkable power of combining with animal or vegetable substances,[2] and it cannot be extracted from the combination by hydrochloric acid. Barium chloride solution may be boiled with the compound without undergoing any change. Meat treated with ferric sulphate solution retains its red colour, but becomes exceedingly hard, so that it can hardly be scratched with the finger-nail.

Numerous basic salts[3] occur in nature (see p. 25), chief amongst which are *amarantite*, $Fe_2O_3.2SO_3.7H_2O$; *fibro-ferrite*, $Fe_2O_3.2SO_3.10H_2O$; *castanite*, $Fe_2O_3.2SO_3.8H_2O$; α *copiapite*, $3Fe_2O_3.8SO_3.27H_2O$[4] or $2Fe_2O_3.5SO_3.18H_2O$,[5] and *planoferrite*, $Fe_2O_3.SO_3.15H_2O$.

Botryogen contains ferrous and magnesium oxides associated with ferric sulphate, thus : $FeO.MgO.Fe_2(SO_4)_3.18H_2O$.

A basic sulphate, of formula $2Fe_2O_3.SO_3$ or $Fe_2(SO_4)_3.5Fe_2O_3$,[6] is precipitated from dilute solutions of ammonium iron alum upon prolonged standing,[7] but no basic sulphates are formed by mixing ferric sulphate solutions with freshly precipitated ferric hydroxide.[8] On heating ferric sulphate solution in sealed tubes at 150° C. and 275° C. respectively, crystalline products have been obtained,[9] corresponding to the formulæ $3Fe_2O_3.4SO_3.9H_2O$ and $10Fe_2O_3.SO_3.H_2O$.

A basic ferric sulphate under the name of *chemical sand* is used commercially to neutralise the alkali present in waste soap lyes from which the glycerine is to be recovered. It is manufactured by mixing dry and finely powdered iron ore (oxide) with concentrated sulphuric acid, and allowing the fluid mass to spread out on an iron floor. When solidification has taken place, the mass is broken up and heated at a temperature of 200° to 280° C. for some hours, when it is ready for use, and consists essentially of ferric oxide and ferric sulphate.[10]

An acid sulphate, termed **ferric tetrasulphate,** $Fe_2(SO_4)_3.H_2SO_4.8H_2O$, may be obtained by dissolving the anhydrous sulphate in 10-normal sulphuric acid, and allowing the white crystalline product to dry.[11] It is produced, together with α copiapite, when a neutral solution of ferric sulphate is concentrated.[5] It is soluble in water, and decomposes at 100° C. The sulphuric acid may be replaced by sulphates of the alkali and other metals yielding well-defined compounds, for which reason the salt is frequently termed **ferri disulphuric acid**, the formula being expressed as $H[Fe(SO_4)_2]4H_2O$. When exposed over concentrated sulphuric acid it slowly loses five molecules of water, yielding $2H[Fe(SO_4)_2]3H_2O$, the same change taking place rapidly at 98° C.

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[1] Manchot, *Annalen*, 1910, 372, 179.

[2] Rohart, *Compt. rend.*, 1883, 96, 1705.

[3] See list by Mackintosh, *Amer. J. Sci.*, 1889, (3), 38, 242. It is not here suggested that these are all definite compounds

[4] Wirth and Bakke, *Zeitsch. anorg. Chem.*, 1914, 87, 13. Ordinary copiapite is termed α to distinguish it from a similar substance called β copiapite, the composition of which is slightly different, namely, $2Fe_2O_3.5SO_3.18H_2O$ (Wirth and Bakke's formula).

[5] Scharizer, *Zeitsch. Kryst. Min.*, 1907, 43, 113 ; 1909, 46, 427.

[6] Pickering, *Trans. Chem. Soc.*, 1883, 43, 182 ; 1880, 37, 807.

[7] See p. 164 ; also Pickering, *Trans. Chem. Soc.*, 1907, 91, 1981.

[8] Cameron and Robinson, *J. Physical Chem.*, 1907, 11, 641.

[9] Athanasesco, *Compt. rend.*, 1886, 103, 271.

[10] See Martin, *Industrial and Manufacturing Chemistry* (*Organic*) (Lockwood, 1913), p. 123.

[11] Scharizer, *Zeitsch. Kryst. Min.*, 1901, 35, 345 ; Recoura, *Compt. rend.*, 1903, 137, 118 ; Komar, *Chem. Zeit.*, 1906, 30, 15 ; Wirth and Bakke, *loc. cit.*

Double Sulphates.

$Fe_2(SO_4)_3.FeSO_4.4(NH_4)_2SO_4.3H_2O$ is obtained[1] as colourless needles when ferrous sulphate is added to fused ammonium sulphate, the latter being in excess. The salt dissolves slowly in cold water. Density 2·02.

$Fe_2(SO_4)_3.3(NH_4)_2SO_4$ results[1] on heating the preceding compound in the presence of excess ammonium sulphate. It crystallises in white prismatic needles, of density 2·31 at 14° C.

$Fe_2(SO_4)_3.(NH_4)_2SO_4$ is obtained[1] in a similar manner to the preceding salt, the heating being more prolonged. It yields hexagonal crystals, of density 2·45 at 14° C. When further heated it yields ferric sulphate, $Fe_2(SO_4)_3$, and at higher temperatures ferric oxide, Fe_2O_3.

Mixed double sulphates, such as $(Cr, Fe)_2(SO_4)_3.(NH_4)_2SO_4$, and $(Al, Fe)_2(SO_4)_3.(NH_4)_2SO_4$, have also been prepared.[2]

Ferri-Sulphates.

Ammonium ferri-disulphate, $NH_4[Fe(SO_4)_2]$, is prepared by heating a solution of ferric ammonium alum with sulphuric acid for some hours.[3] It is a white crystalline powder, sparingly soluble in water.

The **potassium** salt, $K[Fe(SO_4)_2]H_2O$, is obtained in a similar manner.[3]

Trisodium ferri-trisulphate, $Na_3[Fe(SO_4)_3]3H_2O$, occurs in nature as *ferro-natrite,* in Chili. It may be prepared by heating sodium sulphate decahydrate, $Na_2SO_4.10H_2O$, until it melts in its combined water, and then adding sulphuric acid and ferric sulphate.[4] It separates as a white substance, which is slowly dissolved by water with decomposition. The salt may also be obtained by allowing a mixture of acid sodium sulphate and ferri-disulphuric acid to remain in contact with a moist atmosphere for several months, when the complex salt crystallises out in greenish white hexagonal crystals. It is completely dehydrated at 100° C.[5]

A basic salt, $2Na_2O.Fe_2O_3.4SO_3.7H_2O$, has also been prepared.[6]

When barium chloride is added to sulphuric acid or soluble sulphate solutions containing dissolved ferric salts, the precipitated barium sulphate is contaminated with iron. This has been variously attributed to adsorption of ferric compounds, and to the formation of solid solutions of ferric salts and barium sulphate. Smith, however, does not regard either of these explanations as satisfactory, and attributes the phenomenon to the formation of insoluble **barium ferri-disulphate,** $Ba[Fe(SO_4)_2]_2.xH_2O$, which is admixed with barium sulphate.[7]

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[1] Lachaud and Lepierre, *Compt. rend.*, 1892, 114, 915.

[2] Klobb, *Compt. rend*, 1893, 117, 311.

[3] Weinland and Ensgraber, *Zeitsch. anorg. Chem.*, 1913, 84, 340.

[4] Skrabal, *Zeitsch. anorg. Chem.*, 1904, 38, 319.

[5] Scharizer, *Zeitsch. Kryst. Min.*, 1905, 41, 209.

[6] Skrabal, *loc. cit.*

[7] G. M'P. Smith, *J. Amer. Chem. Soc.*, 1917, 39, 1152. See also Karavglanow, *Zeitsch. anal. Chem.*, 1917, 56, 225.

Ferric Alums.

Ferric sulphate unites with sulphates of the alkali metals and ammonium to yield well-defined crystalline salts of general formula :—

$$M_2SO_4.Fe_2(SO_4)_3.24H_2O.$$

The iron alums are isomorphous, not merely with one another, but with the wide series of salts known as alums of generic formula :—

$$M_2SO_4.R_2(SO_4)_3.24H_2O,$$

in which M may, as before, be ammonium or an alkali metal, whilst R may stand not merely for Fe, but also for Al, Cr, Co, Ga, In, Mn, Rh, Ti, or V. All possible combinations of these have not as yet been prepared, but such as are known crystallise in the cubic system as regular octahedra or as combinations of the octahedron and cube.

The internal structure of crystals of various alums has been studied by Bragg's X-ray method,[1] and the conclusion arrived at is that the water of crystallisation is not to be regarded as in any way distinct from the other constituents of the molecule, since its removal necessitates the destruction of the crystalline structure. Werner's generic formula for the alums is in complete harmony with this, namely :—

$$\left[R[(H_2O)_2]_6\right]\begin{matrix}SO_4\\SO_4M.\end{matrix}$$

Sometimes the formula for an alum is written as

$$MR(SO_4)_2.12H_2O,$$

indicative of an associated sulphate anion. The trivalent metal, however, figures among the cations along with the alkali metal, and does not enter the anion. Thus, for example, in the case of the iron alums, the iron is one of the positive radicles ; it does not constitute part of the negative radicle, as in the case of the ferrocyanides. Hence a solution of an iron alum gives all the reactions of a ferric salt. Raoult[2] has shown that the molecular depression of the freezing-point of water by—to quote a specific example—ferric potassium alum, namely 85·0° C., is practically identical with the sum of the molecular depressions produced separately by potassium sulphate and ferric sulphate, namely 82·1° C. In aqueous solution, therefore, the alum appears to be dissociated into its constituents.

The refractive indices for the D-line and densities of the iron alums are as follow :—

Alum.	Refractive Index.	Density.
Ammonium	1·48482	1·713
Potassium	1·48169	1·806
Rubidium	1·48234	1·916
Cæsium	1·48378	2·061
Thallium	1·52365	2·385

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[1] Vegard and Schjelderup, *Ann. Physik*, 1917, (2), 54, 146.

[2] Raoult, *Compt. rend.*, 1884, 99, 914.

The refractive index is seen to increase with the molecular weight, except in the case of the iron ammonium alum.[1]

The solubilities of the alums in water at 25° C. are as follow :—[2]

Alum.	Gram-molecules dissolved per Litre of Water.	Grams of (Anhydrous) Alum per Litre of Water.
Ammonium	1·659	..
Rubidium	0·293	97·4
Cæsium	0·045	17·1
Thallium	0·799	..

The relatively low solubility of the cæsium salt is remarkable in view of the great solubility of ferrous cæsium sulphate (see p. 156).

Ferric ammonium alum or **Iron ammonium alum**, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, has been obtained by electrolysing a solution of ferrous sulphate and ammonium sulphate.[3] The cathode consists of platinum wire immersed in acidified ferrous sulphate solution contained in a porous pot. An acidulated solution of ferrous and ammonium sulphates surrounds the pot, and is contained in a platinum dish which serves as anode. A current of 0·04 ampère is passed through the cell, and after several hours crystals of the alum are deposited round the anode.

Aqueous solutions of the alum rapidly become turbid when dilute, although concentrated solutions remain clear for several months. Addition of ammonium sulphate increases the hydrolysis, whilst sulphuric acid exerts a marked retarding influence. The precipitate consists of a basic sulphate of iron, $2Fe_2O_3.SO_3$, and the hydrolysis is believed [4] to follow the course indicated by the equations :—

$$2Fe_2(SO_4)_3+2(NH_4)_2SO_4+5H_2O \rightleftharpoons 2Fe_2O_3.SO_3+5H_2SO_4+2(NH_4)_2SO_4;$$

or, expressing the change ionically :

$$4Fe^{\cdot\cdot\cdot}+4NH_4^{\cdot}+8SO_4''+5H_2O \rightleftharpoons 2Fe_2O_3.SO_3+10H^{\cdot}+4NH_4^{\cdot}+7SO_4'',$$

or

$$4Fe^{\cdot\cdot\cdot}+SO_4''+5H_2O \rightleftharpoons 2Fe_2O_3.SO_3+10H^{\cdot}.$$

The fact that ferric hydroxide is not one of the products of hydrolysis explains why ammonium sulphate does not retard the reaction.[5]

On addition of concentrated sulphuric acid to a solution of the alum a white precipitate is obtained which contains ferric and ammonium sulphates in some uncertain state of combination. The precipitate when dry is stable in air, slowly soluble in cold water, but readily soluble in hot hydrochloric acid, and is possibly an ammonium salt of ferri-sulphuric acid (see p. 162).

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[1] Soret, *Compt. rend.*, 1884, 99, 867.

[2] Locke, *Amer. Chem. J.*, 1901, 26, 166, 332.

[3] Howe and O'Neal, *J. Amer. Chem. Soc.*, 1898, 20, 759.

[4] Rae, *Trans. Chem. Soc.*, 1916, 109, 1331.

[5] See also Wagner, *Monatsh.* 1913, 34, 95.

The densities of various concentrations of iron-ammonium alum solutions in water at 32·5° C. are as follow :—[1]

Grams $(NH_4)_2SO_4.Fe_2(SO_4)_3$ $24H_2O$ in 100 Grams H_2O.	Density.
20 00	1·07960
15·00	1·05907
10·00	1·03801
5 02	1·01670
2·01	1·00376
0·80	0·99849

Ferric potassium alum, $K_2SO_4.Fe_2(SO_4)_3.24H_2O$, may be obtained by mixing together concentrated solutions of potassium and ferric sulphates in the requisite proportions and allowing to stand for some days at 0° C., when the salt crystallises out in violet octahedra.

It cannot be obtained as readily by electrolysis as the ammonium salt, owing to the relatively slight solubility of potassium sulphate.

Addition of potassium hydroxide to a solution of the alum, and subsequent evaporation yields a crop of crystals yellowish brown in colour and possessing peculiar optical properties like tourmaline. Their composition is given as $5K_2SO_4.2Fe_2(SO_4)_2.(OH)_2.16H_2O$. The crystals decompose to iron alum and a basic salt.

The densities of various concentrations of the alum in water at 17·5° C. are given[2] as follow :—

Iron alum (per cent.) .	5	10	15	20	25	30
Density .	1·0268	1 0466	1·0672	1·0894	1·1136	1·1422

Ferric rubidium alum, $Rb_2SO_4.Fe_2(SO_4)_3.24H_2O$, and **ferric cæsium alum,** $Cs_2SO_4.Fe_2(SO_4)_3.24H_2O$, have been obtained[3] by electrolysis in an analogous manner to the iron ammonium alum. They are of a delicate violet colour, turning slightly greenish upon exposure to air. Their solubilities in water with rise of temperature are as follow :—[4]

Temperature, °C.	25	30	35	40
Grams $Rb_2SO_4.Fe_2(SO_4)_3$ per litre of water	97·4	202·4	(5)	(5)
Grams $Cs_2SO_4.Fe_2(SO_4)_3$ per litre of water	17·1	25·2	37·5	60·4

Ferric magnesium alum, $MgSO_4.Fe_2(SO_4)_3.24H_2O$, has also been obtained.[6]

Ferroso-ferric sulphates occur in nature. *Rœmerite* (see p. 26) is a mineral with yellow triclinic crystals and a composition represented by $FeSO_4.Fe_2(SO_4)_3.12H_2O$. Its crystallographic elements are :—[1]

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[1] Rae, *loc. cit.*
[2] Franz, *J. prakt. Chem.*, 1872, (2), 5, 274.
[3] Howe and O'Neal, *loc. cit.*
[4] Locke, *Amer Chem. J.*, 1901, 26, 166, 332.
[5] Decomposition into basic salt takes place at this temperature.
[6] Bastick, *J. Pharm. Chim.*, 1854, 13, 639.

$$a : b : c = 0{\cdot}8791 : 1 : 0{\cdot}8475,$$
$$\alpha = 89° 44', \quad \beta = 102° 17', \quad \gamma = 85° 18'.$$

The salt may be prepared artificially by allowing a mixture of powdered ferrous sulphate and acid ferric sulphate to remain in contact with moist air for several months. It is then obtained as a reddish brown, crystalline powder.[2] It decomposes in moist air, yielding ferrous and ferric sulphates, the latter giving α-copiapite and the acid sulphate.

In *voltaite* the iron is partly replaced by other metals yielding isomorphous salts. By adding ferrous sulphate to fused ammonium sulphate a compound of ferroso-ferric sulphate with ammonium sulphate has been obtained—namely, **ferroso-ferric tetrammonium sulphate,**[3] $FeSO_4.Fe_2(SO_4)_3.4(NH_4)_2SO_4.3H_2O$—as colourless needles, of density 2·02. It dissolves slowly in cold water, yielding a basic salt on warming. When heated with ammonium sulphate it yields ferric triammonium sulphate, referred to above.

The following acid salts have also been obtained :—[4]

$$FeSO_4.Fe_2(SO_4)_3.2H_2SO_4,$$
$$NiSO_4.Fe_2(SO_4)_3.2H_2SO_4, \text{ and}$$
$$2MnSO_4.Fe_4(SO_4)_3.3H_2SO_4.$$

Ferrous amido-sulphonate, $Fe(SO_3.NH_2)_2.(?)5H_2O$, is obtained by dissolving iron wire in aqueous amido-sulphonic acid, and concentrating *in vacuo.*[5] The crystals are bluish green in colour, deliquescent, and exceedingly soluble in water, from which they are not precipitated by alcohol, thereby differing from ferrous sulphate. The crystals appear to contain 5 molecules of combined water.

Ferric amido-sulphonate, $Fe(SO_3.NH_2)_3$, is prepared[5] by dissolving ferric hydroxide and amido-sulphonic acid together in water. The solution obtained is bright brown in colour, and dries up into an opaque, amorphous, brittle mass, which is brown in colour, very soluble in water, but not at all deliquescent. It possesses the astringent taste of ferric salts of inorganic acids, and not that of the citrate or tartrate, the inference being that the iron constitutes the positive ion and is not included in the negative radicle.

Ferrous thiosulphate, $FeS_2O_3.5H_2O$, may be prepared by passing hydrogen sulphide through a cold solution of ferrous sulphate and sodium thiosulphate. The precipitate consisting of sulphur and ferrous sulphide is washed and suspended in water through which a current of sulphur dioxide diluted with hydrogen is passed. The reactions are :—[6]

$$2FeS + 3SO_2 = 2FeS_2O_3 + S,$$
$$FeS + 3SO_2 = FeS_4O_6,$$
$$FeS + 3SO_2 = FeS_3O_6 + S.$$

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[1] Blaas, *Monatsh.*, 1883, 4, 833.
[2] Scharizer, *Zeitsch. Kryst. Min.*, 1903, 37, 529.
[3] Lachaud and Lepierre, *loc. cit.*
[4] Etard, *Compt. rend.*, 1878, 87, 602.
[5] Divers and Haga, *Trans. Chem. Soc*, 1896, 69, 1634.
[6] Feld, *Zeitsch angew. Chem.*, 1911, 24, 290.

A further quantity of the sulphide is then added to remove excess sulphur dioxide and to reduce the polythionates :—

$$FeS_4O_6+FeS=2FeS_2O_3+S,$$
$$FeS_3O_6+FeS=2FeS_2O_3.$$

The salt may also be obtained by triturating a concentrated solution of ferrous sulphate with barium thiosulphate,[1] but it is less pure, as it contains some tetrathionate as well.[2] It results when sulphur is digested with ferrous sulphate solution, and when iron is dissolved in aqueous sulphurous acid.[3] This latter reaction is somewhat complicated, ferrous sulphite being first produced, thus :—

$$Fe+H_2SO_3=FeSO_3+2H.$$

The nascent hydrogen then attacks either the sulphurous acid (or ferrous sulphite), reducing it to thiosulphuric acid (or ferrous thiosulphate). Thus :—

$$Fe+2H_2SO_3+2H=FeS_2O_3+3H_2O.$$

On concentration ferrous sulphite, being much less soluble, crystallises out first, leaving the thiosulphate in solution (see p. 145).

The salt yields green crystals, readily soluble in water. They belong to the triclinic system, their crystallographic elements being as follow :—[4]

$$a : b : c=0{\cdot}37673 : 1 : 0{\cdot}57844.$$
$$\alpha=104^\circ\ 57'.\quad \beta=98^\circ\ 8{\cdot}5'.\quad \gamma=89^\circ\ 40'.$$

The salt readily oxidises in air, yielding a basic ferric compound.

The *double salt*, $Fe_2S_2O_3.3Na_2S_2O_3.8H_2O$, is obtained[5] by precipitating a mixed solution of ferrous iodide and sodium thiosulphate with alcohol. It forms bright green crystals, readily soluble in water.

Ferrous disulphate or **Ferrous pyrosulphate,** FeS_2O_7, is precipitated as a white powder by mixing a saturated solution of ferrous sulphate with several times its volume of concentrated sulphuric acid. Examined under the microscope, it is seen to consist[6] of fine prismatic crystals, which absorb water on exposure to air.

Ferrous tetrathionate, FeS_4O_6, results in unstable solution on adding ferrous thiosulphate solution in small quantities at a time to ferric chloride :—

$$2FeCl_3+2FeS_2O_3=FeS_4O_6+3FeCl_2.$$

The product readily decomposes, evolving sulphur dioxide. Thus :—

$$FeS_4O_6=FeSO_4+SO_2+2S.$$

Ferrous dithionate, FeS_2O_6, is readily obtained by double decomposition of solutions of the barium salt and ferrous sulphate. The dithionate is also formed by dissolving ferric hydroxide in sulphurous acid,[1] and allowing to stand for some hours. If the ferric hydroxide is pure and well washed, it dissolves exceedingly slowly [2]; the ordinary, freshly precipitated hydroxide dissolves rapidly. On standing, the yellow solution becomes green, as the ferric iron becomes reduced to ferrous. The reaction apparently takes place in stages involving the intermediate formation of ferric sulphite—which salt, however, has not been isolated. Thus :—

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[1] Vortmann and Padberg, *Ber.*, 1889, 22, 2637; Rammelsberg, *Pogg. Annalen*, 1842, 56, 306.

[2] Feld, *loc. cit.*

[3] Berthollet, *Ann. Chim. Phys.*, 1830, (2), 2, 58; Vogel, *J. prakt. Chem.*, 1836, 8, 102; Fordos and Gélis, *J. Pharm. Chim.*, 1843, (3), 4, 333.

[4] Fock and Kluss, *Ber.*, 1889, 22, 3310.

[5] Vortmann and Padberg, *Ber.*, 1889, 22, 2637.

[6] Bolas, *Trans. Chem. Soc.*, 1874, 27, 212.

$$2Fe(OH)_3+3SO_3=Fe_2(SO_3)_3+3H_2O,$$
$$Fe_2(SO_3)_3=FeS_2O_6+FeSO_3.$$

On passing sulphur dioxide into cold solutions of ferric sulphate, ferrous dithionate is formed.[3] With a 2 per cent. solution of ferric sulphate, 80 per cent. of the sulphate is converted into dithionate at 0° C., but this amount diminishes as the temperature rises, none being formed at 95° C. The equilibrium may be represented by the equation :—

$$Fe_2(SO_4)_3+3SO_2+2H_2O \rightleftharpoons 2FeS_2O_6+2H_2SO_4.$$

It is interesting to note that ruthenium sulphate behaves in a precisely similar manner.[4] On concentration bluish green crystals are obtained, which are unstable in air. They contain 5 or 7 molecules of combined water, and belong to the triclinic system. At 18·5° C., 1 part of the heptahydrate dissolves in 0·59 part of water.[5]

The following **double salts** have been prepared :—[6]

$FeS_2O_6.3(NH_4)_2S_2O_6.6H_2O$ (monoclinic), and
$4FeS_2O_6.18(NH_4)_2S_2O_6.33H_2O$.

Ferric dithionate has not been isolated, as its solution decomposes yielding ferric sulphate, ferrous dithionate, sulphurous and sulphuric acids.

IRON AND SELENIUM.

When iron and selenium are heated together to a high temperature, combination takes place, but the product usually contains more selenium than corresponds to the **monoselenide** or **ferrous selenide,** FeSe. By heating the product in hydrogen, however, the monoselenide results,[7, 8] further reduction to a sub-selenide not taking place, although the selenides of nickel and cobalt are reduced to sub-selenides under like conditions.

Ferrous selenide was first obtained by Divers and Shimidzu [9] by heating a mixture of wrought-iron filings and selenium in a graphite pot. When the mixture had grown hot, a considerable portion of the selenium had volatilised and a further portion was added which combined with the iron with very little loss, causing vivid ignition and complete liquefaction. The product thus obtained closely resembles iron sulphide. It is not very sensitive to acids, but when warmed with dilute hydrochloric acid, after first powdering, hydrogen selenide is steadily evolved. The heat of formation of solid, crystalline ferrous selenide is 184,400 calories.[1]

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[1] Gélis, *Ann. Chim. Phys.*, 1862, (3), 65, 222.
[2] Carpenter, *Trans. Chem. Soc.*, 1902, 81, 1.
[3] Anthony and Manasse, *Gazzetta*, 1899, 29, i. 483.
[4] This volume, Part I., p. 149.
[5] Kluss, *Annalen*, 1888, 246, 179 ; *Chem. Zentr*, 1888, p. 215.
[6] Klüss, *loc. cit.*
[7] Fabre, *Thèse de Doctorat*, 1886 ; *Ann. Chim.*, 1887, 10, 520.
[8] Fonzes-Diacon, *Compt. rend.*, 1900, 130, 1710 ; *Bull. Soc. chim.*, 1900, 23, 811.
[9] Divers and Shimidzu, *Trans. Chem. Soc.*, 1885, 47, 441.

Ferric selenide or **iron sesqui-selenide,** Fe_2Se_3, was obtained by Little [2] by heating iron to redness in selenium vapour, cooling, and fusing the product with excess of selenium under a layer of borax. It also results when hydrogen selenide is passed over ferric oxide at red heat.[3] It is a grey crystalline powder.

Iron diselenide, $FeSe_2$, is prepared by heating anhydrous ferric chloride to dull red heat in hydrogen selenide.[3] When ignited in oxygen, it yields ferric oxide and selenium dioxide.

Two other selenides, namely Fe_3Se_4 and Fe_7Se_8 or $Fe_3Se_4.4FeSe$, have been described.[3]

Iron Selenites.—Although metallic iron does not appear to be soluble in selenous acid, yet selenites of iron are readily obtained in a variety of ways. When sodium selenite is added to ferrous sulphate solution, a white precipitate of **ferrous selenite,** $FeSeO_3$, is obtained.[4] This becomes darker on exposure to air in consequence of oxidation. If the white precipitate is dissolved in hydrochloric acid, a portion of the selenium separates out, whilst ferric chloride and selenous acid remain in solution. Thus :—

$$4FeSeO_3+12HCl=Se+4FeCl_3+3SeO_2+6H_2O.$$

Several **ferric selenites** have been described, and may be divided into three groups, namely *basic*, *neutral*, and *acid salts*.[5]

Basic Salts.—The salt, $3Fe_2O_3.8SeO_2.28H_2O$, is obtained as a yellow, voluminous precipitate on adding sodium selenite solution to one of ferric chloride [6] at room temperature. This, when heated to 230°–250° C. for several hours with water in a sealed tube, yields insoluble yellow crystals [5] of $Fe_2O_3.2SeO_2$. This latter salt may also be obtained by heating the decahydrated neutral salt in the same manner.

Neutral Salts, $Fe_2O_3.3SeO_2.xH_2O$.—The following hydrates have been described: decahydrate,[5] nonahydrate,[6] heptahydrate,[6] trihydrate,[4, 5] monohydrate.[5]

Acid Salts.—The following salts are known: $Fe_2O_3.4SeO_2.8H_2O$,[6] $Fe_2O_3.4SeO_2.9H_2O$,[6] $Fe_2O_3.4SeO_2.H_2O$,[5] and $Fe_2O_3.6SeO_2.2H_2O$.[5]

Ferrous selenate, $FeSeO_4$.—Iron dissolves in aqueous selenic acid, yielding ferrous selenate and a deposit of selenium,[7] which collects upon the surface of the undissolved metal and shields it from further attack. The rate of solution is thereby so greatly retarded that as a method of preparing ferrous selenate it is not to be recommended.[8] The net result of the action may be represented by the equation :—

$$3Fe+4H_2SeO_4=3FeSeO_4+Se+4H_2O.$$

---

[1] Fabre, *Compt. rend.*, 1886, 103, 345.

[2] Little, *Annalen*, 1859, 112, 211.

[3] Fonzes-Diacon, *Compt. rend.*, 1900, 130, 1710; *Bull. Soc. chim.*, 1900, 23, 811.

[4] Muspratt, *J. Chem Soc.*, 1848, 2, 52.

[5] Boutzoureano, *Ann. Chim. Phys.*, 1889, (6), 18, 289; *Bull. Soc. chim.*, 1887, (2), 48, 209.

[6] Nilson, *Bull. Soc. chim.*, 1875, 23, 494.

[7] No hydrogen is evolved. Presumably the selenium is produced by the action of nascent hydrogen upon the selenic acid; thus :—

$$6H+H_2SeO_4=4H_2O+Se.$$

[8] Tutton, *Proc. Roy. Soc.*, 1918, A, 94, 352.

Ferrous carbonate is likewise but slowly attacked by selenic acid; a better method of preparing ferrous selenate consists in dissolving ferrous sulphide in a concentrated solution of the acid.[1] The hydrogen sulphide evolved reduces a portion of the selenic acid in accordance with the equation :—

$$H_2SeO_4+3H_2S=Se+3S+4H_2O.$$

The solution is therefore filtered and when allowed to crystallise at 0° C. yields monoclinic crystals of the *heptahydrate*, $FeSeO_4.7H_4O$, isomorphous with ferrous sulphate, $FeSO_4.7H_2O$. The crystals are much less stable, however, rapidly becoming opaque. When crystallised from warm solutions the *pentahydrate*, $FeSeO_4.5H_2O$, is obtained, isomorphous with copper sulphate, $CuSO_4.5H_2O$,[2] and ferrous sulphate, $FeSO_4.5H_2O$.

Double Selenates.

Ferrous selenate yields double selenates with salts of the alkali metals. Their general formula is :—

$$M_2SeO_4.FeSeO_4.6H_2O,$$

and they all crystallise in the holohedral class of the monoclinic system, and are isomorphous with the other salts of this series (see p. 155). The crystals rapidly decompose at temperatures very little above 0° C., so that a study of their crystallographic elements and optical properties is a task of considerable difficulty. The following salts have been studied :—[3]

Potassium ferrous selenate, $K_2SeO_4.FeSeO_4.6H_2O$.

$a : b : c = 0{\cdot}7490 : 1 : 0{\cdot}5044. \quad \beta = 103° 50'.$
Density at 20° C., 2·494.
Molecular volume, 210·39.

Rubidium ferrous selenate, $Rb_2SeO_4.FeSeO_4.6H_2O$.

$a : b : c = 0{\cdot}7424 : 1 : 0{\cdot}5000. \quad \beta = 104° 57'.$
Density at 20° C., 2·800.
Molecular volume, 220·29.

Cæsium ferrous selenate, $Cs_2SeO_4.FeSeO_4.6H_2O$.

$a : b : c = 0{\cdot}7308 : 1 : 0{\cdot}4979. \quad \beta = 106° 2'.$
Density at 20° C., 3·048.
Molecular volume, 233·21.

Ammonium ferrous selenate, $(NH_4)_2SeO_4.FeSeO_4.6H_2O$.

$a : b : c = 0{\cdot}7433 : 1 : 0{\cdot}5019. \quad \beta = 106° 9'.$
Density at 20° C., 2·191.
Molecular volume, 220·39.

Ferric Selenium Alums.

Ferric rubidium selenium alum, $Rb_2SeO_4.Fe_2(SeO_4)_3.24H_2O$, is obtained when the requisite amount of rubidium carbonate is added to a solution of freshly precipitated ferric hydroxide in excess of aqueous selenic acid.[1]

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[1] Tutton, *Proc. Roy. Soc.*, 1918, A, 94, 352.
[2] Wohlwill, *Annalen*, 1860, 114, 169.
[3] Tutton, *Phil. Trans.*, 1919, A, 218, 395.

The alum crystallises out in pale violet crystals, belonging to the cubic system. Its density at 15° C. is 2·1308. At 40° to 45° C. the crystals melt in their combined water, yielding a red liquid.

Ferric cæsium selenium alum, $Cs_2SeO_4.Fe_2(SeO_4)_3.24H_2O$, prepared in an analogous manner to the preceding salt,[1] yields violet crystals of density 3·6176 at 15° C. These melt in their combined water at 55° to 60° C.

IRON AND TELLURIUM.

Iron combines with tellurium when the two elements are heated together in an inert atmosphere, yielding **ferrous telluride,**[2] FeTe, as a hard grey crystalline mass. Stable in moist air, it is but slowly attacked by acids in the cold, although bromine water readily effects its solution.[3]

Ferric tellurite occurs in nature as the mineral *durdenite* in Honduras,[4] associated with metallic tellurium. Hardness 2 to 2 5. Its chemical composition closely approaches that represented by the formula $Fe_2O_3.3TeO_2.4H_2O$, or $Fe(TeO_3)_3.4H_2O$. *Emmonsite* is another naturally occurring ferric tellurite found in Colorado [5] as yellowish green scales, associated with lead carbonate and quartz.

IRON AND CHROMIUM.[6]

Ferrous chromite, $FeO.Cr_2O_3$, occurs in nature as *chromite* (see p. 13). It may be prepared in the laboratory by heating to a high temperature an intimate mixture of iron filings, ferrous carbonate, and potassium bichromate, covered with a thin layer of cryolite. The cooled product is extracted with water and concentrated acids in succession ; a residue is obtained containing chromite as small octahedra, cubo-octahedra, and cubes.[7]

Ferrous chromate does not appear to be capable of existing. When solutions of ferrous sulphate and chromic acid, or its alkali salts, are mixed at low temperatures, the iron is oxidised, basic ferric sulphates resulting, the chromium being correspondingly reduced. If the ferrous sulphate is in excess, ferroso-ferric sulphate results.

Numerous **basic double ferric chromates** have been prepared,[8] namely :—

$3K_2O.6Fe_2O_3.2CrO_3$—obtained by the action of ferrous sulphate on potassium chromate at 0° C., at which temperature it is dried with alcohol and ether. It is black in appearance, but brown when moist.

$4K_2O.3Fe_2O_3.4CrO_3$—a yellowish brown micro-crystalline precipitate, obtained by addition of excess of potassium chromate to ferrous sulphate solution.

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[1] Roncagliolo, *Gazzetta*, 1905, 35, ii. 553.
[2] Margottet, *Thèse de Paris*, 1879.
[3] Fabre, *Ann. Chim. Phys.*, 1888, (6), 14, 110.
[4] Dana and Wells, *Amer. J. Sci*, 1890, 40, 78.
[5] Hillebrand, *ibid*, p. 81 ; *Zeitsch. Kryst. Min*, 1887, 12, 492.
[6] For alloys of iron and chromium, see this volume, Part III.
[7] Meunier, *Compt. rend.*, 1888, 107, 1153.
[8] Lepierre, *ibid.*, 1894, 119, 1215.

$4Na_2O.7Fe_2O_3.10CrO_3$ and $6(NH_4)_2O.5Fe_2O_3.6CrO_3$ are obtained in a similar manner to the preceding salt, but replacing potassium chromate by sodium and ammonium chromates respectively.

Other complexes that have been prepared are :—[1]

$7K_2O.6Fe_2O_3.10CrO_3$; $4K_2O.3Fe_2O_3.11CrO_3.9H_2O$;
$6K_2O.2Fe_2O_3.9CrO_3.6H_2O$; $6K_2O.3Fe_2O_3.10CrO_3.5H_2O$;
$2K_2O.2Fe_2O_3.7CrO_3.7H_2O$;
$3K_2O.2Fe_2O_3.6CrO_3$; $5K_2O.4Fe_2O_3.16CrO_3.8H_2O$.

Ferric ammonium chromate, $(NH_4)_2CrO_4.Fe_2(CrO_4)_3.4H_2O$, and **ferric potassium chromate,** $K_2CrO_4.Fe_2(CrO_4)_3.4H_2O$, have been prepared [2] as dark red crystalline plates by the slow evaporation of mixed solutions of ferric chloride and ammonium (or potassium) dichromate.

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[1] Lepierre, *loc. cit*

[2] Hensgen, *Ber.*, 1879, 12, 1656.

CHAPTER VIII.

IRON AND THE ELEMENTS OF GROUP V.

IRON AND NITROGEN.

Iron nitride, Diferro-nitride, Fe_2N or Fe_4N_2.—That iron combines with nitrogen was first observed by Depretz,[1] who gave to the compound the formula Fe_4N_2. A natural nitride of iron has been found in the lava of Etna [2] as the mineral *siderazote.* When heated in hydrogen ammonia is evolved, metallic iron constituting the residue. The importance of carefully studying the manner in which iron combines with nitrogen has been increasingly emphasised within the last decade, because the presence of nitrogen in steel has been shown to affect very materially the mechanical properties of the metal. For example, the absorption of 0·3 per cent. of nitrogen entirely suppresses the critical changes occurring in pure iron,[3] and prolonged heating *in vacuo* is necessary to effect the complete expulsion of the gas. Nitrogenised steels are brittle, showing an increase in hardness and tenacity, accompanied by a decrease in elongation and ductility—these properties resulting from the tendency of the nitrogen to retain the iron in the gamma form, and the carbide in solution. Tubes of malleable iron, after exposure for several days to ammonia at 800° C., become so brittle that they can be broken like porcelain with a blow from a hammer. A rod of soft charcoal iron, after like treatment, becomes so hard that it can be used as a drill.[4]

Nitrogen is slightly soluble in iron, the solubility being proportional to the square root of the pressure.[5]

Iron and steel absorb small quantities of nitrogen when heated to above 1200° C.,[6] and when melted under a high pressure of the gas.[7] Under ordinary conditions, however, merely heating the metal in nitrogen yields no perceptible quantity of nitride.[8]

Continuous heating of the reduced metal is stated to result in a small amount of nitrogen absorption,[9] as also exposure of the finely divided reduced metal at the ordinary temperature to nitrogen.[10]

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[1] Depretz, *Ann Chim. Phys.*, 1829, (2), 42, 122.

[2] Silvestri, *Pogg. Annalen,* 1876, 157, 165.

[3] Andrews, *J. Iron Steel Inst.*, 1912, II., 210.

[4] Beilby and Henderson, *Trans. Chem. Soc.*, 1901, 79, 1250. See also Tschischevski, *J. Iron Steel Inst.*, 1915, II., 47 ; Braune, *Rev. Metallurgie,* 1905, 2, 497.

[5] Jurisch, *Stahl und Eisen,* 1914, 34, 252.

[6] Sieverts and Krumbhaar, *Ber.*, 1910, 43, 893.

[7] Andrews, *loc. cit.* ; Rogstadius, *J. prakt Chem* , 1862, 86, 307.

[8] See Baur and Voerman, *Zeitsch. physikal. Chem.*, 1905, 52, 467.

[9] Sieverts, *ibid.*, 1907, 60, 129.

[10] Rogstadius, *J. prakt. Chem.*, 1862, 86, 307; Briegleb and Geuther, *Annalen,* 1862, 123, 228.

To obtain iron nitride indirect methods must be adopted. These may be enumerated as follows :—

1. Heating ferrous chloride in a current of dry ammonia,[1] the optimum temperature for the reaction being 480° C.[2] Ferrous bromide may be used instead of the chloride.[3]

2. Heating reduced iron in a current of dry ammonia at about 414° C., when hydrogen is rapidly evolved.[4] The heating is continued until the reaction is complete and no more hydrogen is liberated.

3. Heating electrolytic iron foil in dry ammonia at temperatures ranging from 600° to 1000° C. Hanemann [5] by this means succeeded in preparing iron nitride containing 11·1 per cent. of nitrogen, the product thus corresponding to the formula Fe_2N or Fe_4N_2. The most favourable temperature appears to be 650° to 700° C., in a rapid current of ammonia, the nitride peeling off in thin flakes if the metal is thick. Any carbon combines with the nitrogen and is removed.[6]

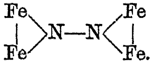
4. Heating spongy iron in dry ammonia, the optimum temperature being 450° to 475° C.[7]

5. Iron amalgam when heated in ammonia vapour loses its mercury content and is gradually converted into nitride.[8]

As prepared by any of the above methods, iron nitride is a grey powder of density about 6·25,[8] and soluble in dilute hydrochloric and sulphuric acids, yielding ferrous and ammonium salts. Nitric acid, even when concentrated, only acts slowly. Gaseous hydrogen chloride attacks it at 220° C., the reaction becoming vigorous at 350° C., ammonium and ferrous chlorides resulting. When heated in oxygen, ferric oxide is produced, nitrogen (not its oxides) being set free ; the reaction is detectable at 200° C. Hydrogen reduces it, the reaction beginning at 350° C. and being very rapid at 600° C.

Heated *in vacuo* or in nitrogen it begins to decompose at 500° C., and at 600° C. nitrogen is rapidly evolved. This reduction takes place even under a pressure of 18 atmospheres of nitrogen. For this reason there is no nitride formation when iron is heated at these temperatures in nitrogen.[9]

It has been suggested [10] that the constitution of iron nitride is represented by the formula :—[11]



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[1] Frémy, *Compt. rend.*, 1861, 52, 322 ; Warren, *Chem. News*, 1887, 55, 155 ; G. J. Fowler, *Chem. News*, 1900, 82, 245 ; *Trans. Chem. Soc.*, 1901, 79, 285.

[2] Girardet, *Bull. Soc. chim.*, 1910, (4), 7, 1028.

[3] Fowler, *Trans. Chem. Soc.*, 1901, 79, 285.

[4] Stahlschmidt, *Pogg. Annalen*, 1865, 125, 37 ; Fowler, *loc. cit.* ; *Chem. News*, 1893, 68, 152 ; Beilby and Henderson, *Trans. Chem. Soc.*, 1901, 79, 1245.

[5] Hanemann, *Inaugural Dissertation*, Technische Hochschule, Berlin, 1913.

[6] Charpy and Bonnerot, *Compt. rend.*, 1914, 158, 994. See also Braune, *Rev. Metallurgie*, 1905, 2, 497 Allen (*Chem. News*, 1880, 41, 231) heated iron wire in ammonia and obtained a product containing 2·5 per cent. of nitrogen.

[7] White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, 28, 1343.

[8] Fowler, *loc. cit.*

[9] Charpy and Bonnerot, *loc. cit.* See also Maxted, *J. Soc. Chem. Ind.*, 1918, 37, 105.

[10] Fowler and Hartog, *Trans. Chem. Soc.*, 1901, 79, 299.

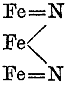
[11] White and Kirschbraun (*loc. cit.*) suggest that this nitride may be a solid solution of iron nitride in iron, namely,

$$Fe_3N_2 + Fe \rightarrow Fe_4N_2.$$

The heat of formation of iron nitride is as follows :—[1]

$$2[Fe]+(N)=[Fe_2N]+3040 \text{ calories.}$$

Two other nitrides of iron have been prepared,[2] namely, **ferrous nitride,** Fe_3N_2, and **ferric nitride,** FeN. The former is described as a black, oxidisable powder, obtained by heating lithium nitride with ferrous potassium chloride. The ferric nitride, FeN, resulted when lithium nitride was heated with ferric potassium chloride. It is a black substance, which, on being heated in air, oxidises to ferric oxide. These substances are, presumably, ferrous and ferric substituted ammonias, the constitutional formulæ being :—



and $Fe\equiv N$.

respectively.

Nitro-iron, $Fe_2(NO_2)$.—Attempts to prepare nitro-iron, analogous to nitro-nickel and nitro-cobalt, have been successful. It presumably results as an intermediate product when nitrogen peroxide diluted with nitrogen is passed over reduced iron. The peroxide is absorbed, but the resulting compound deflagrates even in a greatly diluted atmosphere of nitrogen peroxide. The corresponding cobalt and nickel derivatives, namely $Co_2(NO_2)$ and $Ni_2(NO_2)$, respectively, are considerably more stable.[3]

Several **triple nitrites** of iron have been prepared, namely :—

Ferrous lead potassium nitrite[4];
Ferrous barium potassium nitrite,[4] $FeBaK_2(NO_2)_6$;
Ferrous calcium potassium nitrite[4, 5];
Ferrous strontium potassium nitrite[4, 5];
Ferrous lead thallium nitrite.[6]

Ferrous nitrate.—The anhydrous salt has not been prepared. The *hexahydrate,* $Fe(NO_3)_2.6H_2O$, is very unstable, and is, in consequence, somewhat difficult to isolate. It may be obtained in solution by dissolving either ferrous sulphide or metallic iron in dilute nitric acid, of density ranging from 1·034 to 1·115. If metallic iron and acid of lower density be employed, the iron dissolves without any evolution of gas, and with the formation of ferrous nitrate and ammonium nitrate. By using iron and acid within the above-mentioned range of densities, ferrous nitrate is obtained, together with some ferric nitrate, the percentage of the latter increasing with the density of the acid. If the acid density is greater than 1·115, ferric nitrate is the main product.[7]

Ferrous nitrate may also be obtained in solution by grinding lead nitrate with an equivalent quantity of ferrous sulphate in the presence of dilute alcohol; double decomposition takes place, the ferrous nitrate passing into solution. Upon evaporation at room temperature the salt crystallises out as bright green rhombic prisms, which are faintly stable at 0° C. They melt at 60·5° C., but rapidly decompose when the temperature is raised by even a very small amount above this point. At higher temperatures a residue of ferric oxide is obtained.[1]

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[1] Fowler and Hartog, *loc. cit.*
[2] Guntz, *Compt. rend.*, 1902, 135, 738.
[3] Sabatier and Senderens, *Bull. Soc. chim.*, 1893, (3), 9, 669.
[4] Przibylla, *Zeitsch. anorg. Chem.*, 1897, 15, 419.
[5] No simple formula has been assigned.
[6] Przibylla, *Zeitsch. anorg. Chem.*, 1898, 18, 448.
[7] Scheurer-Kestner, *Ann. Chim. Phys.*, 1859, (3), 55, 330.

The solubility of ferrous nitrate in water at various temperatures is given as follows :—[2]

Temperature, °C. . . .	−9	0	18	24	25	50	60·5	
Grams $Fe(NO_3)_2$ per 100 grams solution.	39·68	41·53	45·14	46·51	..	..	62·50	(Funk)
	..	41·67	..	..	44·44	46·94	..	(Ordway)
Density of solution .	..	..	..	..	1·48	1·50	..	

Between −9° and 24° C. the composition of the saturated solution is given by the expression :—

$$Fe(NO_3)_2+(14{\cdot}198-0{\cdot}11242t)H_2O.$$

A break in the solubility curve at −12° C. indicates the formation of another hydrate, namely, the *nonahydrate*, $Fe(NO_3)_2.9H_2O$, which, however, has not been isolated. Its solubility in water is as follows :—

Temperature, °C. . . .	−27	−21·5	−19	−15·5
Grams $Fe(NO_3)_2$ per 100 grams solution . .	35·66	36·10	36·56	37·17

The heat of formation of the dissolved salt is :—

$$[Fe]+(N_2)+3(O_2)+Aq.=Fe(NO_3)_2.Aq.+119{,}000 \text{ calories.}$$
$$2HNO_3.Aq.+[Fe(OH)_2]=Fe(NO_3)_2.Aq.+21{,}500 \quad ,,$$

Ferric nitrate, $Fe(NO_3)_3$, is conveniently obtained by dissolving iron in nitric acid of density[3] 1·3 until the colour of the solution changes through green to dark red. An equal bulk of nitric acid of density 1·43 is now added, and the liquid allowed to cool.[4]

The salt separates out in hydrated crystals, which are usually pale violet in colour, the extent of hydration varying according to circumstances. Two definite hydrates are known[5]: namely, the *nonahydrate*,[6] $Fe(NO_3)_3.9H_2O$, which yields pale red deliquescent monoclinic crystals,[7] of the following crystallographic elements :—

$$a:b:c=1{\cdot}1296:1:1{\cdot}9180, \quad \beta=131° \ 34',$$

and the *hexahydrate*,[8] $Fe(NO_3)_3.6H_2O$, which crystallises in cubes, melting at 60·5° C.[9]

The crystals readily dissolve in water to a yellowish brown solution. In nitric acid they are much less soluble, and admit of ready recrystallisation from this acid. The crystals of nonahydrate melt at 40° C., yielding a dark red liquid (Ordway).

Although ferric nitrate crystals are usually pale violet in colour, when perfectly pure the salt is colourless. Ordway mentions having obtained colourless crystals, and this is confirmed by the more recent work of Lambert and Thomson,[1] who took elaborate precautions to prepare a very pure salt. A pure specimen of ferric chloride, free from arsenic, sulphate, alkali, or alkaline earth metals, was dissolved in conductivity water and electrolysed between iridium electrodes. The deposit of iron on the cathode was dissolved in pure diluted nitric acid, and the solution concentrated on the water-bath. The salt was crystallised from solution in concentrated nitric acid, separated from the mother liquor, and recrystallised several times from the concentrated acid. The crystals so obtained were colourless, or white when seen in bulk.

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[1] Ditte, *Compt. rend.*, 1879, 89, 641.

[2] Funk, *Ber.*, 1899, 32, 96; Ordway, *Amer. J. Sci.*, 1865, 40, 325.

[3] With more dilute acid ferrous nitrate is apt to be formed. See p. 175.

[4] Ordway, *Amer. J. Sci.*, 1850, 9, 30.

[5] Ditte (*loc. cit.*) has described a third—namely, the *trihydrate*, $Fe(NO_3)_3.3H_2O$.

[6] Ordway, *J. prakt. Chem*, 1851, 53, 64.

[7] Surgunoff, *Bull. Acad. Sci. Petrograd*, 1913, p. 407.

[8] Hausmann, *Annalen*, 1854, 89, 109; Wildenstein, *J. prakt. Chem.*, 1861, 84, 243.

[9] Funk, *Ber.*, 1899, 32, 96.

Ferric nitrate in aqueous solution is reduced by metallic silver to the ferrous condition, equilibrium being ultimately attained according to the equation

$$Ag+Fe(NO_3)_3 \rightleftharpoons AgNO_3+Fe(NO_3)_2.$$[2]

In dilute solution ferric nitrate is hydrolysed, yielding colloidal ferric hydroxide and free nitric acid. Such solution gives no coloration with potassium ferrocyanide. In less dilute solutions, to which potassium ferrocyanide has already been added, the blue colour gradually intensifies owing to the continued re-formation of ferric nitrate, as the equilibrium represented by the equation

$$Fe(OH)_3+3HNO_3 \rightleftharpoons Fe(NO_3)_3+3H_2O$$

is disturbed, owing to removal of ferric nitrate as insoluble Prussian blue.[3]

Aqueous solutions of ferric nitrate containing less than 0·1 per cent. are quite colourless.

The heat of formation of ferric nitrate is given by Berthelot as follows:—

$$2[Fe]+3(N_2)+9(O_2)+Aq.=2Fe(NO_3)_3.Aq.+314{,}300 \text{ calories.}$$

Numerous **basic ferric nitrates** have been described. They are uncrystallisable substances, and contain varying amounts of water. Hausmann,[4] by boiling solutions of ferric nitrate, obtained the following supposed compounds:—$8Fe_2O_3.2N_2O_5.3H_2O$, $36Fe_2O_3.N_2O_5.48H_2O$, and $8Fe_2O_3.N_2O_5.12H_2O$.

Scheurer-Kestner[5] identified $2Fe_2O_3.N_2O_5.H_2O$, $2Fe_2O_3.N_2O_5.2H_2O$, and $4Fe_2O_3.N_2O_5.3H_2O$. Cameron and Robinson,[6] however, have proved that no definite basic nitrates of iron are formed from solution at 25° C., the solid phase under these conditions consisting of a solid solution of ferric oxide, nitric acid, and water. It seems unlikely, therefore, that the substances described by Hausmann and Scheurer-Kestner are definite compounds.

An **acid nitrate,** $Fe_2O_3.4N_2O_5.18H_2O$ or $2Fe(NO_3)_3.2HNO_3.17H_2O$, appears also to have been prepared,[7] although later attempts to obtain the salt proved abortive.

With cæsium nitrate the double salt, $CsNO_3.Fe(NO_3)_3.7H_2O$, is formed[8] as pale yellow deliquescent crystals, melting at 33° to 36° C.

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[1] Lambert and Thomson, *Trans. Chem. Soc.*, 1910, 97, 2426.

[2] Noyes and Brann, *J. Amer. Chem. Soc.*, 1912, 34, 1016.

[3] Antony and Gigli, *Gazzetta*, 1896, 26, i. 293.

[4] Hausmann, *Annalen*, 1854, 89, 109.

[5] Scheurer-Kestner, *Ann. Chim. Phys*, 1859, (3), 55, 330.

[6] Cameron and Robinson, *J. Physical Chem.*, 1909, 53, 64.

[7] Cameron and Robinson, *loc. cit.*

[8] Wells and collaborators, *Amer. Chem. J.*, 1901, 26, 275.

NITROSO SALTS.

Ferrous salts readily combine in solution with nitric oxide to form nitroso derivatives, in which one molecule of nitric oxide is combined for each atom of ferrous iron. These substances, several of which are described in connection with their respective negative radicles (see pp. 93, 95, 105, 153, 161), readily dissociate in solution in accordance with the reversible reaction :—

$$Fe(NO)^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot} + NO.$$

By lowering the temperature, by raising the pressure, or by increasing the concentration of the free acid, the equilibrium is shifted from right to left, the amount of the nitroso salt being proportionately increased, but never in excess of the above-mentioned ratio.[1] When the increase is due to addition of acids, the colour of the solution changes, and the absorption band in the yellow region of the spectrum disappears. This is indicative of a change of constitution, complex anions being formed which are more stable than the nitroso cations.

Ferro-heptanitroso Sulphides, $MFe_4(NO)_7S_3$.

Nitroso derivatives of a more complex and more stable character than the foregoing were discovered by Roussin in 1858.[2] This investigator observed that a black voluminous precipitate is obtained when a mixture of ammonium sulphide and alkali nitrite is added to an aqueous solution of ferrous sulphate. On boiling, the precipitate passes into solution. The liquid is filtered, and, upon cooling, black crystals separate out, the composition of which has been the subject of considerable discussion. The reaction does not proceed in perfectly neutral solution, a green liquor only being produced, consisting of sulphides of iron and sodium, entirely free from any nitroso derivative. The presence of a small quantity of acid, however, results in the formation of the nitroso derivative, probably because it liberates nitrous acid, which acts direct upon the ferrous salt.

Roussin, as the result of his analyses, attributed to the nitroso derivative a formula which, translated into modern equivalents, becomes $H_2Fe_3(NO)_4S_5$.

Other later investigators have obtained similar substances either by an exact repetition of Roussin's method or by adopting slight modifications of the same. The various formulæ suggested by them for the nitroso derivative are given in the accompanying table :—

Formula.	Authority.
$Fe_3(NO)_4S_3.2H_2O$ . .	Porczinsky, *Annalen*, 1863, **125**, 302.
$Fe_2(NO_2)_2S_2(NH_2)_2$ . .	Demel, *Ber.*, 1879, **12**, 461, 1948.
$K_2Fe_7(NO)_{12}S_5.2H_2O$.	Pavel, *ibid.*, p. 1407, 1949.
$Fe_6(NO)_{10}S_5.4H_2O$ . .	Rosenberg, *ibid.*, p. 1715.
$2[Fe_3(NO)_4S_2NO_2]3H_2O$.	Marie and Marquis, *Compt. rend.*, 1896, **122**, 137.

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[1] See Kohlschütter and Sazanoff, *Ber.*, 1911, **44**, 1423 ; Gay, *Ann. Chim. Phys.*, 1885, (6), **5**, 145 ; Peligot, *ibid.*, 1833, (2), **54**, 17.

[2] Roussin, *Compt. rend.*, 1858, **46**, 224 ; *Ann. Chim. Phys.*, 1858, (3), **52**, 285.

In 1882, however, Pavel reconsidered his formula, and suggested

$$MFe_4(NO)_7S_3,$$

where M represents ammonium or one of the alkali metals.[1] This formula has since been accepted by the majority of workers in this field.[2]

Cryoscopic measurements of the sodium and potassium salts give values for the molecular weights equal to half those corresponding to the simple formula $MFe_4(NO)_7S_3$, and thus indicate that the salts are completely dissociated into the ions $M^\cdot$ and $Fe_4(NO)_7S'_3$; also electric conductivity measurements show that the salts are derived from a monobasic acid, and that they have the simple molecular formula :—[3]

$$[MFe_4(NO)_7S_3]_n, \text{ where } n=1.$$

The ferro-heptanitroso sulphides constitute a well-defined series of crystalline salts. In so far as the salts of the alkali metals are concerned, the order of their solubilities in water is as follows :—

Potassium, sodium, ammonium, rubidium, and cæsium.

The potassium salt is the most soluble, whilst the cæsium salt is quite insoluble in water. Both the rubidium and the cæsium salts may be prepared by double decomposition of dilute solutions of their chlorides with the nitroso salts of sodium or potassium. The thallium salt may be prepared in a similar manner by means of thallium sulphate. The nitroso salts of the alkaline earth metals—calcium, barium, and magnesium—are very soluble in water.

Potassium ferro-heptanitroso sulphide, $KFe_4(NO)_7S_3.H_2O$.—To prepare this salt, Pavel [4] raised a solution of potassium nitrite to boiling, added sodium sulphide, and, finally, with repeated shaking, a solution of ferrous sulphate in small quantities at a time. Upon crystallisation the nitroso derivative separated out in monoclinic crystals which were purified by recrystallisation from warm water and carbon disulphide in succession, and finally dried over phosphorus pentoxide.

The same compound results when a dilute solution of potassium sulphide or sulphydrate is added to one of ferrous sulphate containing nitric oxide.

When a solution of potassium ferro-dinitroso thiosulphate, $KFe(NO)_2S_2O_3.H_2O$, is boiled, sulphur dioxide is expelled, and ferric hydroxide precipitated. Upon concentrating the clear solution obtained by filtering, crystals of potassium ferro-heptanitroso sulphide are obtained.[5]

When acted upon with dilute sulphuric acid, the potassium salt yields the free acid, **hydrogen ferro-heptanitroso sulphide,** $HFe_4(NO)_7S_3$, as an insoluble, amorphous precipitate. It is very unstable. When boiled with dilute potassium hydroxide solution, the potassium heptanitroso derivative yields potassium ferro-dinitroso sulphide, $KFe(NO)_2S.2H_2O$ (see p. 181).

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[1] Pavel, *Ber.*, 1882, 15, 2600.

[2] See Rosenberg, *Arkiv Kem. Min. Geol.*, 1911, 4, (3), 1 ; Cambi, *Atti R. Accad. Lincei*, 1908, (5), 17, i. 202 ; 1907, (5), 16, ii. 658 ; Bellucci and Cesaris, *ibid.*, 1908, (5), 17, i 424 ; 1907, (5), 16, ii 740 ; Bellucci and Venditori, *ibid.*, 1905, (5), 14, i 28, 98 ; Hofmann and Wiede, *Zeitsch. anorg. Chem.*, 1895, 9, 296 ; Marchlewski and Sachs, *ibid.*, 1892, 2, 175.

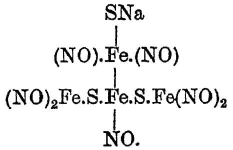
[3] Bellucci and Carnevali, *Atti R. Accad Lincei*, 1907, (5), 16, ii. 584.

[4] Pavel, *Ber.*, 1879, 12, 1407.

[5] Hofmann and Wiede, *Zeitsch. anorg. Chem.*, 1895, 9, 295.

Sodium ferro-heptanitroso sulphide, $NaFe_4(NO)_7S_3.2H_2O$, may be obtained in a similar manner to the potassium salt by boiling a solution of sodium ferro-dinitroso thiosulphate, as also by the action of sodium nitrite and sulphide solutions upon ferrous sulphate. In this latter reaction the sodium sulphide may be replaced by sodium thiocarbonate, Na_2CS_3.

The constitution [1] of this salt has been represented as follows :—



$$\begin{array}{c} \mathrm{SNa} \\ | \\ \mathrm{(NO).Fe.(NO)} \\ | \\ \mathrm{(NO)_2Fe.S.Fe.S.Fe(NO)_2} \\ | \\ \mathrm{NO.} \end{array}$$

Upon crystallisation the salt is obtained as monoclinic needles. It is more readily soluble in water than the potassium salt. It begins to decompose at 80° C., evolving nitric oxide. Heated with concentrated sulphuric acid, the salt decomposes, evolving nitric oxide, nitrogen, and hydrogen sulphide ; sulphur is precipitated out, and, upon evaporating the filtered solution, ferric sulphate and sodium and ammonium sulphates are left. On the other hand, when treated with ice-cold concentrated sulphuric acid, a portion only of the sodium heptanitroso derivative is decomposed, and the liberated iron atoms replace those of sodium in the remaining unattacked portion, yielding **ferrous ferro-heptanitroso sulphide,** $Fe[Fe_4(NO)_7S_3]_2$. This salt may also be obtained by double decomposition of the sodium salt with ferrous sulphate. The resulting precipitate is washed, recrystallised from ether, and finally from water. It begins to decompose at 55° C.

Ammonium ferro-heptanitroso sulphide, $NH_4Fe_4(NO)_7S_3.H_2O$, is readily obtained by double decomposition of the sodium salt with ammonium carbonate. The precipitated salt is washed and recrystallised from warm water rendered faintly alkaline with ammonia. It may be prepared by passing nitric oxide for some ten hours into freshly precipitated ferrous sulphide suspended in water, without previous addition of ammonia. The salt is extracted from the excess of ferrous sulphide with warm alcohol, and recrystallised from water.[2]

It also results when nitric oxide is passed through a mixture of ferrous hydroxide and carbon disulphide saturated with ammonia. The ferrous hydroxide is obtained by precipitation from ferrous sulphate, and the passage of nitric oxide is maintained for some eight hours. The ammonium salt is extracted from the mixture with hot alcohol. The same salt is formed even without the addition of ammonia, by the action of nitric oxide on ferrous hydroxide suspended in carbon disulphide.[2]

The crystals are monoclinic prisms, less soluble than those of the sodium salt, but, like the latter, they begin to decompose at 80° C.

By warming the solutions of this salt with the hydroxides of the alkaline earth metals until ammonia ceases to escape, the corresponding salts of **calcium, barium,** and **magnesium** have been obtained. These, however, are less stable than the ammonium salt.

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[1] Rosenberg, *Arkiv Kem. Min. Geol.*, 1911, 4, (3), 1.

[2] Hofmann and Wiede, *Zeitsch. anorg. Chem.*, 1895, 9, 295.

Tetramethyl ammonium ferro-heptanitroso sulphide, $N(CH_3)_4.Fe_4(NO)_7S_3$, yields triclinic crystals :—[1]

$$a:b:c=0{\cdot}8648:1:1{\cdot}3125. \quad \alpha=87^\circ\ 29{\cdot}5'. \quad \beta=106^\circ\ 7'.$$
$$\gamma=93^\circ\ 44'. \quad \text{Density, } 2{\cdot}056.$$

The **tetra-ethyl salt** is likewise triclinic, possessing the following crystallographic elements :—[2]

$$a:b:c=1{\cdot}0221:1:1{\cdot}0247. \quad \alpha=85^\circ\ 8'. \quad \beta=97^\circ\ 8'.$$
$$\gamma=99^\circ\ 17{\cdot}5'. \quad \text{Density, } 1{\cdot}883.$$

Heptanitroso ferro-sulphides of the following metals have also been obtained :—[2]

Cæsium, $CsFe_4(NO)_7S_3.H_2O$,
Rubidium, $RbFe_4(NO)_7S_3.H_2O$, and
Thallium, $TlFe_4(NO)_7S_3.H_2O$.

Of these the first-named is readily obtained by adding a solution of cæsium chloride to one of sodium heptanitroso ferro-sulphide, when the **cæsium** derivative is precipitated as an insoluble black crystalline powder. The **rubidium** derivative, obtained in an analogous manner, presents a similar appearance. The **thallium** salt is likewise difficultly soluble in water, and is obtained by double decomposition with thallium sulphate and the potassium derivative.

The **hydrazine,** $N_2H_4.Fe_4(NO)_7S_3$, and the **hydroxylamine,** $NH_2OH.Fe_4(NO)_7S_3$, derivatives have been prepared.[3]

Ferro-dinitroso Sulphides, $MFe(NO)_2S$.

On boiling potassium ferro-heptanitroso sulphide with dilute potassium hydroxide, ferric hydroxide is deposited, and, upon concentration of the filtered liquid, dark red crystals of **potassium ferro-dinitroso sulphide**[4] are obtained, to which the formula $KFe(NO)_2S.2H_2O$ is ascribed. The reaction may be represented as follows :—

$$2KFe_4(NO)_7S_3+4KOH=6KFe(NO)_2S+Fe_2O_3+N_2O+2H_2O.$$

The reverse transformation is effected by treatment with carbon dioxide, dilute acids, or ferrous chloride.[5]

The **sodium** salt, $NaFe(NO)_2S.4H_2O$, may be prepared in an analogous manner. It was the first salt of this series to be obtained, and Roussin,[6] its discoverer, gave to it a formula which, translated into modern equivalents, becomes $3Na_2S.Fe_2S_3(NO)_2$.

The **ammonium** salt cannot be obtained by boiling the ammonium hepta derivative with ammonium hydroxide, nor by the action of ammonia upon the free acid. It results, however, when the free acid is treated with ammonium sulphide. It is very unstable. The **cæsium, iron,** and **thallium** salts have been prepared. The last-named is quite insoluble in water and in alcohol.

The **free acid** is obtained by decomposing the sodium or potassium salt with dilute mineral acid. It is a yellowish brown amorphous substance, insoluble in water, more soluble in alcohol, and readily soluble in carbon disulphide. It slowly decomposes on standing.

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[1] Zambonini, *Zeitsch. Kryst. Min.*, 1910, 47, 620.
[2] Pavel, *Ber.*, 1879, 12, 1407.
[3] Bellucci and Cecchetti, *Atti R. Accad. Lincei*, 1906, (5), 15, ii. 467.
[4] Pavel, *Ber.*, 1882, 15, 2600.
[5] See Rosenberg, *Arkiv Kem. Min. Geol.*, 1911, 4, (3), 1.
[6] Roussin, *Compt. rend.*, 1858, 46, 224.

Ferro-dinitroso Thiosulphates, $MFe(NO)_2S_2O_3$.

Potassium ferro-dinitroso thiosulphate,[1] $KFe(NO)_2S_2O_3.H_2O$, results when nitric oxide is passed into a concentrated mixed solution of ferrous sulphate and potassium thiosulphate at room temperature. The solution becomes deep brown in colour, and reddish brown crystals of the potassium salt are obtained on concentration. The salt is but slightly soluble in cold water, and is insoluble in water-free alcohol and in ether. Concentrated sulphuric acid dissolves it without decomposition, yielding a greenish yellow solution.

Alkalies partly decompose the salt in the warm, whilst ammonia effects its complete decomposition.

The **sodium** salt,[1] $NaFe(NO)_2S_2O_3.2H_2O$, is obtained in a similar manner to the preceding salt. It yields either laminated or needle-shaped crystals, which are glistening black in appearance. They are appreciably more soluble in water than those of the potassium salt, and yield a deep brown solution. The salt is fairly stable below 0° C., but above that temperature continuously evolves nitric oxide. When its aqueous solution is boiled, sulphur dioxide is expelled and ferric hydroxide precipitated. Upon concentrating the clear solution obtained by filtering, crystals of sodium ferro-heptanitroso sulphide, $NaFe_4(NO)_7S_3.H_2O$, separate out.[2]

The **ammonium** salt,[1] $(NH_4)Fe(NO)_2S_2O_3.H_2O$, may be prepared in an analogous manner. It may be recrystallised from warm water, when it yields flat prisms, black in colour.

The **rubidium** and **cæsium** salts [2] have also been prepared, namely $RbFe(NO)_2S_2O_3.H_2O$ and $CsFe(NO)_2S_2O_3$. Thallium, apparently, does not yield an analogous salt under like conditions.

Nitroso pentacyanoferrates, $M_2[Fe(CN)_5NO]$.

For a discussion of these salts see Chapter IX.

IRON AND PHOSPHORUS.

Iron Phosphides.—Iron unites with phosphorus in several proportions. Nine supposed phosphides have been described, and four of them certainly exist [3]; these are, Fe_3P, Fe_2P, FeP, and Fe_2P_3.

Triferro phosphide, Fe_3P, occurs as crystals embedded in a eutectic mixture of this phosphide and iron when phosphorus and iron containing more than 84·4 per cent. of iron are fused together. Its density is 6·74, and melting-point 1110° C. It dissolves in concentrated aqueous hydrogen chloride, evolving pure hydrogen. Thus:—[3]

$$Fe_3P+6HCl+4H_2O=3FeCl_2+H_3PO_4+11H.$$

Triferro phosphide has been found in a cavity of pig iron from a blast furnace near Middlesbrough, in the form of small tin-white needles, strongly magnetic and lustrous. The crystals belong to the sphenoidal-hemihedral class of the tetragonal system,[1] with the ratio

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[1] K. A. Hofmann and Wiede, *Zeitsch anorg. Chem*, 1895, 8, 318.

[2] Hofmann and Wiede, *ibid.*, 1895, 9, 295.

[3] Le Chatelier and Wologdine, *Compt. rend.*, 1909, 149, 709.

$$a : c = 1 : 0{\cdot}3469.$$

Save for the absence of nickel the crystals are identical with rhabdite (see p. 26).

Diferro phosphide, Fe_2P, may be obtained by heating finely divided iron with copper phosphide in an electric furnace.[2] On dissolving the residue in nitric acid crystalline needles remain, of density 6·56, and melting at 1290° C. Diferro phosphide may also be obtained by fusing iron and phosphorus together and subsequently separating the more magnetic impurities. It is insoluble in acids, except aqua regia. Fluorine attacks it at red heat. When heated in air it oxidises to a basic ferric phosphate.

Iron monophosphide, FeP, results when vaporised phosphorus is passed over diferro phosphide at red heat, until no further increase in weight occurs.[3] It has also been prepared by heating phosphorus and iron together at red heat,[4] and also by the action of hydrogen phosphide upon ferric chloride,[5] ferrous sulphide,[6] or ferrous chloride [7] at red heat.

Heated in air it loses part of its phosphorus, ferric phosphate remaining.

Iron sesqui-phosphide, Fe_2P_3, may be prepared by heating ferric chloride to dull redness in phosphorus vapour,[8] or by the action of phosphorus iodide upon reduced iron.[9] It crystallises in brilliant grey needles, is not magnetic, and is insoluble in hydrochloric and in nitric acid, as also in aqua regia. It loses phosphorus when heated in air at bright red heat, and is slowly attacked by chlorine at dull red heat.

In addition to the foregoing, several other phosphides have been described, but the evidence in favour of these being separate chemical entities is not so convincing.[10] Rose believed that he had prepared **triferro tetraphosphide,** Fe_3P_4, by the action of hydrogen phosphide upon pyrites :—

$$4PH_3 + 3FeS_2 = Fe_3P_4 + 6H_2S.$$

The product is bluish grey in appearance, permanent in air, but, when heated to a high temperature, it oxidises to phosphorus pentoxide and an iron phosphate, the former being evolved as fumes. Density 5·04. It is not magnetic.[11]

By reduction of iron phosphate in hydrogen, or by passing vapours of phosphorus trichloride, tribromide, or tri-iodide over reduced iron at red heat, Granger obtained [12] grey prismatic crystals of composition

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[1] Spencer, *Min. Mag.*, 1916, 17, 340.

[2] Maronneau, *Compt. rend*, 1900, 130, 656 ; Le Chatelier and Wologdine, *loc. cit.*

[3] Le Chatelier and Wologdine, *loc. cit.*

[4] Schrotter, *Sitzungsber K Akad. Wiss. Wien*, 1849, 2, 301.

[5] Freeze and Rose, *Pogg. Annalen*, 1832, 24, 301.

[6] Struve, *Bull. Acad. Sci. Petrograd*, 1860, 1, 453.

[7] Dennis and B. S. Cushman, *J. Amer. Chem. Soc*, 1894, 16, 477.

[8] Granger, *Compt. rend.*, 1896, 122, 936 ; *Bull. Soc. chim.*, 1896, (3), 15, 1086 ; *Chem. News*, 1898, 77, 227.

[9] Le Chatelier and Wologdine, *loc. cit.*

[10] For further details of the iron-phosphorus alloys see this volume, Part III.

[11] Rose, *Pogg. Annalen*, 1826, 6, 212 ; Freeze and Rose, *ibid.*, 1832, 24, 301 ; Freeze, *ibid.*, 1867, 132, 225.

[12] Granger, *Compt. rend.*, 1896, 123, 176 ; *Bull. Soc. chim.*, 1896, (3), 15, 1086 ; *Chem. News*, 1898, 77, 227.

Fe_4P_3. Fe_5P_2 has also been described[1] as forming glistening needles, almost insoluble in concentrated nitric and in dilute sulphuric acid, but readily soluble in aqua regia.

Ferrous hypophosphite, $Fe(H_2PO_2)_2$, results on dissolving iron in hypophosphorous acid, air being carefully excluded.[2] The metal dissolves with evolution of hydrogen gas, and the salt passes into solution. It is also obtained by double decomposition of solutions of ferrous sulphate and the barium salt.[3] Ferrous hypophosphite crystallises in green octahedra, which readily oxidise on exposure to air.

Ferric hypophosphite, $Fe(H_2PO_2)_3$, is obtained[4] as an insoluble white powder on dissolving freshly precipitated ferric hydroxide in dilute hypophosphorous acid in the cold, and allowing to evaporate. It decomposes on warming, yielding a mixture of ferrous and ferric hypophosphites; on warming with acids an evolution of hydrogen phosphide takes place.

Ferrous phosphite, $FeHPO_3$, is prepared[5] as a white powder on saturating phosphorus trichloride with ammonia and mixing with a solution of ferrous sulphate. The precipitate is washed with hot water and dried in a vacuum over sulphuric acid. When heated it decomposes with incandescence, evolving hydrogen gas.

Ferric phosphite, $Fe_2(HPO_3)_3$, has been obtained only in solution[6] by dissolving freshly precipitated ferric hydroxide in phosphorous acid. On dilution with water a basic phosphite is obtained of probable composition $Fe_2(HPO_3)_3 2Fe(OH)_3$.

A **basic ferric phosphite,** $Fe_4(HPO_3)_6.Fe(OH)_3.5H_2O$, has been described.[7]

Ferrous orthophosphate occurs in nature in the octahydrated form as *vivianite* (see p. 26), $Fe_3(PO_4)_2.8H_2O$, in monoclinic crystals.[8] When perfectly pure the crystals are colourless,[9] but most specimens are tinged with a greenish blue in consequence of slight oxidation.[10] They melt at 1114° C.[11]

The salt may be obtained by heating diferrous orthophosphate with water to 250° C.[12]; by heating in a sealed tube mixed solutions of sodium phosphate and ferrous sulphate[13] in an atmosphere of carbon dioxide; or by electrolysis of sodium phosphate solution, using an iron anode.[14]

A powder containing at least 90 per cent. of the octahydrated ferrous phosphate is obtained by mixing solutions of sodium acetate (2 parts), sodium phosphate (10 parts), and ferrous sulphate (8 parts), and allowing to stand in the absence of air for several days. The precipitate is collected on a calico filter and dried at 40° C.[15] If the liquid and precipitate are maintained together at a temperature of 60° to 80° C. for a week, small crystals develop.

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[1] Kuhn, *Chem. Zeit.*, 1910, 34, 45.

[2] Rose, *Pogg. Annalen*, 1828, 12, 292.

[3] Wurtz, *Ann. Chim. Phys.*, 1846, (3), 16, 196.

[4] Rose, *loc. cit.*

[5] Rose, *Pogg. Annalen*, 1827, 9, 35.

[6] Grutzner, *Arch. Pharm.*, 1897, 235, 693.

[7] Berger, *Compt. rend.*, 1904, 138, 1500.

[8] Rammelsberg, *Pogg. Annalen*, 1845, 64, 251, 405.

[9] Colourless crystals have been found at Delaware in Pennsylvania.

[10] Deville, *Compt. rend.*, 1864, 59, 40.

[11] Cusack, *Proc Roy. Irish Acad.*, 1897, (3), 4, 399.

[12] Debray, *Ann. Chim. Phys.*, 1861, (3), 61, 437.

[13] Horsford, *Sitzungsber. K. Akad. Wiss. Wien*, 1873, 67, 466.

[14] Becquerel, *Ann. Chim. Phys.*, 1833, (2), 54, 149.

[15] E. J. Evans, *Pharm. J.*, 1897, (4), 4, 141.

The salt is insoluble in water; it readily oxidises in air, becoming bluish in colour.

The *hexahydrate*, $Fe_3(PO_4)_2.6H_2O$, has been prepared by the prolonged heating at 83° C. of finely powdered ferrous carbonate held in suspension in an aqueous solution of ammonium phosphate. The same substance results if a solution of ferrous carbonate in carbonic acid is heated with ammonium phosphate.[1] Gautier suggests that the mineral vivianite has originated in a similar manner to this, but that the reaction has proceeded for a longer time and at a lower temperature, which would explain the higher water content of the mineral.

Ferrous hydrogen orthophosphate, $FeHPO_4.H_2O$, has been obtained by dissolving iron in boiling phosphoric acid solution. The salt crystallises out in colourless needles which become bluish in air; it is insoluble in water, but readily dissolves in dilute acids and in ammonia. When heated with water to 250° C., it is converted into vivianite.[2]

On adding ammonium phosphate solution to ferrous chloride in alcohol saturated with nitric oxide at 0° C., a viscid oily liquid is precipitated, which crystallises when placed in a freezing mixture. Upon careful purification at low temperatures, brown flaky crystals are obtained, which melt at 16° C., and have the composition represented by the formula $FeHPO_4.NO$.[3] Upon exposure to air it oxidises slowly, yielding white ferric phosphate.

Ferrous dihydrogen orthophosphate, $Fe(H_2PO_4)_2.2H_2O$, is obtained by dissolving iron in excess of phosphoric acid solution in a current of hydrogen gas. Excess of acid is removed by washing with ether, and the substance dried in hydrogen.[4] Obtained in this way the salt is a white, crystalline powder, which readily oxidises in air, yielding a ferric salt. It is insoluble in alcohol, but readily dissolves in water.

Ferric orthophosphate.—The dihydrate, $FePO_4.2H_2O$, occurs in nature as *strengite* (see p. 27), and may be obtained in the laboratory in crystalline form by heating a concentrated solution of ferric chloride with phosphoric acid in a sealed tube at 180° to 190° C. for several hours, when it separates out as small rose-coloured monoclinic crystals, of density 2·74 at 15° C. The crystals closely resemble those of strengite, but the latter are rhombic. They are insoluble in nitric acid, but dissolve in hydrochloric acid.[5]

The amorphous dihydrate results as a yellowish-white precipitate on mixing solutions of sodium phosphate and ferric chloride or sulphate.[6] It may also be formed by dissolving iron in excess of phosphoric acid and exposing to the air[2]; by saturating a 48 per cent. solution of phosphoric acid on the water-bath with iron powder[7]; by boiling solutions of ferric metaphosphate, ferric dihydrogen orthophosphate, or of acid ferric phosphate; or by evaporating a mixed solution of ferric chloride (4 molecules) and disodium hydrogen phosphate (1 molecule) with an excess of nitric acid. As the liquid becomes syrupy, a copious separation of the phosphate occurs.[1]

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[1] Gautier, *Compt. rend.*, 1893, 116, 1491.

[2] Debray, *Ann. Chim. Phys.*, 1861, (3), 61, 437.

[3] Manchot, *Ber.*, 1914, 47, 1601.

[4] Erlenmeyer, *Annalen*, 1878, 194, 176

[5] de Schulten, *Compt. rend.*, 1885, 100, 1522.

[6] Heydenreich, *Chem. News*, 1861, 4, 158.

[7] Erlenmeyer, *Annalen*, 1878, 194, 176.

For the preparation of the pure salt, Caven [2] recommends addition of ferric chloride solution to one of orthophosphoric acid—made by boiling glacial metaphosphoric acid with water until it ceases to give any precipitate with barium chloride—in such proportions that rather more than twice as much acid, calculated as H_3PO_4, is present as is required to precipitate the iron. The precipitate thus obtained appears, when suspended in water, perfectly white; when strained on calico, it possesses a slightly bluish tint. Since hot water hydrolyses the salt, the washing should be conducted in the cold.

The resulting salt, whilst readily soluble in dilute mineral acids, is insoluble in cold acetic acid, phosphoric acid, and sodium phosphate. It is slightly soluble in citric and tartaric acid solutions, and readily dissolves in neutral aqueous ammonium citrate, yielding a green solution with a brownish tint.[3] The salt is insoluble in water, but hot water hydrolyses it, and boiling with excess of ammonia solution converts it into a mixture of ferric hydroxide [4] and ferric phosphate, or if the ammonia is present in great excess the ferric phosphate may be entirely decomposed. Thus :—

$$FePO_4+3NH_4OH \rightleftharpoons Fe(OH)_3+(NH_4)_3PO_4.$$

The reaction is reversible, and on boiling a suspension of freshly precipitated ferric hydroxide in an aqueous solution of ammonium phosphate, ammonia is liberated and ferric phosphate remains.[5] In consequence of this reversibility, and owing to the volatility of ammonia and the active mass of the ammonium phosphate produced, it is not easy to carry the first-named reaction to completion, namely, in the direction of from left to right in the foregoing equation.

These facts have an important bearing on the separation and estimation of iron by means of ferric phosphate.

The *trihydrate,* $FePO_4.3H_2O$, occurs in nature as the mineral *Koninckite* (see p. 27).

By heating molecular proportions of ferric chloride or acetate with phosphoric acid on the water-bath for two days, the *pentahydrated salt,* $2FePO_4.5H_2O$, is obtained as a pink powder, sparingly soluble in water and dilute acids. It may be regarded as the ferric salt of hydrogen ferri-diorthophosphate, $H_3[Fe(PO_4)_2]5H_2O$, and therefore written as $Fe[Fe(PO_4)_2]5H_2O$. Several alkali derivatives are known, the more important of which are as follow :—

Sodium ferri-diorthophosphate, $NaH_2[Fe(PO_4)_2]H_2O$, is obtained by heating for a prolonged period on the water-bath a solution of ferric hydroxide in phosphoric acid and sodium hydroxide. It yields pale, pink crystals, which gradually absorb moisture, yielding the *trihydrate.*

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[1] Arth, *Bull. Soc. chim.*, 1889, (3), 2, 324.

[2] Caven, *J. Soc. Chem Ind*, 1896, 15, 17.

[3] Heydenreich, *Chem. News*, 1861, 4, 158.

[4] Caven, *loc. cit.*; Rammelsberg, Watts' *Dictionary of Chemistry*, edition 1877, Art. "Phosphates" (Longmans).

[5] The colloidal phosphate, prepared by the action of concentrated ammonium hydroxide on ferric phosphate, has been studied by Holmes and Rindfusz, *J. Amer. Chem. Soc.*, 1916, 38, 1970.

Ammonium ferri-diorthophosphate, $NH_4.H_2[Fe(PO_4)_2]$, was first obtained by Danziger[1] by addition of a large excess of di-ammonium hydrogen phosphate to a strongly acid solution of ferric chloride. It is then formed as a white precipitate. If obtained in an analogous manner to the preceding salt, it yields pink, microscopic, hexagonal crystals. In the absence of a sufficient quantity of ammonia the acid salt, $[Fe(PO_4)_2.H_3]NH_3.7H_2O$, is obtained.

Sodium ferri-triorthophosphate, $NaH_5[Fe(PO_4)_3]H_2O$, results when sodium chloride or phosphate is heated on the water-bath with a solution of ferric hydroxide in phosphoric acid. It is a pale red, crystalline powder, sparingly soluble in water.

Colloidal ferric phosphate is obtained by dissolving ferric phosphate in ammoniacal di-ammonium hydrogen phosphate and dialysing the solution until all electrolytes have been washed away. The colloidal solution thus obtained is tasteless and without action on litmus. Addition of electrolytes, such as alkali chlorides, effects its gelatinisation.

Both potassium ferrocyanide and thiocyanate cause gelatinisation also, but induce no colour change, showing the absence of free ions from the solution.[2]

Ferric dihydrogen orthophosphate, $Fe(H_2PO_4)_3$, results when ferric oxide is dissolved in phosphoric acid until a precipitate begins to appear. The solution is washed free from excess of acid with ether and dried,[3] whereby a pink crystalline powder is obtained. When boiled with water, it yields ferric orthophosphate, $FePO_4.2H_2O$.

With water at the ordinary temperature it yields the anhydrous phosphate $FePO_4$ and free phosphoric acid. The greater the proportion of water, the more complete the decomposition.[4]

With a large excess of cold water a precipitate of composition $6Fe_3PO_4.Fe_2(HPO_4)_3$ has been obtained.

Acid ferric orthophosphate, $Fe_2O_3.2P_2O_5.8H_2O$ or $(FePO_4.H_3PO_4)_2.5H_2O$, is obtained in the form of pink crystals when ferric phosphate is dissolved in excess of phosphoric acid and the solution concentrated over sulphuric acid.[3] When boiled with water, neutral ferric orthophosphate, $FePO_4.2H_2O$, results.

Basic ferric phosphates occur in nature as the minerals *dufrenite,* $Fe_2(OH)_3(PO_4)$; *beraunite,* $FePO_4.2Fe_2(PO_4)(OH)_3.4H_2O$.

Ferrous metaphosphate, $Fe(PO_3)_2$, is prepared by the action of fused metaphosphoric acid on ferrous phosphate, oxalate, or chloride, or even metallic iron, at red heat in a current of carbon dioxide. The salt is obtained as a white insoluble powder, unaffected by hydrochloric or nitric acid, but attacked by hot concentrated sulphuric acid.[5]

Ferric metaphosphate, $Fe_2O_3.3P_2O_5.6H_2O$ or $Fe(PO_3)_3.3H_2O$, has been prepared[6] by dissolving ferric oxide in glacial phosphoric acid at 100° C. and maintaining the liquid at this temperature for several hours. The salt separates out in small crystals which take the form of pink rhombic plates derived from a monoclinic prism. The crystals are decomposed by water.

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[1] See Cohen, *J. Amer. Chem. Soc.*, 1907, 29, 714.

[2] Sell, *Proc. Camb. Phil. Soc*, 1904, 12, 388. See also Schneider, *Zeitsch. anorg. Chem.*, 1894, 5, 84.

[3] Erlenmeyer, *Annalen*, 1878, 194, 176

[4] Otto, *Chem Zentr.*, 1887, p 1563

[5] Colani, *Compt. rend.*, 1914, 158, 794; Ludert, *Zeitsch. anorg. Chem.*, 1894, 5, 37.

[6] Hautefeuille and Margottet, *Compt. rend.*, 1888, 106, 135.

If the foregoing reaction is carried out at 150° to 200° C., crystals of the *dihydrate*, $Fe(PO_3)_3.2H_2O$, are obtained as pink, rectangular lamellæ which are more stable towards water and are not attacked by alcohol.

At temperatures above 200° C. the *anhydrous* salt, $Fe(PO_3)_3$, is obtained, the form of which depends upon the temperature at which crystallisation is allowed to take place.[1] This salt was not first made known to science by this method, however, but [2] by addition of ferric chloride to an excess of diluted metaphosphoric acid, concentration of the liquid, and finally heating the residue to 315° C. (600° F.).

It may also be prepared by addition of ferric oxide, phosphate,[3] or of anhydrous ferrous sulphate [4] to metaphosphoric acid until no more of the salt will dissolve. The whole is then heated until the sulphuric acid has been expelled and crystallisation sets in.

As obtained in this manner, the salt is insoluble in water and in dilute acid, but soluble in concentrated sulphuric acid. Density 3·02.

Ferrous pyrophosphate, $Fe_2P_2O_7$, is obtained [5] as an unstable white powder by double decomposition of ferrous sulphate and sodium pyrophosphate; by heating ferrous orthophosphate; and by reduction of ferric phosphate with hydrogen. Upon exposure to air it turns green and ultimately brown.

Ferric pyrophosphate, $Fe_4(P_2O_7)_3.9H_2O$, is obtained as a white precipitate on adding ferric chloride solution to an equivalent amount of sodium pyrophosphate.[6] It is soluble in ferric chloride, in excess of sodium pyrophosphate, and also in acids.

When precipitated ferric hydroxide is dissolved in a 48 per cent. aqueous solution of phosphoric acid, in the proportion of one molecule of $Fe(OH)_3$ to seven of H_3PO_4, a solution is obtained from which :—[7]

(i.) With excess of cold water, a greyish yellow precipitate is obtained, of composition $4FePO_4.Fe_2(HPO_4)_3$.

(ii.) With boiling water, a precipitate of formula $6FePO_4.Fe_2(HPO_4)_3$ results.

(iii.) On boiling the filtrate from (ii.), the precipitate has the formula $4FePO_4.2Fe_2(HPO_4)_3$.

(iv.) On precipitation with alcohol, a substance $2FePO_4.3Fe_2(HPO_3)_3$ is obtained.

Are these to be regarded as definite compounds ?—Probably not.

Complex pyrophosphates analogous to ferri-orthophosphates in which atoms of iron enter the negative radicle, have been prepared.[8] Thus, **sodium ferri-pyrophosphate,** $Na_6[Fe_2(P_2O_7)_3].9H_2O$, analogous to sodium ferricyanide, is deposited at 30° C. as a pale violet microcrystalline precipitate from a 15 per cent. solution of sodium pyrophosphate saturated with ferric pyrophosphate. The *copper* and *silver* salts, $Cu_3[Fe_2(P_2O_7)_3].12H_2O$ and $Ag_6[Fe_2(P_2O_7)_3].4H_2O$ respectively, have been obtained from the sodium salt by double decomposition.

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[1] Hautefeuille and Margottet, *loc cit.*

[2] Maddrell, *Phil. Mag.*, 1847, 30, 322.

[3] Hautefeuille and Margottet, *Compt. rend.*, 1883, 96, 849, 1142.

[4] Johnson, *Ber.*, 1889, 22, 976.

[5] Schwarzenberg, *Annalen*, 1848, 65, 153.

[6] Ridenour, *Amer. J. Pharm.*, 72, 125.

[7] Erlenmeyer, *Annalen*, 1878, 194, 176.

[8] Pascal, *Compt. rend.*, 1908, 146, 231; Rosenheim and Triantaphyllides, *Ber.*, 1915, 48, 582.

Hydrogen ferri-pyrophosphate, $H_6[Fe_2(P_2O_7)_3].7H_2O$, results as a white solid when ferric pyrophosphate is heated for twelve hours at 50° C. with syrupy pyrophosphoric acid in acetone.

Sodium ferro-pyrophosphate, $Na_8Fe_2(P_2O_7)_3$, and **sodium ferro- and ferri-metaphosphates,** $Na_4Fe(PO_3)_6$ and $Na_3Fe(PO_3)_6$, have similarly been prepared.[1]

Alkali ferro-pyrophosphates reduce solutions of gold and silver salts in the cold, the free metals being obtained in the colloidal condition. Mercuric salts are reduced, yielding first mercurous salts and finally colloidal mercury, which is grey by reflected light, but a reddish brown colour by transmitted light. Cupric salts are reduced to colloidal cuprous hydroxide, which is yellow by transmitted light and affords a delicate reaction for copper. At 100° C. metallic copper is deposited as a thin film on glass. Solutions of platinum salts are not reduced even on boiling.[2]

Two series of complex ammonio-salts have been prepared of general formulæ :—[3]

$$\text{I. } [Fe_4(NH_3)_{24-4n}(P_2O_7)_n](P_2O_7)_{3-n}$$

and

$$\text{II. } [Fe_4(NH_3)_{12-4m}(P_2O_7)_{3+m}]R_{4m},$$

where R is an acid radicle, and n and m are small, whole numbers, of the order of 2 or 3.

Triphosphates.—A series of salts termed triphosphates, of general formula $MNa_3P_3O_{10}$, has been described,[4] where M represents a divalent metal. The ferrous salt, $2FeNa_3P_3O_{10}.23H_2O$, results on adding sodium triphosphate, $Na_5P_3O_{10}$, to a solution of ferrous sulphate. It crystallises in silky, white needles, which are stable when dry, but rapidly oxidise in contact with water.

The negative radicle of these salts appears to be compounded of the pyrophosphate, P_2O_7'''', and metaphosphate, PO_3', radicles, so that the anhydrous salt may be written as $FeNa_3(P_2O_7.PO_3)$.

Ferrous thio-orthophosphite, $Fe_3(PS_3)_2$ is prepared[5] by heating a mixture of ferrous sulphide, sulphur, and red phosphorus. It crystallises in black, hexagonal laminæ which are very stable, resisting markedly the action of acids and alkalies.

Ferrous thio-orthophosphate, $Fe_3(PS_4)_2$, results[6] on heating together ferrous sulphide and phosphorus pentasulphide, the latter being present in excess of that required by the equation

$$3FeS+P_2S_5=Fe_3(PS_4)_2.$$

The excess of pentasulphide distils away, leaving a black residue contaminated with ferrous sulphide, from which it is readily freed by treatment with dilute hydrochloric acid.

Ferrous thio-orthophosphate is a black crystalline substance which leaves a mark like graphite. When heated it does not fuse but burns, leaving a brown residue. It is insoluble in water and dilute acids.

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[1] Pascal, *Comp. rend.*, 1908, 146, 231; Rosenheim and Triantaphyllides, *Ber.*, 1915. 48, 582.

[2] Pascal, *Compt. rend*, 1908, 146, 862.

[3] Pascal, *ibid.*, 1908, 146, 279.

[4] Stange, *Zeitsch. anorg. Chem.*, 1896, 12, 444.

[5] Ferrand, *Compt. rend.*, 1896, 122, 621; *Ann. Chim. Phys.*, 1899, 17, 409.

[6] Glatzel, *Zeitsch. anorg. Chem.*, 1893, 4, 186.

Ferrous thio-pyrophosphite, $Fe_2P_2S_6$, has been obtained [1] by heating a mixture of sulphur and red phosphorus with excess of iron wire to redness and maintaining at this temperature for several hours. It yields greyish black hexagonal plates which appear brown by transmitted light. They are attacked by nitric acid, but more easily by this acid containing a little potassium chlorate.

Ferrous thio-pyrophosphate, $Fe_2P_2S_7$, has been obtained by heating the metal or its sulphide with sulphur and phosphorus as in the preparation of the preceding salt. It crystallises in lustrous lamellæ, which are insoluble in cold nitric acid.[2]

IRON AND ARSENIC.

Iron sub-arsenide, Fe_2As.—The possibility that this substance can exist is indicated by the shape of the freezing-point curve of arsenic-iron alloys.[3]

Iron mon-arsenide, FeAs, is obtained by heating iron in excess of arsenic in the absence of air. This may be effected by heating iron in a current of arsenic vapour at 335° to 385° C.,[4] or with arsenic in a bomb tube at 680° C.[5] It also results when the di-arsenide, $FeAs_2$, is reduced at 680° C. in a current of hydrogen.

As obtained by these methods, iron mon-arsenide is a silver-white crystalline substance, of density 7·83, and melting at 1020° C. It is non-magnetic.

Iron mon-arsenide has been found as dark, steel-grey rhombic crystals, of density 7·94, in the hearth of an old furnace in Cornwall.[6]

Iron sesqui-arsenide, Fe_2As_3, results when iron is heated in arsenic vapour at 395° to 415° C.[7] Density 7 22.

Iron di-arsenide, $FeAs_2$, occurs as the mineral *lolingite,* and may be prepared artificially by heating iron in arsenic vapour at 430° to 618° C.[7] Hilpert and Dieckmann [5] recommend heating finely powdered iron and arsenic in a bomb tube to *c.* 700° C. On treatment with dilute acid the pure di-arsenide is obtained as a silver-grey powder, of density 7·38. Insoluble in hydrochloric acid, both dilute and concentrated, it is slowly oxidised by nitric acid, yielding arsenic acid. Heated with concentrated sulphuric acid, sulphur dioxide is evolved. When heated in air it burns, yielding arsenious oxide and ferric oxide. It is non-magnetic.

Iron thio-arsenide, FeAsS, or $FeS_2.FeAs_2$, occurs in nature as the mineral *mispickel, arsenical pyrites* or *arsenopyrite* (see p. 24, where crystallographic data are given). If cobalt is also present, the mineral is known as *glaucodote,* (Fe, Co)AsS. When the arsenide is in excess, the mineral is called *pacite,* $FeS_2.4FeAs_2$.

Constitution.—Many suggestions have been made as to the constitution of mispickel. The structural formula suggested by Beutell[1] may be written

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[1] Friedel, *Bull. Soc. chim.*, 1894, 11, 1057; *Compt. rend.*, 1894, 119, 260.

[2] Ferrand, *Compt. rend.*, 1896, 122, 886.

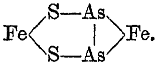
[3] Friedrich, *Metallurgie*, 1907, 4, 129.

[4] Beutell and Lorenz, *Centr Min*, 1916, p. 10

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

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

[7] Beutell and F. Lorenz, *Centr. Min*, 1916, p. 10.



This, however, offers no explanation for the fact that the percentage of sulphur in the crystals obtained from various localities shows considerable variation, as little as 18 05 per cent. and as much as 22·47 per cent. having been found.[2]

Chemical methods for determining the constitution lead to conflicting conclusions, precisely as in the case of iron pyrites (see p. 141), owing to uncertainty as to the state of valency of the iron in the mineral. The formula usually accepted is $FeS_2.FeAs_2$.

When heated in the absence of air, mispickel loses much of its arsenic.[3] This is explained on the assumption that the iron disulphide decomposes into free sulphur and ferrous sulphide:—

$$FeS_2 = FeS + S.$$

The sulphur then attacks the di-arsenide, causing the expulsion of the arsenic:—

$$FeAs_2 + S = FeS + 2As.$$

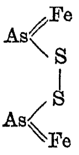
Combining the above reactions, the equation may be represented as

$$FeAs_2.FeS_2 = 2FeS + 2As.$$

Loczka therefore favours the formula $FeAs_2.FeS_2$ for mispickel.

On the other hand, when mispickel is heated in hydrogen, the whole of the sulphur is evolved as hydrogen sulphide,[4] whereas both pyrites and marcasite under similar conditions lose only half their sulphur, being converted into ferrous sulphide, FeS (see p. 141). These facts suggest that the pyrites molecule is absent, and that if iron disulphide is actually present, it is in some other form than ordinary pyrites.

The formula [4]



is suggestive.

Ferrous met-arsenite, $FeO.As_2O_3$ or $Fe(AsO_2)_2$ has been obtained by the action of potassium hydrogen arsenite, $K_2O.As_2O_3.H_2O$, upon a dilute solution of ferrous sulphate. It is greenish in colour, becoming brown upon exposure to air.[5] When a hot, saturated solution of arsenious acid containing ferrous iodide is allowed to cool, crystals of the compound $FeI_2.4As_2O_3.12H_2O$ are obtained, which slowly oxidise in air, and *in vacuo* over concentrated sulphuric yield up all their combined water. The iodide character of the salt is suppressed, from which it may be inferred that the iodine has combined with the arsenious oxide to yield a complex negative radicle.[1]

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[1] Beutell, *Centr. Min.*, 1911, p. 316.

[2] Arzruni and Baerwald, *Jahrb. Min.*, 1884, I., Ref 10.

[3] Loczka, *Zeitsch. Kryst. Min.*, 1889, 15, 41.

[4] Starke, Shock, and E. F. Smith, *J. Amer. Chem. Soc.*, 1897, 19, 948; Lightfoot, *ibid.*, 1894, 16, 624. See also Rammelsberg, *Jahrb. Min.*, 1897, II., 45.

[5] Reichard, *Ber.*, 1894, 27, 1019.

Ferric arsenite, $4Fe_2O_3.As_2O_3.5H_2O$, may be prepared by shaking freshly precipitated ferric hydroxide with an aqueous solution of arsenious oxide, or by adding sodium arsenite (or an aqueous solution of arsenious oxide) to ferric acetate. It is brown in colour, and oxidised by the air when moist.[2]

By the action of potassium hydrogen arsenite, $K_2O.As_2O_3.H_2O$, on dilute aqueous ferric chloride a yellow powder of composition $Fe_2O_3.As_2O_3$ or $FeAsO_3$ has been obtained.[3] A substance of similar chemical composition has been found in a crystalline deposit formed during the Deacon process of making chlorine. The crystals of the pure salt are monoclinic, their crystallographic elements being :—[4]

$$a : b : c = 0{\cdot}9405 : 1 : 0{\cdot}6234. \qquad \beta = 105^\circ\ 10{\cdot}5'.$$

The *pentahydrate*, $FeAsO_3.5H_2O$, found with the preceding salt, crystallises in the rhombic system.

On adding freshly precipitated ferric arsenite to potassium hydroxide solution until no more dissolves, and subsequently evaporating, the soluble potassium salt, $6K_2O.5Fe_2O_3.9As_2O_3.24H_2O$, is obtained as a reddish brown amorphous substance, which dissolves in water, yielding an alkaline solution.[5]

Ferrous ortho-arsenate, $Fe_3(AsO_4)_2.6H_2O$, occurs in nature as the mineral *simplesite.*

It may be prepared by the action of disodium hydrogen arsenate upon ferrous sulphate solution :—[6]

$$4FeSO_4+4Na_2HAsO_4=Fe_3(AsO_4)_2+Fe(H_2AsO_4)_2+4Na_2SO_4,$$

and gradually undergoes oxidation upon exposure to moist air, yielding ferric arsenate and ferric oxide.[7]

Ferric ortho-arsenate occurs in nature as the mineral *scorodite,* $FeAsO_4.2H_2O$, and may be produced artificially by heating iron to 150° C. with a solution of arsenic acid,[8] or by heating ferric arsenate in a similar manner with arsenic acid.[9]

The *monohydrate,* $FeAsO_4.H_2O$, is precipitated from solution.

The salt, when dried in air, is a dull white insoluble substance, containing one molecule of water. When heated at 100° C. it becomes anhydrous. On treatment with sodium hydrogen carbonate solution, both the monohydrate and the anhydrous salt cause effervescence to take place, a soluble double arsenate being produced. It would appear, therefore, that the hydrated salt is acidic, and determinations of its basicity indicate that its formula is $FeO.AsO_2(OH)_2$.[7]

Colloidal ferric arsenate is prepared by the action of ammonium hydroxide on the insoluble salt.[10]

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[1] Weinland and Gruhl, *Arch. Pharm.*, 1917, 255, 467.

[2] See Fehling, *Annalen,* 1850, 74, 87.

[3] Reichard, *Ber.*, 1894, 27, 1019.

[4] Arzruni and Schutz, *Zeitsch. Kryst Min.*, 1894, 23, 529.

[5] Dobbin, *Pharm. J.*, 1904, (4), 18, 585.

[6] Wittstein, *Jahresber.*, 1866, 19, 243.

[7] Duncan, *Pharm. J.*, 1905, (4), 20, 71.

[8] Verneuil and Bourgeois, *Compt. rend.*, 1880, 90, 223.

[9] Metzke, *Jahrb. Min.*, 1898, I., 169.

[10] Holmes and Rindfusz, *J. Amer. Chem. Soc.*, 1916, 38, 1970.

The *anhydrous* salt has been found as a deposit in the Deacon process for the preparation of chlorine, in the form of black prismatic crystals, belonging to the monoclinic system. Its crystallographic elements are :—

$$a : b : c = 0\ 6155 : 1 : 0\ 3221. \qquad \beta = 77° 8'.$$

Density 4·32.[1]

A hydrated *acid salt*, $2Fe_2(HAsO_4)_3.9H_2O$, results when solutions of disodium hydrogen arsenate and ferric chloride are mixed. The salt separates out as a white precipitate, soluble in aqueous hydrogen chloride.

On addition of disodium arsenate, Na_2HAsO_4, to iron ammonium alum, in the proportion of two molecules of the former to one of the latter, a precipitate of composition, $Fe_2O_3.As_2O_5$, is obtained, which varies in tint according to circumstances.[2] Thus, on adding a small quantity of the arsenate to the alum solution a white precipitate is obtained ; but, on reversing the procedure, the precipitate is brownish. The white precipitate turns yellow, and finally brown, however, when washed with water. In the presence of large excess of either constituent the basic salt, $3Fe_2O_3.2As_2O_5$, is obtained. The following substances have also been prepared : $4Fe_2O_3.3As_2O_5$, $Fe_2O_3.As_2O_5.17H_2O$, $2Fe_2O_3.3As_2O_5.22{\cdot}5H_2O$, and $Fe_2O_3.3As_2O_5.16{\cdot}7H_2O$.

Several basic arsenates occur as minerals, namely, *iron sinter* or *pharmaco-siderite*, $3FeAsO_4.Fe(OH)_3.6H_2O$; *Yukonite*, $(Ca_3, Fe_2)As_2O_8.2Fe(OH)_3.5H_2O$.

The double arsenates, **ammonium ferric ortho-arsenate,** $(NH_4)H_2AsO_4.FeAsO_4$, and **potassium ferric arsenate,**[3] possibly represented by the formula $KH_2AsO_4.FeAsO_4$, have been obtained.

An arsenate containing copper—namely, $CuFe_4As_4O_{17}$ or $CuO.2Fe_2O_3.2As_2O_5$—has been found in the form of rhombic crystals as a deposit during the manufacture of chlorine by the Deacon process.[4]

Other double ferric arsenates are : $K_2O.Fe_2O_3.2As_2O_5$, $Na_2O.Fe_2O_3.2As_2O_5$, $3K_2O.2Fe_2O_3.3As_2O_5$, and $3Na_2O.2Fe_2O_3.3As_2O_5$.[5]

IRON AND ANTIMONY.

Ferro mono-antimonide, FeSb.—By heating iron and antimony together in a crucible alloys of the two metals, in varying proportions, have been obtained. Laborde[6] concluded, as a result of studying the density and specific heat, that a compound, Fe_3Sb_4, is formed ; but Maey,[7] from an examination of the specific volumes of the alloys, concludes that the compound formed is more correctly represented by the formula FeSb.

The **di-antimonide,**[8] $FeSb_2$, is obtained in an analogous manner, and occurs as crystals in raw antimony obtained in the commercial extraction of this metalloid.

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[1] Ježek and Šimek, *Zeitsch. Kryst Min.*, 1914, 54, 188.
[2] Metzke, *Zeitsch. anorg. Chem* , 1899, 19, 457.
[3] Curtman, *J. Amer. Chem. Soc.*, 1910, 32, 626.
[4] Arzruni and Schutz, *Zeitsch. Kryst. Min.*, 1894, 23, 529.
[5] Lefevre, *Compt. rend.*, 1890, 111, 36.
[6] Laborde, *ibid.*, 1896, 123, 227.
[7] Maey, *Zeitsch. physikal. Chem.*, 1901, 38, 292.
[8] Kurnakoff and Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 227.

It crystallises according to the rhombic system,[1] the axial ratios being

$$a : b : c = 0\ 75909 : 1 : 0{\cdot}96872.$$

It melts at 732° C., and at that temperature undergoes partial decomposition into **triferro di-antimonide,** Fe_3Sb_2 :—

$$3FeSb_2 \rightleftharpoons Fe_3Sb_2 + 4Sb.$$

Ferrous thio-antimonite, $Fe_3Sb_2S_6$ or $3FeS.Sb_2S_3$, is obtained by precipitation from a solution of a soluble ferrous salt with a dilute solution of potassium thio-antimonite.[2] It is readily oxidised, and always contains potassium if prepared from concentrated solutions.

Ferrous metantimonate, $Fe(SbO_3)_2.FeO$ or $2FeO.Sb_2O_5$, occurs in nature as *tripuhyte* (see p. 28).

Ferric metantimonate, $2Fe(SbO_3)_3.13H_2O$, has also been obtained.[3]

Ferric ortho-antimonate, $Fe_2O_3.Sb_2O_5$ or $FeSbO_4$, is obtained in the heptahydrated condition, $2FeSbO_4.7H_2O$, by addition of excess of a concentrated solution of a ferric salt to a boiling solution of sodium antimonate.[4] The **di-antimonate,** $Fe_2O_3.2Sb_2O_5.11H_2O$, prepared by precipitating iron ammonium alum with potassium antimonate,[3] is a yellow salt which becomes anhydrous at 100° C.

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[1] Iskull, *Zeitsch Kryst. Min*, 1906, 42, 374.

[2] Pouget, *Compt. rend.*, 1899, 123, 104.

[3] Beilstein and Blase, *Chem Zentr.*, 1889, p. 803.

[4] Ebel, *Ber*, 1889, 22, 3044.

CHAPTER IX.

IRON AND THE ELEMENTS OF GROUPS IV. AND III.

IRON AND CARBON.

Triferro carbide, Fe_3C, known to the metallurgist as *cementite,* occurs in meteorites associated with the carbides of nickel and cobalt, as the mineral *Cohenite,* $(Fe, Co, Ni)_3C$ (see p. 12). It occurs normally in steel, and was first isolated [1] by acting on steel with a solution of potassium bichromate in sulphuric acid. The metal dissolves, leaving the cementite as a black powdery residue.

A variation of this method consists in using bars of steel as anodes in baths of dilute acid, platinum plates suspended in porous cells serving as cathodes.[2]

A better method consists in first preparing a steel very rich in carbide and then effecting the isolation of the latter by dissolution of the free metal in acid.[3] To this end 1000 grams of iron are heated with arc-lamp or sugar carbon (100 grams), to white heat, and poured on to a large iron plate to solidify. After removing any scale, etc., the mass is powdered, digested for several weeks with normal acetic acid, and then with $\frac{1}{5}$-normal hydrochloric acid. Any remaining carbon is removed by levigation, and the residual cementite washed with alcohol and ether, and finally dried in a vacuum.

As obtained in this manner, cementite is grey in colour and very brittle; it can be powdered in the hand. Its hardness is 3 2 to 3 3; density [4] at 21° C. 7·396; molecular volume 24·34. It crystallises in pseudo-hexagonal form.[5] The specific heat of cementite, as calculated from data obtained with carbon steels, is 0·1581.[6]

The heat of formation of cementite has been determined by different investigators with very varying results, as indicated in the accompanying table:—

$$3[Fe]+[C]=[Fe_3C]+x \text{ calories.}$$

---

[1] Abel, *Iron,* 1883, I, 76; 1885, I, 115; *Proc. Inst. Mech. Eng.,* 1883, p. 56; 1885, p. 30.

[2] Osmond and Werth, *Ann. Mines,* 1885, 8, 5; Arnold and Read, *Trans. Chem. Soc.,* 1894, 65, 788; Mylius, Foerster, and Schoene, *Zeitsch. anorg. Chem.,* 1896, 13, 38; Campbell, *Amer. Chem. J.,* 1897, 18, 836.

[3] Moissan, *Compt. rend.,* 1897, 124, 716; Ruff and Gersten, *Ber.,* 1912, 45, 63.

[4] Moissan (*Compt. rend.,* 1897, 124, 716) finds a density of 7 07 at 16° C.

[5] Groth, *Chemische-Krystallographie,* 1906, vol. i.

[6] Oberhoffer and Meuthen, *Metallurgie,* 1908, 5, 173.

Value of x (calories).	Authority
$-15,300$	Ruff and Gersten, *Ber.*, 1913, **46**, 394; 1912, **45**, 63.
No sensible heat evolution.	Baykoff, *Rev. Metallurgie, Mem.*, 1911, **8**, 315.
$+2270$	Jermiloff, *J. Russ. Metall. Soc.*, 1911, p. 351.
$+8940$	Schenk, Semiller, and Falke, *Ber.*, 1907, **40**, 1704.
$+8494$	Campbell, *J. Iron Steel Inst.*, 1901, **I.**, 211.

The evidence is admittedly conflicting, but the balance of evidence is distinctly in favour of the view that cementite is an endothermic substance, as indicated by the results of Ruff.

The suggestion has frequently been made that cementite is not a compound, but a solid solution of carbon in iron.[1] This view is not generally accepted, however, as otherwise a whole series of solid solutions containing varying percentages of carbon might be expected to exist, which is not the case.

When damp, cementite is rapidly oxidised in air, yielding a mixture of hydrated oxide and carbonaceous material. It is not altered by exposure to dry air; when very finely divided, it burns in air below 150° C., becomes incandescent in bromine vapour at about 100° C., in chlorine at a somewhat lower temperature, and in sulphur vapour at about 500° C.[2] Although insoluble in concentrated nitric acid, cementite dissolves in nitric acid of density 1·18 to 1·2, yielding a brown-coloured solution, the depth of colour being proportional, other things being equal, to the amount of carbide in solution. By dissolving a given weight of steel in nitric acid, therefore, and comparing the colour obtained with that when the same weight of a steel of known composition is employed, it is possible to estimate with considerable accuracy the amount of cementite in the first steel. This is known as the *Eggertz test*, and is largely used in steel works.

Cementite is less readily attacked than metallic iron by dilute hydrochloric acid; it is gradually dissolved by a normal solution of the acid, and readily in a concentrated solution, the gaseous products being hydrogen and hydrocarbons.[3]

The molecule of cementite is probably not represented by the simple formula Fe_3C, but by $(Fe_3C)_n$, where n is some whole number greater than unity. At present there appears to be no method of determining the value to be assigned to n.

When iron containing cementite is maintained at a temperature a little above 700° C. for some time, the carbide dissociates almost completely into γ iron and graphite.[4] This is quite in accordance with the view that cementite is an endothermic compound.

A consideration of the influence of cementite upon the metallurgical properties of iron is reserved for later discussion.[5]

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[1] See, for example, Baykoff, *loc cit.*

[2] Moissan, *loc. cit.*

[3] Mylius, *loc cit*; Campbell, *loc cit*

[4] Ruff and Goecke, *Metallurgie*, 1911, 8, 417; *Zeitsch. angew. Chem.*, 1911, 24, 1134.

[5] See this volume, Part III.

Diferro carbide, Fe_2C.—By heating pure iron in a graphite crucible in contact with carbon, in an electric vacuum furnace, Ruff and Goecke [1] have been able to determine the solubility of carbon in liquid iron at temperatures ranging from 1220° to 2626° C., and to prepare a diferro carbide, Fe_2C, the existence of which was suspected as resulting when cementite is subjected to prolonged annealing below 600° C.[2] The results were obtained by suspending the crucible in the furnace, and when the desired temperature had been reached and maintained for a sufficient length of time the crucible was released by a mechanical device and dropped into ice water. The metal was thus rapidly quenched without fear of dissociation due to slow cooling. The combined carbon was then estimated, the results being as follows :—

Temperature. °C.	Combined Carbon. Per cent.	Temperature. °C.	Combined Carbon. Per cent.
1220	4·58	2169	8·21
1305	4·81	2220	9·60
1522	5·46	2271	8·97
1623	5·78	2320	8·61
1823	6·59	2420	8·09
2020	6·95	2475	7·78
2122	7·51	2626	7·45

These results, when plotted in the form of a curve (see fig. 8), exhibit a break at 1837° C., corresponding to the composition of cementite, Fe_3C. A maximum occurs at 2220° C., with 9·60 per cent. of combined carbon, which corresponds to diferro carbide, Fe_2C. Up to this temperature

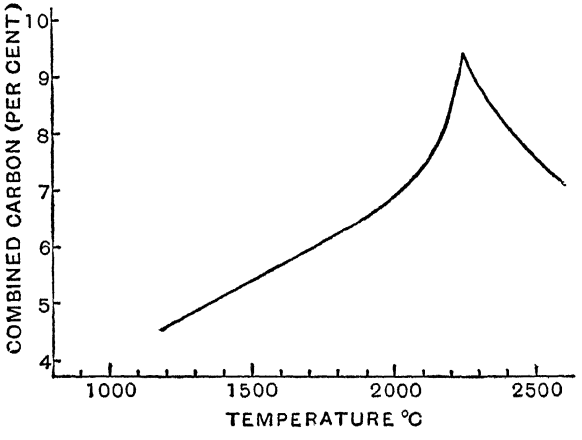

FIG. 8.

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[1] Ruff and Goecke, *Zeitsch. angew. Chem.*, 1911, 24, 1134 ; *Metallurgie*, 1911, 8, 417 ; Ruff, *ibid.*, pp. 456, 497.

[2] E. D. Campbell and Kennedy, *J. Iron Steel Inst.*, 1902, II., 288 ; Benedicks, *Metallurgie*, 1909, 6, 567.

it was observed that the molten mass remained uniformly liquid, with a bright reflecting surface. Above this temperature graphite began to separate out, but the temperature had to be raised very carefully, as otherwise the whole mass became suddenly ejected from the crucible, in consequence of the violent decomposition of the diferro carbide into iron and free graphite, with evolution of heat, the compound being endothermic.

Both carbides, Fe_3C and Fe_2C, are thus endothermic compounds at temperatures above 700° C., and the diminished solubility of graphite in iron above 2220° C. is due to dissociation of the diferro carbide. Below 2220° C. the reaction

$$3Fe_2C \rightleftharpoons 2Fe_3C+C$$

obtains, whilst at 1837° C. the cementite dissociates:—

$$Fe_3C \rightleftharpoons 3Fe+C.$$

Iron dicarbide, FeC_2.—A substance of this composition has been prepared [1] by allowing melts of iron, containing from 6 to 10 per cent. of carbon, to cool. Crystallisation begins at 2380° to 2000° C., a pale yellow carbide separating out, with a silvery reflex. It is slowly attacked by nitric acid, and, when immersed in dilute copper sulphate solution, becomes coated with a film of metallic copper.

When ammonium ferrocyanide, or its double compound with ammonium chloride, is heated, a black magnetic powder is obtained. This, upon ignition in air, is completely transformed into ferric oxide without any change in weight, and is believed [2] to be the dicarbide, FeC_2.

Several other carbides have been described, namely, the **monocarbide,**[3] FeC; **tetraferro carbide,**[3] Fe_4C (which decomposes into γ iron and graphite at temperatures below 1130° C.); FeC_4,[4] Fe_3C_2,[4] Fe_5C,[5] and $Fe_{12}C$.[5] The two last-named are obtained by the prolonged action of carbon monoxide on iron at red heat. $Fe_{12}C$ is more readily soluble in sulphuric acid than Fe_5C, which enables the latter to be separated:—

$$Fe_{12}C+12H_2SO_4=12FeSO_4+CH_4+10H_2.$$

Iron Carbonyls.

Several compounds of iron and carbon monoxide are known. Mond and Quincke [6] were the first to obtain experimental evidence of the existence of volatile iron carbonyls; they succeeded in volatilising reduced iron in a current of carbon monoxide to a very slight extent, and concluded that a tetracarbonyl, $Fe(CO)_4$, had been produced corresponding to the nickel analogue, $Ni(CO)_4$, which had been prepared the previous year.[7] A few months later Mond and Langer [8] succeeded in isolating the iron carbonyl, and found it to be not the tetra but the penta derivative.

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[1] Wittorf, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1613.
[2] Ljubavin, *ibid.*, 1912, 44, 609.
[3] Wittorf, *loc. cit.*
[4] Franck, *Stahl und Eisen*, 1896, 16, 585; *Chem. Zentr.*, 1896, II., 573.
[5] Gautier and Clausmann, *Compt rend.*, 1910, 151, 16.
[6] Mond and Quincke, *Trans. Chem. Soc*, 1891, 59, 604.
[7] Mond, Langer, and Quincke, *ibid.*, 1890, 57, 749.
[8] Mond and Langer, *ibid.*, p 1090.

Iron pentacarbonyl, $Fe(CO)_5$, was obtained by Mond and Langer by allowing finely divided iron, obtained by reduction of ferrous oxalate in a current of hydrogen, to remain twenty-four hours in an atmosphere of carbon monoxide. The gas was gradually absorbed, and, on warming the whole to 120° C., the carbonyl distilled over and condensed in a tube kept at −20° C.[1]

As obtained in this way iron pentacarbonyl is a somewhat viscous liquid, pale yellow in colour, which solidifies at about −21° C. to a mass of yellow needle-shaped crystals. On heating the vapour it dissociates into metallic iron and carbon monoxide, dissociation being practically complete at 216° C.[2]

The empirical formula, $Fe(CO)_5$, has been confirmed in several analyses, and the fact that the molecule is single and correctly represented by the above formula, when the carbonyl is dissolved in benzene, has been proved by cryoscopic measurements. The solid carbonyl melts at −19·5° to −20° C., and the liquid boils at 102·5° C., under 760 mm. pressure. Its density at various temperatures has been determined as follows:—

Temperature. °C.	Density.
0	1·4937
21·1	1·4565
40	1·4330
60	1·3825

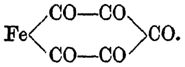
Its mean coefficient of expansion with rise of temperature is 0·00138. Its vapour pressure at various temperatures is as follows:—

Temperature, °C. . . .	−7	0	16·1	18·4	35	57	78
Vapour pressure in mm.	14·0	16·0	25·9	28·2	52·0	133·0	311·2

The halogens decompose solutions of the carbonyl in carbon tetrachloride with the formation of ferrous salts. In the presence of excess of chlorine, however, ferric chloride is formed. The velocity of reaction falls rapidly from chlorine to iodine.

Iron pentacarbonyl is adsorbed by metallic iron.[3]

The fact that the halogens decompose the pentacarbonyl, yielding ferrous salts, apparently suggests that the iron is merely divalent in the carbonyl. If so, the structural formula is presumably: [4]



Gaseous hydrogen chloride and bromide are without action upon liquid iron pentacarbonyl, but hydrogen iodide reacts with it, yielding ferrous iodide, carbon monoxide, and hydrogen. When exposed to sunlight, the pentacarbonyl, either alone or in solution, decomposes,[1] yielding :—

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[1] Stoffel (*Chem. Weekblad,* 1911, 8, 722) has investigated the conditions governing the formation of $Fe(CO)_5$ and shows that the presence of ammonia accelerates the reaction.

[2] Dewar and H. O. Jones, *Proc. Roy. Soc*, 1905, A, 76, 558.

[3] Stoffel, *Eighth Inter. Cong. App. Chem.*, 1912, 2, 225.

[4] Mond, *loc. cit.*; Gladstone, *Phil. Mag.*, 1893, (5), 35, 204; Friend, *The Theory of Valency* (Longmans, 1909), p. 117; contrast Silva, *Bull. Soc. chim.*, 1897, (3), 15, 835.

Diferro nonacarbonyl, $Fe_2(CO)_9$, which separates out as orange-red crystals, which are stable in dry air. The reaction is as follows :—

$$2Fe(CO)_5 \rightleftharpoons Fe_2(CO)_9 + CO.$$

The electric arc only induces the above change slowly, whilst the acetylene flame has very little influence. Blue light is most effective, the activity falling as the red end of the spectrum is approached. Variation of pressure up to 125 atmospheres is without influence, whilst heating to 60° or 100° C. entirely inhibits the change. The reaction induced by light is slowly reversed in the dark. The reaction proceeds more readily in ether, alcohol, or light petroleum solution than in benzene.

To obtain the nonacarbonyl in a pure condition, the penta derivative is dissolved in dry ether or light petroleum, and exposed to sunlight. The resulting crystals are dried over sulphuric acid and solid paraffin. The nonacarbonyl is practically insoluble in ether, benzene, or light petroleum ; slightly more soluble in ethyl alcohol or acetone ; and more so in pyridine. Its density at 18° C. is 2 085. On warming, it decomposes at about 100° C., yielding the pentacarbonyl, free iron, and carbon monoxide. Thus :—

$$2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + 3CO.$$

When crystals of the nonacarbonyl are warmed with certain solvents to from 50° to 90° C., in an atmosphere of carbon dioxide, they dissolve, yielding green solutions which contain a third carbonyl, namely :—

Iron tetracarbonyl, $Fe(CO)_4$, the analogue of nickel carbonyl. Dewar and Jones[2] obtained it in the form of dark green prismatic crystals from the green toluene solution. Iron tetracarbonyl is stable under ordinary conditions, but dissociates into metallic iron and carbon monoxide at 140° to 150° C. The crystals have a density of 1 996 at 18° C., and are soluble in toluene, light petroleum, etc., yielding dark green solutions which slowly decolorise at 100° C., and rapidly at 140° C., metallic iron being deposited. From cryoscopic measurements it appears that the tetracarbonyl has a high molecular weight when dissolved in benzene.

Ferro-nickel nonacarbonyl, $FeNi(CO)_9$, appears to be formed when iron pentacarbonyl is dissolved in nickel tetracarbonyl.[3]

Ferrous carbonate, $FeCO_3$, occurs in nature as *spathic iron ore* (see p. 20), which, however, is not pure, even in the crystalline form, as it contains several other isomorphous carbonates. When crystalline, the mineral is generally known as *chalybite* or *siderite*. The crystals belong to the hexagonal system, and are brown in colour. Upon exposure to moisture and air they are gradually converted into hydrated ferric oxide. When heated, they begin to decompose at about 400° C.[4] in air.

In the laboratory ferrous carbonate may be obtained as a white precipitate by adding sodium carbonate to a solution of ferrous sulphate in the absence of air. If air is present, the precipitate rapidly turns green in consequence of oxidation, carbon dioxide is evolved, and ultimately the mass consists almost entirely of ferric hydroxide.

---

[1] Dewar and Jones, *Proc. Roy. Soc.*, 1905, A, 76, 558 ; 1907, A, 79, 66.
[2] Dewar and Jones, *loc. cit.*
[3] Dewar and Jones, *ibid*, 1905, A, 76, 558.
[4] Friedrich and L G. Smith, *Centr. Min*, 1912, pp. 616, 651, 684.

If the air is entirely excluded, the original white precipitate may be washed and dried and kept in a hermetically sealed tube.

Microscopic crystals of ferrous carbonate have been obtained by precipitating the salt from a ferrous solution with sodium hydrogen carbonate, and heating the mixture in closed tubes for twelve to thirty-six hours at 150° C.

The heat of formation of ferrous carbonate is [1]

$$[FeO]+(CO_2)=[FeCO_3]+25,200 \text{ calories.}$$

Ferrous hydrogen carbonate or **ferrous bicarbonate**, $FeH_2(CO_3)_2$, exists in solutions obtained by dissolving ferrous oxide or carbonate in water charged with excess of carbon dioxide. On exposure to air carbon dioxide is evolved, and a precipitate is obtained consisting essentially of ferric hydroxide.[2]

The solubility of ferrous carbonate in water and in aqueous solutions of certain mineral salts under a pressure of two atmospheres of carbon dioxide is as follows :—[3]

Salt.	Concentration in Grams per Litre.	$FeCO_3$ Grams per Litre at 14° to 18° C.
..	0·0	6·1907
$MgCl_2.6H_2O$ . .	86·9	5·8403
	700·0	4·5553
	1150·0	4·4587
	1437·5	4·6934
	1725	5·3975
	2300	9·0524
$Na_2SO_4.10H_2O$ . .	137·7	7·9428
	Saturated at 14° C.	9·578
$MgSO_4.7H_2O$ . .	105·3	6·2423
	Saturated at 18° C.	7·3922

Ferrous potassium carbonate, $FeK_2(CO_3)_2.4H_2O$, may be prepared by mixing, out of contact with air, a concentrated solution of ferrous chloride with excess of potassium carbonate. At first a white precipitate of ferrous carbonate is formed, which soon dissolves to a greenish solution from which the double salt crystallises in nearly white scales.[4]

Ferric carbonate is too unstable to exist in the dry state. It is produced when a ferric salt is precipitated with sodium carbonate, but rapidly loses carbon dioxide, leaving a precipitate consisting mainly of ferric hydroxide.

---

[1] Le Chatelier, *Compt rend.*, 1895, 120, 623

[2] Just (*Ber.*, 1907, 40, 3695) has studied the kinetics of the autoxidations of ferrous hydrogen carbonate in water.

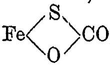
[3] Ehlert and Hempel, *Zeitsch. Elektrochem*, 1912, 18, 727.

[4] W. C. Reynolds, *Trans. Chem. Soc.*, 1898, 73, 262.

Complex Iron Carbonates.—Complex ammonium iron carbonates have been prepared in solution by adding excess of ammonium carbonate to ferrous or ferric salts in aqueous solutions. Ferric ammonium carbonate solution is blood-red in colour, and stable when kept in a closed vessel, but deposits ferric hydroxide on evaporation. Ferrous ammonium carbonate yields a colourless solution, which, upon oxidation in a limited supply of air, yields doubly refracting green prisms of basic ferroso-ferric ammonium carbonate, $NH_4.CO_3.Fe.CO_3.Fe.CO_3.FeO.2H_2O$. This, when treated with alkali hydroxides, yields magnetic ferroso-ferric oxide (see p. 144).[1]

A basic carbonate is obtained by grinding crystals of ferric chloride with a slight excess of crystallised sodium carbonate until no more carbon dioxide is evolved. The now liquid mixture is mixed with water, and the precipitate allowed to settle, and dried. The proportion of carbon dioxide present is liable to vary, as washing the precipitate induces hydrolysis. A substance of composition approximating to $7Fe_2O_3.CO_2.8H_2O$ has been obtained.[2]

Ferrous thiocarbonate, $FeCS_3$.—On adding an alkali thiocarbonate to ferrous sulphate solution a red liquid is obtained, which gradually becomes darker in colour on standing. The solution is believed to contain ferrous thiocarbonate (Berzelius).

Ferrous oxythiocarbonate,  $\mathrm{Fe}<\begin{smallmatrix}S\\O\end{smallmatrix}>\mathrm{CO}$, is sometimes formed in natural waters in solution as the result of combination between ferrous sulphide and carbon dioxide. It has been detected in the waters of the Rhone.[3]

Ferrous thiocarbonate hexammoniate, $Fe_2C_2S_7.6NH_3.2H_2O$, is prepared by warming a mixture of ferrous hydroxide, aqueous ammonia, and carbon disulphide. It yields black tetragonal prisms, with violet iridescence. On exposure to air it decomposes with heat, ferric hydroxide resulting.[4]

IRON AND CYANOGEN.

Ferrous cyanide is obtained [5] as a yellow powder on heating hydrogen ferrocyanide, $H_4Fe(CN)_6$, in the absence of air to 300° C. Hydrogen cyanide is evolved. It is also obtained on heating ammonium ferrocyanide in the absence of air.[6] Ferrous cyanide is stable, in the absence of oxygen, but even in cold air it rapidly becomes warm, and when gently heated it glows, yielding ferric oxide.[7]

The constitution of ferrous cyanide is discussed by Browning, who suggests that it is really an *iso*cyanide, for, when warmed with potassium ethyl sulphate in a current of hydrogen, it yields ethyl *iso*cyanide. The formula for ferrous cyanide is thus $Fe(NC)_2$, rather than $Fe(CN)_2$.

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[1] Hauser, *Ber.*, 1905, 38, 2707

[2] Feist, *Arch. Pharm.*, 1909, 247, 439.

[3] Causse, *Compt. rend*, 1900, 131, 947.

[4] Wiede and K. A. Hofmann, *Zeitsch. anorg. Chem.*, 1896, 11, 379.

[5] Robiquet (see Dammer, *Handbuch der anorganischen Chemie*, 1893, III, 364) believed that ferrous cyanide resulted when Prussian blue was reduced by hydrogen sulphide Hofmann (*Annalen*, 1907, 352, 54) shows that this cannot be correct.

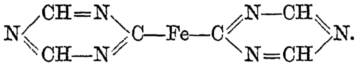
[6] Berzelius, *Ann. Chim. Phys.*, 1820, (1), 15, 228.

[7] Browning, *Trans. Chem. Soc.*, 1900, 77, 1234.

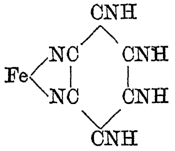
Ferric cyanide is not known, but large numbers of complex derivatives of both ferrous and ferric cyanides have been prepared in which the iron enters into the negative radicle. These are known as *ferro-* and *ferri-cyanides* respectively.

CONSTITUTION OF FERRO- AND FERRI-CYANIDES.

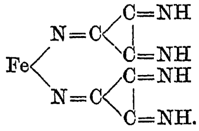
The constitution of hydrogen and alkali ferrocyanides has for many years been a matter of dispute. Both Graham and Erlenmeyer[1] believed that the cyanogen radicles were present in groups of three, as in cyanuric acid, $C_3N_3(OH)_3$, so that the formula for hydrogen ferrocyanide becomes :—



Etard and Bémont[2] and Friedel[3] suggested the cyclic formula :—



whilst Browning[4] writes hydrogen ferrocyanide as :—



The results obtained for the osmotic pressures and electric conductivities of aqueous solutions of calcium and strontium ferrocyanides (see pp. 208 and 220) indicate that these molecules possess the double formula, $M_4[Fe(CN)_6]_2$. On the other hand, tetra-ethyl ferrocyanide is known to have the single formula, $(C_2H_5)_4Fe(CN)_6$.[5]

Each of the two latter graphical formulæ as written above assumes that the iron and hydrogen are attached directly to the nitrogen and not to the carbon atoms. This is supported, in so far as the hydrogen atoms are concerned, by Freund's[6] preparation of ethyl ferrocyanide from silver ferrocyanide and ethyl iodide :—

$$4C_2H_5I+Ag_4[Fe(CN)_6]=4AgI+(C_2H_5)_4[Fe(CN)_6].$$

The ester, on heating, decomposed, yielding ethyl *iso*cyanide, C_2H_5NC.

As has already been mentioned, hydrogen ferrocyanide, when heated in the absence of air, yields ferrous cyanide, and if the *iso*cyanide constitution be accepted for this salt, it may be inferred that the same grouping, namely $Fe(NC)_2$, occurs in hydrogen ferrocyanide.

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[1] Graham, *Elements of Chemistry*, 1842, 1, 200 ; Erlenmeyer, *Lehrbuch der organischen Chemie*, 1867, 148.

[2] Etard and Bémont, *Compt. rend.*, 1884, 99, 972, 1024.

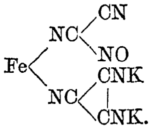
[3] Friedel, *ibid.*, 1887, 104, 994.

[4] Browning, *Trans Chem. Soc.*, 1900, 77, 1234.

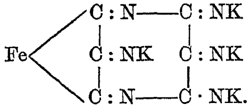
[5] Buchbock, *Zeitsch. physikal. Chem.*, 1897, 23, 157.

[6] Freund, *Ber.*, 1888, 21, 931.

To this extent, therefore, the two foregoing formulæ agree, but Browning suggests that his formula is probably more nearly correct as it offers a more ready explanation for the formation of nitroprussides, etc., no rupture of a hexatomic ring being necessary. Thus, potassium nitroprusside becomes :—



Neither formula, however, explains the fact that the potassium atoms are labile, whilst the iron atom is not. Denigès [1] overcomes this difficulty by the formula :—

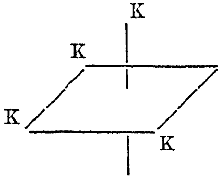


In common with Browning's formula, this scheme admits of the ready formation of nitroprussides without disrupting a ring. Furthermore, since the iron is not attached in the same way as the potassium atoms, being linked to carbon instead of nitrogen, a difference in stability may reasonably be expected.

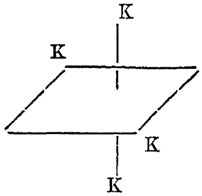
The weakness of this formula lies in the fact that the only available evidence on the subject points to the conclusion that the iron is attached directly to nitrogen, and not to the carbon as here represented, ferrous cyanide having the isocyanic structure.[2]

According to Werner's theory (see this series, Vol. X.), the formulæ of hydrogen ferro- and ferri-cyanide should be written $[Fe(CN)_6]H_4$ and $[Fe(CN)_6]H_3$ respectively, the six cyanogen groups being co-ordinated with the iron atom, and constituting the nucleus around which hover the replaceable hydrogen atoms.

In 1911 Briggs [3] believed that he had succeeded in isolating two isomerides of potassium ferrocyanide,[4] and suggested their representation by the following stereo-isomeric schemes :—



1, 2, 3 4 position.



1, 2, 4, 6 position.

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[1] Denigès, *Bull Soc. chim* , 1916, 20, 79.

[2] Browning *loc. cit*

[3] Briggs, *Trans. Chem Soc.*, 1911, 99, 1019. See also p. 212.

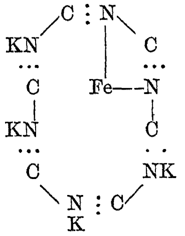
[4] In 1899 Locke and Edwards concluded that potassium ferricyanide exists in two isomeric forms. This has been disputed ; and the evidence is certainly even less substantial than in the case of the ferrocyanide under discussion. See Locke and Edwards, *Amer. Chem. J.*, 1899, 21, 193, 413 ; Bellucci and Sabatini, *Atti R. Accad. Lincei*, 1911, (5), 20, i. 176.

although it was not possible to determine which isomeride corresponded to each particular scheme.

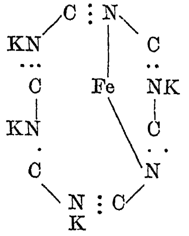
Bennett,[1] however, dissented from this view. Having prepared the two "isomerides" according to the directions given by Briggs and measured their angles, he concluded that there can be no doubt of their crystallographic identity. Briggs[2] therefore reinvestigated the problem, and showed that the so-called β ferrocyanides are in reality mixed crystals of ferrocyanide and aquopentacyanoferrite, $K_3[Fe(CN)_5H_2O]$. (See p. 215.)

There still remains, however, the possibility of isomerism of the inorganic ferrocyanides being ultimately discovered, comparable with the undoubted isomerism manifested by the tetramethyl salt, $(CH_3)_4Fe(CN)_6$.[3]

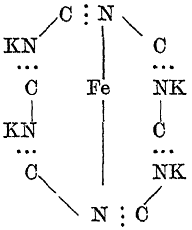
Now, Werner's formula does not admit of the possibility of isomerism of ferrocyanides. This is not the case, however, with the formulæ of Denigès, Browning, and of Etard, several rearrangements being possible. According to Friend's[4] shell theory three isomerides, namely, ortho, meta, and para, are possible Thus :—



1, 2, or ortho salt.



1, 3, or meta salt.



1, 4, or para salt.

In an analogous manner three isomerides are, theoretically, possible for potassium ferricyanide, $K_3Fe(CN)_6$, in which the central iron atom is trivalent. All of these cyclic schemes are in harmony with the isocyanic structure of ferrous cyanide, They also serve to explain why the potassium ions are ionisable, whereas the iron atom, bound within the centre of the shell, constitutes part of the negative radicle.

When a solution of potassium ferrocyanide reacts with rather less than one equivalent of a ferric salt, a blue hydrated precipitate of α-soluble Prussian blue, or ferric potassium ferrocyanide $Fe^{\cdot\cdot\cdot}K[Fe^{\cdot\cdot}(CN)_6]$, is obtained. Now, Hofmann and his co-workers[5] have shown that this precipitate is identical with that prepared under precisely similar conditions by the addition of a ferrous salt to potassium ferricyanide, although in this case ferrous potassium ferricyanide, $Fe^{\cdot\cdot}K[Fe^{\cdot\cdot\cdot}(CN)_6]$, might be expected. It is therefore assumed that the latter salt is unstable, and, at the moment of formation, undergoes intramolecular rearrangement to the former complex.

By adopting the shell formulæ, however, the difficulty at once disappears, for the two salts are seen to be identical without rearrangement. For example, 1, 4 ferrocyanide reacts with a ferric salt yielding 2, 3, 5 ferric 6 potassium 1, 4 ferrocyanide, which is clearly the same as 1, 4 ferrous 6 potassium 2, 3, 5 ferricyanide obtained by the action of a ferrous salt on potassium 1, 2, 4 ferricyanide. Thus :—[1]

---

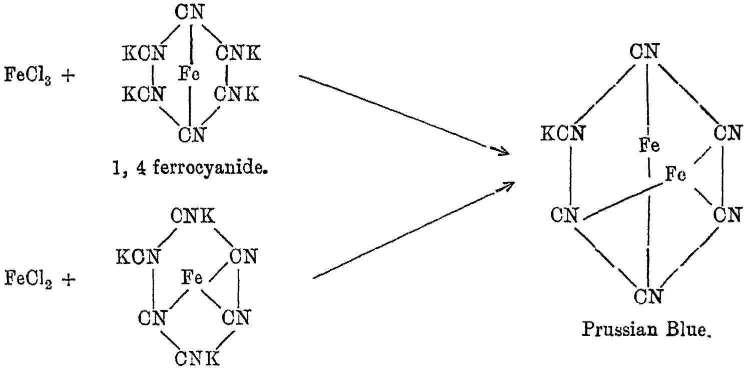
[1] Bennett, *Trans. Chem. Soc.*, 1917, 111, 490. See also Piutti, *Ber.*, 1912, 45, 1830; Hauser and Biesalski, *ibid.*, p. 3516; Wells, *Amer. Chem. J.*, 1913, 49, 205.

[2] Briggs, *Trans. Chem. Soc.*, 1920, 117, 1026.

[3] Hartley, *ibid.*, 1913, 103, 1196.

[4] Friend, *ibid.*, 1916, 109, 715.

[5] Hofmann and co-workers, *Annalen*, 1904, 337, 1.



1, 4 ferrocyanide.

2, 3, 5 ferricyanide.

Prussian Blue.

Ferrocyanides, $M_4[Fe(CN)_6]$.

The reactions of soluble ferrocyanides are in general typified by those of the potassium salt, the properties of which are therefore discussed in detail (see p. 212).

Hydrogen ferrocyanide, Ferro-cyanic acid, $H_4[Fe(CN)_6]$, is conveniently prepared by adding concentrated aqueous hydrogen chloride solution to a saturated solution of potassium ferrocyanide, in the cold :—

$$K_4[Fe(CN)_6]+4HCl=4KCl+H_4[Fe(CN)_6].$$

The precipitate, dried in the absence of air, is dissolved in alcohol and re-precipitated as a white powder on addition of ether,[2] but apparently combined with two molecules of ether, which, however, evaporate away upon exposure to air, leaving the pure acid as a residue.[3]

Ferrocyanic acid is also obtained when a solution of insoluble Prussian blue in hot, concentrated hydrochloric acid is allowed to stand (see p. 227).

Hydrogen ferrocyanide is soluble in water and possesses a strong acid reaction. The solution decomposes on boiling, evolving gaseous hydrogen cyanide, and yielding a white precipitate of ferrous cyanide. Thus :—[4]

$$H_4[Fe(CN)_6]=4HCN+Fe(CN)_2.$$

---

[1] These views have been vigorously attacked by E. E. Turner, *Trans. Chem. Soc.*, 1916, 109, 1130.

[2] Liebig, *Annalen*, 1853, 87, 127; Joannis, *Ann. Chim. Phys.*, 1882, (5), 26, 484.

[3] Etard and Bémont, *Compt. rend.*, 1884, 99, 972, 1024.

[4] Berzelius, *Schweigger's J.*, 1820, 30, 57; Adie and Browning, *Trans. Chem. Soc.*, 1900, 77, 150.

Upon exposure to air hydrogen ferrocyanide absorbs oxygen, yielding hydrogen cyanide and a ferric salt of the original acid. Thus :—

$$7H_4[Fe(CN)_6]+O_2=24HCN+2H_2O+Fe_4[Fe(CN)_6]_3.$$

Heated in the absence of air to 300° C., a pale yellow powder (ferrous cyanide) is obtained,[1] hydrogen cyanide being evolved.[2]

The heat of neutralisation of ferrocyanic acid with 4 molecules of potassium hydroxide is

$$H_4Fe(CN)_6+4KOH=K_4Fe(CN)_6+4H_2O+57,900 \text{ calories}$$

at 12° C.[3] The heat of formation of ferrocyanic acid from its elements is $-122,000$ calories.[4]

Aluminium ferrocyanide, $Al_4[Fe(CN)_6]_3.17H_2O$, is formed when solutions of alum and potassium ferrocyanide are mixed in the cold,[5] the alum being (presumably) in excess [6]; otherwise the double aluminium ammonium salt is produced.

Aluminium ammonium ferrocyanide, $Al(NH_4)Fe(CN)_6.4H_2O$, is formed as a jelly on mixing equivalent solutions of aluminium chloride and ammonium ferrocyanide.[6] The salt is difficult to isolate, but is obtained as a precipitate by centrifugating at 3000 revolutions per minute. The precipitate is washed with acetone and ether and dried *in vacuo*. It resembles the potassium salt in appearance, being dark green and transparent in lumps, but a light bluish green when powdered. At 100° C. it becomes anhydrous and assumes a deep blue colour.

Aluminium potassium ferrocyanide (see p. 218).

Ammonium ferrocyanide, $(NH_4)_4Fe(CN)_6.3H_2O$, may be obtained either by the action of ammonium hydroxide upon Prussian blue, or by neutralising hydrogen ferrocyanide with ammonia.[7] On concentrating the solution over potassium hydroxide in a vacuum, the salt crystallises out in thin, greenish-yellow plates, or the salt may be precipitated from solution with alcohol.[8] When heated in the absence of air, ammonium ferrocyanide yields ferrous cyanide.[9] The aqueous solution of the salt is very unstable, being decomposed on merely warming, yielding, amongst other products, ammonium cyanide.[8] When boiled in contact with air, it yields a dull green deposit of $Fe^{\cdot\cdot\cdot}{}_2Fe^{\cdot\cdot}(NH_4)_8[Fe''(CN)_6]_4.3H_2O$.[10]

The *double salt* with ammonium chloride, $(NH_4)_4Fe(CN)_6.NH_4Cl.3H_2O$, is obtained as pale yellow or brown crystals by cooling warm, mixed solutions of ammonium ferrocyanide and ammonium chloride in the presence of sodium cyanide or of acetic acid respectively.[11] The anhydrous salt has also been obtained.[8]

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[1] Browning, *Trans. Chem. Soc*, 1900, 77, 1234. See also Rammelsberg, *Pogg. Annalen*, 1851, 38, 364; 1851, 42, 111; Etard and Bémont, *Compt. rend*, 1884, 99, 972, 1024.

[2] See Robiquet, *Ann. Chim. Phys.*, 1819, (1), 12, 277; Etard and Bémont, *loc. cit.*; Reemann and Carius, *Annalen*, 1860, 113, 39; Adie and Browning, *Trans. Chem. Soc.*, 1900, 77, 150.

[3] Chrétien and Guinchant, *Compt. rend.*, 1903, 137, 65. Compare Joannis, *Compt. rend.*, 1882, 94, 725.

[4] Berthelot, *Thermochimie*, II., 294.

[5] Wyrouboff, *Ann. Chim. Phys.*, 1879, (5), 18, 446.

[6] Robinson, *Trans. Chem. Soc.*, 1909, 95, 1353.

[7] Bunsen, *Pogg. Annalen*, 1835, 36, 404; Briggs, *Trans. Chem. Soc.*, 1911, 99, 1019.

[8] Etard and Bémont, *Compt. rend.*, 1885, 100, 108.

[9] Berzelius, *Ann. Chim. Phys.*, 1820, (1), 15, 228.

[10] Williams, *Proc. Chem. Soc.*, 1913, 29, 54.

[11] Briggs, *loc. cit.*

Barium ferrocyanide,[1] $Ba_2Fe(CN)_6.6H_2O$, is readily prepared by boiling Prussian blue (see p. 225) with the requisite quantity of barium hydroxide solution. It also results when ferrous sulphate and barium cyanide solutions interact.

Upon concentration the salt crystallises in monoclinic prisms.

Cadmium ferrocyanide.—On addition of potassium ferrocyanide to solutions of cadmium salts, complex precipitates containing cadmium and potassium in varying proportions are obtained.

The *hepta-ammoniate* has been prepared, namely $Cd_2Fe(CN)_6.7NH_3$.[2]

Cadmium ammonium and **cadmium potassium ferro cyanides** are known.[3]

Cæsium ferrocyanide, $Cs_4Fe(CN)_6+(?)6H_2O$, has been prepared by neutralising hydrogen ferrocyanide with cæsium hydroxide.[4]

Calcium ferrocyanide, $Ca_2Fe(CN)_6.xH_2O$ (where $x=11$,[5] or 12,[6]), may be obtained by boiling Prussian blue with the calculated quantity of milk of lime. It is also formed when hydrogen cyanide is passed into a suspension of lime and ferrous hydroxide in water. The salt crystallises in pale yellow triclinic prisms, which are more soluble in cold water than in hot.

The density of the salt is 1·68. At 500° C., in the absence of air or oxygen, it decomposes, yielding calcium cyanamide. Thus :—

$$Ca_2Fe(CN)_6=2CaCN_2+Fe+N_2+4C.$$

The osmotic pressures of solutions of calcium ferrocyanide in water have been determined for various concentrations,[5] and the results indicate that the negative radicles are associated, yielding the double ion $[Fe(CN)_6]_2''''''''$.

Calcium ammonium ferrocyanide, $(NH_4)_2CaFe(CN)_6$, results on mixing cold concentrated solutions of calcium chloride and ammonium ferrocyanide, in equimolecular proportions, washing the precipitate and drying in air or at 100° C. It also results on boiling potassium calcium ferrocyanide (see p. 219) with water containing a large excess of ammonium chloride.[7]

One part of the salt dissolves in 388 parts of water at 15° to 17° C.

Cerium ammonium ferrocyanide, $(NH_4).CeFe(CN)_6$, is obtained[8] on mixing, in the cold, concentrated solutions of cerium chloride and ammonium ferrocyanide. No description of the salt has been given.

Cerium potassium ferrocyanide (see p. 219).

Cerium sodium ferrocyanide (see p. 220).

Cobalt ferrocyanide, $Co_2Fe(CN)_6.7H_2O$,[9] is obtained by neutralising the free acid with cobalt hydroxide. It is less stable than the corresponding nickel salt. It is green in colour; oxidised by chlorine water to ferricyanide and by bromine water to hydrated cobaltic oxide.[10]

---

[1] Howe and Campbell, *J. Amer Chem. Soc.*, 1898, 20, 29.

[2] Peters, *Zeitsch anorg. Chem.*, 1912, 77, 137.

[3] See Miller and Falk, *J Amer. Chem. Soc.*, 1904, 26, 952; Miller and Fisher, *ibid.*, 1900, 22, 537; 1902, 24, 226.

[4] Briggs, *loc cit*

[5] Berkeley, Hartley, and Burton, *Phil. Trans*, 1908, A, 209, 177; Berkeley, Hartley, and Stephenson, *ibid*, p. 319.

[6] Joannis, *Compt rend*, 1882, 94, 725.

[7] Brown, *Trans Chem. Soc.*, 1907, 91, 1826.

[8] Robinson, *ibid.*, 1909, 95, 1353

[9] Wyrouboff, *Jahresber*, 1876, 29, 311

[10] Werner, *Zeitsch. anal. Chem*, 1919, 58, 23.

On boiling with concentrated hydrochloric acid, the acid salt $CoH_2Fe(CN)_6.4H_2O$, is obtained.[1]

The *tri-ammoniate*, $Co_2Fe(CN)_6.3NH_3$, has been prepared.[2]

Copper (cupric) ferrocyanide, $Cu_2[Fe(CN)_6].+Aq.$, is obtained as a brown precipitate by mixing solutions of copper sulphate and potassium ferrocyanide, the former salt being present in excess.[3] An interesting experiment consists in preparing in a gas jar a saturated solution of copper sulphate and diluting some 50 per cent. A drop of saturated potassium ferrocyanide solution is now introduced by means of a pipette and rapidly sinks to the bottom of the jar. It does not mix with the copper sulphate solution, for its surface which came into contact with the latter solution is now covered with a thin and invisible membrane of copper ferrocyanide. After lying at the bottom of the jar a little while, the drop will be seen to increase slightly in bulk, and then rise up through the copper sulphate solution to the top of the jar. This is due to water passing through the copper ferrocyanide membrane and reducing the density of the potassium ferrocyanide solution.[4]

Evidence has been obtained suggestive of the possible existence of the *trihydrate*, $Cu_2Fe(CN)_6.3H_2O$.[5]

The salt is largely used in experimental work dealing with osmosis.[6]

The pores in a copper ferrocyanide membrane are exceedingly fine, ranging from 8 to 60 $\mu\mu$ in diameter, the average being from 15 to 20 $\mu\mu$.[7] The osmotic action is not due to a selective mechanical filtration, but to selective adsorption on the surface of the membrane. Hence such membranes as have the smallest pores and expose the greatest superficial area are the most efficient semipermeable structures.

Copper ferrocyanide may be obtained in colloidal form of high chemical purity by prolonged dialysis of the solution obtained by mixing equivalent solutions of sodium ferrocyanide and copper chloride (or sulphate).[8]

The molecular weight of colloidal copper ferrocyanide has been calculated [9] as 700,000.

When boiled with concentrated nitric acid, a ferroferricyanide is obtained [10] of the composition

$$Cu_7[Fe''Fe'''(CN)_{12}]_2 30H_2O.$$

When boiled with concentrated hydrochloric acid, the *acid salt* $CuH_2Fe(CN)_6.4H_2O$, is obtained as a yellow, insoluble substance.[11] This, when digested with solutions of the chlorides of the alkali metals, liberates hydrochloric acid, yielding alkali cupriferrocyanides. Thus, for example, with potassium chloride :—

---

[1] Williams, *Proc. Chem. Soc*, 1912, 28, 317.

[2] Peters, *Zeitsch. anorg. Chem.*, 1917, 77, 137.

[3] Namely, at least five molecules of copper sulphate to one of potassium ferrocyanide (E. Muller and co-workers, *J. prakt. Chem.*, 1912, 86, 82).

[4] Thiel, *Zeitsch. Elektrochem*, 1906, 12, 229.

[5] Tinker, *Proc. Roy. Soc*, 1917, A, 93, 268.

[6] See Tinker, *loc. cit* ; Beutner, *J. Physical Chem.*, 1913, 17, 344.

[7] Tinker, *Proc Roy Soc.*, 1916, A, 92, 357. By μ is generally understood 0·001 mm and by $\mu\mu$ 0·000001 mm.

[8] Pappada, *Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 136. See also Duclaux, *Compt. rend.*, 1904, 138, 144.

[9] Duclaux, *J. Chim. phys.*, 1909, 7, 303.

[10] Williams, *Proc. Chem. Soc.*, 1913, 29, 54.

[11] Williams, *ibid.*, 1912, 28, 317.

$$CuH_2Fe(CN)_6+2KCl=CuK_2Fe(CN)_6+2HCl.$$

With sodium chloride solution in the cold only half the hydrogen is replaced, thus :—

$$CuH_2Fe(CN)_6+NaCl=CuNaHFe(CN)_6+HCl.$$

This latter salt, when digested with potassium or ammonium chloride yields $CuNaKFe(CN)_6$ or $CuNaNH_4Fe(CN)_6$ respectively.

The acid salt $CuH_2Fe(CN)_6$ thus behaves as a dibasic acid, namely *cupriferrocyanic acid*, and gives rise to a definite series of salts known as *cupriferrocyanides*, which are discussed on p. 211.

Cuproferrocyanides, $M_2Cu_2Fe(CN)_6$.

Ammonium cuproferrocyanide, $(NH_4)_2Cu_2Fe(CN)_6$, results[1] when cuprous cyanide is boiled with a solution of ammonium ferrocyanide containing ammonium sulphite, and hydrogen passed through the mixture. It may also be obtained by double decomposition of the sodium salt with ammonium nitrate. It crystallises in small, colourless six-sided prisms, which readily decompose both under water and on mere exposure to air or in a vacuum.

Barium cuproferrocyanide,[1] $BaCu_2Fe(CN)_6$ and **calcium cuproferrocyanide,**[1] $CaCu_2Fe(CN)_6$, are obtained by boiling copper cyanide with the corresponding ferrocyanides. They crystallise in colourless, hexagonal prisms which cannot be distinguished from one another.

Lithium cuproferrocyanide,[2] $Li_2Cu_2Fe(CN)_6$, is obtained by boiling cuprous cyanide with a solution of lithium ferrocyanide containing lithium sulphite, hydrogen gas being simultaneously bubbled through the solution. It crystallises in colourless, hexagonal prisms.

Magnesium cuproferrocyanide, $MgCu_2Fe(CN)_6$, results[1] on boiling cuprous cyanide with a solution of magnesium ferrocyanide. It crystallises in colourless, hexagonal prisms which, however, are unstable, turning brown on keeping.

Potassium cuproferrocyanide, $K_2Cu_2Fe(CN)_6$, is prepared[1] by boiling cuprous cyanide with a solution of potassium ferrocyanide containing a little potassium sulphite ; or by boiling cuprous chloride or potassium cuprous cyanide with potassium ferrocyanide solution. When rapidly cooled, the solution yields colourless cubes, but the crystals are liable to undergo partial oxidation, turning yellow or brown in colour.

Sodium cuproferrocyanide, $Na_2Cu_2Fe(CN)_6$, results[1] on adding a cold, saturated solution of sodium copper cyanide to a hot solution of sodium ferrocyanide ; or by boiling a solution of sodium ferrocyanide with cuprous cyanide in the presence of a little sodium sulphite, and cooling in an atmosphere of hydrogen. It crystallises in minute, colourless hexagonal prisms, which are conveniently dried over sulphuric acid in a vacuum.

It retains 27·5 per cent. of water. In air it slowly oxidises, turning brown. It is insoluble in water, alcohol, and ether.

Strontium cuproferrocyanide, $SrCu_2Fe(CN)_6$, is obtained[1] in a similar manner to the barium salt, which it closely resembles.

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[1] Messner, *Zeitsch. anorg. Chem.*, 1895, 8, 368.

[2] Messner, *ibid*, 1895, 9, 126.

Cupriferrocyanides, $M_2CuFe(CN)_6$.

Ammonium cupriferrocyanide, $(NH_4)_2CuFe(CN)_6$, is prepared[1] by boiling a mixed solution of cupric and ammonium ferrocyanides. It crystallises in brownish red cubes, and is best dried in a vacuum over sulphuric acid. The following four salts are obtained in an analogous manner:—

Barium cupriferrocyanide,[1] $BaCuFe(CN)_6$, and **calcium cupriferrocyanide,**[1] $CaCuFe(CN)_6$, yield small, brown, quadratic prisms.

Lithium cupriferrocyanide,[2] $Li_2CuFe(CN)_6$, crystallises in red plates or brownish red needles.

Magnesium cupriferrocyanide,[1] $MgCuFe(CN)_6$, separates in violet-brown crystals, containing 44·3 to 44·5 per cent. of water.

Potassium cupriferrocyanide, $K_2CuFe(CN)_6$, results[2] on boiling cuprous cyanide with an excess of potassium ferricyanide solution:—

$$2CuCN+4K_3Fe(CN)_6=2K_2CuFe(CN)_6+2K_4Fe(CN)_6+(CN)_2,$$

and by digesting cupriferrocyanic acid with potassium chloride solution.[3] It crystallises in brownish red, quadratic prisms.

Potassium ferrous cupriferrocyanide, $K_2Fe_2Cu[Fe(CN)_6]_2$.—Probably this is the beautiful violet compound[1] obtained when a solution of a cupric salt acts on ferrous potassium ferrocyanide, $K_2Fe[Fe(CN)_6]$.

Sodium cupriferrocyanide, $Na_2CuFe(CN)_6$, is prepared by boiling solutions of cupric salts and sodium ferrocyanide, and by boiling cupric ferrocyanide with sodium ferrocyanide and, after filtering, allowing the clear solution to evaporate in air.[1] It yields lustrous brown crystals, insoluble in cold water, but decomposed when boiled with water, dilute acids, or alkalies.

Strontium cupriferrocyanide, $SrCuFe(CN)_6$, is obtained in a similar manner to the calcium salt, which it closely resembles.

When a copper sulphate solution is added to excess potassium ferrocyanide, a mixture of *di-potassium cupric* and *di-potassium tricupric ferrocyanides* is produced, namely $K_2CuFe(CN)_6$ and $K_2Cu_3[Fe(CN)_6]_2$ respectively.

If cuprous chloride is substituted for cupric sulphate, then different *cuprous potassium ferrocyanides* are obtained according to circumstances, namely $K_2Cu^{\cdot}_2[Fe(CN)_6]$; $KCu^{\cdot}Cu^{\cdot}_3[Fe(CN)_6]_2$; and $KCu^{\cdot}_3[Fe(CN)_6]$. The last of these is obtained, when cuprous chloride is in great excess, as a white precipitate.

Ferrous ferrocyanide (see p. 227).

Lead ferrocyanide,[4] obtained by precipitation with potassium ferrocyanide, always contains some of this latter salt, from which it cannot be freed by washing.

Lithium ferrocyanide, $Li_4Fe(CN)_6.9H_2O$, yields deliquescent monoclinic crystals.

Magnesium ferrocyanide, $Mg_2Fe(CN)_6+Aq.$, may be prepared as pale yellow needles, in similar ways to the calcium salt. The amount of water is uncertain, being of the order of 10 [1] or 12 [2] molecules.

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[1] Messner, *Zeitsch. anorg. Chem.*, 1895, 8, 368.
[2] Messner, *ibid.*, 1895, 9, 126.
[3] Williams, *Proc Chem. Soc.*, 1912, 28, 317.
[4] Miller and Fisher, *J. Amer. Chem. Soc*, 1900, 22, 537.

Magnesium ammonium ferrocyanide, $Mg(NH_4)_2Fe(CN)_6$, is obtained[3] by mixing concentrated solutions of magnesium chloride and ammonium ferrocyanide in equivalent proportions. The anhydrous salt separates out as small white crystals which remain unaltered at 120° C. A saturated solution of the salt contains 2·48 grams per litre.

Magnesium potassium ferrocyanide (see p. 219).

Manganese ferrocyanide, $Mn_2Fe(CN)_6$, is a white substance, which is turned green by chlorine water and oxidised to brown ferricyanide by bromine water.[4]

On boiling with concentrated hydrochloric acid, the *acid salt*, $MnH_2Fe(CN)_6.5H_2O$, is obtained.[5]

The *di-ammoniate*, $Mn_2Fe(CN)_6.2NH_3$, has been prepared.[6]

Mercuric ferrocyanide, $Hg_2Fe(CN)_6$,[7] is white in appearance. Chlorine water turns it green, and bromine water brown.

Double Salts with Mercuric Cyanide.

A series of stable salts has been prepared [8] containing mercuric cyanide associated with the ferrocyanide molecule. The first to be discovered was the **potassium** salt, $K_4Fe(CN)_6.3Hg(CN)_2.4H_2O$, by Kane,[7] which is readily obtained by allowing a mixed solution of potassium ferrocyanide and mercuric cyanide to evaporate. Other salts in this series are those of

Ammonium,[5] $(NH_4)_4Fe(CN)_6.3Hg(CN)_2.2H_2O$;
Cæsium,[9] $Cs_4Fe(CN)_6.3Hg(CN)_2$; and
Rubidium,[5] $Rb_4Fe(CN)_6.3Hg(CN)_2.4H_2O$.

Nickel ferrocyanide, $Ni_2Fe(CN)_6.Aq.$,[10] is bluish green in colour, stable towards chlorine water, but oxidised to brown ferricyanide with bromine water.[4]

On boiling with concentrated hydrochloric acid, the *acid salt*, $NiH_2Fe(CN)_6.3H_2O$, is obtained.[5]

The following *ammoniates* have been prepared: namely, $Ni_2Fe(CN)_6.5NH_3.4H_2O$,[11] and $Ni_2Fe(CN)_6.7NH_3$.[6]

Potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, is the most important salt of ferrocyanic acid, and is known in commerce by the more familiar name of *yellow prussiate of potash*.[12] It results when a solution of potassium cyanide is added in excess to one of a ferrous salt, so that the precipitate first formed completely redissolves. It may also be prepared by allowing iron to dissolve in an air-free solution of potassium cyanide :—

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[1] Bette, *Annalen*, 1836, 22, 152 ; 1836, 23, 115.

[2] Coleman, see Roscoe and Schorlemmer, *A Treatise on Chemistry*, vol. ii. (Macmillan & Co), 1907, p 1232.

[3] Robinson, *Trans. Chem. Soc*, 1909, 95, 1353.

[4] F. F. Werner, *Zeitsch anal. Chem.*, 1919, 58, 23.

[5] Williams, *Proc. Chem. Soc*, 1912, 28, 317.

[6] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[7] Kane, *J. prakt. Chem.*, 1840, 19, 405.

[8] Williams, *Proc. Chem. Soc.*, 1912, 28, 317 ; Stromholm, *Zeitsch. anorg. Chem.*, 1913, 84, 208.

[9] Stromholm, *Zeitsch. anorg Chem*, 1914, 90, 370.

[10] Wyrouboff, *Jahresber*, 1876, 29, 311.

[11] Reynoso, *ibid*, 1850, p 358 ; Gintl, *ibid*, 1868, p. 305.

[12] This salt has been studied by Bunsen, *Pogg Annalen*, 1835, 36, 404 ; Wyrouboff, *Ann. Chim. Phys.*, 1869, (4), 16, 293 ; Dufet, *Compt. rend.*, 1895, 120, 377 ; Briggs, *Trans. Chem. Soc*, 1911, 99, 1019.

$$6KCN+Fe+2H_2O=K_4[Fe(CN)_6]+2KOH+H_2,$$

and by the action of potassium hydroxide solution on ferrous cyanide :—

$$3Fe(CN)_2+4KOH=K_4Fe(CN)_6+2Fe(OH)_2.$$

The old commercial method of preparing the salt lay in heating nitrogenous material, such as horn, wool, feathers, blood, etc., with potash and iron turnings. The mass was ultimately heated to fusion to complete the reaction, cooled, and extracted with boiling water. The solution contained potassium ferrocyanide, thiocyanate, carbonate, and sulphide. The first-named was crystallised out, but the yield was seldom more than 20 per cent. of the quantity theoretically obtainable from the nitrogen content of the organic material consumed.

The chemistry of the reactions involved has been made the subject of considerable study.[1]

Another method [2] consists in passing the vapour of trimethylamine into a retort at red heat. The resulting products are passed into sulphuric acid, whereby ammonium cyanide is converted into hydrogen cyanide, which is now absorbed in potash to yield the corresponding cyanide. Ferrous hydroxide, prepared by addition of milk of lime to a solution of ferrous chloride, is added to the cyanide solution, and the liquid, after filtering, deposits a relatively pure crop of potassium ferrocyanide.

Alkali thiocyanates may be made the starting-point for the preparation of ferrocyanides. The potassium salt is mixed with twice the weight of iron filings necessary to form ferrous sulphide, and with double the quantity of ferrous hydroxide, in a freshly precipitated condition, to form ferrocyanide. The mixture is maintained for some twelve hours under agitation in a closed vessel at 110° to 120° C. Potassium ferrocyanide is formed, together with Prussian blue, and extracted from the residue with water.[3]

From 1885 to 1895 potassium ferrocyanide was manufactured very largely from *spent oxide* of iron, used in purifying coal gas from hydrogen sulphide. Coal gas, as it leaves the retorts, contains hydrogen cyanide, formed by the action of ammonia on red-hot carbon. Thus :—

$$NH_3+C=HCN+H_2.$$

The hydrogen cyanide yields ammonia again in contact with heated water vapour :—

$$HCN+H_2O=NH_3+CO,$$

the ammonia uniting with the free acid to form ammonium cyanide.

The relative proportions of ammonia and cyanide in coal gas thus vary with the conditions.

The oxide of iron employed in gas works is the hydrated ferric compound. It absorbs the hydrogen sulphide in the coal gas, yielding ferrous and ferric sulphides; the ammonium cyanide, also present in the gas, reacts with the iron compounds, forming ferrocyanide and, ultimately, Prussian blue. The last-named was frequently converted into calcium ferrocyanide by intimate admixture with lime, and dissolved in cold water. Potassium chloride solution was next added, whereby the potassium calcium ferrocyanide, $K_2CaFe(CN)_6$, was precipitated, to be converted into potassium ferrocyanide by boiling with potassium carbonate.

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[1] See Liebig, *Annalen*, 1841, 38, 20 ; R. Hoffmann, *ibid.*, 1860, 113, 81 ; Ewan, article on "Cyanides," *Dictionary of Applied Chemistry*, Thorpe (Longmans, 1912).

[2] Willm, *Bull. Soc. chim.*, 1884, 41, 449.

[3] Sternberg, *Dingl. Poly. J.*, 1885, 257, 539.

Wet methods are now largely employed for the preparation of potassium ferrocyanide from coal gas, and, whilst several have been patented and found to work well, it will suffice, for present purposes, to mention one method only.

The crude coal gas is washed with ferrous sulphate solution, whereby the latter is converted into a suspension of ferrous sulphide in ammonium sulphate solution. This reacts with the ammonium cyanide, yielding ferrous ferrocyanide, $Fe_2[Fe(CN)_6]$, or ammonium ferrous ferrocyanide, $(NH_4)_2Fe[Fe(CN)_6]$, according to circumstances. Potassium ferrocyanide may be obtained from these by treatment with lime, as in the spent oxide process. By repeatedly dissolving in water and precipitating with alcohol, the salt can be obtained in a very pure state.[1]

What appeared to be two forms of the salt, designated as α and β respectively, were prepared by Briggs.[2] The former was obtained from the pure commercial salt by dissolving it in water with 1 per cent. of its weight of potassium cyanide. After twenty-four hours alcohol was added, and a white crystalline precipitate of the α salt obtained. Upon recrystallisation, if the crystals were large, they were lemon-yellow in colour, but otherwise quite white; density at 20° C. 1·889. At 20° C. 100 grams of saturated solution contained 25·0 grams of the α trihydrated salt, $K_4[Fe(CN)_6].3H_2O$. The β salt was obtained by dissolving the pure commercial salt in water with 1 per cent. of its weight of dilute acetic acid (1 part acid, 10 parts water), and allowing to stand in the absence of air. After twenty-four hours the addition of alcohol yielded a cream-coloured precipitate. Upon recrystallisation orange-coloured crystals were obtained, of more intense colour than the α salt; of slightly less density, namely 1·882 at 20° C., and rather less soluble in water, 100 grams of saturated solution at 20° C. containing 24·6 grams of the salt.

Solutions of the α salt, upon prolonged standing, are converted into the β variety, a process that is hastened by the addition of 1 per cent. of acetic acid. Cyanides, alkalies, and ammonia induce the reverse transformation.

Bennett,[3] however, having prepared these two "isomerides" according to the directions given by Briggs, and measured their angles, concluded that the two forms are identical crystallographically. He drew attention to the fact that the more intense colour of the β salt might easily arise from slight decomposition induced by its acid method of preparation; in support of this, it is significant that the most striking difference of colour occurs in the ammonium salt, which is the most unstable of all, its aqueous solution being decomposed on simply warming. The differences in density and solubility are too slight to be very definite evidence either way. Again, Kolthoff[1] found no difference in the physical properties of solutions of α and β ferrocyanide, except their colour.

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[1] Mecklenburg, *Zeitsch. anorg. Chem.*, 1910, 67, 322.

[2] Briggs, *loc. cit.* See also p. 204

[3] Bennett, *Trans. Chem Soc.*, 1917, III, 490 See also Piutti, *Ber*, 1912, 45, 1830; Hauser and Biesalski, *ibid.*, p. 3516; Wells, *Amer. Chem. J.*, 1913, 49, 205.

Briggs[2] therefore reinvestigated the matter, and showed that the supposed isomeride or β variety consists of mixed crystals of potassium ferrocyanide and aquopentacyanoferrite, $K_3[Fe(CN)_5H_2O]$, the amount of the latter being too small to detect by qualitative analysis. Since the β salt is formed when the α variety is repeatedly recrystallised from water, it is concluded that the compounds are, in aqueous solution, in a state of equilibrium, thus :—

$$H_2O + K_4[Fe(CN)_6] \rightleftharpoons K_3[Fe(CN)_5.H_2O] + KCN.$$

It must not be overlooked, however, that isomerism has been definitely discovered[3] in the case of tetramethyl ferrocyanide, $(CH_3)_4Fe(CN)_6$, and it is always possible that isomerides of inorganic salts of ferrocyanic acid may be capable of existence.

Potassium ferrocyanide crystallises with three molecules of water, which are completely expelled at 110° C., leaving the anhydrous salt in the form of a white powder. Crystals of potassium ferrocyanide, in common with the few other hydrated crystals which have been examined, are permeable to water vapour. This has been demonstrated[4] by cementing crystals with wax into the necks of small flasks containing phosphorus pentoxide, and noting any alteration in weight after exposure to moist air. An increase was observed, which was slow but steady and continuous. It is not suggested that the crystals are porous in the ordinary mechanical sense in which, for example, unglazed earthenware is porous. Rather is it believed that the layers of the crystal inside the flask give up their moisture to the dry air in contact with the phosphorus pentoxide; these dehydrated layers take up water from the next layers, and so on, until the layers are reached in direct contact with the moist air. The net result is thus that the water passes through the crystal from the wet to the dry atmosphere.

The crystals of potassium ferrocyanide are tough and difficult to powder. They are non-poisonous, but act as an aperient. When the dry anhydrous salt is heated to incipient fusion in a vacuum no gas is evolved, potassium cyanide and ferrous potassium ferrocyanide being produced :—[5]

$$2K_4Fe(CN)_6 = FeK_2Fe(CN)_6 + 6KCN.$$

At red heat the latter salt is further decomposed, evolving free cyanogen. Thus :—

$$FeK_2Fe(CN)_6 = 2Fe + 2KCN + 2C_2N_2.$$

This is a convenient method of preparing potassium cyanide, although wasteful in so far as the nitrogen is concerned, in that one-third of this element is lost as cyanogen.

The solubility of potassium ferrocyanide in water has been determined by a number of investigators, but the results do not harmonise.[1] The only reliable figures appear to be those of Briggs,[2] quoted above; of Harkins and Pearce,[3] namely, that at 25° C. 100 grams of water dissolve 24·796 grams of $K_4Fe(CN)_6$; and of Grube,[4] that one litre of saturated solution at 25° C. contains 319·4 grams of $K_4Fe(CN)_6.3H_2O$. The solubility is increased by the presence of sodium ferrocyanide.

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[1] Kolthoff, *Chem. Weekblad*, 1919, 16, 1406.

[2] Briggs, *Trans. Chem. Soc.*, 1920, 117, 1026.

[3] Hartley, *ibid.*, 1913, 103, 1196.

[4] Baker and Adlam, *ibid.*, 1911, 99, 507.

[5] Etard and Bémont, *Compt. rend.*, 1885, 100, 108.

The density of potassium ferrocyanide solution at 8·9° C., saturated and in contact with crystals of the salt, is 1·1191,[5] and at 25° C. 1 09081.[6] The contractions resulting when given volumes of potassium ferrocyanide solutions are mixed with equal volumes of water have been measured by Wade.[7]

Solutions of potassium ferrocyanide are gradually decomposed by light, ferric hydroxide being precipitated.[8] Addition of an alkali sulphide to a fresh solution of the ferrocyanide effects the gradual precipitation of ferrous sulphide in sunlight[9] but not in the dark. The reason appears[10] to be as follows :—

1. Potassium ferrocyanide dissociates normally in solution into potassium and ferrocyanogen ions :—[11]

$$K_4Fe(CN)_6 \rightleftharpoons 4K^{\cdot} + Fe(CN)_6''''.$$

2. Under the influence of light the ferrocyanogen ion dissociates thus :—

$$Fe(CN)_6'''' \rightleftharpoons Fe^{\cdot\cdot} + 6CN'.$$

This reaction is reversible, proceeding from right to left in the dark. It is these iron ions which are precipitated as ferrous sulphide, in the presence of an alkali sulphide, or as ferric hydroxide in neutral or alkaline solution by the action of atmospheric oxygen.

Upon prolonged exposure to light, a solution of potassium ferrocyanide deposits ***Prussian blue*** (see p. 225), whilst on continued boiling ammonia is evolved. With ferrous salts it yields an immediate white precipitate of *ferrous potassium ferrocyanide*, $K_2Fe[Fe(CN)_6]$, which readily absorbs oxygen, becoming blue. The presence of dilute hydrochloric or sulphuric acid, or the employment of excess of the ferrous salt, accelerates the formation of the blue colour, and the reaction is exceedingly delicate.[12]

With ferric salts Prussian blue (see p. 225) is obtained, but the reaction is a time-reaction, and is retarded by the presence both of acids and salts. In very dilute solution no colour may be produced, or only an indefinite green after several hours,[13] although the blue colour may be produced by the addition of concentrated solutions of many salts to the dilute solutions of the reagents. Probably the explanation lies in the precipitation by the salts of Prussian blue, which is first formed in colourless colloidal form.[1]

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[1] Wallace, *Trans. Chem. Soc*, 1855, 7, 80; Etard, *Ann. Chim. Phys.*, 1894, [7], 2, 526; Schiff, *Annalen*, 1860, 113, 350; Michel and Krafft, *Ann. Chim. Phys.*, 1858, [3], 41, 478.

[2] Briggs, *loc. cit.*

[3] Harkins and Pearce, *J. Amer. Chem Soc.*, 1916, 38, 2714.

[4] Grube, 1914 Taken from Seidell, *Solubilities* (Crosby Lockwood, 1920).

[5] Sonstadt, *Trans. Chem. Soc.*, 1906, 89, 343.

[6] Harkins and Pearce, *loc. cit*

[7] Wade, *Trans. Chem Soc*, 1899, 75, 254.

[8] Matuschek, *Chem. Zeit.*, 1901, 25, 565

[9] See Berthelot, *Ann. Chim. Phys*, 1900, (7), 21, 204. He does not mention that light is necessary to effect this decomposition.

[10] Haber, *Zeitsch. Elektrochem*, 1905, 10, 847; Foster, *Trans. Chem. Soc.*, 1906, 89, 912.

[11] Contrast Jones and Bassett, *Amer. Chem. J.*, 1905, 34, 290.

[12] Vorlander, *Ber.*, 1913, 46, 181.

[13] Vorlander, *loc. cit.*

Carbon dioxide decomposes potassium ferrocyanide solution at 72° to 74° C., liberating hydrogen cyanide and precipitating ferrous potassium ferrocyanide.[2] Continued passage of carbon dioxide through a boiling solution of potassium ferrocyanide results in the precipitation of ferric hydroxide and the formation of potassium carbonate and hydrogen cyanide, or its decomposition products, ammonia and formaldehyde.[3]

When potassium ferrocyanide is heated with concentrated sulphuric acid, carbon monoxide is evolved. This reaction has been known for many years,[4] but it was not until 1900 that the reaction was thoroughly investigated.[5]

Concentrated sulphuric acid dissolves dry anhydrous potassium ferrocyanide, yielding potassium hydrogen sulphate and hydrogen ferrocyanide :—

$$K_4Fe(CN)_6+4H_2SO_4=4KHSO_4+H_4Fe(CN)_6.$$

This solution is decomposed on warming, carbon monoxide being evolved, although even at 200° C. the rate of evolution is slow.

If a little water is present, carbon monoxide is readily formed on warming, the best result being attained with acid of concentration corresponding to $H_2SO_4.2H_2O$, when dry anhydrous potassium ferrocyanide is employed ; the reaction is then complete at 180° C. :—[6]

$$K_4[Fe(CN)_6]+8(H_2SO_4.2H_2O)$$
$$=4KHSO_4+FeSO_4+3(NH_4)_2SO_4+6CO+10H_2O.$$

This is a very convenient method of preparing pure carbon monoxide.

When heated with dilute sulphuric acid hydrogen cyanide is evolved, and Everitt's salt remains behind :—[7]

$$2K_4[Fe(CN)_6]+3H_2SO_4=3K_2SO_4+\underset{\text{(Everitt's salt)}}{K_2Fe^{\cdot\cdot}[Fe^{\cdot\cdot}(CN)_6]}+6HCN$$

Its aqueous solution upon saturation with chlorine darkens in colour, and upon concentration yields potassium ferricyanide, $K_3[Fe^{\cdot\cdot\cdot}(CN)_6]$:—

$$2K_4[Fe^{\cdot\cdot}(CN)_6]+Cl_2\rightleftharpoons 2KCl+2K_3[Fe^{\cdot\cdot\cdot}(CN)_6].$$

Potassium ferrocyanide is similarly oxidised by potassium bromate in acid solution ; thus :—

$$6K_4Fe(CN)_6+KBrO_3+6HCl=6K_3Fe(CN)_6+KBr+6KCl+3H_2O,$$

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[1] Kato, *Mem. Col. Sci. Eng. Kyōto*, 1908, 1, 352.

[2] Autenrieth, *Arch. Pharm.*, 1893, 231, 99

[3] Matuschek, *Chem. Zeit.*, 1901, 25, 815. See also Autenrieth, *Chem. Zeit*, 1898, 22, 866 ; *Kurze Anleitung zur Auffindung der Gifte*, 1892, p. 2 ; Gigli, *Chem. Zeit*, 1898, 22, 775.

[4] Doebereiner, *Schweigger's J.*, 1820, 28, 107 ; Fownes, *Phil. Mag.*, 1844, (3), 24, 21.

[5] Adie and Browning, *Trans. Chem. Soc.*, 1900, 77, 150.

[6] Adie and Browning, *loc. cit.*

[7] Everitt, *Phil. Mag.*, 1835, (3), 6, 97.

the reaction being quantitative under certain well-defined conditions.[1] It probably takes place in three stages, namely :—

(1) $2KBrO_3+12HCl=2KCl+Br_2+5Cl_2+6H_2O.$
(2) $2K_4Fe(CN)_6+Br_2=2KBr+2K_3Fe(CN)_6.$
(3) $10K_4Fe(CN)_6+5Cl_2=10KCl+10K_3Fe(CN)_6.$

With potassium permanganate oxidation to ferricyanide proceeds quantitatively in acid solution, the reaction affording a useful volumetric method of estimating ferrocyanides if carried out under certain well-defined conditions.[2]

Mixed solutions of potassium ferrocyanide and *p*-nitroso dimethyl aniline are at first yellow in colour, but become green very rapidly on exposure to light, due, perhaps, to the production of colloidal Prussian blue under the influence of a catalyst generated by the nitroso compound.[3]

Solutions of potassium ferrocyanide are catalytically decomposed when boiled with cuprous chloride in the presence of hydrochloric acid.[4] The action appears to consist in the alternate formation of cuprous cyanide and regeneration of cuprous chloride, hydrogen cyanide being evolved. By collecting the evolved acid in alkali, and afterwards titrating excess of the latter, the amount of ferrocyanide originally present may be conveniently estimated.

If a few drops of potassium ferrocyanide solution are added to dilute hydrogen peroxide (1 per cent.), and kept in the dark, decomposition of the latter is exceedingly slow. On placing in direct sunlight for a few moments, however, brisk evolution of oxygen takes place and continues, even after removal from the light. The effect is not due to rise of temperature, but, presumably, to some catalyst generated under the influence of the light.[5]

Potassium ferrocyanide finds application in commerce in the manufacture of Prussian blue, and also for case-hardening of steel.[6]

Double Salts.—When equal parts of potassium ferrocyanide and ammonium chloride are dissolved in water at 100° C. and allowed to cool, pale yellow hexagonal crystals are obtained of composition $NH_4KH_2Fe(CN)_6.2NH_4Cl$. The neutral salt, $(NH_4)_3KFe(CN)_6.2NH_4Cl$, has also been obtained.[7]

Potassium aluminium ferrocyanide, $KAlFe(CN)_6.4H_2O$.—Considerable difficulty attends the preparation of this salt,[8] which forms a jelly on mixing equivalent solutions of aluminium chloride and potassium ferrocyanide. By centrifugating at 3000 revolutions per minute it may be isolated as a precipitate, washed with acetone and ether, and dried *in vacuo*. The salt is dark green, and transparent when in bulk, but when powdered is light bluish green. At 100° C. it becomes anhydrous and assumes a deep blue colour.

Potassium barium ferrocyanide, $K_2BaFe(CN)_6.3H_2O$, results as a crystalline deposit on mixing dilute solutions of potassium ferrocyanide and barium chloride.[1]

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[1] de Koninck and Joassart, *Bull. Soc chim. Belg*, 1914, 28, 144

[2] See E Muller and Diefenthäler, *Zeitsch. anorg. Chem.*, 1910, 67, 418; Mecklenburg, *ibid.*, 1910, 67, 322.

[3] Gallenkamp, *Chem. Zeit.*, 1916, 40, 235.

[4] Williams, *J. Soc. Chem. Ind*, 1912, 31, 468.

[5] Kistiakowsky, *Zeitsch. physikal. Chem.*, 1900, 35, 431.

[6] See this volume, Part III.

[7] Etard and Bémont, *Compt. rend*, 1885, 100, 108.

[8] Robinson, *Trans. Chem. Soc.*, 1909, 95, 1353.

Potassium calcium ferrocyanide, $K_2CaFe(CN)_6$, is obtained by mixing cold concentrated solutions of potassium ferrocyanide and calcium chloride in molecular proportions. The precipitate is washed in cold water and dried in air or at 100° C.

One part of the salt dissolves in 244 parts of water at 15° to 17° C.[2]

Potassium cerium ferrocyanide, $KCeFe(CN)_6$, is obtained as a white crystalline precipitate on mixing cold concentrated solutions of cerium chloride and potassium ferrocyanide.[3] The salt undergoes no change when heated to 100° C.

Potassium magnesium ferrocyanide, $K_2MgFe(CN)_6$, is obtained in the anhydrous condition by mixing cold concentrated solutions of potassium ferrocyanide and magnesium chloride.[3] After a short time a white micro-crystalline precipitate is formed, which is not affected by heating to 120° C. When moist the salt soon becomes cream-coloured, owing to slight decomposition, possibly under the influence of atmospheric carbon dioxide.

A saturated aqueous solution of the salt contains 1·95 grams per litre.

The *heptahydrate*, $2K_2MgFe(CN)_6.7H_2O$, is prepared by mixing dilute solutions of potassium ferrocyanide and magnesium chloride at the boiling-point.

Potassium mercuric ferrocyanide, $K_2HgFe(CN)_6$, may be obtained as a faintly blue powder by the interaction of mercuric chloride and potassium ferrocyanide solutions.[4] It is insoluble in water, but is decomposed by acids.

Potassium ammonium barium ferrocyanide, $K_2BaFe(CN)_6.4(NH_4)_2BaFe(CN)_6.15H_2O$; **potassium ammonium cadmium ferrocyanide,** $K_2CdFe(CN)_6.4(NH_4)_2CdFe(CN)_6.2H_2O$; **potassium ammonium calcium ferrocyanide,** $K_2CaFe(CN)_6.4(NH_4)_2CaFe(CN)_6.2H_2O$; and **potassium ammonium magnesium ferrocyanide,** $K_2MgFe(CN)_6.5(NH_4)_2MgFe(CN)_6.10H_2O$; have been prepared.[5]

Silver ferrocyanide, $Ag_4Fe(CN)_6$, is obtained as a white precipitate by double decomposition of a silver salt with potassium ferrocyanide. With nitric acid it yields orange-red silver ferricyanide.[6]

Sodium ferrocyanide, $Na_4Fe(CN)_6.10H_2O$, may be prepared in an analogous manner to the potassium salt.[7] It may also be prepared by boiling Prussian blue with aqueous solutions of sodium carbonate or hydroxide.

Its solubility in water is as follows :—[8]

Temperature, °C. . . .	20	30	42	60	80	98·5
Grams $Na_4Fe(CN)_6$ per 100 grams H_2O	17·9	23·5	30·2	42·5	59·2	63·0

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[1] Bunsen, *Pogg. Annalen*, 1835, 36, 404. Wyrouboff gives 5 molecules of combined water (*Ann. Chim. Phys.*, 1870, 21, 279).

[2] Brown, *Trans. Chem. Soc.*, 1907, 91, 1826.

[3] Robinson, *ibid.*, 1909, 95, 1353.

[4] Fernekes, *J. Amer. Chem. Soc.*, 1906, 28, 87.

[5] Dains, *ibid.*, 1907, 29, 727.

[6] See Valenta, *Chem. Zeit.*, 1916, 40, 398.

[7] It was studied by Bunsen (*Pogg. Annalen*, 1835, 36, 413) and Pebal (*Annalen*, 1886, 233, 165).

[8] Conroy, *J. Soc. Chem. Ind.*, 1898, 17, 104.

At 25° C., 20·725 grams of $Na_4Fe(CN)_6$ dissolve in 100 grams of water,[1] the density of the solution being 1·0595. It yields beautiful monoclinic crystals, pale yellow in colour. Alcohol precipitates the *nonahydrate*, $Na_4Fe(CN)_6.9H_2O$, from the aqueous solution of the salt.

Sodium cerium ferrocyanide, $NaCeFe(CN)_6$, is obtained [2] on mixing cold concentrated solutions of cerium chloride and sodium ferrocyanide. No description of the salt is given.

Strontium ferrocyanide, $Sr_2Fe(CN)_6.14H_2O$, is obtained as a soluble salt by neutralising hydrogen ferrocyanide with the hydroxide or carbonate of strontium. The salt crystallises in monoclinic prisms containing 14 molecules of water,[3] of which seven are lost on exposure to air and a further six when kept over concentrated sulphuric acid.

A study of the osmotic pressures and electric conductivities of solutions of strontium ferrocyanide in water leads to the conclusion [4] that the negative radicles are associated to double ions, namely $[Fe(CN)_6]_2''''''''$.

Thallium ferrocyanide, $Tl_4Fe(CN)_6.2H_2O$ has been prepared.[5] It is formed as yellow crystals by adding a hot concentrated solution of thallous sulphate to one of potassium ferrocyanide and allowing to cool.[6] It is sparingly soluble in cold water but more readily in hot [7] and in potassium ferrocyanide solution. If dilute solutions of thallous sulphate and potassium ferrocyanide are mixed and alcohol added, a complex **potassium thallium ferrocyanide,** $K_4Fe(CN)_6.K_3TlFe(CN)_6.6H_2O$, is obtained.[8]

Zinc ferrocyanide, $Zn_2Fe(CN)_6.(3 \text{ or } 4)H_2O$ [9] is a white powder.

The following *ammoniates* have been prepared, namely $Zn_2Fe(CN)_6.6NH_3.2H_2O$ [10] and $Zn_2Fe(CN)_6.7NH_3$.[11]

Zinc potassium ferrocyanide, $Zn_3K_2[Fe(CN)_6]_2$, is obtained as an insoluble precipitate on adding an excess of potassium ferrocyanide to a zinc salt in aqueous solution.[12]

By adding sulphuric acid to a portion of the clear solution and estimating the excess of potassium ferrocyanide by titration with permanganate, the method may be made a convenient one for the estimation of zinc.[13]

Ferricyanides.

Hydrogen ferricyanide, Ferricyanic acid, $H_3[Fe(CN)_6]$, may be obtained as crystalline brown needles by the action of dilute sulphuric acid upon lead ferricyanide and subsequent concentration of the decanted solution. The product is not pure, however.[1] A pure acid is believed to result on decomposition with hydrochloric acid, silver ferricyanide, prepared by the action of silver nitrate on potassium ferricyanide.[2]

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[1] Harkins and Pearce, *J. Amer. Chem Soc*, 1916, 38, 2714.

[2] Robinson, *Trans. Chem. Soc.*, 1909, 95, 1353.

[3] Coleman, quoted by Roscoe and Schorlemmer, *A Treatise on Chemistry*, vol. ii. (Macmillan & Co.), 1907, p. 1232; Berkeley, Hartley, and Stephenson, *Phil Trans.*, 1909, A, 209, 319. Bette (*Annalen*, 1836, 22, 148) and Wyrouboff (*Ann. Chim Phys.*, 1869, (4), 16, 287; 1870, (4), 21, 274) gave $15H_2O$.

[4] Berkeley, Hartley, and Stephenson, *loc. cit.*

[5] Kuhlmann, *Compt. rend*, 1862, 55, 607; Lamy and Descloiseaux, *ibid.*, 1868, 66, 1146, Robinson, *Trans Chem. Soc.*, 1909, 95, 1353.

[6] T. Fischer and Benzian, *Chem. Zeit.*, 1902, 26, 49

[7] See Crookes, *Chem. News*, 1861, 3, 303.

[8] Fischer and Benzian, *loc. cit.*

[9] Schendeler, *Mag. Pharm*, 35, 71, Wyrouboff, *loc. cit.*

[10] Tissier, *Compt. rend.*, 1857, 45, 232.

[11] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[12] Miller and Falk, *J. Amer. Chem. Soc.*, 1904, 26, 952.

[13] Meurice, *Ann. Chim. anal.*, 1913, 18, 342.

Ammonium ferricyanide, $2(NH_4)_3[Fe(CN)_6].H_2O$, may be prepared in a similar manner to the potassium salt (*vide infra*). It yields red monoclinic prisms, which readily dissolve in water. The solution hydrolyses upon standing, and is more sensitive to the action of light in this respect than is the potassium salt.[3]

Barium ferricyanide, $Ba_3[Fe(CN)_6]_2.20H_2O$, is prepared by neutralising ferricyanic acid with barium carbonate and evaporating to crystallisation *in vacuo*.[2] It also results on boiling a solution of barium ferrocyanide with lead dioxide.[4] It yields reddish brown crystals. These are soluble in water without decomposition. The salt is decomposed on warming with acids. The compound $Ba_3[Fe(CN)_6]_2.2BaBr_2.20H_2O$, has been obtained.[5]

Barium potassium ferricyanide, $BaKFe(CN)_6.4H_2O$, first isolated by Bette,[6] who regarded it as a trihydrate, is conveniently prepared by addition of the requisite quantity of potassium sulphate to a solution of barium ferricyanide and allowing the filtered liquid to evaporate.[7]

Barium sodium ferricyanide, $BaNaFe(CN)_6.3H_2O$, and **Barium ammonium ferricyanide,** $BaNH_4.Fe(CN)_6.4H_2O$, have also been prepared.

Bismuth ferricyanide.—This salt is precipitated from bismuth salts by solutions of potassium ferricyanide. It is straw-coloured and insoluble in concentrated nitric acid.[8]

Calcium ferricyanide, $Ca_3[Fe(CN)_6]_2(?)12H_2O$, may be obtained [9] by oxidising aqueous calcium ferrocyanide with calcium plumbate and carbon dioxide under pressure, at the ordinary temperature. The solid salt is separated by evaporation under reduced pressure. The salt may also be obtained by oxidation of calcium ferrocyanide with chlorine [10] and by neutralising ferricyanic acid with calcium carbonate. It yields needle-shaped crystals, which are stable in dry air.

Calcium potassium ferricyanide, $CaK.Fe(CN)_6.3H_2O$, crystallises in deep red plates, and is more stable than the simple calcium salt.

Calcium ammonium ferricyanide, $CaNH_4.Fe(CN)_6.3H_2O$, and **Calcium sodium ferricyanide,** $CaNa.Fe(CN)_6.5H_2O$, have also been obtained.

Cobalt ferricyanide, $Co_3[Fe(CN)_6]_2$, is a red precipitate resulting when potassium ferricyanide and cobalt sulphate solutions are mixed. The *ammoniates* $Co_3[Fe(CN)_6]_2.4NH_3.6H_2O$ [11] and $Co_3[Fe(CN)_6]_2.8NH_3$ [12] have been prepared.

Copper ferricyanide, $Cu_3[Fe(CN)_6]_2$, is a greenish brown precipitate obtained on mixing solutions of copper sulphate and potassium ferricyanide.[13] The precipitate has a constant composition, no matter what relative proportions of the two salts are used.

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[1] Joannis, *Compt. rend.*, 1882, 94, 449.

[2] Fischer and P. Muller, *Chem. Zeit.*, 1901, 25, 321.

[3] Eder, *Monatsh.*, 1885, 6, 495.

[4] Schuler, *Jahresber.*, 1873, p. 330

[5] Rammelsberg, *J. prakt. Chem.*, 1889, (2), 39, 455.

[6] Bette, *Ann. Pharm.*, 1837, 23, 124.

[7] Fischer and Muller, *loc. cit.*

[8] Locke and Edwards, *Amer. Chem. J.*, 1899, 21, 193.

[9] Kassner, *Chem. Zeit*, 1893, 17, 1712.

[10] Bette, *loc. cit.*

[11] Braun, *Annalen*, 1863, 125, 164.

[12] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[13] E. Müller, Wegelin, and Kellerhof, *J. prakt. Chem.*, 1912, 86, 82.

If ammoniacal cupric hydroxide is added to potassium ferricyanide the *pent-ammoniate*, $Cu_3[Fe(CN)_6]_2.5NH_3$, is obtained as black, stable crystals.[1] The salt $Cu_3[Fe(CN)_6]_2.16NH_3$ has also been obtained.[2]

Lead ferricyanide, $Pb_3[Fe(CN)_6]_2.16H_2O$, is obtained by double decomposition of lead nitrate with potassium ferricyanide. It yields dark reddish brown crystals.

Lead ferricyanide nitrate, $Pb_3[Fe(CN)_6]_2.Pb(NO_3)_2.12H_2O$, and **Lead potassium ferricyanide,** $PbK[Fe(CN)_6].3H_2O$, have been described.[3]

Magnesium ferricyanide, $Mg_3[Fe(CN)_6]_2.10H_2O$, is prepared in an analogous manner to the barium salt, and dried over sulphuric acid. The aqueous solution decomposes when warmed.[4]

Magnesium ammonium ferricyanide, $MgNH_4.Fe(CN)_6.4H_2O$.

Magnesium potassium ferricyanide, $MgK.Fe(CN)_6.4H_2O$, and **Magnesium sodium ferricyanide,** $MgNaFe(CN)_6.6H_2O$, have also been obtained.

Mercuric ferricyanide, $Hg_3[Fe(CN)_6]_2$, may be obtained by adding a concentrated aqueous solution of potassium ferricyanide to a solution of mercuric chloride in alcohol and ether. The precipitate is bright yellow in colour, and fairly stable when dry.[5]

Mercurous ferricyanide, $Hg_3[Fe(CN)_6]$, is obtained as a flocculent cream-coloured precipitate on the addition of mercurous nitrate to potassium ferricyanide solution.[5] It turns blue on exposure to air.

Potassium ferricyanide, $K_3[Fe(CN)_6]$, known commercially as *red prussiate of potash*, was discovered by Gmelin in 1822, and is obtained by the chlorination of potassium ferrocyanide :—[6]

$$2K_4[Fe(CN)_6]+Cl_2 \rightleftharpoons 2K_3[Fe(CN)_6]+2KCl,$$

and subsequent re-crystallisation, whereby the more soluble potassium chloride remains in solution. It yields dark red monoclinic prisms of density 1·8, which dissolve in water to a yellow solution.[7] The solubility is as follows :—[8]

Temperature, °C. .	4·4	10	15·6	37·8	100
Grams $K_3[Fe(CN)_6]$ in 100 grams H_2O .	33·0	36·6	39 7	58·8	77·6

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[1] Bhaduri, *Zeitsch. anorg. Chem* , 1913, 81, 406

[2] Peters, *ibid* , 1912, 77, 137.

[3] Schuler, *Sitzungsber. Akad Wiss. Wien*, 1879, 79, 302 ; Rammelsberg, *J. prakt Chem.*, 1889, (2), 39, 455.

[4] Fischer and Muller, *Chem Zeit* , 1901, 25, 321 ; Bette, *Ann. Pharm.*, 1837, 23, 124.

[5] Fernekes, *J. Amer. Chem. Soc.*, 1906, 28, 602

[6] This reaction has been studied by Gillet, *Bull Soc. chim. Belg.*, 1912, 26, 236.

[7] A supposed isomeride named *potassium β ferricyanide*, $K_3[Fe \cdot(CN)_6]\,H_2O$, was described as obtained (Locke and Edwards, *Amer. Chem. J.*, 1899, 21, 193, 413) from the α salt by treatment with small quantities of mineral acids. It is formed on concentration as olive-coloured crystals, which readily dissolve in water. It reacts similarly to the α salt, yielding characteristic precipitates with solutions of salts of the heavy metals, although in some cases the β ferricyanides thus obtained are appreciably different from the more common α salts. The evidence, however, is far from conclusive. With reference to the constitution of this salt see I. Bellucci and Sabatini, *Atti R Accad. Lincei*, 1911, (5), 20, i. 176, 239 ; *Gazzetta*, 1920, 50, i 23 ; Piutti, *Ber* , 1912, 45, 1830 ; Wells, *Amer Chem. J.*, 1913, 49, 205. Hauser and Biesalski (*Ber* , 1912, 45, 3516) suggest that the β salt is the ordinary one containing some Prussian blue as impurity. Since the foregoing was written, Briggs (*Trans. Chem. Soc.*, 1920, 117, 1026) has shown, however, that the β salt consists of mixed crystals of potassium ferricyanide and aquopentacyanoferrate, $K_2[Fe(CN)_5.H_2O]$. (See p 235)

[8] Wallace, *Trans. Chem. Soc.*, 1855, 7, 80.

The above data are only approximately correct, and further research on the subject would be welcome. According to Grube,[1] one litre of saturated solution at 25° C. contains 385 5 grams of $K_3Fe(CN)_6$. The solution on exposure to light yields a blue precipitate, ferrocyanide remaining in solution. It is reduced by sodium amalgam to ferrocyanide, and hydrogen peroxide has the same effect :—

$$4K_3[Fe^{\cdot\cdot}(CN)_6]+2H_2O_2=3K_4[Fe^{\cdot\cdot}(CN)_6]+H_4[Fe^{\cdot\cdot}(CN)_6]+2O_2.$$

When oxidised, *di-potassium perferricyanide*, $K_2Fe(CN)_6$, is stated to be produced,[2] but the salt is probably a *pentacyanoferrate*, $K_2Fe^{\cdot\cdot}(CN)_5$.[3] With solutions of ferrous salts potassium ferricyanide yields a deep blue precipitate, originally called *Turnbull's blue*, but now believed to be identical with Prussian blue.[4]

In neutral solution potassium ferricyanide undergoes hydrolysis to a small extent, ferric hydroxide being precipitated. Thus :—[5]

$$K_3Fe(CN)_6+3HOH=Fe(OH)_3+3KCN+3HCN.$$

The hydrolysis is accelerated by light.[6] Hydrolysis also appears[7] to take place to a slight extent according to the equation—

$$K_3Fe(CN)_6+H_2O\rightleftharpoons K_2Fe(CN)_5H_2O+KCN,$$

aquo penta-cyanoferrate resulting. The solution is reduced by hydrogen sulphide, slowly at the ordinary temperature, but rapidly on warming. Thus :—[8]

$$6K_3Fe(CN)_6+3H_2S=4K_4Fe(CN)_6+K_2Fe.Fe(CN)_6+6HCN+3S.$$

Potassium ferricyanide is reduced in alkaline solution to ferrocyanide—in other words, the salt under these conditions is able to function as an oxidiser, thus :—

$$2K_3Fe(CN)_6+2KOH\rightleftharpoons 2K_4Fe(CN)_6+H_2O+O.$$

The reaction velocity has been studied[9] at 90° C., with interesting results. The velocity at first decreases slightly, then increases rapidly to a maximum, after attaining which it falls again. The reason for the increased velocity lies in the autocatalytic action of the potassium ferrocyanide produced during the reaction.

Below 60° C. and in the dark, the alkaline solution of potassium ferrocyanide is stable.[10]

An aqueous solution of potassium ferricyanide is readily reduced by hydrochloric acid into ferrocyanide. Thus :—

$$2H_3Fe(CN)_6+2HCl\rightleftharpoons 2H_4Fe(CN)_6+Cl_2,$$

the reaction proceeding to completion if the chlorine is removed as, for example, by addition of reduced silver. Ferric chloride acts similarly—

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[1] Grube, 1916. Taken from Seidell, *opus cit.*

[2] Stadeler, *Annalen*, 1869, 151, 1.

[3] Cambi, *Gazzetta*, 1911, 41, i. 157.

[4] Hofmann, Heine, and Hochtlen, *Annalen*, 1904, 337, 1. Also see p. 227.

[5] See Foster, *Trans. Chem. Soc.*, 1906, 89, 916 ; Matuschek, *Chem. Zeit.*, 1901, 25, 411, 522, 565.

[6] See Eder, *Monatsh.*, 1885, 6, 495.

[7] Briggs, *loc. cit.*

[8] Venditori, *Atti R. Accad. Lincei*, 1906, (5), 15, i. 370.

[9] Grube, *Zeitsch. anorg. Chem.*, 1914, 84, 190 ; Prudhomme, *Bull. Soc. chim*, 1903, (3), 29, 1010 ; Fredenhagen, *Zeitsch. anorg. Chem.*, 1902, 29, 396.

[10] Kassner, *Arch. Pharm.*, 1896, 234, 330.

not because it dissociates on solution into ferrous chloride and chlorine, but because it undergoes hydrolysis, the liberated hydrochloric acid acting as indicated above.

Hydrobromic acid, ferric bromide, and the chlorides and bromides of zinc and aluminium all react in an analogous manner.[1] With potassium iodide in the presence of a zinc salt the reaction is quantitative, and may be used in the volumetric estimation of ferricyanides:—[2]

$$2K_3Fe(CN)_6+2KI\rightleftharpoons 2K_4Fe(CN)_6+I_2.$$

Potassium ferricyanide is reduced to ferrocyanide by an alkaline solution of ferrous sulphate.

Potassium ferricyanide is quantitatively reduced by an alkaline solution of hydrazine sulphate, the reaction proceeding as follows:—

$$4K_3Fe(CN)_6+4KOH=4K_4Fe(CN)_6+2H_2O+O_2,$$
$$N_2H_4+O_2=N_2+2H_2O.$$

By effecting the reduction in a nitrometer and measuring the nitrogen evolved, the amount of hydrazine or potassium ferricyanide originally present can readily be calculated.[3]

Hydroxylamine similarly reduces the salt, yielding nitrous oxide and nitrogen.[3] Thus:—

$$4NH_2.OH+O_2=2N_2+6H_2O,$$
$$6NH_2.OH+O_2=2N_2O+2NH_3+6H_2O.$$

Indigo is readily bleached by the salt.

When distilled with potassium cyanide, potassium ferrocyanide, hydrogen cyanide, and ammonium carbonate are produced:—[4]

$$2K_3Fe(CN)_6+2KCN+2H_2O=2K_4Fe(CN)_6+HCN+NH_3+CO_2.$$

Continued passage of carbon dioxide through a boiling solution of potassium ferricyanide results in the precipitation of ferric hydroxide and the formation of potassium carbonate and hydrogen cyanide or its decomposition products, ammonia and formic acid.[5]

Sodium ferricyanide, $2Na_3[Fe(CN)_6].H_2O$, may be obtained in a similar manner to the preceding salt. It yields deliquescent ruby-red prisms, soluble in water.

Strontium ferricyanide, $Sr_3[Fe(CN)_6]_2.14H_2O$, obtained in an analogous manner to the barium salt, crystallises in reddish brown prisms.[6]

Strontium potassium ferricyanide, $SrKFe(CN)_6.3H_2O$; **Strontium sodium ferricyanide,** $SrNaFe(CN)_6.3H_2O$; and **Strontium ammonium ferricyanide,** $SrNH_4Fe(CN)_6.3H_2O$; have also been prepared.

Thallium ferricyanide does not appear to have been obtained, but various double potassium thallium salts have been isolated. When potassium ferricyanide and thallous sulphate solutions are mixed and allowed to crystallise, red needles of $K_2Tl[Fe(CN)_6]$ are obtained. These are decomposed by pure water.[1]

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[1] Gillet, *Bull Soc. chim. Belg.*, 1912, 26, 236. For the action of bromine on potassium ferricyanide see Reynolds, *Trans. Chem. Soc.*, 1888, 53, 767.

[2] Mecklenburg, *Zeitsch. anorg. Chem.*, 1910, 67, 322. The kinetics of this reaction have been studied by Donnan and le Rossignol, *Trans. Chem. Soc.*, 1903, 83, 703; Just, *Zeitsch. physikal. Chem.*, 1908, 63, 513.

[3] Rây and Sen, *Zeitsch. anorg. Chem.*, 1912, 76, 380.

[4] Bloxam, *Chem. News*, 1883, 48, 73.

[5] Matuschek, *Chem. Zeit.*, 1901, 25, 815.

[6] Fischer and P. Muller, *Chem. Zeit.*, 1901, 25, 321.

Zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$, is precipitated as an insoluble orange-coloured salt on adding potassium ferricyanide to a solution of a zinc salt.

The *ammoniate*, $Zn_3[Fe(CN)_6]_2.12NH_3$, has been isolated.[2]

Iron Derivatives of Ferro- and Ferri-cyanides.

Some of these derivatives, such as Prussian blue, are of considerable commercial importance on account of their characteristic deep colour. As a general rule, the derivatives which are devoid of colour contain iron in one stage of oxidation only within the molecule, whilst the coloured compounds possess divalent and trivalent atoms of iron respectively. It would appear, therefore, that the colour is in some way connected with the presence of similar atoms in more than one stage of oxidation. Thus, ferrous potassium ferrocyanide, $Fe^{\cdot\cdot}K_2[Fe^{\cdot\cdot}(CN)_6]$, is white, the iron atoms in the positive and negative radicles respectively being divalent. Upon oxidation, however, Prussian blue, $Fe^{\cdot\cdot\cdot}K[Fe^{\cdot\cdot}(CN)_6]$ is obtained, the iron atom of the negative radicle remaining divalent, whilst the positive iron ion is trivalent.

An analogous case is afforded by the deep indigo colour of sulphur sesqui-oxide, S_2O_3, which contains sulphur atoms in two degrees of valency,[3] whereas sulphur dioxide and trioxide are both colourless.

Ferrous hydrogen ferrocyanide, $H_2Fe[Fe(CN)_6]$, results when hydrogen ferrocyanide solution is heated to 110°–120° C.[4] with exclusion of air. It readily oxidises to **ferric hydrogen ferrocyanide,** $Fe^{\cdot\cdot\cdot}H[Fe^{\cdot\cdot}(CN)_6].H_2O$, which is a blue compound, insoluble in water, oxalic acid, and ammonium oxalate solutions.

Ferrous potassium ferrocyanide, $FeK_2[Fe(CN)_6]$, is obtained as a white precipitate when potassium ferrocyanide reacts with an equimolecular quantity of a ferrous salt:—

$$FeCl_2+K_4[Fe(CN)_6]=FeK_2[Fe(CN)_6]+2KCl.$$

It readily absorbs oxygen, yielding Prussian blue.

Everitt's salt also has the formula $FeK_2[Fe(CN)_6]$ and is isomeric with the previous salt. It is obtained when dilute sulphuric acid and potassium ferrocyanide are heated together:—[5]

$$2K_4[Fe(CN)_6]+3H_2SO_4=3K_2SO_4+K_2Fe[Fe(CN)_6]+6HCN.$$

It is a pale yellow crystalline powder which, upon oxidation with hydrogen peroxide, yields *Williamson's violet* (see p. 226).

The Prussian Blues.—Several of these are known, namely: *a* **soluble Prussian blue,** $4Fe^{\cdot\cdot\cdot}K[Fe^{\cdot\cdot}(CN)_6].7H_2O$. This compound is obtained when a solution of potassium ferrocyanide interacts with rather less than one equivalent of a ferric salt.[6] It occurs as a deep blue precipitate, which when washed with alcohol and dried yields a beautiful blue powder exhibiting a bronze cast by reflected light. It is soluble in pure water, but is precipitated on the addition of salts. Aqueous solutions of oxalic acid dissolve it, whilst alkalies decompose it, precipitating ferric hydroxide.[1] A similar blue-coloured precipitate, known as **Turnbull's blue** (the soluble variety), is formed when rather less than one equivalent of a ferrous salt interacts with potassium ferricyanide. According to Skraup[2] and Hofmann,[3] the two precipitates are identical, but this is denied by Müller.[4]

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[1] T. Fischer and Benzian, *Chem. Zeit.*, 1902, 26, 49.

[2] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[3] See this series, Volume VII.

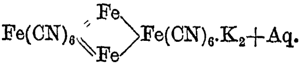
[4] Reemann and Carius, *Annalen*, 1860, 113, 39; Etard and Bémont, *Compt. rend.*, 1884, 99, 1024; Hofmann, Arnoldi, and Hiendlmaier, *Annalen*, 1907, 352, 54.

[5] Everitt, *Phil. Mag.*, 1835, (3), 6, 97.

[6] See Volschin, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 480.

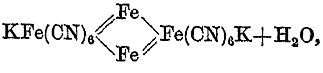
β **soluble Prussian blue** is produced when molecular proportions of a ferrous salt and potassium ferrocyanide are brought together in *neutral* solution and oxidised with hydrogen peroxide. It is rapidly decomposed by ammonia, but is not soluble in oxalic acid solution.[5] It is isomeric with the γ variety, and the formula $Fe^{\cdots}K[Fe(CN)_6].H_2O$ is attributed to it.

γ **soluble Prussian blue** is obtained when molecular proportions of a ferrous salt and potassium ferrocyanide are brought together in *cold, acid* solution and oxidised with nitric acid or hydrogen peroxide. Hofmann regards it as consisting of two molecules of $KFe[Fe(CN)_6]+Aq.$ and suggests the asymmetrical formula



$$Fe(CN)_6\begin{matrix}\diagup Fe \diagdown \\ \diagdown Fe \diagup\end{matrix}Fe(CN)_6.K_2+Aq.$$

Isomeric with this salt is: **Williamson's violet** or **Williamson's blue,** $KFe^{\cdots}[Fe(CN)_6]+H_2O$, obtained by suspending Everitt's salt in one per cent. sulphuric acid and adding nitric acid or hydrogen peroxide. A ferric salt may be used as oxidising agent.[6] The compound is insoluble in water, but forms a suspension which appears dark purple by reflected light, but greenish blue by transmitted light. It is insoluble in oxalic acid and is not decomposed by dilute mineral acids or by digestion with ferric chloride, but 4 per cent. ammonium hydroxide converts it after some hours into ferric hydroxide and alkali ferrocyanide.[5] Hofmann and Resenscheck suggest the symmetrical constitutional formula :—



$$KFe(CN)_6\begin{matrix}\diagup Fe \diagdown \\ \diagdown Fe \diagup\end{matrix}Fe(CN)_6K+H_2O,$$

the water also being constitutional in some way.

When ferric ammonium alum and potassium ferricyanide are acted upon with hydrogen peroxide in the presence of free hydrochloric acid, a blue substance, $Fe_7(CN)_{18}.10H_2O$, is obtained, having properties similar to Williamson's violet, but less stable towards dilute ammonium hydroxide.[7]

Insoluble Prussian blue, $Fe^{\cdots}{}_4[Fe(CN)_6]_3+Aq.$, is obtained when potassium ferrocyanide is treated with an excess of a ferric salt, the ratio, in the case of ferric chloride,[1] $FeCl_3/K_4Fe(CN)_6$, being greater than 1·33. The same product is obtained when a soluble Prussian blue is acted upon by a ferric salt, and is stated to be identical with **insoluble Turnbull's blue,**[2] which is the salt obtained by addition of excess ferrous salt to potassium ferricyanide and washing in full exposure to air; but this is denied by Muller,[3] who gives it the formula $KFe^{\cdot\cdot}Fe^{\cdot\cdot\cdot}{}_3[Fe(CN)_6]_3$.

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[1] Guignet, *Compt. rend.*, 1889, 108, 178.

[2] Skraup, *Annalen*, 1877, 186, 371.

[3] Hofmann, Heine, and Hochtlen, *loc. cit.*; Hofmann, *J. prakt. Chem.*, 1909, 80, 150.

[4] E. Müller and Stanisch, *J. prakt. Chem.*, 1909, (2), 79, 81.

[5] K. A. Hofmann and Resenscheck, *Annalen*, 1905, 340, 267.

[6] Messner, *Zeitsch. anorg. Chem.*, 1895, 9, 126.

[7] Hofmann and Resenscheck, *loc. cit.*

The substance is insoluble in water and in dilute mineral acids, but dissolves in oxalic acid, yielding a blue solution at one time largely used for ink. When dried, the salt contains 9–10 molecules of water, and if heated strongly in air it burns, leaving a residue of ferric oxide. Alkalies decompose it, precipitating ferric hydroxide, soluble ferrocyanides passing into solution :—

$$Fe_4[Fe(CN)_6]_3+12NaOH=4Fe(OH)_3+3Na_4[Fe(CN)_6],$$

whilst hot concentrated hydrochloric acid effects its solution, hydrogen ferrocyanide eventually separating out. Heated with concentrated sulphuric acid, the cyanogen group is decomposed, the nitrogen yielding ammonium sulphate. When fused with a mixture of ammonium nitrate and sulphate, sulphate of iron is produced.

Commercial Preparation and Uses of Prussian Blue.—Prussian blue was discovered accidentally in 1704 by Diesbach,[4] and is highly valued as a pigment on account of its remarkable intensity of colour. It was manufactured in Great Britain in 1770, and sold at 2 guineas per lb. One pound of Prussian blue will perceptibly tinge some 600 lbs. of white lead. The pigment is sometimes prepared commercially by the direct method of adding a ferric salt to a solution of potassium ferrocyanide ; but it is more usual to adopt an indirect method, namely to add a ferrous salt to potassium ferrocyanide and subsequently to oxidise the white precipitated mass of ferrous potassium ferrocyanide.[5] Chemically it consists of a variable mixture of some or all of the Prussian blues already described.

Ferrous ferrocyanide, $Fe_2[Fe(CN)_6]$, is formed when an aqueous solution of hydrogen ferrocyanide is heated until hydrogen cyanide ceases to be evolved.[6]

Ferric ammonium ferrocyanide, $FeNH_4[Fe(CN)_6]$, results when potassium ferrocyanide is heated with a solution of hydroxylamine hydrochloride. It is a deep blue insoluble powder.[7] The hydrated salt $FeNH_4[Fe(CN)_6].H_2O$ is known as *Monthiers' blue*,[8] having been obtained by Monthier as the result of oxidising the white precipitate thrown down by the action of potassium ferrocyanide upon ammoniacal ferrous chloride solution. It may also be prepared by dissolving iron wire in a solution containing ammonia, ammonium chloride, and potassium ferrocyanide, and oxidising the green precipitate, thereby obtained, with hydrogen peroxide.[1]

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[1] Müller and Stanisch, *J. prakt. Chem.*, 1909, (2), 80, 153.

[2] Hofmann, Heine, and Hochtlen, *loc. cit.*

[3] E. Muller and Stanisch, *J. prakt. Chem.*, 1909, (2), 79, 81.

[4] Kopp, *Geschichte der Chemie*, 1843–47, 4, 369.

[5] For details of the various processes the reader is referred to *A Treatise on Colour Manufacture*, by Zerr and Rubenkamp, translated by C. Mayer (Chas. Griffin & Co.), 1908.

[6] E. Muller and Treadwell, *J. prakt. Chem*, 1909, (2), 80, 170.

[7] Hofmann and Arnoldi, *Ber.*, 1906, 39, 2204.

[8] Monthiers, *J. Pharm.*, 1846, (3), 9, 262.

A compound of the same formula is obtained by oxidation in neutral solution of the compound obtained by reducing Prussian blue with hydrogen sulphide.

The corresponding potassium salt, $FeK[Fe(CN)_6].H_2O$, has already been described under the name of *Williamson's violet.* This when treated with excess of chlorine yields a green hydrated mass known as *Prussian green.* Its composition corresponds to the formula $Fe(CN)_3$, but its constitution is probably represented by $(Fe[Fe(CN)_6])_n$, *i.e.* ferric ferricyanide.[2]

PENTACYANIDE DERIVATIVES OF IRON.

One of the cyanogen groups of both ferro- and ferri-cyanides is capable of being replaced by other radicles, such as CO, SO_3, NO, NO_2, H_2O, NH_3, AsO_2, etc., thereby yielding pentacyanide derivatives of the types $M_x[Fe^{\cdot\cdot}(CN)_5R]$ and $M_{x-1}[Fe^{\cdot\cdot\cdot}(CN)_5R]$ respectively,[3] the value for x varying according to the negative radicle introduced.

Nitroso Penta-Cyano-ferrates or Nitroso Penta-ferricyanides, $M_2[Fe(CN)_5NO]$.

Hydrogen nitroso ferricyanide or **nitroprussic acid,** $H_2[Fe(CN)_5NO]$, is obtained by decomposition of the silver salt with hydrochloric acid or by the action of dilute sulphuric acid upon the barium salt. It is also formed when nitric oxide is bubbled through an acidified solution of potassium ferrocyanide.[4] The reaction proceeds in two stages, namely, (*a*) oxidation to the ferricyanide, and (*b*) substitution of the cyanogen radicle by NO :—

$$H_3[Fe(CN)_6]+NO=H_2[Fe(CN)_5NO]+HCN.$$

Concentration *in vacuo* yields dark-red needles, which readily deliquesce. Its most important salt is

Sodium nitroprusside,[5] $Na_2[Fe(CN)_5NO]2H_2O$, which is usually obtained by decomposing the potassium salt with sodium carbonate. Potassium carbonate is exceedingly soluble in water, so that sodium nitroprusside is readily obtained in pure form by crystallisation.

It may be conveniently prepared by heating potassium ferrocyanide with 50 per cent. nitric acid solution on a water-bath until a drop of the solution gives no colour with ferrous sulphate. The whole is cooled, the liquid poured from the precipitate, neutralised with sodium carbonate, and taken to dryness. Extraction with water, filtration from the insoluble iron compounds, and crystallisation from the clear aqueous solution yields the salt in ruby-coloured, rhombic prisms. The reactions involved may be represented as follows :—

$$2K_4Fe(CN)_6+3HNO_3=2K_3Fe(CN)_6+2KNO_3+H_2O+HNO_2.$$
$$2K_3Fe(CN)_6+3HNO_2=2K_2[Fe(CN)_5NO]+2KCN+H_2O+HNO_3.$$
$$K_2[Fe(CN)_5NO]+Na_2CO_3=Na_2[Fe(CN)_5NO]+K_2CO_3.$$

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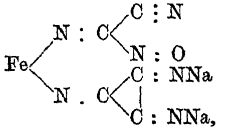
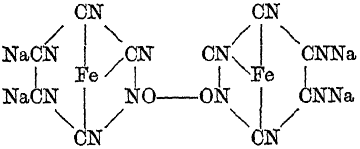
[1] Hofmann, Arnoldi, and Hiendlmaier, *Annalen,* 1907, 352, 54.
[2] Messner, *Zeitsch. anorg. Chem.,* 1895, 9, 136
[3] For the nomenclature of these substances see Hofmann, *Annalen,* 1903, 312, 1.
[4] Playfair, *Phil. Mag.,* 1850, (3), 36, 197, 271, 348.
[5] Playfair, *Annalen,* 1852, 74, 317 ; Kyd, *ibid.,* 340.

Another method [1] consists in dissolving 34·5 grams of sodium nitrate in 150 grams of water at 70° C., and mixing with 216 grams of sodium hydrogen sulphite and a solution of 82 grams of potassium ferricyanide in 250 grams of water, also at 70° C. The mixture is boiled until evolution of gas ceases and the cooled liquid mixed with 54 grams of sodium hydrogen sulphite. The deep red liquid deposits crystals of sodium nitroprusside.

When potassium ferricyanide is warmed with a solution of bleaching powder to 70° C. a considerable evolution of gas takes place, and a reddish deposit of ferric oxide and calcium carbonate is formed. The filtered solution is concentrated and the potassium nitroprusside extracted with alcohol, and converted into the insoluble copper salt by addition of cupric chloride. This latter is decomposed with sodium hydroxide, yielding the sodium salt, which may be further purified by dissolving in a little water, addition of alcohol, and subsequent evaporation after filtering off any insoluble material.[2] The *constitution* to be assigned to sodium nitroprusside in particular, and hence to nitroprussides in general, has been a subject of debate. Browning's [3] formula is :—



whilst Friend [4] suggests



in harmony with his shell theory of complex salts. From a combined study of the electric conductivity in dilute aqueous solution and the depression of the freezing-point in water, it has been concluded that the salt under these conditions yields the following ions :—

$$Na^{\cdot},\ Na^{\cdot},\ \text{and}\ Fe(CN)_5NO''.$$

The suggestion is therefore made that the salt is more correctly represented by the single formula, $Na_2[Fe(CN)_5NO]$, than by the double formula [5] given above. In order to harmonise the double cyclic formula with this, it is merely necessary to assume that the double negative radicle $[Fe(CN)_5NO]_2''''$ itself dissociates into two $Fe(CN)_5NO''$ ions in solution.

This assumption has its parallel in the case of triphenylmethyl, $C(C_6H_5)_3$, which in solution has the simple formula, but is regarded as associated in the solid condition to hexaphenyl ethane, $(C_6H_5)_3C-C(C_6H_5)_3$.[6]

[1] Prudhomme, *Compt. rend.*, 1890, 111, 45.
[2] Jensen, *J. Pharm.*, 1885, (5), 11, 315.
[3] Browning, *Trans. Chem. Soc.*, 1900, 77, 1238.
[4] Friend, *ibid.*, 1916, 109, 721.
[5] Burrows and Turner, *ibid.*, 1919, 115, 1429.
[6] Tschitschibabin, *Ber.*, 1905, 38, 771; Piccard, *Annalen*, 1911, 381, 347.

Further, a study of the dehydration of the solid sodium salt supports the suggestion that the salt has the double formula[1] $[Na_2Fe(CN)_5NO]_2.4H_2O$, for its complete dehydration is a matter of some difficulty, the last molecule of water clinging tenaciously to the salt. If the single formula, $Na_2Fe(CN)_5NO.2H_2O$, be assumed, it is necessary to postulate the existence of half a molecule of water.

Properties.—An aqueous solution of sodium nitroprusside deposits Prussian blue on exposure to light. In the presence of alkali sulphides—as, for example, ammonium sulphide—it yields a beautiful purple colour, which is very characteristic, and so sensitive that the presence of 0·0000018 gram of hydrogen sulphide in 0·004 c.c. can easily be detected.[2] Ammonium hydroxide does not hinder the colour formation, but caustic alkalies destroy it. It gradually fades on standing, in consequence of oxidation of the sulphide to sulphite. The composition of the purple substance is uncertain, but Hofmann[3] suggests the formula $Na_3[Fe(CN)_5(O:N.SNa)]$, since, by the action of thio-urea, $CS(NH_2)_2$, upon sodium nitroprusside, he obtained the complex derivative $Na_3[Fe(CN)_5(O:N.SCNH.NH_2)]$, as a carmine-red powder, closely similar to the substance under discussion.[4]

Hydrochloric acid decomposes sodium nitroprusside, yielding hydrogen cyanide and ferric chloride. The ferric chloride then reacts with excess of the nitroprusside to form ferric nitroprusside.[5]

Concentrated sulphuric acid decomposes the salt, but the reactions involved are very complex.[6] In part they appear to proceed as follows :—

$$\begin{aligned}2Na_2Fe(CN)_5NO+7H_2SO_4+5H_2O=2H(NO)SO_4&+NaHSO_4\\&+NH_4HSO_4+FeSO_4\\&+2(NH_4)_2SO_4\\&+5CO+Na_3Fe(CN)_5.\end{aligned}$$

The pentacyanide derivative unites with the carbon monoxide to yield sodium carbonyl ferrocyanide, $Na_3[Fe(CN)_5.CO]$, which again interacts with the ferrous sulphate to yield the ferrous derivative, $Fe_3[Fe(CN)_5CO]_2$, characterised by its violet colour (see p. 232).

Neutral potassium permanganate is without action on the salt. Sodium amalgam[7] reduces it to sodium ferrocyanide and ammonia. Thus :—

$$\begin{aligned}&12Na_2[Fe(CN)_5.NO]+16Na+54H\\&\qquad=10Na_4Fe(CN)_6+12NH_3+Fe_2O_3+9H_2O.\end{aligned}$$

Reduction in neutral solution with a zinc-copper couple causes the evolution of nitrogen. In acid solution (dilute sulphuric) sodium amalgam causes the formation of Prussian blue.

Sodium hydroxide solution converts the salt into the nitrito derivative, $Na_4[Fe(CN)_5.NO_2]10H_2O$ (see p. 234), whilst ammonium hydroxide yields, at 0° C., the ammoniate $Na_3[Fe(CN)_5.NH_3]$, and at the ordinary temperature $Na_2(NH_4)[Fe(CN)_5.NH_3]$ (see p. 234).

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[1] Guareschi, *Atti R. Accad Sci. Torinò*, 1915, 50, 881.

[2] Reichard, *Zeitsch. anal. Chem*, 1904, 43, 222.

[3] Hofmann, *Annalen*, 1900, 312, 1.

[4] Pereirà, using potassium sulphide in metanol, obtained a violet, hygroscopic precipitate, readily oxidised in air, to which he gave the formula $Na_2Fe(CN)_5.K_4S_2.2H_2O$ (*Anal. Fis Quim.*, 1915, 13, 27, 69).

[5] Bhaduri, *Zeitsch anorg Chem*, 1913, 84, 95.

[6] Pereirà, *Anal. Fis. Quim*, 1915, 13, 166. Compare also Bhaduri, *loc. cit.*

[7] Bhaduri, *loc. cit.*

When heated to 440° C. in a vacuum, sodium nitroprusside decomposes, evolving nitric oxide and cyanogen.[1]

Sodium nitroprusside is a convenient reagent to use in preparing nitroprussides of the heavy metals, such as copper and nickel, which yield insoluble nitroprussides, and may therefore be estimated volumetrically in this manner by titration, using sodium sulphide as indicator.[2] In this connection it is well to note that solutions of sodium nitroprusside may be preserved for months unaltered if stored in the dark in a bottle of non-alkaline glass. A trace of sulphuric acid greatly enhances the stability of the solution against the effect of light and of alkali from glass.[3] Light rapidly induces decomposition.[4]

The *di-ammoniate*, $Na_2Fe(CN)_5.NO.2NH_3$, has been prepared.[5]

Ammonium nitroprusside, $(NH_4)_2[Fe(CN)_5NO]$, obtained by decomposing the barium salt with ammonium sulphate, crystallises in reddish plates, which are readily soluble in water.[6]

Barium nitroprusside, $Ba[Fe(CN)_5NO]3H_2O$, is prepared by precipitating a solution of the sodium salt with zinc sulphate and boiling the zinc salt thus obtained with a suspension of precipitated barium carbonate. The filtered solution of the barium salt is evaporated under reduced pressure, and the salt crystallised from alcohol.[6]

Cobalt nitroprusside, $Co[Fe(CN)_5NO]$, obtained by double decomposition of a soluble cobalt salt with sodium nitroprusside, is a red salt, possessing an appreciable solubility in water. It dissolves in acids, but is insoluble in potassium hydroxide or ammonia solution. This latter property enables it to be separated from the corresponding nickel salt, which readily dissolves in ammonia.[7]

Nickel nitroprusside, $Ni[Fe(CN)_5NO]$, obtained in a similar manner to the preceding salt,[8] is dark green when anhydrous, but upon exposure to moist air becomes ashen grey. It is insoluble in acids, but readily dissolves in ammonia to a brownish yellow liquid. Potassium hydroxide turns it lemon-yellow.

Potassium nitroprusside, $K_2[Fe(CN)_5NO]$, may be obtained by the interaction of a ferrous salt with the nitrite and cyanide of potash :—[9]

$$5KCN+2FeSO_4+KNO_2+H_2O \\ =K_2[Fe(CN)_5NO]+Fe(OH)_2+2K_2SO_4,$$

or by the action of potassium nitrite on ferricyanides at 100° C.[10]

A convenient method consists in decomposing the barium salt with the calculated amount of potassium sulphate, and, after filtering off the insoluble barium sulphate, evaporating at low temperature under reduced pressure. The residue is purified by recrystallisation from 95 per cent. alcohol, when it separates as pale pink, anhydrous crystals.[11]

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[1] Etard and Bémont, *Compt. rend.*, 1884, 99, 972, 1024.

[2] Zuccari, *Ann. Chim. Applicata*, 1914, 2, 287 ; 1915, 3, 277 ; *Boll. Chim. Farm.*, 1914, 53, 321.

[3] Zuccari, *loc. cit.*

[4] Eder, *Monatsh.*, 1885, 6, 495.

[5] Peters, *Zeitsch. anorg. Chem.*, 1912, 77, 137.

[6] Burrows and Turner, *Trans. Chem Soc.*, 1919, 115, 1429.

[7] Zuccari, *Ann. Chim. Applicata*, 1915, 3, 277 ; Cavalli, *Gazzetta*, 1897, 27, ii 95.

[8] Cavalli, *loc. cit.* ; Zuccari, *loc. cit.*

[9] Stadeler, *Annalen*, 1869, 151, 1.

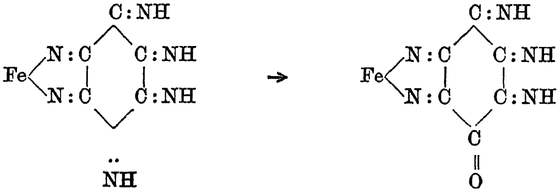
[10] Prudhomme, *Compt. rend.*, 1890, 111, 45.

[11] Burrows and Turner, *loc. cit*

Carbonyl Penta-Cyanoferrites or *Carbonyl Penta-Ferrocyanides*, $M_3[Fe(CN)_5CO]$.

Addition of ferric chloride to certain liquors produced in the manufacture of Prussian blue in a French factory by the methylamine method (see p. 213) resulted in the precipitation of a violet compound.[1] Several hundred grams of this were isolated by Muller, warmed with potassium carbonate and hydroxide successively, and the filtered solution allowed to crystallise. The product thus isolated crystallised in thin scales and rectangular prisms, and proved to be the potassium salt of an entirely new acid, namely *hydrogen carbonyl ferrocyanide*, $H_3Fe(CN)_5.CO$. Following up this discovery, Muller succeeded in preparing a series of well-defined salts.

Constitution.—The constitution to be assigned to these derivatives depends very largely upon the views accepted for the constitution of ferrocyanides in general. The carbonyl group clearly replaces a C : NH group in the ferrocyanide molecule, or, regarded from another standpoint, divalent oxygen replaces the divalent NH group without effecting any alteration in the carbon nucleus of the molecule. Adopting his cyclic formula (see p. 203) for ferrocyanic acid, Friedel[2] therefore suggests the following graphical representation of the change :—



(ferrocyanide) (carbonyl ferrocyanide).

Hydrogen carbonyl ferrocyanide, or carbonyl ferrocyanic acid, $H_3[Fe(CN)_5.CO]H_2O$, is obtained[3] by the action of hydrogen sulphide on the copper salt in solution. Upon evaporation in the dark over potassium hydroxide, the acid separates in colourless tabular crystals. It is acid to litmus, and is sufficiently powerful to decompose alkali carbonates.

The heat of combustion of carbonyl ferrocyanic acid is 809,800 calories, the products being nitrogen, carbon dioxide, water, and ferric oxide.[4] The heat of formation of the anhydrous acid is −48,600 calories[5]; the acid is thus less strongly endothermic than ferrocyanic acid (−122,000 calories).

Barium carbonyl ferrocyanide, $Ba_3[Fe(CN)_5.CO]_2 11H_2O$, is readily prepared by decomposing the copper salt with a soluble barium salt, or by neutralising the free acid with barium hydroxide. It loses 10 molecules of water at 19° C. *in vacuo*, and becomes anhydrous at 130° C. The heats of solution are :—[6]

$$[Ba_3[Fe(CN)_5CO]_2]+Aq.=Ba_3[Fe(CN)_5CO]_2Aq.+16{,}900 \text{ calories},$$
$$[Ba_3[Fe(CN)_5CO]_2 11H_2O]+Aq.=Ba_3[Fe(CN)_5CO]_2Aq.-\ 6{,}900 \text{ calories},$$

---

[1] J. A. Muller, *Compt. rend.*, 1887, 104, 994.

[2] Friedel, *ibid.*, 1887, 104, 995.

[3] Muller, *Ann. Chim. Phys.*, 1889, (6), 17, 93.

[4] Muller, *Compt rend.*, 1906, 142, 1516.

[5] Muller, *loc. cit.*

[6] Muller, *Bull. Soc. chim.*, 1914, (4), 15, 491.

whence the heat of hydration of the anhydrous salt is 23,800 calories at 17·5° C.

Copper carbonyl ferrocyanide, $Cu_3[Fe(CN)_5.CO]_2$, is obtained[1] by double decomposition in aqueous solution of copper sulphate and potassium carbonyl ferrocyanide. It forms as a yellowish green gelatinous precipitate, which is insoluble in dilute nitric or sulphuric acid, and which becomes an anhydrous dark brown powder at 110° C.

Ferric carbonyl ferrocyanide, $Fe[Fe(CN)_5CO]$, is prepared by double decomposition of an excess of ferric chloride solution and the potassium salt.[1] It resembles indigo in appearance, and contains about 4 per cent. of combined water.[2] Dried at a moderate temperature, it yields a friable resinous mass with a brilliant conchoidal fracture.[1]

Potassium carbonyl ferrocyanide, $2K_3[Fe(CN)_5CO].7H_2O$.—The discovery and early preparation of this salt have already been described (see p. 232). It may be prepared in the laboratory by passing moist carbon monoxide over potassium ferrocyanide at 130° C. Thus :—[3]

$$K_4Fe(CN)_6+CO+2H_2O=K_3Fe(CN)_5.CO+NH_3+H.COOK.$$

It crystallises in thin scales and rectangular prisms. 100 parts of water at 18° C. dissolve 148 parts of the salt.[4]

The salt is more stable than potassium ferrocyanide towards oxidising media, being unaffected by potassium persulphate, and but slightly oxidised by permanganate or ozone in the absence of sulphuric acid.[5] The salt becomes anhydrous at 120° C. The heats of solution are as follow :—[6]

$$[K_3Fe(CN)_5CO]+Aq.= K_3Fe(CN)_5CO.Aq.- 5{,}200 \text{ calories},$$
$$[2K_3(Fe(CN)_5CO)7H_2O]+Aq.=2K_3Fe(CN)_5CO.Aq.-21{,}800 \text{ calories},$$

whence the heat of hydration of the anhydrous salt is 5700 calories at 18° C.

Chlorine appears to oxidise the salt to an unstable carbonyl ferricyanide. Prolonged exposure to chlorine results in the formation of potassium ferricyanide.[7]

Silver carbonyl ferrocyanide, $Ag_3[Fe(CN)_5CO]$, is obtained as a white curdy precipitate on addition of the potassium salt to silver nitrate solution in the presence of acetic acid.[4] It rapidly darkens even when protected from the light. Insoluble in boiling acetic acid, it is slightly soluble in dilute mineral acids evolving hydrogen cyanide. Potassium hydroxide liberates silver oxide, potassium carbonyl ferrocyanide being simultaneously produced.

Sodium carbonyl ferrocyanide, $Na_3[Fe(CN)_5CO].7H_2O$, is obtained in a similar manner to the potassium salt. It crystallises in pale yellow monoclinic needles, which become anhydrous at 110° C.

The heats of solution are as follow :—[6]

$$[Na_3Fe(CN)_5.CO]+Aq.=Na_3Fe(CN)_5CO.Aq.+4800 \text{ calories},$$
$$[Na_3Fe(CN)_5CO.7H_2O]+Aq.=Na_3Fe(CN)_5CO.Aq.-7500 \text{ calories},$$

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[1] Muller, *Ann. Chim. Phys.*, 1889, (6), 17, 93.

[2] Stoecker, *Chem. Zentr.*, 1904, I., 1406, from *J. Gasbeleuchtung*, 1904, 47, 338.

[3] See also Lecocq, *Bull. Soc. chim. Belg.*, 1911, 25, 72; F. Smith, *Gas World*, 1903, 39, 55; Stoecker, *J. Gasbeleuchtung*, 1904, p. 338.

[4] Muller, *Compt. rend.*, 1887, 104, 994.

[5] Muller, *Bull. Soc. chim.*, 1903, (3), 29, 1158.

[6] Muller, *ibid.*, 1914, (4), 15, 491.

[7] Muller, *ibid*, 1903, (3), 29, 1161.

whence the heat of hydration of the anhydrous salt is 12,300 calories at 15·9° C.

Strontium carbonyl ferrocyanide, $Sr_3[Fe(CN)_5CO]_2.4H_2O$, may be prepared in a similar manner to the barium salt. It is a yellow hygroscopic powder, which becomes anhydrous at 200° C. The heats of solution are as follow:—[1]

$$[Sr_3(Fe(CN)_5CO)_2]+Aq.=Sr_3(Fe(CN)_5CO)_2.Aq.+39{,}900 \text{ calories},$$
$$[Sr_3(Fe(CN)_5CO)_2.4H_2O)]+Aq.=Sr_3(Fe(CN)_5CO)_2.Aq.+32{,}400 \text{ calories},$$

whence the heat of hydration of the anhydrous salt at 13·3° C. is 7500 calories.

Uranyl carbonyl ferrocyanide, $(UO_2)_3[Fe(CN)_5CO]_25H_2O$, is obtained[2] as an orange-yellow gelatinous precipitate on adding the potassium salt to uranium nitrate. At 70° C. it becomes red, but acquires the yellow colour again on powdering.

Potassium calcium carbonyl ferrocyanide, $CaK.Fe(CN)_5.CO.5H_2O$, has been obtained as straw-coloured crystals.[3]

Nitrito Penta-Cyanoferrites or *Nitrito Penta-Ferrocyanides*, $M_4[Fe(CN)_5.NO_2]$.

When aqueous sodium nitroprusside solution is treated with sodium hydroxide, the quaternary nitrito **sodium salt,** $Na_4[Fe(CN)_5NO_2]10H_2O$, is obtained.[4] It crystallises in yellowish red monosymmetric tablets, and is very soluble in water, yielding a dark red coloration with ammonium sulphide.

When sodium hydroxide is allowed to react on a solution of sodium nitroprusside in methyl alcohol, the **monohydrated** [5] salt is obtained. Thus:—

$$Na_2Fe(CN)_5.NO.2H_2O+2NaOH=Na_4Fe(CN)_5.NO_2.H_2O+2H_2O.$$

With potassium hydroxide the double **sodium potassium monohydrated** salt, $Na_2K_2[Fe(CN)_5NO_2].H_2O$, is obtained.

The **silver salt,** $Ag_4[Fe(CN)_5.NO_2]2H_2O$, and alkyl nitroso derivatives have also been obtained,[4] and numerous other complex salts are described.[6]

Ammino Penta-Cyanoferrites or *Ammonio Penta-Ferrocyanides*, $M_3[Fe(CN)_5.NH_3]$.

Sodium ammonio ferrocyanide, $Na_3Fe(CN)_5.NH_3$, is obtained when ammonium hydroxide is allowed to act at 0° C. on a solution of sodium nitroprusside in methyl alcohol.[5]

If the reaction is allowed to proceed at the ordinary temperature, the **sodium ammonium** salt, $Na_2(NH_4)[Fe(CN)_5.NH_3]$, is obtained. Thus:—

$$Na_2Fe(CN)_5.NO+3NH_3+H_2O=Na_2(NH_4)Fe(CN)_5.NH_3+NH_4NO_2.$$

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[1] Muller, *Bull. Soc. chim.*, 1914, (4), 15, 491.
[2] Muller, *Ann. Chim. Phys.*, 1889, (6), 17, 93.
[3] Lecocq, *Bull. Soc. chim. Belg.*, 1911, 25, 72.
[4] Hofmann, *Annalen*, 1900, 312, 1; *Zeitsch. anorg. Chem.*, 1896, 11, 278.
[5] Pereirà, *Anal. Fis. Quim*, 1915, 13, 144.
[6] Hofmann, *loc. cit.*; Pereirà, *Anal. Fis. Quim*, 1915, 13, 144, 166.

Aquo Penta-Cyanoferrites or *Aquo Penta-Ferrocyanides*, $M_3[Fe(CN)_5.H_2O]$.

Potassium aquo ferrocyanide, $K_3Fe(CN)_5.H_2O$, is obtained by reducing potassium aquo penta-ferricyanide, $K_2Fe(CN)_5.H_2O$, with alkaline hydroxylamine chloride, with alkali sulphide, or with formaldehyde and acetone in the presence of alkali.[1]

Sodium aquo ferrocyanide,[2] $Na_3Fe(CN)_5.H_2O$, results when sodium nitroprusside reacts with hydroxylamine, etc., or when the salt is oxidised by potassium hypobromite or hydrogen peroxide.

Aquo Penta-Cyanoferrates or *Aquo Penta-Ferricyanides*, $M_2[Fe(CN)_5.H_2O]$.

Potassium aquo ferricyanide, $K_2Fe(CN)_5.H_2O$, is obtained by the prolonged action of chlorine upon potassium ferrocyanide solution. At first potassium ferricyanide is formed, which undergoes further decomposition, the chlorine abstracting one (CN) group, water taking its place. Thus :—[1]

$$2K_4Fe(CN)_6+Cl_2=2K_3Fe(CN)_6+2KCl,$$

followed by

$$K_3Fe(CN)_6+Cl_2=K_3Fe(CN)_5Cl+CN.Cl.$$
$$K_3Fe(CN)_5Cl+H_2O=K_2Fe(CN)_5.H_2O+KCl.$$

The same salt is produced by the action of a mixed solution of sodium chlorate and hydrochloric acid upon potassium ferrocyanide.

The solution is intensely violet, but the salt is readily precipitated by addition of alcohol. Reduction with alkaline hydroxylamine chloride solution yields **potassium aquo penta-ferrocyanide,** $K_3Fe(CN)_5.H_2O$, whilst with alkaline potassium sulphite the **sulphito penta-ferrocyanide,** $K_5Fe(CN)_5.SO_3$, is obtained.

In earlier literature this salt is referred to as **potassium perferricyanide,** the formula, $K_2Fe(CN)_6$, being ascribed to it.[3]

Sodium aquo penta-ferricyanide, $Na_2Fe(CN)_5.H_2O$, is readily obtained[2] by the action of nitrous acid or bromine water upon the corresponding ferrite, $Na_3Fe(CN)_5.H_2O$.

Sulphito Penta-Cyanoferrites or *Sulphito Penta-Ferrocyanides*, $M_5[Fe(CN)_5.SO_3]$.

Potassium sulphito ferrocyanide, $K_5Fe(CN)_5.SO_3$, is obtained by reduction of potassium aquo ferricyanide, $K_2Fe(CN)_5.H_2O$, with excess of potassium sulphite in potassium hydroxide.[1] It crystallises from aqueous alcohol in small yellow prisms.

Ferrous thiocyanate, $Fe(CNS)_2.3H_2O$, is obtained by dissolving iron in an aqueous solution of the free acid. It crystallises in monoclinic prisms, and is readily oxidised by exposure to air.[4]

Ferric thiocyanate, $Fe(CNS)_3.6H_2O$, may be prepared by dissolving ferric hydroxide in aqueous thiocyanic acid, as also by metathetical decomposition of a ferrous salt and potassium thiocyanate.[1] It crystallises in cubes, deep red in colour, which slowly dissolve in water, yielding an intensely red solution. The formation of this red colour constitutes a delicate method of detecting the presence of traces of ferric iron (see p. 242).

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[1] Cambi, *Gazzetta*, 1911, 41, i. 157.

[2] Hofmann, *Annalen*, 1900, 312, 1; *Zeitsch. anorg. Chem.*, 1896, 11, 278.

[3] See Bong, *J. Chem. Soc.*, 1876, 29, 907; Dammer, *Handbuch der anorg. Chem.*, 3, 378; Moissan, *Traité de Chimie Minérale*, 1905, 4, 417.

[4] Claus, *Annalen*, 1856, 99, 49.

In very dilute solution the intensity of colour produced is not quite proportional to the amount of iron present—indeed, the more concentrated solution becomes decolorised on dilution, as also by addition of oxalates, tartrates, etc. The decoloration on dilution is usually explained on the assumption that the water hydrolyses the red undissociated salt into yellow colloidal ferric hydroxide and free thiocyanic acid :—

$$2Fe(CNS)_3+3H_2O \rightleftharpoons 2Fe(OH)_3+6HCNS.$$

The effect of the organic acids is attributed to their union with the iron ions of the dissociated ferric thiocyanate, thereby displacing the equilibrium

$$Fe^{\cdot\cdot\cdot}+3CNS' \rightleftharpoons Fe(CNS)_3$$

in the direction of right to left—that is, reducing the concentration of the undissociated coloured salt.[2]

A modification of this view lies in the theory that the coloured compound is the undissociated double salt[3] $Fe(CNS)_3.9KCNS$, and not simply the simple undissociated molecule $Fe(CNS)_3$. This is apparently supported by the observation that a maximum coloration is produced, save in very dilute solutions, with twelve molecules of potassium thiocyanate to one of ferric chloride. Thus :—

$$FeCl_3+12KCNS=Fe(CNS)_3.9KCNS+3KCl.$$

In dilute solution even more potassium thiocyanate is required, no doubt on account of dissociation, as explained above.

Tarugi,[4] on the other hand, attributes the colour to the formation of ferrous peroxy thiocyanic acid, $FeH(CNOS)_3$, according to the reversible reaction :—

$$12FeCl_3+6KCNS+6H_2O=2FeH(CNOS)_3+6KCl+10FeCl_2+10HCl.$$

The free acid, $H_3(CNOS)_3$, as well as its acid salts, have a red colour. The decolorising influence of oxalates, etc., is attributable to their converting the acid or its acid salts into colourless normal salts.

This theory, however, has not met with a wide acceptance.

Ferric thiocyanate solution gradually loses its intensity of colour when kept, a reduction of the iron from the ferric to the ferrous condition being observable.[5]

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[1] Claus, *loc. cit.*

[2] Bongiovanni, *Boll. Chim. Farm.*, 1911, 50, 694 ; *Gazzetta*, 1908, 38, ii. 5, 299 ; 1907, 37, i 472 ; Rosenheim and Cohn, *Zeitsch. anorg. Chem.*, 1901, 27, 280 ; Magnanini, *Zeitsch. physikal. Chem.*, 1891, 8, 1. See also Ley, *Zeitsch. physikal. Chem.*, 1899, 30, 193 ; Gladstone, *Chem. News*, 1893, 67, 1 ; Vernon, *ibid*, 1893, 67, 66 ; 1892, 66, 177, 191, 202, 214 ; Schultze, *Chem. Zeit.*, 1893, 17, 2 ; Riban, *Bull. Soc. chim.*, 1892, (3), 6, 916 , Tatlock, *J. Soc. Chem. Ind.*, 1887, 6, 276, 352 ; Shilton, *Chem. News*, 1884, 50, 234 H. Werner, *Zeitsch. anal. Chem.*, 1883, 22, 44 ; Dupré, *Chem. News*, 1875, 32, 15 ; Pelouse, *Ann. Chim. Phys.*, 1830, (1), 44, 214.

[3] Kruss and Moraht, *Ber.*, 1889, 22, 2054, 2061 ; *Zeitsch anorg. Chem.*, 1892, 1, 399.

[4] Tarugi, *Gazzetta*, 1904, 34, ii 326.

[5] Stokes and Cain, *J. Amer. Chem. Soc.*, 1907, 29, 412.

The exact course of this reduction is uncertain, but the carbon of the acid radicle is oxidised to carbon dioxide and the sulphur to sulphuric acid. The equation might therefore be written as :—

$$8Fe(CNS)_3+6H_2O=8Fe(CNS)_2+7HCNS+CO_2+H_2SO_4+NH_3.$$

This equation, however, postulates the production of more ammonia than is actually found, by about 50 per cent. The nitrogen therefore appears only partly as ammonia, and no definite information has been obtained as to the product or products into which the remaining portion of the element is converted.[1]

The beautiful colour of the amethyst is thought to be due to ferric thiocyanate, and this is supported by the fact that, on heating, the colour of the stone becomes yellow, its absorption spectrum now closely resembling that of ferric oxide or a ferric compound. The calcined stone closely resembles the natural *citrine*, which latter may have been obtained in an analogous manner from the amethyst through natural agencies.[2]

$Fe(CNS)_3.9KCNS.4H_2O$ is obtained[3] by dissolving freshly precipitated ferric hydroxide in thiocyanic acid, adding the requisite quantity of potassium thiocyanate, and concentrating over sulphuric acid. The salt yields dark red rhombic prisms, with a greenish reflex. It is fairly stable, but slowly deliquesces upon exposure to moist air. Its solution in pure water is stable, but traces of electrolytes induce decomposition. The corresponding ammonium, sodium, lithium, and cæsium salts have been prepared.

The anhydrous salt, $Fe(CNS)_3.3KCNS$, has been obtained, and is described below.

Ferro Hexathiocyanates or *Hexathiocyanoferrites*, $M_4Fe(CNS)_6.xH_2O$.

Sodium ferrothiocyanate, $Na_4Fe(CNS)_6.12H_2O$, is prepared by dissolving ferrous carbonate in thiocyanic acid and adding sodium thiocyanate.[4] The salt crystallises in colourless tablets, which are soluble in water, as also in alcohol, yielding bright rose-coloured solutions.

Ferri Hexathiocyanates or *Hexathiocyanoferrates*, $M_3Fe(CNS)_6.xH_2O$.

Sodium ferrithiocyanate, $Na_3Fe(CNS)_6.12H_2O$, is formed by allowing a mixed solution of sodium and ferric thiocyanates to crystallise over sulphuric acid.[4] It crystallises in dark green hexagonal or rhombic crystals. These dissolve in water to a deep red solution, and are partially decomposed. In alcohol a violet solution is obtained, from which the salt may be recrystallised unchanged.

The **potassium salt,** $K_3Fe(CNS)_6$, is obtained by dissolving freshly precipitated ferric hydroxide in thiocyanic acid and adding the requisite quantity of potassium thiocyanate.[5] The solution is concentrated over sulphuric acid, when the salt separates out in small hexagonal crystals. The aqueous solution possesses an intensely red colour.

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[1] Philip and Bramley, *Trans. Chem. Soc.*, 1913, 103, 795.

[2] Nabl, *Monatsh.*, 1899, 20, 272.

[3] Krüss and Moraht, *Ber.*, 1889, 22, 2061; *Annalen*, 1890, 260, 206. See also Wells, *Amer. Chem. J.*, 1902, 28, 245.

[4] Rosenheim and Cohn, *Zeitsch. anorg. Chem.*, 1901, 27, 280.

[5] Krüss and Moraht, *Ber.*, 1889, 22, 2061.

IRON AND SILICON.

When heated together, iron absorbs silicon, even at temperatures considerably below 950° C.,[1] a silicide or silicides being produced according to circumstances.

Iron silicides are, in general, hard and brittle, thus forming good abrasives. They are white or grey in colour, and may take a good polish. Unattacked by air and water, they are but slowly decomposed by acids, except hydrofluoric, which readily dissolves them. In general their density falls with rise of silicon content.

The freezing-point curves of alloys of iron and silicon[2] indicate the existence of two silicides of iron, namely, the *subsilicide*, Fe_2Si, and the *monosilicide*, FeSi; and Jouve regards these as the only two definite silicides that exist.[3] A study of the density curves of solutions of silicon in iron[4] suggests the possible existence of Fe_2Si, FeSi, $FeSi_2$, Fe_2Si_3, Fe_3Si_2, and Fe_3Si_4. Of these the *disilicide*,[5] and the *triferro disilicide*, Fe_3Si_2,[6] are claimed as having been isolated, but the evidence is not conclusive. A *triferro silicide*, Fe_3Si, is described by Naske.[7]

Diferro silicide or **Iron subsilicide**, Fe_2Si, is the form in which silicon occurs in cast iron, and may be obtained[8] in several ways: namely, (1) by heating iron in a porcelain dish brasqued with silicon; (2) by heating iron with 10 per cent. of silicon in an electric furnace; and (3) by similarly heating ferric oxide with excess of silicon.

It may also be prepared by heating iron in silicon tetrachloride vapour at 1100° C. :—[9]

$$SiCl_4+4Fe=Fe_2Si+2FeCl_2,$$

or by heating iron and copper silicide containing 10 per cent. of silicon.[10]

Diferro silicide, as obtained by these methods, occurs as small prismatic crystals, possessed of metallic lustre, magnetic, and of density 7·00 at 22° C. Hydrogen fluoride attacks it readily, and aqua regia decomposes it, yielding silica and ferric chloride. Hot potassium hydroxide is without action on it. It is decomposed by chlorine with incandescence.

Iron silicide or **Iron monosilicide**, FeSi, is prepared by heating a mixture of copper silicide and iron filings in an electric furnace. The resulting product is treated with 50 per cent. nitric acid to decompose any copper silicide, and washed. Obtained in this way, iron silicide occurs as tetrahedral crystals, with a brilliant metallic lustre; they are extremely hard, and have a density of 6·17 at 15° C. Fluorine attacks them at ordinary temperatures, whilst chlorine and bromine decompose them at red heat. Molten alkali hydroxides attack the silicide, as also do fused mixtures of the alkali nitrates and carbonates.[11]

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[1] Lebeau, *Bull Soc. chim.*, 1902, (3), 27, 44.

[2] Guertler and Tammann, *Zeitsch. anorg. Chem.*, 1905, 47, 163

[3] Jouve, *Bull. Soc. chim.*, 1901, (3), 25, 290; *Compt. rend.*, 1902, 134, 1577.

[4] Frilley, *Revue Metallurgie*, 1911, 8, 457.

[5] Chalmot, *J. Amer. Chem. Soc*, 1895, 17, 923; 1899, 21, 59; Lebeau, *Compt. rend.*, 1901, 132, 681.

[6] Chalmot, *loc. cit.*

[7] Naske, *Chem. Zeit.*, 1903, 27, 481.

[8] Moissan, *Compt rend.*, 1895, 121, 621.

[9] Vigouroux, *ibid*, 1905, 141, 828.

[10] Lebeau, *ibid.*, 1900, 131, 583.

[11] Lebeau, *ibid.*, 1899, 128, 933; Guertler and Tammann, *loc. cit.*; Vanzetti, *Gazzetta*, 1906, 36, i 498.

Iron disilicide, $FeSi_2$.—A substance containing iron and silicon in the proportions necessary to the formula $FeSi_2$ is produced by heating iron in excess of silicon in an electric furnace. It occurs as small lustrous crystals.[1]

Ferric silicide, triferro disilicide, Fe_3Si_2, is obtained by heating a mixture of iron filings, sand, and charcoal in an electric furnace. It is white, crystalline, and of density 6·36; only slightly magnetic. It is a good conductor of electricity. Cold aqua regia slowly attacks it; fusion with potassium nitrate and sodium carbonate rapidly decomposes it. Hydrofluoric acid also breaks it up.[2]

Ferrous orthosilicate, iron olivine or **Fayalite,** Fe_2SiO_4, occurs as tabular rhombs in iron slags, of which it is one of the commonest constituents. Its name is derived from Fayal Island (Azores), where it was first found, although probably even that specimen was originally a lump of slag from a ship's ballast. Its crystal elements are:—[3]

$$a : b : c = 0{\cdot}4632 : 1 : 0{\cdot}5835.$$

It is the most fusible silicate present in slag, and melts at about 1260° C.[4] When heated in hydrogen, reduction begins at 225° C.

Ferrous magnesium orthosilicate, $(Fe,Mg)SiO_4$ or $Fe_2SiO_4 + xMg_2SiO_4$, where x ranges from 3 to 12, occurs as green rhombic crystals, usually small in size. It is present in slag, being the silicate of highest melting-point, namely, about 1400° C. Natural olivines usually melt between 1363° and 1378° C.[5]

The refractive index of olivine progressively increases with the iron content, and may be used as a criterion of the chemical composition of rock sections.[6]

Olivine readily decomposes upon exposure, yielding *serpentine*, $Mg_3Si_2O_7.2H_2O$.

Ferrous metasilicate, $FeSiO_3$, has been prepared by fusing the calculated quantities of ferric oxide and silica at 1600° C. Density, 3·44. It melts at 1500°–1550° C.[7]

The heat of formation of ferrous metasilicate is:—

$$[FeCO_3] + [SiO_2] = [FeSiO_3] + (CO_2) - 7600 \text{ calories.}^8$$
$$[FeO] + [SiO_2] = [FeSiO_3] + 5000 \text{ calories}^{\,8} \text{ (5905 calories}^{\,9}\text{).}$$

Double **metasilicates of magnesium and iron** occur as the minerals *hypersthene* and *anthophyllite* $(Mg,Fe)SiO_3$. A **sodium ferrous metasilicate,** $NaFe(SiO_3)_2$, occurs as dark brown or green prisms in quartz under the name of *acmite* or *ægirite*, and a crystalline substance of similar composition has been prepared by Weyberg[10] by fusing silicic acid, ferric hydroxide, and sodium carbonate with excess of sodium chloride. The potassium analogue $KFe(SiO_3)_2$ has been prepared,[1] but does not apparently occur in nature.

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[1] Lebeau, *Compt. rend.*, 1901, 132, 681; de Chalmot, *Amer. Chem. J.*, 1897, 19, 118; also de Chalmot, *J. Amer. Chem. Soc.*, 1895, 17, 923.

[2] de Chalmot, *loc cit*

[3] G. O. Smith, *Johns Hopkins Univ. Circulars*, 1894, 13, 82.

[4] Sélivanov, *Rev. Soc. Russe Métall.*, 1915, 11, 328.

[5] Cusack, *Proc. Roy. Irish Acad.*, 1897, (3), 4, 399.

[6] Backlund, *Abstr. Chem. Soc.*, 1911, ii. 616, from *Trav. Musée Géol. Pierre le Grand Acad. Sci. Petrograd*, 1909, 3, 77.

[7] G. Stein, *Zeitsch. anorg. Chem.*, 1907, 55, 159.

[8] Le Chatelier, *Compt. rend.*, 1895, 120, 623.

[9] Wologdine, *ibid.*, 1913, 157, 121.

[10] Weyberg, *Centr. Min.*, 1905, p. 717.

Crystals of **ferrous manganese metasilicate** $(Fe, Mn)SiO_3$, or *iron rhodonite*, have been obtained from Bessemer slags. They belong to the triclinic system, and closely resemble crystals of the mineral.[2]

Ferric silicate.—Several silicates containing ferric iron are known in a natural state, chief among which are *Anthosiderite*, $2Fe_2O_3.9SiO_2.2H_2O$; *Cronstedtite*, $3FeO.Fe_2O_3.2SiO_2.3H_2O$; *Hisingerite*, $4Fe_2O_3.9SiO_2.18H_2O$; and *Nontronite*, $Fe_2O_3.3SiO_2.5H_2O$. A sodium ferric metasilicate occurs as *Crocidolite*, $2NaFe^{\cdots}(SiO_3)_2.Fe\ SiO_3.Na_2SiO_3$.[3]

Ferrous fluosilicate, $FeSiF_6.6H_2O$, has been prepared. It is isomorphous with the corresponding salts of cobalt and nickel.[4]

IRON AND BORON.

Iron sub-boride or **diferro boride,** Fe_2B, is obtained by heating reduced iron and boron in a porcelain tube in an atmosphere of hydrogen.[5] It occurs as steel-grey prisms, of density 7·37 at 18° C., and is attacked by dry air at dull red heat only, whilst moist air readily attacks it at ordinary temperatures. It dissolves in hot aqueous solutions of the mineral acids.

Iron monoboride, FeB, is readily formed by heating iron in a stream of vaporised boron chloride. It also results when iron and boron are heated together in the electric furnace.[6] Obtained in this way iron boride forms brilliant yellow-grey crystals, of density 7·15 at 18° C. It does not alter in dry air or oxygen, but moist air renders it ochreous. Chlorine and bromine attack it at red heat and, when heated in oxygen, it burns brilliantly.

Bromine attacks it at red heat with incandescence; chlorine is less vigorous in its action, whilst iodine and hydrogen iodide have no action, even at 1100° C. The chlorate and nitrate of potassium do not affect it at their melting-points, but at higher temperatures decompose it with incandescence. Fused alkali hydroxides and carbonates decompose it rapidly. Concentrated sulphuric acid is without action in the cold, but with the boiling acid ferrous sulphate is produced. Dilute nitric acid dissolves it when hot, and the concentrated acid acts vigorously. Dilute hydrochloric acid is without action, and the hot concentrated acid acts only slowly.

Iron diboride, FeB_2, has been prepared in a similar manner to the sub-boride, and represents the maximum limit of combination of iron with boron. Its density is 5; it is slightly yellow in colour, hard, and friable, being readily oxidised by moist air.[7]

Other complexes, such as Fe_5B_6, Fe_3B_4, Fe_2B_3, have been prepared,[8] but are probably not all separate chemical entities.

Ferrous chlorborate, $FeCl_2.6FeO.8B_2O_3$ or $FeCl_2.6FeB_2O_4.2B_2O_3$, is obtained by passing the vapour of ferric chloride over an intimate mixture of iron wire and calcium borate heated to 330° C. The ferric chloride is reduced to ferrous, which immediately reacts with the calcium borate. The mass, on cooling, is extracted with water, any unattacked iron being removed magnetically. Ferrous chlorborate yields greyish, transparent cubes. It is slowly attacked by nitric acid; fused alkalies rapidly decompose it.[1]

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[1] Niggli, *Zeitsch. anorg. Chem.*, 1913, 84, 31.

[2] Tacconi, *Zeitsch. Kryst. Min.*, 1914, 54, 392.

[3] See Tschirwinsky, *Centr. Min.*, 1907, p. 435.

[4] Dufet, *Bull. Soc. Min.*, 1901, 24, 118.

[5] du Jassonneix, *Compt. rend*, 1907, 145, 121.

[6] Moissan, *ibid.*, 1895, 120, 173.

[7] du Jassonneix, *loc. cit.*

[8] J. Hoffmann, *Chem. Zeit.*, 1910, 34, 1349.

Ferrous bromborate, $FeBr_2.6FeO.8B_2O_3$ or $FeBr_2.6FeB_2O_4.2B_2O_3$, is prepared by passing bromine vapour over an intimate mixture of iron (in excess) and boro-natro-calcite, $Na_2B_4O_7.Ca_2B_6O_{11}.16H_2O$. It yields greyish white cubes and octahedra.[2]

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[1] Rousseau and Allaire, *Compt. rend.*, 1893, 116, 1195.
[2] Rousseau and Allaire, *ibid.*, 1893, 116, 1445.

CHAPTER X.

DETECTION AND ESTIMATION OF IRON.

IRON readily lends itself both to detection and estimation.[1] In this chapter the more important methods of detecting and estimating iron in its compounds are discussed. For methods of analysing steels and other alloys the reader is referred to Part III. of this volume.

Detection of Iron.

Dry Tests.—Iron salts, when moistened with hydrochloric acid and heated on a loop of platinum wire in a Bunsen flame, emit a shower of sparks. When heated on charcoal with sodium carbonate in the blow-pipe flame, the compound is converted into a dark-coloured residue. If potassium cyanide is added to the sodium carbonate and iron compound, and the whole heated on charcoal in the inner flame of the blow-pipe, metallic iron is obtained as a grey, magnetic powder.

If a little of the iron compound is heated with borax on platinum wire in the outer blow-pipe flame, on cooling, a yellow transparent bead is obtained, which becomes bottle-green upon heating in the inner or reducing flame of the blow-pipe, in consequence of reduction to the ferrous condition.[2]

Wet Tests.—The presence of iron in solution may readily be detected by a considerable number of sensitive reactions. Thus *ferrous iron* gives a green precipitate of ferrous hydroxide upon addition of excess of ammonium hydroxide. With potassium ferricyanide and a trace of acid, a deep blue precipitate—Turnbull's blue—is obtained. With potassium ferrocyanide a white precipitate is obtained in the entire absence of any ferric salt. Ferric iron, on the other hand, is usually characterised by its deep yellow or brown colour. Addition of concentrated hydrochloric acid deepens the colour. With excess of ammonium hydroxide, brown flocculent ferric hydroxide is precipitated. With potassium ferrocyanide solution, a deep blue colour is obtained in acid solution, whilst with potassium ferricyanide there is no action. Potassium thiocyanate gives in acid solution a deep red colour, which is not destroyed by heat. Salicylic acid gives a violet colour, provided no free mineral acid is present.

It is usual, in systematic qualitative analysis, to remove silver, lead, and mercury from the solution to be analysed, by precipitation as chlorides on addition of hydrochloric acid. The metals capable of precipitation as sulphides with hydrogen sulphide in acid solution are next removed, and the filtrate, boiled to expel any dissolved hydrogen sulphide, is treated with ammonium chloride and excess of ammonium hydroxide. In the absence of phosphates, the precipitate may contain the hydroxides of iron, aluminium, and chromium. The presence of iron is evidenced by the brown colour, if the metal is in the ferric condition. In any case, the precipitate is treated with sodium peroxide and water, whereby any aluminium is dissolved as sodium aluminate, any chromium as sodium chromate, the iron remaining as insoluble ferric hydroxide. If desired, a confirmatory test may be applied. For example, the precipitate may be dissolved in hydrochloric acid and potassium ferrocyanide added. The characteristic blue colour indicates iron.

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[1] As this is not a text-book of analysis, the various methods of qualitative and quantitative analysis are not discussed in experimental detail References, however, are appended, so that the student desirous of attempting any of the methods may know where to seek for details.

[2] The green colour of ordinary bottle glass is due to the presence of ferrous iron

If a phosphate was present, the precipitate obtained on addition of ammonium chloride and hydroxide may contain phosphates of such metals as calcium, etc., which are normally precipitated in later groups in systematic analysis. The precipitate is therefore dissolved in dilute hydrochloric acid, and the solution nearly neutralised with sodium carbonate. Sodium acetate is now added, and the whole boiled. The precipitate contains the phosphates of aluminium, chromium, and iron, and is treated, as already indicated, with sodium peroxide and water.

Estimation of Iron.

Gravimetric Methods.—If the iron is already in solution, it is first oxidised to the ferric condition and precipitated as ferric hydroxide by addition of ammonia to the boiling solution. The precipitate is well washed, dried in an oven, ignited in a crucible, and weighed as anhydrous ferric oxide, Fe_2O_3.

If the iron is not already in solution, the solid to be analysed is digested with hydrochloric acid, or aqua regia, or is brought into a soluble condition by fusion with potassium carbonate or hydrogen sulphate. Silica is filtered off, any copper, lead, etc., precipitated with hydrogen sulphide, and the iron oxidised to the ferric condition with nitric acid. Addition of ammonium chloride and hydroxide precipitates the iron, which is filtered off and weighed as Fe_2O_3. If aluminium and chromium are likely to be present, these are first removed, as in qualitative analysis, by adding sodium peroxide to the precipitated hydroxide, prior to ignition. After washing away any sodium aluminate and chromate, the pure ferric hydroxide is ignited, as already indicated.

If manganese was originally present, some of it will precipitate out with the iron, and be weighed as Mn_3O_4 along with the Fe_2O_3. If it is desired to remove the manganese, the hydroxides, prior to ignition, are dissolved in a minimum quantity of hydrochloric acid, and ammonium carbonate added, under constant agitation, until the precipitate first formed just re-dissolves, leaving the liquid slightly opalescent. Acetic acid and ammonium acetate are now added, the solution boiled for a few moments, filtered hot, and the precipitate, consisting of basic ferric acetate, washed twice with boiling water. The filtrate will be colourless if the operations have been successfully carried out, and contains the bulk of the manganese as acetate. A small quantity of manganese, however, will still be entangled in the precipitate, which latter is therefore re-dissolved in acid and precipitated a second time in a precisely similar manner, washed, and ignited to Fe_2O_3.

"*Cupferron*" or amino nitroso phenyl hydroxylamine[1] may be used for the direct precipitation of iron in acid solution, in the presence of aluminium, chromium, cobalt, nickel, and zinc. Copper is precipitated along with the iron, but is easily removed afterwards by treatment with ammonia, in which it is soluble.

The precipitating solution is made by dissolving 6 grams of the amino derivative in 100 grams of water, and may be kept for a week if protected from the light. The solution containing the iron is acidified with concentrated hydrochloric acid and the reagent added until no further precipitation of iron takes place. The precipitate, which is reddish brown in colour, is allowed to settle, washed with twice-normal hydrochloric acid, then with water, ammonia, and water in succession, and finally ignited to Fe_2O_3.

a-nitroso β-naphthol is a convenient reagent for precipitating iron,[2] particularly if aluminium is present, since this latter metal is not precipitated by the naphthol.[3] The naphthol solution should be made up fresh once a month, as it is rather unstable. For this purpose 4 grams of the solid are dissolved in 150 c.c. of cold glacial acetic acid, and the solution subsequently diluted with an equal quantity of water. The iron should be present in solution as chloride or sulphate, and may be in any state of oxidation—not necessarily all as ferric or all as ferrous metal. The slightly acid solution is mixed with an equal volume of 50 per cent. acetic acid, and an excess of the β-naphthol added. After 6 to 8 hours the solution is filtered, the precipitate,[4] washed first with cold 50 per cent. acetic acid and then with water, dried, and ignited, being weighed as Fe_2O_3.

Volumetric methods are largely employed for the rapid estimation of iron in solution. As a rule, the iron must be present in the ferrous condition, and any ferric iron must first be reduced, the reagents employed varying somewhat with the method of titration. If both the ferrous and ferric contents of a solution are required, the ferrous iron is first determined by titration, then the whole is reduced, and the total iron determined. Subtraction gives the amount of ferric iron originally present.

Bichromate Method.[5]—The iron is reduced with stannous chloride or sodium sulphite,[6] and the solution acidified, preferably with sulphuric acid.[7] Potassium bichromate solution is now added from a burette until a spot of the mixture removed on the tip of a glass rod fails to give a blue coloration when mixed with a drop of freshly prepared potassium ferricyanide solution on a white, glazed earthenware tile. The whole of the iron has then been oxidised to the ferric state in accordance with the equation:—

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[1] Baudisch, *Chem. Zeit.*, 1905, 33, 1298; 1911, 35, 913; Baudisch and King, *J. Ind. Eng. Chem.*, 1911, 3, 627.

[2] Ilinski and von Knorre, *Ber.*, 1885, 18, 2728.

[3] Meineke, *Zeitsch. angew. Chem.*, 1888, p. 252.

[4] The ferric precipitate is a voluminous black mass of $Fe(C_{10}H_6O.NO)_3$; the ferrous salt, $Fe(C_{10}H_6O.NO)_2$, is green.

[5] See p. 82; also Penny, *Chem. Gaz.*, 1850, 8, 330; Schabur, *Sitzungsber. K. Akad. Wiss. Wien*, 1851, 6, 1851; Kessler, *Zeitsch. anal. Chem.*, 1872, 11, 249.

[6] The reduction may also be effected with zinc in dilute sulphuric acid; but it does not give such a clear end-point, owing to formation of zinc ferricyanide with the indicator.

[7] A sharper end-point is obtained than with excess of hydrochloric acid.

$$6FeSO_4+K_2Cr_2O_7+7H_2SO_4=3Fe_2(SO_4)_3+K_2SO_4+Cr_2(SO_4)_3+7H_2O.$$

In the absence of acid, the results obtained are too high, the amount of dichromate required to complete the reaction increasing with dilution of the ferrous salt. With dry ferrous sulphate the result closely approaches the theoretical.[1]

Permanganate Method.—The iron is conveniently reduced with zinc or magnesium in the presence of dilute sulphuric acid. A blank experiment should be carried out with the zinc or magnesium alone, in order that a correction may be applied in the event of traces of iron being present as impurity in the metal, and for any carbon which is also liable to affect the titration by reducing a portion of the permanganate.[2] No special indicator is required by this method, for the permanganate is added to the solution, acidified with sulphuric acid until a faint pink colour persists, indicating that the permanganate is now present in slight excess, having oxidised all the iron. Thus (see p. 82):—

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

The end-point is unstable in the presence of fluorides, but satisfactory results can, in these circumstances, be obtained by addition of fairly concentrated sulphuric or boric acid solutions.[3]

Hydrochloric acid also renders the estimation unreliable unless special precautions are taken, the amount of permanganate used being too great. This has been attributed to the intermediate formation of a higher chloride of manganese during the reduction of the permanganate, which only relatively slowly oxidises the ferrous iron to the ferric condition according to the equation

$$MnCl_{(x+2)}+xFeCl_2 \rightleftharpoons xFeCl_3+MnCl_2$$

until equilibrium is established. Consequently, if the titration is carried out rapidly, more permanganate is added than is theoretically necessary before the ferrous iron is completely oxidised, and the pink colour indicative of the end-point appears. An excess of the higher manganese chloride remains in solution.

Addition of manganous sulphate, phosphoric acid, and of other substances to the liquid to be titrated has been found to reduce the error.[5]

Stannous chloride is often a convenient reagent to use, as it enables a determination to be made of the quantity of ferric iron in the presence of ferrous. The reaction hinges on the fact that stannous chloride reduces ferric chloride to the colourless ferrous salt. Thus :—

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[1] Neidle and Witt, *J. Amer. Chem. Soc.*, 1915, 37, 2360.

[2] Mackintosh, *Chem. News*, 1884, 50, 75.

[3] Barnebey, *J. Amer. Chem. Soc.*, 1915, 37, 1481.

[4] Friend, *Trans. Chem. Soc.*, 1909, 95, 1228. See also Skrabal, *Zeitsch. anal. Chem.*, 1903, 42, 373; Harrison and Perkin, *Analyst*, 1908, 33, 43; Birch, *Chem. News*, 1909, 99, 61; Buchanan, *Proc. Roy. Soc. Edin.*, 11, 191.

[5] See Kessler, *Annalen*, 1861, 118, 48; *Zeitsch. anal. Chem.*, 1863, 1, 329; Zimmermann, *Ber.*, 1881, 14, 779; Hauffe, *Chem. Zeit.*, 1897, 21, 894; Willenz, *Chem. Zentr.*, 1899, I., 638; Baxter and Frevert, *Amer. Chem. J.*, 1905, 34, 109; Harrison and Perkin, *loc. cit.*; Birch, *loc. cit.*; Friend, *loc. cit.*; A. Müller, *Stahl und Eisen*, 1906, 26, 1477; Jones and Jeffery, *Analyst*, 1909, 34, 306; Hough, *J. Amer. Chem Soc*, 1910, 32, 539; Barnebey, *J. Amer. Chem. Soc.*, 1914, 36, 1429; Brandt, *Chem. Zeit.*, 1918, 42, 433, 450.

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4.$$

Concentrated hydrochloric acid is added to the iron solution, the whole raised to boiling and quickly titrated with stannous chloride solution until the solution becomes colourless.

To determine the total iron content, the solution is first oxidised with potassium chlorate, and the ferric iron solution thus obtained titrated as above. The difference between two such determinations gives the amount of ferrous iron.

In order that the results should be accurate, especial care must be taken to ensure uniformity of conditions.[1]

Colorimetric Tests.—A sensitive test for iron consists in adding a small quantity of hydrazine sulphate to a dilute solution of the iron salt to reduce it to the ferrous condition. Ammonia is now added in excess, and an alcoholic solution of dimethyl glyoxime.[2] The solution is heated to boiling, and then cooled. A faint but detectable rose-red coloration is obtained in the presence of 1 part of iron per 100,000,000 parts of solution.[3]

This method may be applied in the gravimetric estimation of iron. Iron may be detected also by the yellow coloration produced in concentrated hydrochloric acid, 1 part of iron per 100,000 being observable. The colour varies with the concentration of the acid, the maximum intensity occurring with 28 per cent. acid.[4]

Iron in natural waters is frequently estimated colorimetrically by means of the red colour produced by ferric salts with potassium thiocyanate.[5] The iron is best oxidised with nitric acid, as the results appear to be more trustworthy than when oxidation is effected with hydrochloric acid and potassium chlorate.[6] One part of iron in 1,600,000 parts of solution may be detected in this manner.[7]

A delicate reaction for ferrous iron consists in adding a solution of sodium phospho-tungstate, acidified with hydrochloric acid, to the solution suspected of containing a ferrous salt. The whole is rendered alkaline with caustic soda, when a blue coloration is produced if a ferrous salt is present.[8] This reaction is more delicate than that with potassium ferricyanide.

Colorimetric methods are often uncertain in the presence of copper salts, but an accurate method has been worked out,[9] whereby 0·00002 gram of iron can be detected in the presence of 0·2 gram of copper. The method hinges on the violet colour produced when salicylic acid dissolved in acetic acid is added to ferric chloride in the presence of excess of sodium acetate. Under these conditions the depth of colour is proportional to the amount of iron present. The blue or green colour of the copper, which might mask the red produced by the iron, is first removed, where necessary, by addition of dilute potassium cyanide solution.

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[1] For details the reader is referred to text-books of analysis. See, for example, Scott, *Standard Methods of Chemical Analysis*, 2nd edition (New York, 1918), p. 221.

[2] Conveniently prepared by dissolving 10 grams of the solid in a litre of 98 per cent. alcohol.

[3] Tschugaev and Orelkin, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 1874; *Zeitsch. anorg. Chem.*, 1914, 89, 401.

[4] Hüttner, *Zeitsch. anorg. Chem.*, 1914, 86, 341.

[5] Proposed by Herapath, *J. Chem. Soc.*, 1853, 5, 27. See also Jassilly, *Bull. Soc. chim.*, 1913, (4), 13, 34; Mayer, *Mon. Sci.*, 1913, 3, i. 81; *Chem. Zeit.*, 1912, 36, 552; Lunge, *Zeitsch. angew. Chem.*, 1896, p. 3; Schulze, *Chem. Zeit.*, 1893, 17, 2; Zega, *ibid.*, p. 1564, also this volume, p. 236.

[6] Gothe, *Zeitsch. Nahr. Genussm.*, 1914, 27, 676.

[7] Wagner, *Zeitsch. anal. Chem.*, 1881, 20, 349. Compare E. E. Smith (*ibid.*, 1880, 19, 350), who states 1 part in 8,000,000.

[8] Richaud and Bidot, *J. Pharm. Chim.*, 1909, (6), 29, 230.

[9] Gregory, *Trans. Chem. Soc.*, 1908, 93, 93.

The red colour produced by ferric iron with acetyl acetone is recommended as the basis of a useful method of estimating the metal colorimetrically.[1]

In acid solution ferrous iron gives an intense blue colour with potassium ferricyanide—the so-called Turnbull's blue (see p. 227). The intensity of the colour is so great that one part of iron in 500,000 parts of solution can be detected.[2]

Iron may also be determined **electrolytically.**[3]

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[1] Pulsifer, *J. Amer. Chem. Soc.*, 1904, 26, 967.

[2] Wagner, *Zeitsch. anal. Chem.*, 1881, 20, 349.

[3] See Classen, *Ber.*, 1884, 17, 2467. See also this volume, pp. 34–36

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