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THE PERIODIC TABLE.*

PERIODS.	GROUP O.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period . .	2 He 4·00	1 H 1·008 3 Li 6·940	4 Be 9·02	5 B 10·82	6 C 12·000	7 N 14·008	8 O 16·000	9 F 19·00	
Second short period .	10 Ne 20·2	11 Na 22·997	12 Mg 24·32	13 Al 26·97	14 Si 28·06	15 P 31·027	16 S 32·064	17 Cl 35·457	
First long period { Even series .	18 A 39·91	19 K 39·096	20 Ca 40·07	21 Sc 45·10	22 Ti 48·1	23 V 50·96	24 Cr 52·01	25 Mn 54·93	26 Fe 55·84 27 Co 58·94 28 Ni 58·69
First long period { Odd „ .		29 Cu 63·57	30 Zn 65·38	31 Ga 69·72	32 Ge 72·60	33 As 74·96	34 Se 79·2	35 Br 79·916	
Second long period { Even series .	36 Kr 82·9	37 Rb 85·44	38 Sr 87·63	39 Y 88·9	40 Zr 91·0	41 Nb 93·1	42 Mo 96·0	43 ...	44 Ru 101·7 45 Rh 102·91 46 Pd 106·7
Second long period { Odd „ .		47 Ag 107·880	48 Cd 112·41	49 In 114·8	50 Sn 118·70	51 Sb 121·77	52 Te 127·5	53 I 126·932	
Third long period . .	54 X 130·2	55 Cs 132·81	56 Ba 137·37	57 La 138·90	58 Ce 140·25 59 Pr 140·92	60 Nd 144·27 61 ...	62 Sm 150·43 63 Eu 152·0	64 Gd 157·26 65 Tb 159·2	
Fourth long period. .		66 Dy 162·52 67 Ho 163·4	68 Er 167·7 69 Tm 169·4	70 Yb 173·6 71 Lu 175·0	72 Ct [180·8]	73 Ta 181·5	74 W 184·0	75 ...	76 Os 190·8 77 Ir 193·1 78 Pt 195·23
Fifth long period { Even series .		79 Au 197·2	80 Hg 200·61	81 Tl 204·39	82 Pb 207·20	83 Bi 209·00	84 Po [210]	85 ...	
Fifth long period { Odd „ .	86 Rn 222	87 ...	88 Ra 225·95	89 Ac ...	90 Th 232·15	91 Pa ...	92 U 238·17		
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* The International Atomic Weights for 1925 are adopted in this Table.

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LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

Abbreviated Title.	Journal.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914 +).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à 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, Beiblättes.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B.A. Reports	British Association Reports.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Akad. Ber.	See *Sitzungsber. K. Akad. Wiss. Berlin*
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. franc. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Drude's Annalen	Annalen der Physik (1900–1906).
Electroch. Met. Ind.	Electrochemical and Metallurgical Industry.

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

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

TABLE OF DATES OF ISSUE OF JOURNALS

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

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

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* 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
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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
1855	6, 7	29, 30	10	227–231	...	4–6	7, 8	223	18	43, 44	51, 52	...	9
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89	11	37, 38	14	250–255	...	16–18	15, 16	227	22	(3) 1, 2	59, 60	4, 5	13

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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
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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
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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

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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
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03	29, 30	15, 16	28	326–329	28–30	3, 4	241	36	29, 30	87, 88	32, 33	...	27	136, 137
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1905	33, 34	19, 20	30	338–343	4–6	7, 8	243	38	33, 34	91, 92	36, 37	...	29	140, 141
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08	39, 40	25, 26	33	358–363	13–15	13, 14	246	41	3, 4	97, 98	42, 43	5	32	146, 147
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1910	43, 44	29, 30	35	372–377	19–21	17, 18	248	43	7, 8	101, 102	46, 47	7	34	150, 151
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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

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1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279–282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283–286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287–290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291–294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295–298	25	17	67, 68	...	(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
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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
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06	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
07	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
08	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
09	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
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13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
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18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
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1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	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
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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
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04	203	5	20	72, 73, 74	23	113	24		43	17	38–42	10	39, 40	47–49
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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 TEXT-BOOK OF

INORGANIC CHEMISTRY.

VOLUME III. PART II.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. III. THE ALKALINE EARTH METALS AND THEIR ASSOCIATES.

PART II. BERYLLIUM AND ITS CONGENERS.

(Subgroup B.)

CHAPTER I.

INTRODUCTORY.

In Group II. of the Periodic Table beryllium and magnesium form a connecting link between the alkaline earth and zinc-cadmium-mercury groups. On the whole, beryllium has the closer relation to the zinc group and magnesium to the alkaline earths, with which it was once classed.

Group II.	
A. Alkaline Earths.	B. Zinc Group.
	Be
	Mg
Ca	
	Zn
Sr	
	Cd
Ba	
	..
..	
	Hg
Ra	

Beryllium was originally believed to resemble aluminium more than magnesium. It is, however, divalent like the members of Group II. The solubility of its hydroxide in caustic alkalies, which partly suggested its relationship with aluminium, is repeated by zinc. Mercury forms two well-marked series of salts, and the chloride of the monovalent series resembles silver chloride. The tendency to the extra monovalent series is faintly discernible in cadmium, as in cadmous hydroxide.

Both the alkaline earth metals and the members of the magnesium group are more or less white and metallic in appearance. Beryllium and magnesium are light: their approximate densities being 1·84 and 1·74. Calcium, with an atomic weight of 40·07, has an approximate density of 1·54; the approximate density of barium, atomic weight 137·37, is 3·78. The approximate densities of zinc and cadmium, with atomic weights of 65·38 and 112·41 respectively, are 6·92 and 8·65. The high density of mercury, 13·6, completes the tendency of zinc and cadmium to exceed the alkaline earths in density.

Beryllium melts at about 1280° C. Magnesium melts at the much lower temperature of *c.* 650° C. Barium melts some 200° above magnesium; calcium and strontium about 50° below barium, which is distinctly higher than magnesium. Zinc melts at about 419° C., and this tendency of zinc to melt more easily than the alkaline earth metals culminates in the low melting-point of mercury at −38·89° C. Zinc, cadmium, and mercury, with respective boiling-points of about 918° C., 778° C., and 357° C., very distinctly tend to greater volatility with increasing atomic weight. Magnesium boils at about 1100° C. and barium at about 950° C.

Water acts more readily on the alkaline earth metals than on the zinc group: cold water acts very slowly on beryllium; steam acts on zinc at a red heat and on heated cadmium vapour, but mercury is hardly attacked at all by water. Magnesium reacts readily in the presence of a little platinic chloride or when amalgamated. The alkaline earth metals also oxidise more readily than those of their sister group.

The zinc group metals greatly incline to form basic salts, and magnesium, though it tends to relations with the alkaline earth metals, shares somewhat in their inclination.

Calcium, strontium, and barium form hydrides. Magnesium, tending to resemble them, also has a hydride, but the zinc group has, in general, very little tendency to hydride formation, for the existence of a hydride of beryllium is very doubtful, and hydrides have not been discovered for zinc, cadmium, and mercury.

The fluorides of calcium, strontium, and barium are only very slightly soluble. Beryllium fluoride is very soluble. A litre of water only dissolves 7·6 mgm. of magnesium fluoride. Even anhydrous zinc fluoride is sparingly soluble, but cadmium fluoride, which dissolves to the extent of about 45 grm. in a litre of water at 25° C., returns to the general tendency towards solubility manifested by beryllium fluoride. Hydrolysis obscures the continuation of this tendency in mercury fluorides.

Beryllium chloride is very sensitive to moisture; zinc and magnesium chlorides form basic salts when their aqueous solutions are evaporated to dryness; hydrolysis is much less marked in cadmium chloride solutions and virtually absent in those of mercuric chloride. The heats of formation of beryllium and magnesium chlorides are approximately 155 and 151 Cal. respectively. In the alkaline earth group the heat of formation of the anhydrous chloride tends to rise with increasing molecular weight. Thus the approximate figure for strontium chloride is 184 Cal. and for barium chloride 194 Cal. The heat of formation of anhydrous zinc chloride is much lower than that of beryllium or magnesium—about 97 Cal. The figure is a little less for cadmium—about 93 Cal.—and, from the recorded results, very distinctly less for mercury.

The oxides of beryllium and magnesium are white, as are those of the alkaline earth metals. A tendency to colour is evident in zinc oxide, which is yellow when hot. The oxides of cadmium and mercury are coloured at ordinary temperatures. There is a tendency towards peroxide formation in the whole group.

The oxides of the alkaline earth metals dissolve appreciably in water to form hydroxide solutions. The hydroxides of the zinc group are only very slightly soluble in water, and are not formed by direct union between water and the oxides. Water is easily expelled from them by heat, and in the case of mercury, precipitation of salts by alkaline hydroxide solutions produces an oxide. The basic character of the hydroxides of the zinc group decreases with increasing atomic weight.

Hydrogen sulphide does not precipitate sulphides from solutions of salts of beryllium, magnesium, or the alkaline earth metals. Zinc sulphide is precipitated from alkaline or slightly acid solutions. Cadmium sulphide is less soluble in acids than zinc sulphide, though hydrogen sulphide does not precipitate it when the acid concentration is at all high. The increasing insolubility of the sulphides with increasing molecular weight is evident in the great resistance of mercuric sulphide to acid attack.

Nitrogen tarnishes calcium and strontium at ordinary temperatures. Beryllium and magnesium also form nitrides by direct combination with nitrogen. This tendency to direct union falls off perceptibly with zinc, though mercury still forms a nitride more indirectly.

The alkaline earth metals form well-marked carbides, and carbides of magnesium and beryllium are also known. Calcium, strontium, and barium form well-defined, stable carbonates. Magnesium carbonate is also well-defined and stable; but the tendency to form basic carbonates, apparent in magnesium, makes it difficult or impossible to obtain the carbonates of other metals in the group free from basic admixture.

The solubility of magnesium sulphate separates it from the sulphates of calcium, strontium, and barium, which decrease with increasing atomic weight from sparing to very slight solubility. Magnesium indicates its connection with the zinc group both by the solubility of its sulphate and the isomorphism between it and zinc sulphate. The sulphates of the zinc group are both more soluble and less stable than the alkaline earth sulphates. Their stability decreases with increasing atomic weight of the element.

CHAPTER II.

BERYLLIUM AND ITS COMPOUNDS.

BERYLLIUM.

Symbol, Be. Atomic Weight, 9·02 (O=16).

Occurrence.—Beryllium, since the difficulty of separating it from aluminium makes it difficult to detect in small quantities, may be more widely distributed than is supposed, though Hartley, from spectroscopic evidence, thinks this is doubtful.[1] *Beryl*, a double silicate of beryllium and aluminium, $3BeO.Al_2O_3.6SiO_2$, is the chief source of the element and its compounds. Beryl crystallises in the hexagonal system, and usually in simple forms. Its density is 2·7, and its hardness, 7·5–8, is intermediate between quartz and topaz. When free from colouring matter and flaws it is clear and transparent like glass. *Aquamarine* is a yellowish-green, bluish-green, or sea-green variety of the gem, and rich grass-green beryl is well known as *emerald*. The emerald has been valued as a gem from early times, and the Egyptian beads and scarabs, made from the products of Cleopatra's emerald mines in Upper Egypt, which were worked as early as 1650 B.C., had probably both a magical and an æsthetic value. Emeralds also occur in the Urals and at Salzburg, but the most valued gems come from Colombia in S. America.[2] The colour of the emerald is probably due to chromium.[3] Pink beryls have been found in Madagascar and California.

Very large crystals of beryl have been found in Norway, and some New Hampshire specimens have actually weighed from one to two tons. Beryl occurs frequently in some granites : in Bavaria, as a transparent blue variety in the Mourne Mountains, and as an opaque variety in Dublin, Donegal, and Banffshire.

Aquamarine of gem quality is found mostly in Brazil, the Urals, and Siberia.[2]

Beryl is not attacked by acids, except perhaps, when finely divided, by hydrofluoric acid.[4] It has been artificially prepared.[5]

The following analyses have been published :—

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[1] Hartley, *Proc. Roy. Soc.*, 1902, 69, 283.

[2] Spencer, *The World's Minerals* (W. & R. Chambers), 1911, p. 163.

[3] Wöhler and Rose, *Compt. rend.*, 1864, 58, 1180 ; Williams, *Phil. Mag.*, 1873, [4], 46, 314.

[4] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721 ; Britton, *J. Soc. Chem. Ind.*, 1922, 41, 349T.

[5] Williams, *Phil. Mag.*, 1873, [4], 46, 314 ; Hautefeuille and Perrey, *Compt. rend.*, 1888, 106, 1800 ; Traube, *Jahrb. Miner.*, 1894, 1, Mem., 275.

	1.[1]	2.[1]	3.[2]	4.[2]	5.[2]	6.[2]	7.[3]
Loss on ignition . .	1·46	1·41	..	..	..	..	..
SiO_2	66·06	65·80	64·02	66·24	65·23	66·53	64·41
Al_2O_3	16·1	16·40	16·44	17·64	17·72	17·11	18·82
BeO	14·33	14·21	12·91	11·06	12·37	12·24	11·65
FeO	..	..	..	..	..	..	1·46
Fe_2O_3	1·2	0·9	0·68	1·36	1·35	0·94	..
Mn_3O_4 . . .	0·13	0·11	..	..	..	..	..
NiO and ZnO . .	..	..	..	..	..	..	0·74
Cu	..	..	..	..	..	..	trace
MgO	0·55	0·61	0·23	0·09	0·37	0·20	0·02
CaO	0·17	0·14	0·50	0·36	0·61	0·43	0·65
K_2O	..	..	2·76	0·30	0·35	0·22	..
Cs_2O	..	..	..	..	..	0·12	..
Na_2O	..	..	0·25	0·60	0·53	0·97	..
Li_2O	..	..	0·05	0·14	0·06	0·17	..
Alkali chlorides . .	..	..	..	..	..	..	0·68
Alkalies and titanic acid	trace	trace	..	..	..	..	..
H_2O	..	..	1·76	2·06	1·49	1·49	1·22
P_2O_5	0·11	0·09	0·26	0·78	0·14	trace	..
	100·11	99·67	99·86	100·63	100·22	100·45	99·65

Beryllium also occurs in combination with silica in *phenacite*, Be_2SiO_4; in combination with alumina in *chrysoberyl* (cymophane), $Be(AlO_2)_2$; in combination with silica and alumina in *euclase*, $Be(AlOH)SiO_4$; and in combination with boric acid in *hambergite*, $Be_2(OH)BO_3$. It also occurs in other complex combinations containing silicic acid, as in *gadolinite*, $BeF_3(YO)_2(SiO_4)_2$; *leucophane*, $Na(BeF)Ca(SiO_3)_2$; *helvite*, $(Mn,Fe)_2(Mn_2S)Be_3(SiO_4)_3$; *danalite*, $(Zn,Fe)_2(Fe_2S)Be_3(SiO_4)_3$; *epididymite*, $HNaBeSi_3O_3$; *trimerite*, $MnBeSiO_4$; etc. *Berylonite* is sodium beryllium orthophosphate, $NaBePO_4$.[4]

The beryls and chrysoberyls often contain helium.[5]

Lockyer found beryllium lines in the sun's spectrum.[6]

History.—There have been two hesitancies over beryllium—a minor hesitancy over its name and a major hesitancy over its valency. It is still called both "beryllium" and "glucinum," but the name "beryllium" is adopted in this series. Beryllium is now almost universally regarded as divalent, though there may be a few compounds in which its valency is higher.

Vauquelin discovered *la terre du béril* in 1797. Haüy had emphasised the close resemblance between beryl and the emerald; Vauquelin examined the two minerals carefully and proved their chemical identity—confirming an opinion mentioned by Pliny. Klaproth had found in them silica, alumina, and ferric oxide; their present constitution, double silicates of beryllium and aluminium,

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[1] Lebeau, *Compt. rend.*, 1895, **121**, 601 (emerald).

[2] de Benneville, *J. Amer. Chem. Soc.*, 1894, **16**, 65 (beryl).

[3] Pollok, *Trans. Chem. Soc.*, 1904, **85**, 603 (Limoges beryl). Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 721, found small quantities of zinc in some beryls.

[4] Joy, *Chem. News*, 1863, 8, 183, 197, gave a useful list of the beryllium minerals and their literature as they were in 1863.

[5] Piutti, *Atti R. Accad. Lincei*, 1913, [5], **22**, i, 140.

[6] Lockyer, *Proc. Roy. Soc.*, 1878, **27**, 279.

$3BeO.Al_2O_3.6SiO_2$, is the result of Vauquelin's discovery that the alumina was accompanied by beryllia. He discovered the new oxide by its deposition from a boiling solution of potassium hydroxide, and distinguished it from alumina mainly by its solubility in ammonium carbonate, his failure to obtain potash alum from it, its higher basicity, its complete precipitation by ammonia, and by the sweetness of its salts, as well as by a number of other differences.[1] Subsequent research has fully confirmed his discovery.

A tendency soon developed to call the new earth "glucine," because its salts were sweet, and Vauquelin's own name for it, derived from its source, was superseded in France by the newer term. "Beryllerde" was, however, preferred in Germany, because sweet salts were not peculiar to the new earth. The names "glucinum" and "beryllium" were subsequently adapted from the original terms to denote the metal itself, and both are still in use.

Thirty years after Vauquelin's isolation of beryllia, Bussy[2] and Wöhler,[3] working independently, isolated the metal itself by reducing the chloride with metallic potassium.

Towards the end of the nineteenth century electrolytic methods for isolating beryllium were discovered, and the metal is now usually prepared by electrolysing its compounds in the presence of a fluoride. In 1916 it was obtained of 99·5 per cent. purity.[4]

Since beryllium is intimately associated with aluminium in nature and resembles it in many ways, it was natural to assume its trivalency, but, after a long controversy, the determination of the vapour density of its chloride by Nilson and Pettersson, in 1884 and 1886, indicated that it was divalent, like magnesium.[5] Humpidge confirmed this result in 1885, and drew the same conclusion from his determination of the vapour density of the bromide.[6] The run of the data in the light of the Periodic Classification and modern methods of checking or determining atomic weights clearly indicate for beryllium an atomic weight of about 9·1 and a valency of 2. Anode-ray analysis indicates that beryllium is a "simple element" with an atomic weight of $9{\cdot}0 \pm 0{\cdot}1$ ($Na=23$).[7]

Pollok's suggestion, in 1904, that the beryllium of Limoges beryl contains another unknown earth, has not matured.[8]

Beryllium is too rare to have much industrial importance. Crystalline beryllium is one of the most expensive rare metals, and its salts are also costly. The nitrate, however, is used in solutions for impregnating gas mantles.[9]

Extraction of Beryllium Compounds.—Vauquelin originally obtained beryllia by fusing beryl with potassium hydroxide, dissolving the melt in water and boiling the solution to reprecipitate the beryllia.[10]

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[1] Vauquelin, *Ann. Chim.*, 1798, 26, 155, 170, 259.

[2] Bussy, *Dingl. poly. J.*, 1828, 29, 466.

[3] Wöhler, *Ann. Chim. Phys.*, 1828, [2], 39, 77.

[4] Oesterheld, *Zeitsch. anorg. Chem.*, 1916, 97, 1.

[5] Nilson and Pettersson, *Compt. rend.*, 1884, 98, 988; *Ann. Chim. Phys.*, 1886, [6], 9, 554.

[6] Humpidge, *Proc. Roy. Soc.*, 1885, 39, 1.

[7] Thomson, *Phil. Mag.*, 1921, [6], 42, 857.

[8] Pollok, *Trans. Chem. Soc.*, 1904, 85, 1630.

[9] Martin, *Industrial and Manufacturing Chemistry* (*Inorganic*) (Crosby, Lockwood & Son), 1917, ii, 307–8.

[10] Vauquelin, *Ann. Chim.*, 1798, 26, 155.

Since the adequate isolation of beryllia from beryl involves the troublesome separation of the two very similar oxides, beryllia and alumina, a large number of methods have been devised and used to effect it. The best methods can be classified under the two main headings of (A) alkali fusion and (B) fluoride fusion.[1] Beryllia is almost invariably prepared from beryl, though other minerals containing beryllium have been occasionally employed.

(A) In the alkali-fusion method the finely powdered beryl is fused with about twice its weight of potassium carbonate or potassium hydroxide. The melt is ground, covered with water, and treated with excess of sulphuric acid. The whole is then heated, with stirring, until white fumes of sulphuric acid are evolved and the residue is reduced to a fine white powder. This decomposes the silico-aluminate of beryllium and potassium and makes the silica insoluble. After dissolving out the sulphates of beryllium, aluminium, and potassium with water, it has been usual to crystallise out the aluminium as potash alum, after suitable concentration. The mother-liquor from the separated alum contains the beryllium as sulphate, and also potassium sulphate, sulphuric acid, some aluminium sulphate, and small amounts of impurities, including slight amounts of iron. Britton advises, after filtering off the silica, adjusting the concentration of the sulphuric acid to about 5N by adding potassium hydroxide, saturating the boiling solution with potassium sulphate, and crystallising at a low temperature, preferably at 0° C.[2] If alcohol is used to procure a complete separation of the aluminium as alum, some beryllium sulphate also crystallises out.[3] Whether a preliminary separation of aluminium through potash alum is made or not, a final isolation of the beryllia is necessary.

(B) Lebeau fused powdered emerald with twice its weight of fluorspar, poured the molten mass into water and heated the resulting friable mass with sulphuric acid. After volatilisation of the silicon fluoride the bulk of the aluminium was removed as potash alum. He also heated emerald in the electric furnace, which volatilised some of the silica and left a mass easily attacked by hydrofluoric and sulphuric acids.[4]

A solution of beryllium fluoride is obtained by heating beryl to dull redness with 6 parts of ammonium hydrogen fluoride and extracting with water. The solution also contains traces of aluminium and other impurities—including iron.[5]

Copaux heats 1 part of finely powdered beryl with 2 parts of sodium silicofluoride to 850° C. The beryllia is converted into a double fluoride, thus :

$$2BeO + SiF_4 = SiO_2 + 2BeF_2;$$
$$2NaF + BeF_2 = Na_2BeF_4.$$

The alumina is analogously converted into artificial cryolite, Na_3AlF_6. Boiling water extracts the soluble double fluoride of beryllium from the residual mass, and leaves the bulk of the insoluble fluoride of aluminium.[1]

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[1] Critical reviews of the methods for obtaining beryllia from beryl have been given by Joy, *Amer. J. Sci.*, 1863, [2], 36, 83 ; *Chem. News*, 1863, 8, 183, 197 ; Gibson, *Trans. Chem. Soc.*, 1893, 63, 909 ; Britton, *Analyst*, 1921, 46, 359, 437 ; 1922, 47, 50.

[2] Britton, *J. Soc. Chem. Ind.*, 1922, 41, 351T. See also James, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 207.

[3] Pollok, *Trans. Roy. Soc.* (Dublin), 1904, 2, 8, 39.

[4] Lebeau, *Compt. rend.*, 1895, 121, 641.

[5] Gibson, *Trans. Chem. Soc.*, 1893, 63, 909.

The *final isolation* of pure beryllia from the crude products of these and other methods of extraction from beryl is difficult, and many modern improvements have been made on the older methods, which were often very elaborate.

In a much used method the solution containing the beryllium salt and associated impurities is poured into a large quantity of ammonium carbonate solution. Aluminium hydroxide is precipitated. Most of the iron separates on warming, and the rest is thrown down as sulphide by adding ammonium sulphide. On boiling the filtered solution the beryllium is precipitated as basic carbonate. This precipitate is easily washed, and very suitable for conversion into other salts of the metal.[2] In this method appreciable quantities of beryllium hydroxide are carried down by the aluminium hydroxide, and the beryllium precipitate is contaminated with aluminium hydroxide.[3]

The original method employed by Vauquelin, precipitation of beryllium hydroxide from its solution in potassium hydroxide (or sodium hydroxide) by boiling, has been a constant subject of controversy. Several workers have obtained good results by this method, but others concluded that it was quite unreliable.[4] Britton decided that this method affords a satisfactory separation of beryllium hydroxide if the following conditions are observed:—

1. The solution, which should not contain more than about 0·3 grm. BeO and 0·4 grm. Al_2O_3, should be evaporated to 25 c.c., brought to room temperature, and the precipitated hydroxides just redissolved by adding 6*N* NaOH. The beryllium hydroxide subsequently deposits more slowly and incompletely if excess of the alkali is added.

2. The solution should then be diluted to 500 c.c. and boiled for forty minutes. Longer boiling may precipitate some aluminium hydroxide.

3. The precipitate should then be filtered off at once to avoid re-solution of any beryllium hydroxide and decomposition of the sodium aluminate.[5]

Other methods are—

(*a*) The hydroxides of beryllium and aluminium, precipitated by ammonia, are suspended in a concentrated solution of ammonium chloride. If the solution is boiled till ammonia is evolved, the beryllium hydroxide is completely dissolved, while the aluminium hydroxide is not attacked. This method is tedious, and even with careful attention to conditions is probably not quantitative.[6]

(*b*) The hydroxides of beryllium and aluminium are dissolved in sulphurous acid or ammonium sulphite and the solution boiled till the sulphur dioxide has been expelled. Aluminium hydroxide is precipitated and the beryllium remains in solution. All the alumina is precipitated, but it adsorbs some beryllia.[1]

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[1] Copaux, *Compt. rend.*, 1919, 168, 610.

[2] Parsons and Barnes, *J. Amer. Chem. Soc.*, 1906, 28, 1589; Parsons and Roberts, *Science*, 1906, 24, 39.

[3] Britton, *Analyst*, 1921, 46, 437.

[4] Vauquelin, *Ann. Chim. Phys.*, 1798, 26, 155; Gmelin, *Pogg. Annalen*, 1840, 50, 175; Weeren, *Pogg. Annalen*, 1854, 92, 91; Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1904, 38, 377; Wunder and Chéladzé, *Ann. Chim. anal.*, 1911, 16, 205.

[5] Britton, *Analyst*, 1921, 46, 362.

[6] Weeren, *Pogg. Annalen*, 1854, 92, 101; Penfield and Harper, *Amer. J. Sci.*, 1886, iii, 32, 110; Britton, *Analyst*, 1922, 47, 50.

(*c*) Sodium carbonate precipitates nearly all the alumina from a solution containing aluminium and beryllium salts, and the beryllium remains in solution.[2]

✓ (*d*) Pollok, after fusing beryl with sodium hydroxide and separating the silica, precipitated the aluminium as chloride by saturating the solution with hydrogen chloride. Havens originally dissolved the co-precipitated hydroxides of aluminium and beryllium in hydrochloric acid and concentrated to about 10 c.c. The solution, which did not contain more than 0·1 grm. of the respective oxides, was mixed with an equal volume of ether and saturated with hydrogen chloride. After filtering off the aluminium chloride the beryllium can be precipitated from the filtrate by ammonia. The separation from aluminium is complete.[3]

(*e*) The methylamines and ethylamines precipitate beryllium hydroxide and retain aluminium hydroxide in solution. Precipitation can be effected from either nitric acid or hydrochloric acid solution of the two earths, but the beryllium hydroxide precipitated is very gelatinous, and probably adsorbs much alumina.[4]

(*f*) Beryllium can also be separated through its basic acetate. The basic acetate is dissolved away from other elements, including iron and aluminium, by hot glacial acetic acid [5] or chloroform.[6] According to one method, beryllium-containing minerals are heated with acetic acid, the beryllium converted, by a second treatment with acetic acid, into a form soluble in chloroform and extracted with that solvent.[7]

✓ (*g*) Parsons and Barnes treated the hydrochloric acid solution of the beryllium hydroxide with sodium bicarbonate. This precipitates aluminium hydroxide and retains beryllium in solution, as described under the estimation of beryllium (p. 31).[8]

The two preliminary treatments, (A) and (B), have been variously combined with the different methods of final isolation. Britton obtains from beryl a solution of beryllium sulphate, as described in (A), throws down " crystalline " beryllium hydroxide by treating the solution with sodium hydroxide and boiling, as previously described, and dissolves it in nitric acid. The solution is boiled to oxidise any iron, cooled, neutralised, diluted, and saturated with sodium bicarbonate. On boiling for half a minute, with vigorous stirring, any ferric or aluminium hydroxide precipitates completely, and pure beryllium hydroxide can be separated from the filtrate by ammonia. The sodium hydroxide process may be omitted, but care is then needed to prevent the aluminium hydroxide from carrying down some hydroxide of beryllium.[1]

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[1] Berthier, *Ann. Chim. Phys.*, 1843, [3], 7, 74; Britton, *Analyst*, 1921, 46, 440. The use of sodium thiosulphate appears to be unsatisfactory (Britton, *Analyst*, 1922, 47, 54).

[2] Hart, *J. Amer. Chem. Soc.*, 1895, 17, 604; Parsons, *ibid.*, 1904, 26, 721; Britton, *Analyst*, 1921, 46, 442.

[3] Havens, *Chem. News*, 1897, 76, 111; Pollok, *Trans. Chem. Soc.*, 1904, 85, 603; Parsons and Barnes, *J. Amer. Chem. Soc.*, 1906, 28, 1589; Britton, *Analyst*, 1922, 47, 55.

[4] Renz, *Ber.*, 1903, 36, 275; Britton, *Analyst*, 1922, 47, 57.

[5] Parsons and Barnes, *J. Amer. Chem. Soc.*, 1906, 28, 1589; Parsons and Robinson, *ibid.*, 555.

[6] Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1904, 40, 465.

[7] German Patent, 155466 (1903).

[8] Bran and van Oordt, *J. Soc. Chem. Ind.*, 1906, 25, 1147 (French Patent, 367861 (1906)).

Preparation of Metallic Beryllium.—Bussy[2] and Wöhler,[3] working independently, first isolated the metal in an impure state by decomposing the anhydrous chloride with potassium.

Sodium may be used instead of potassium,[4] and the simple chloride may be replaced by the double fluoride of potassium and beryllium, $2KF.BeF_2$.[5] About 1883 it was discovered that metallic beryllium can be obtained by electrolysing this double fluoride, though the halides of beryllium do not conduct electricity in the pure state.[6]

Subsequently, a fused mixture of beryllium chloride and sodium or ammonium chloride was electrolysed,[7] and Lebeau electrolysed the double fluoride of sodium and beryllium in a nickel crucible. The anode was a rod of graphite, and the crucible itself acted as cathode.[8] Beryllium minerals can be electrolysed in the presence of fluorine or one of its compounds: halogen compounds of the alkalies or alkaline earths may be added.[9]

The electrolytic method is now generally used; it consists essentially of electrolysing beryllium compounds in the presence of fluorides, and its development is largely due to Lebeau.

Attempts to reduce beryllium oxide with magnesium have not been very successful.[10] The converse reaction

$$Be + MgO = BeO + Mg$$

occurs more readily.[11]

The metal can be purified by volatilisation in hydrogen.[11] Oesterheld, in 1916, claimed to have secured metallic beryllium of 99·5 per cent. purity.[12]

Physical Properties of Beryllium.—Metallic beryllium was first obtained as a dark grey powder by reducing its chloride with potassium.[13] The product of such reduction methods is usually a similar powder, though crystals of the metal sometimes occur.[14] It assumes "a bright grey or white metallic lustre under the burnisher." [15]

The metal produced by electrolysis is crystalline, with a bright metallic lustre.[8] It crystallises in prismatic and tabular forms of the holohedral division of the hexagonal system,[16] and the density of the crystals is 1·842.[17] This density agrees closely with the 1·85 at 20° C.

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[1] Britton, *J. Soc. Chem. Ind.*, 1922, **41**, 351T.

[2] Bussy, *Dingl. poly. J.*, 1828, **29**, 466.

[3] Wöhler, *Pogg. Annalen*, 1828, **13**, 577.

[4] Debray, *Ann. Chim. Phys.*, 1855, [3], **44**, 5; Reynolds, *Phil. Mag.*, 1876, [5], **3**, 38; Nilson and Pettersson, *Ann. Chim. Phys.*, 1878, [5], **14**, 427; Humpidge, *Phil. Trans.*, 1883, **174**, ii, 601; Pollok, *Trans. Chem. Soc.*, 1904, **85**, 603.

[5] Humpidge, *loc. cit.*; Krüss and Moraht, *Ber.*, 1890, **23**, 727.

[6] Humpidge, *loc. cit.*; Fichter and Jablczyński, *Ber.*, 1913, **46**, ii, 1604.

[7] Borchers, *Chem. Zentr.*, 1895, **2**, 13; *Zeitsch. Elektrochem.*, 1895, **2**, 40.

[8] Lebeau, *Compt. rend.*, 1898, **126**, 744.

[9] Liebmann, *J. Soc. Chem. Ind.*, 1899, **18**, 282 (English Patent, 3497).

[10] Krüss and Moraht, *Annalen*, 1890, **260**, 161; *Ber.*, 1890, **23**, 727; Winkler, *Ber.*, 1890, **23**, 120.

[11] Fichter and Brunner, *Zeitsch. anorg. Chem.*, 1915, **93**, 84.

[12] Oesterheld, *ibid.*, 1916, **97**, 1.

[13] Wöhler, *Ann. Chim. Phys.*, 1828, [2], **39**, 77.

[14] Humpidge, *Proc. Roy. Soc.*, 1885, **39**, 1; Krüss and Moraht, *Ber.*, 1890, **23**, 727.

[15] Pollok, *Trans. Chem. Soc.*, 1904, **85**, 603.

[16] Brogger and Flink, *Ber.*, 1884, **17**, 849.

[17] Fichter and Jablczyński, *ibid.*, 1913, **46**, ii, 1604.

determined on the metal produced by reduction of the chloride with sodium.[1] Lebeau's electrolytic crystals had a density of 1·73 at 15° C.[2]

The small crystals thus obtained cannot be melted together because a coating of oxide prevents coalescence. To obtain a regulus they are compressed and heated in a non-oxidising atmosphere. The freshly filed metal has a steel-grey colour. Its melting-point is 1280±20° C. (Oesterheld gives 1278±5° C.[3]); it scratches glass, is brittle at ordinary temperatures, ductile at higher, and its specific electrical conductivity is $5{\cdot}41 \times 10^4$ reciprocal ohms.[4]

Pollok deduced from some of his experiments that beryllium volatilises without fusion under atmospheric pressure.[5] It is said to volatilise readily at 1530° C. under 5 mm. pressure in hydrogen.[6]

Humpidge[7] expressed the relationship between the specific heat and temperature (t) in the formula—

$$\text{Specific heat} = 0{\cdot}3756 + 0{\cdot}00106t - 0{\cdot}00000114t^2.$$

Its atomic volume has been given as 5·26[8] and its approximate heat of fusion as 341.[3]

It is probably a "simple element,"[9] and its band spectrum resembles that of aluminium.[10]

The stronger lines in the spectrum of beryllium in decreasing order of wave-length (Rowland) are as follows[11]:—

Spark: 4572·9, 3321·5, 3321·2, 3131·2, 3130·6, 2650·7, 2494·7, 2348·7.
Arc : 4572·9, 3321·5, 3321·2, 3131·2, 3130·6, 2650·7, 2494·7, 2348·7.

Chemical Properties of Beryllium.—Beryllium is chemically intermediate between magnesium and aluminium. The metal is unaffected by dry air at the ordinary temperature, but burns brilliantly to the oxide when heated.[12, 13] Cold water has very little action on it, though hot water slowly converts it into the hydroxide. Wöhler originally stated that water had no action on it at all:[12] a surface film of oxide probably protects the metal.[4] Dilute acids dissolve it with evolution of hydrogen. Ammonia does not attack it, but caustic alkalies act on it similarly to aluminium, though some investigators say that the vigour of the attack has been exaggerated.[4] Beryllium sulphate and sulphur dioxide are produced by the action of hot concentrated sulphuric acid.[12] Concentrated nitric acid has hardly any action; at higher dilutions beryllium nitrate is formed and nitric oxide evolved.[12]

Beryllium partially decomposes silicon tetrachloride at 270°–370° C.,[14] and combines directly with fluorine, chlorine, bromine,[1] iodine,[2] and sulphur.[3, 4] Its combination with hydrogen is doubtful;[5] at electric-furnace heat it combines with carbon,[6] boron, and silicon,[1] and above 900° C. with nitrogen.[7]

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[1] Humpidge, *Proc. Roy. Soc.*, 1885, 39, 1.
[2] Lebeau, *Ann. Chim. Phys.*, 1899, [7], 16, 457.
[3] Oesterheld, *Zeitsch. anorg. Chem.*, 1916, 97, 1.
[4] Fichter and Jablczyński, *Ber.*, 1913, 46, ii, 1604.
[5] Pollok, *loc. cit.*
[6] Fichter and Brunner, *Zeitsch. anorg. Chem.*, 1915, 93, 84.
[7] Humpidge, *loc. cit.*
[8] Ephraim, *Ber.*, 1912, 45, i, 1322.
[9] Thomson, *Phil. Mag.*, 1921, [6], 42, 857.
[10] de Boisbaudran and de Gramont, *Compt. rend.*, 1911, 153, 318.
[11] Watts, *Index of Spectra*, Appendix U, 1911 (Wesley & Son, London; Abel Heywood & Son, Manchester). See Rowland and Tatnall, *J. Astroph.*, 1895, i, 14.
[12] Wöhler, *Ann. Chim. Phys.*, 1828, [2], 39, 77.
[13] Lebeau, *ibid.*, 1899, [7], 16, 457.
[14] Rauter, *Annalen*, 1892, 270, 235.

Equivalent, Valency, and Atomic Weight of Beryllium.—Anode-ray analysis indicates that beryllium is a "simple element" with an atomic weight of $9{\cdot}0 \pm 0{\cdot}1$ (Na=23).[8] Other modern supplemental methods of verifying atomic weights, such as the transparency of beryllium oxide to X-rays,[9] indicate a similar value. Modern methods of checking valency, such as the precipitation of colloidal arsenic sulphide by beryllium salts,[10] also indicate that the element is divalent.

Up to 1885 opinion swayed between the trivalency and divalency of beryllium. Berzelius, controverting Vauquelin, wrote its oxide Be_2O_3 and its atomic weight 13·7 (O=16), *i.e.* three times its equivalent.[11] Awdejew [12] and Debray [13] supported the earlier view. Berzelius considered beryllia to be an analogue of alumina because ammonia precipitated its hydroxide from solutions of its salts, because it was insoluble in acids after calcination, and because alumina could be replaced by beryllia in some mineral species. When beryllium chloride was discovered by Rose it appeared to be very similar to aluminium chloride, and when Wöhler isolated the metal it seemed to be analogous to aluminium.[13]

Analogies between beryllium and aluminium constantly appear—their band spectra, for example, are very similar.[14] Humpidge noted, in 1883, that the two metals both formed stable double fluorides with potassium and sodium. He also commented on the tendency of beryllium to form basic compounds.[11]

Awdejew failed to obtain a double sulphate of beryllium and potassium analogous to potash alum, and concluded that the composition of many minerals containing beryllium indicated the formula BeO for beryllia. Debray, reviewing the evidence, decided that, though it was indecisive, beryllia should be regarded as similar in constitution to magnesia rather than to alumina.[13]

Since an atomic weignt of about 9 fitted beryllium comfortably into the periodic system of Mendeleef and Lothar Meyer, subsequent chemists usually accepted this value,[11] and Reynolds, in 1876, confirmed it by a determination of the atomic heat.[15] Atterberg, two or three years before, had urged the determination of the specific heat of the metal, since the formulation of some beryllium compounds seemed to require the formula BeO for beryllium oxide.[16]

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[1] Lebeau, *Ann. Chim. Phys.*, 1899, [7], 16, 457.
[2] Debray, *ibid.*, 1855, [3], 44, 5.
[3] Wöhler, *ibid.*, 1828, [2], 39, 77.
[4] Biltz, *Zeitsch. anorg. Chem.*, 1913, 82, 436.
[5] Winkler, *Ber.*, 1891, 24, 1966.
[6] Lebeau, *Compt. rend.*, 1895, 121, 496.
[7] Fichter and Brunner, *Zeitsch. anorg. Chem.*, 1915, 93, 84.
[8] Thomson, *Phil. Mag.*, 1921, [6], 42, 857.
[9] Benoist and Copaux, *Compt. rend.*, 1914, 158, 859.
[10] Galecki, *Zeitsch. Elektrochem.*, 1908, 14, 467.
[11] Humpidge, *Phil. Trans.*, 1883, 174, ii, 601.
[12] Awdejew, *Ann. Chim. Phys.*, 1843, [3], 7, 155.
[13] Debray, *ibid.*, 1855, [3], 44, 5.
[14] de Boisbaudran and de Gramont, *Compt. rend.*, 1911, 153, 318.
[15] Reynolds, *Phil. Mag.*, 1876, [5], 3, 38.
[16] Atterberg, *Ber.*, 1874, 7, 472.

It was, however, difficult to obtain pure beryllium, and experimenters found specific heats which pointed alternately to about 9 and 13·5 as the atomic weight. The results of Nilson and Pettersson, in 1878, favoured the higher value.[1] Brauner, convinced that Mendeleeff's Periodic Law fixed the atomic weight of beryllium at the lower value, suggested a rise of the specific heat with temperature, and noted the importance of obtaining the vapour density of some volatile compound of beryllium.[2] Reynolds repeated his own determination, and defended his results against Nilson and Pettersson.[3] Humpidge, however, summed up in their favour: reviewing the available data which bore on the atomic weight of beryllium, and arguing that *experimental* results must outweigh Lothar Meyer's "theoretical conceptions arising from a consideration of Mendeleeff's periodic law."[4] Humpidge subsequently determined the specific heat of beryllium, confirmed the higher value for its atomic weight,[5] and, continuing to prefer practical results to theoretical conceptions, remarked that the result was "unfortunate for the periodic law."[6]

Two years after, in 1885, Humpidge agreed to accept the number which "satisfies the requirements of the periodic law," and recognised the "due importance" of the "periodic arrangement." He discovered that the variation in the specific heat of beryllium with the temperature threw doubt on any deduction of its atomic weight. The specific heat of beryllium increases rapidly to 400° C., and then remains very constant at about 0·62 between 400° C. and 500° C. This constant value agrees, according to the Law of Dulong and Petit, more closely with an atomic weight of about 9·1 than with one of about 13·5. The vapour densities of beryllium chloride and bromide decided the issue, and Humpidge, after determining them, represented the two compounds as $BeCl_2$ and $BeBr_2$, "in which the metal is a dyad, and has the atomic weight 9·1."[7] Nilson and Pettersson had, the year before, obtained a similar result for the chloride,[8] and after they verified their result,[9] beryllium may be said to have been confirmed in its divalency and its atomic weight of about 9·1. Three years after, in 1889, Mendeleeff publicly established beryllium in its present position in the Periodic Table.[10]

Rosenheim and Woge confirmed the results of the vapour-density method by determining the molecular weight of beryllium chloride in pyridine. They also described a number of reactions which pointed to the divalency of beryllium.[11] Glassmann has also confirmed its divalency through the molecular weight of the anhydrous picrate.[12]

Mallard observed, in 1889, that crystallised beryllia was isomorphous with crystallised zinc oxide[13]—an indication that beryllium is divalent like zinc. The evidence from isomorphism is, however, not uniform: beryllium silicotungstates, for example, are isomorphous with aluminium silicotungstates.[1] Retgers denied isomorphism between beryllium salts and the salts of the metals of the magnesium group.[2]

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[1] Nilson and Pettersson, *Ann. Chim. Phys.*, 1878, [5], 14, 427; *Ber.*, 1878, 11, 381.

[2] Brauner, *Ber.*, 1878, 11, 872.

[3] Reynolds, *Chem. News*, 1880, 42, 273.

[4] Humpidge, *ibid.*, 42, 261.

[5] Humpidge, *Proc. Roy. Soc.*, 1883, 35, 137.

[6] Humpidge, *Phil. Trans.*, 1883, 174, ii, 601.

[7] Humpidge, *Proc. Roy. Soc.*, 1885, 39, 1.

[8] Nilson and Pettersson, *Compt. rend.*, 1884, 98, 988.

[9] Nilson and Pettersson, *Ann. Chim. Phys.*, 1886, [6], 9, 554.

[10] Mendeleeff, *Trans. Chem. Soc.*, 1889, 55, 650.

[11] Rosenheim and Woge, *Zeitsch. anorg. Chem.*, 1897, 15, 283.

[12] Glassmann, *Ber.*, 1907, 40, 3059.

[13] Mallard, *Compt. rend.*, 1887, 105, 1260.

In 1895 Lebeau implied trivalency for beryllium by comparing its carbide to that of aluminium and formulating it as Be_4C_3.[3] Henry promptly defended the formula Be_2C,[4] and his conclusion, with the implication of divalency for beryllium, is now generally accepted.[5]

In 1904 Pollok suggested that an undiscovered element in Limoges beryl, with a higher equivalent than beryllium and similar properties to it, had confused many of the results in determining the atomic weight of beryllium.[6] This suggestion, however, has not matured.[7]

Tanatar, about the same time, suggested quadrivalency for beryllium and an atomic weight of 18·2, because some of its compounds appear to have the constitution $R_3 : BeOBe : R_3$, and because its specific heat at low temperatures is more suited to an atomic weight of 18·2 than to a lower value.[8] Glassmann criticised his conclusion,[9] and such dissent may be said to be now negligible. The vapour densities of beryllium acetylacetonate[1] and basic beryllium acetate[10] confirm the atomic weight as about 9.

The earlier determinations were usually made from the ratio $BeO : BaSO_4$.[11] Debray[12] analysed the double oxalate, $Be(NH_4)_2.(C_2O_4)_2$, and obtained the ratio $4CO_2 : BeO = 100 : 14·41$. This result, corrected for the atomic weights $O = 16$ and $C = 12·003$, gives an atomic weight of 9·36.

Previous to 1922, the most reliable determinations, recalculated from the fundamental values $O = 16·000$, $S = 32·065$, $C = 12·003$, and $H = 1·00762$, were as follows :—

(*a*) Nilson and Pettersson,[13] ignition of sulphate, $BeSO_4.4H_2O : BeO = 100 : 14·169$ (mean of four determinations), atomic weight 9·113.

(*b*) Krüss and Moraht,[14] ignition of sulphate, $BeSO_4.4H_2O : BeO = 100 : 14·144$ (mean of sixteen determinations), atomic weight 9·061.

(*c*) Parsons,[15] ignition of acetylacetonate, $Be(C_5H_7O_2)_2 : BeO = 100 : 12·112$ (mean of seven determinations), atomic weight 9·101.

(*d*) Parsons,[15] ignition of basic acetate, $Be_4O(C_2H_3O_2)_6 : 4BeO = 100 : 24·698$ (mean of nine determinations), atomic weight 9·108.

Concordant results for the equivalent of beryllium have formerly been difficult to obtain from the chloride, because it is difficult to purify completely.[16] In 1922, however, Hönigschmid and Birckenbach worked with pure beryllium chloride prepared by heating the highly purified oxide with carbon in a current of chlorine. They obtained the ratio $BeCl_2 : 2Ag = 0{\cdot}370465 : 1$ from thirteen determinations, and the ratio $BeCl_2 : 2AgCl = 0{\cdot}278825 : 1$ from five. Both ratios gave $Be = 9{\cdot}018$, if $Ag = 107{\cdot}88$ and $Cl = 35{\cdot}457$.[1]

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[1] Combes, *Compt. rend.*, 1894, **119**, 1221.
[2] Retgers, *Zeitsch. physikal. Chem.*, 1896, **20**, 481.
[3] Lebeau, *Compt. rend.*, 1895, **121**, 496.
[4] Henry, *ibid.*, 600.
[5] Fichter and Brunner, *Zeitsch. anorg. Chem.*, 1915, **93**, 84.
[6] Pollok, *Trans. Chem. Soc.*, 1904, **85**, 1630.
[7] See Parsons, *J. Amer. Chem. Soc.*, 1905, **27**, 233.
[8] Tanatar, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 82; 1906, **38**, 850.
[9] Glassmann, *Chem. Zeit.*, 1907, **31**, 8.
[10] Urbain and Lacombe, *Compt. rend.*, 1901, **133**, 874.
[11] Awdejew, *Ann. Chim. Phys.*, 1843, [3], **7**, 155; Weeren, *Pogg. Annalen*, 1854, **92**, 91; Klatzo, *Bull. Soc. chim.*, 1869, [2], **12**, 131.
[12] Debray, *Ann. Chim. Phys.*, 1855, [3], **44**, 5.
[13] Nilson and Pettersson, *Ber.*, 1880, **13**, 1451.
[14] Krüss and Moraht, *Annalen*, 1891, **262**, 38.
[15] Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 721.
[16] Pollok, *Trans. Chem. Soc.*, 1904, **85**, 1630.

The International Committee on Atomic Weights for 1925[2] has adopted the value

$$Be = 9{\cdot}02.$$

ALLOYS OF BERYLLIUM.

Alloys of copper and beryllium can be prepared by heating an intimate mixture of the oxides, in suitable proportions, with carbon in an electric furnace. Low percentages of beryllium impart a yellow colour; with higher percentages the alloys tend to become white. Small amounts of beryllium also make the metal very sonorous: even 0·5 per cent. of beryllium makes the alloy sonorous and yellow. An alloy containing 1·32 per cent. of beryllium is golden yellow, highly sonorous, and can be readily filed or forged. Alloys with 10 per cent. are nearly white; those with 5 per cent. are more yellow, easily filed or forged, malleable, unaltered by air, tarnished by hydrogen sulphide, and soluble in nitric acid.[3]

Alloys of beryllium with other metals can be prepared by a similar method, or by electrolysing double beryllium-sodium fluorides in a carbon crucible, which acts as anode, containing the other metal in a state of fusion.[3, 4]

The eutectic systems of beryllium with iron, silver, copper, and aluminium have been investigated by Oesterheld. It appears to be impossible to alloy beryllium and magnesium, since the latter boils below the melting-point of the former.[5]

COMPOUNDS OF BERYLLIUM.

Beryllium yields only one series of salts, derived from one oxide. Unanimity is not yet absolute, but beryllium is almost universally regarded as BeO, and the salts as containing divalent beryllium. No acid salts are known, but the existence and nature of basic salts have been vexed questions. In 1906, Parsons and Robinson commented on the necessity either of "exact equivalents of anion and cation," or of "excess of the acid component," in preparing "definite crystalline compounds" of beryllium.[6]

Normal salts of beryllium have an acid reaction in aqueous solution. These aqueous solutions can dissolve relatively large quantities of beryllium oxide. The oxide, or hydroxide, is probably soluble, in the ordinary sense of simple solution, in solid beryllium salts, as camphor is soluble in acetic acid, and also soluble in dissolved beryllium salts, as camphor is soluble in aqueous acetic acid.[1] There is usually very little hydrolysis in dissolved beryllium salts,[2] though the chloride, bromide, iodide,[3] and nitrate [4] are strongly hydrolysed, and the hydrogen ion concentration is reduced virtually to zero by adding very much less beryllia than the solutions will dissolve.[5] Solutions of beryllium hydroxide in aqueous beryllium sulphate are not markedly colloidal, and do not contain beryllium in a complex anion. The solution of the hydroxide also raises the freezing-point and lowers the conductivity.[6]

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[1] Hönigschmid and Birckenbach, *Ber.*, 1922, 55, [B], 4.

[2] *J. Amer. Chem. Soc.*, 1925, 47, 597.

[3] Lebeau, *Compt. rend.*, 1897, 125, 1172.

[4] Lebeau, *ibid.*, 1898, 126, 744.

[5] Oesterheld, *Zeitsch. anorg. Chem.*, 1916, 97, 6.

[6] Parsons and Robinson, *J. Amer. Chem. Soc.*, 1906, 28, i, 555.

Residues of very varying basicity are obtained by evaporating solutions of beryllium salts. The basic acetate,[3, 7] and some other basic salts of organic acids,[7, 8] are definite, and remarkably stable, substances. But a large number of the basic salts described are probably indefinite basic phases.[9]

Solutions of beryllium salts are apparently sweet in proportion to their cation concentration.[10]

Beryllium Hydride.—Winkler has described a very impure hydride which evolves hydrogen in contact with hot water and gives a hydrogen flame on heating. Its existence, which was mainly deduced from an absorption of gas when beryllia and powdered magnesium were heated in an atmosphere of hydrogen, is doubtful.[11]

BERYLLIUM AND THE HALOGENS.

Beryllium Fluoride.—Berzelius [12] dissolved beryllium hydroxide in hydrofluoric acid, evaporated to dryness, and dried the residue at 100° C. Lebeau showed that this residue always retained water, and left an oxyfluoride, $5BeF_2.2BeO$, on heating to redness. This solid oxyfluoride is colourless, almost transparent, soluble in water, and has a density of about 2·01 at 15° C.

The original moist residue is converted into anhydrous beryllium fluoride by heating in a current of hydrogen fluoride. Lebeau also obtained anhydrous beryllium fluoride by igniting the dry double fluoride of ammonium and beryllium, $BeF_2.2NH_4F$, in a current of carbon dioxide. It is a vitreous solid, with a density of 2·1 at 15° C. It softens on heating, becomes fluid at about 800° C., finally volatilises, and forms a crystalline sublimate. It is deliquescent, soluble in water in all proportions, slightly soluble in absolute alcohol, converted into an oxyfluoride by oxygen, and readily decomposed by sulphuric acid. Sodium, potassium, lithium, and magnesium, when heated with anhydrous beryllium fluoride, combine with the fluorine and set metallic beryllium free. Hydrofluoric acid does not dissolve it.[13]

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[1] Parsons, *J. Physical Chem.*, 1907, **11**, 660.

[2] Ley, *Zeitsch. physikal. Chem.*, 1899, **30**, 218; Bruner, *Zeitsch. physikal. Chem.*, 1900, **32**, 133.

[3] Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 721.

[4] Parsons, *Science*, 1906, **25**, 402.

[5] Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 1433.

[6] Parsons, Robinson, and Fuller, *J. Physical Chem.*, 1907, **11**, 655.

[7] Urbain and Lacombe, *Compt. rend.*, 1901, **133**, 874.

[8] Lacombe, *ibid.*, 1902, **134**, 772; Tanatar, *Ber.*, 1910, **43**, 1230.

[9] Parsons and Robinson, *J. Amer. Chem. Soc.*, 1906, **28**, i, 555.

[10] Höber and Kiesow, *Zeitsch. physikal. Chem.*, 1898, **27**, 601.

[11] Winkler, *Ber.*, 1891, **24**, 1966.

[12] Berzelius, *Pogg. Annalen*, 1823, **1**, 22, 196.

[13] Lebeau, *Compt. rend.*, 1898, **126**, 1418; *Ann. Chim. Phys.*, 1899, [7], **16**, 457.

Beryllium Chloride.—Beryllium chloride, $BeCl_2$, has played an important part in the history of beryllium. It was the first source of the metal,[1] and the discovery that its vapour density between 490° and 1520° C. corresponded to the formula $BeCl_2$, was fundamental for the discussion over the valency and atomic weight of the element.[2, 3, 4] The formula has been confirmed by the molecular weight of beryllium chloride in pyridine.[5]

Anhydrous beryllium chloride is a white crystalline solid, of density 1·8995 at 25° C.,[6] which melts at about 440° C. and boils at about 520° C.[7] The fused chloride is a non-conductor.[8] It decomposes when heated in the presence of air, but volatilises without decomposition if water and air are absent.[3]

It dissolves violently in water with loss of hydrogen chloride. With ether it forms a compound, $BeCl_2.2Et_2O$,[9] and dissolves readily in alcohol but not in chloroform, carbon tetrachloride, benzene, or sulphur dichloride. The *tetrahydrate* can be obtained by treatment with hydrogen chloride and ether: [10] alcohol can replace the ether in preparing it.[11] Anhydrous beryllium chloride forms compounds with many organic bases.[8, 12]

Beryllium chloride is easily prepared in solution by dissolving the oxide or hydroxide in hydrochloric acid. When such a solution is evaporated down hydrogen chloride passes off and a gummy basic mass is left. The pure chloride can only be prepared by methods which exclude the presence of water.[13]

Anhydrous beryllium chloride has been prepared by five principal methods. A very pure product was obtained by the action of hydrogen chloride gas on the metal.[14] It has also been prepared by the action of carbon tetrachloride on red-hot beryllia,[15] by passing chlorine and sulphur chloride vapour over the heated oxide,[16] and by the action of chlorine or hydrogen chloride on the heated carbide.[17] Most workers heated a mixture of beryllium oxide and carbon in a current of chlorine.[18, 19, 20] Mieleitner and Steinmetz say that hydrous beryllium chloride, like the compound $BeCl_2.4H_2O$, cannot be completely dehydrated by heating in dry hydrogen chloride or chlorine.[1]

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[1] Bussy, *Dingl. poly. J.*, 1828, **29**, 466; Wöhler, *Pogg. Annalen*, 1828, **13**, 577.

[2] Nilson and Pettersson, *Compt. rend.*, 1884, **98**, 988.

[3] Humpidge, *Proc. Roy. Soc.*, 1885, **39**, 1.

[4] Nilson and Pettersson, *Ann. Chim. Phys.*, 1886, [6], **9**, 554.

[5] Rosenheim and Woge, *Zeitsch. anorg. Chem.*, 1897, **15**, 283.

[6] Hönigschmid and Birckenbach, *Ber.*, 1922, **55**, [B], 4.

[7] Pollok, *Trans. Chem. Soc.*, 1904, **85**, 603.

[8] Lebeau, *Ann. Chim. Phys.*, 1899, [7], **16**, 457.

[9] Atterberg, *Ber.*, 1875, **9**, 856.

[10] Awdejew (*Ann. Chim. Phys.*, 1843, [3], **7**, 155) reported this compound. Parsons subsequently denied the existence of the tetrahydrate (*J. Amer. Chem. Soc.*, 1904, **26**, 721), but Steinmetz succeeded in preparing it five years later and Parsons accepted the correction (Parsons, *The Chemistry and Literature of Beryllium* (The Chemical Publishing Co., Easton, Pa.; Williams & Norgate, London), 1909, p. 9).

[11] Mieleitner and Steinmetz, *Zeitsch. anorg. Chem.*, 1913, **80**, 71.

[12] Lacombe, *Compt. rend.*, 1902, **134**, 772.

[13] Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 721.

[14] Nilson and Pettersson, *Ann. Chim. Phys.*, 1886, [6], **9**, 554.

[15] Meyer (Lothar), *Ber.*, 1887, **20**, 681.

[16] Bourion, *Compt. rend.*, 1907, **145**, 62.

[17] Lebeau, *ibid.*, 1895, **121**, 496.

[18] Rose, *Pogg. Annalen*, 1827, **9**, 39; Wöhler, *ibid.*, 1828, **13**, 577; Awdejew, *ibid.*, 1842, **56**, 100; Debray, *Ann. Chim. Phys.*, 1855, [3], **44**, 5; Klatzo, *Bull. Soc. chim.*, 1869, [2], **12**, 131.

[19] Pollok, *Trans. Chem. Soc.*, 1904, **85**, 603.

[20] Mieleitner and Steinmetz, *Zeitsch. anorg. Chem.*, 1913, **80**, 71.

The sublimed chloride forms a tetra-ammoniate, $BeCl_2.4NH_3$, with dry ammonia. If the mixture becomes hot the composition of the compound approximates to $BeCl_2.2NH_3$.[1, 2]

Some experimenters have noted an action of beryllium chloride upon glass, but Parsons doubts whether it has any action on Jena or hard potash glass. A thin film of oxide, produced by traces of moisture, might be mistaken for corrosion.[3]

The following thermochemical data have been given for beryllium chloride:—

$$[Be]+(2HCl)=[BeCl_2]+(H_2)+121{\cdot}1\text{ Cal.}$$
$$[Be]+(Cl_2)\quad=[BeCl_2]+155\text{ Cal.}$$
$$[BeCl_2]+Aq.\ =BeCl_2.Aq.+44{\cdot}5\text{ Cal.}^4$$

Beryllium Bromide.—Beryllium bromide, $BeBr_2$, closely resembles the chloride. It forms white crystals which melt at about 490° C., and begins to volatilise below its melting-point. By distillation in a current of carbon dioxide it is obtained quite pure.[5] Its vapour density agrees with the formula $BeBr_2$.[6] Water attacks it violently with evolution of hydrogen bromide.[7]

It is easily obtained in solution by dissolving beryllium oxide or hydroxide in hydrobromic acid. Anhydrous beryllium bromide has been prepared by the action of bromine or hydrogen bromide on the metal,[5, 6, 8] by the action of bromine on beryllium carbide,[5] and by passing bromine over a heated mixture of beryllium oxide and carbon.[5]

Beryllium Iodide.—Beryllium iodide, BeI_2, which is very similar to the chloride, occurs in colourless crystals which melt at about 510° C., boil between 585° C. and 595° C., and sublime very perceptibly below their melting-point. Like the chloride and bromide it forms compounds with ammonia, organic bases, and ether. It is insoluble in most organic solvents except alcohol. It can be sublimed in a current of dry carbon dioxide, hydrogen, or nitrogen. Water reacts violently with it, with the evolution of hydrogen iodide.[9] This sensitiveness to water makes beryllium iodide very unstable in moist air, and the salt is, in general, very reactive towards chemical reagents; oxygen or air, for example, readily decompose it, and it takes fire when heated to near redness in oxygen.

Beryllium iodide was first prepared by acting on beryllium with iodine;[10] but our accurate knowledge of it is largely due to Lebeau, who prepared it in considerable quantity by heating beryllium carbide to about 700° C. in a current of hydrogen iodide containing iodine vapour.[11, 12]

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[1] Mieleitner and Steinmetz, *Zeitsch. anorg. Chem.*, 1913, 80, 71.
[2] Ephraim, *Ber.*, 1912, 45, i, 1322.
[3] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721.
[4] Pollok, *Trans. Chem. Soc.*, 1904, 85, 603.
[5] Lebeau, *Ann. Chim. Phys.*, 1899, [7], 16, 457.
[6] Humpidge, *Proc. Roy. Soc.*, 1885, 39, 1.
[7] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721.
[8] Wöhler, *Pogg. Annalen*, 1828, 13, 577.
[9] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721.
[10] Wöhler, *loc. cit.*; Debray, *Ann. Chim. Phys.*, 1855, [3], 44, 5.
[11] Lebeau, *Compt. rend.*, 1898, 126, 1272.
[12] Lebeau, *Ann. Chim. Phys.*, 1899, [7], 16, 457.

Double Halides of Beryllium.—The following double halides have been described: $NaF.BeF_2$, $2NaF.BeF_2$,[1, 2, 3] $KF.BeF_2$,[1, 3] $2KF.BeF_2$,[1, 3, 4, 5] $2NH_4F.BeF_2$,[1, 3, 6] $BeCl_2.AuCl_3$, $BeCl_2.2AuCl_3$,[7] $2BeCl_2.3HgCl_2.6H_2O$,[8] $3BeCl_2.Tl_2Cl_6$,[9] $BeCl_2.CrCl_3.H_2O$,[9] $BeCl_2.FeCl_3.H_2O$,[9] $BeCl_2.PdCl_2.6H_2O$,[10] $BeCl_2.PdCl_4.8H_2O$,[11] $BeCl_2.PtCl_2.5H_2O$,[12] $BeCl_2.PtCl_4.8H_2O$,[13] $Be_2I_6.3PbI_2.10H_2O$.[14]

Beryllium Oxyhalides.—The perchlorate, $BeClO_4.4H_2O$, seems to be the only oxyhalide definitely known. Atterberg mentions the decomposition of the chlorate on evaporating its solution.[8] He describes the perchlorate as needle-shaped, deliquescent crystals, with 4 molecules of water of crystallisation.[7] Marignac says it is very deliquescent, and only crystallises on concentrating its solution to a thick syrup.[1] It is prepared by dissolving beryllium hydroxide in excess of perchloric acid and concentrating the solution.

Atterberg refers to a "gummy mass" of beryllium iodate [8] and to a periodate, $3BeO.I_2O_7+11$ or $13H_2O$, which is nearly insoluble in pure water.[7]

BERYLLIUM AND OXYGEN.

Beryllium Oxide, BeO, obtained by heating the hydroxide, is a white powder which is very refractory and, like alumina, becomes difficultly soluble in acids by heating to redness. It can also be obtained by heating any beryllium salt containing a volatile acid. Concentrated nitric or hydrochloric acid only dissolves it slowly, but concentrated sulphuric acid readily converts it into the anhydrous sulphate. It is reducible by carbon in the electric furnace, and at a lower temperature if copper is present. Fluorine vigorously converts it into the fluoride.[15] It melts at 2450°±56° C., and is very volatile near its melting-point.[16]

When beryllia fuses and volatilises in the electric furnace it cools to hexagonal crystals that are slightly harder than corundum [15] and are isomorphous with zinc oxide.[17] It can also be crystallised from fused alkali silicates.[18] At 4° C. its density is about 3; [19, 20] between 0° C. and 100° C., its specific heat is 0·247, and it is diamagnetic.[19]

Parsons refers to a "light and feathery" oxide of beryllium which he obtained by heating a dry mixture of beryllium and ammonium chlorides.[20] Beryllia obtained by strongly igniting the hydroxide is distinctly hygroscopic.[1] In high *vacuo* beryllia gives a blue fluorescence.[2]

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[1] Marignac, *Ann. Chim. Phys.*, 1873, [4], 30, 45.
[2] Lebeau, *Compt. rend.*, 1898, 126, 744.
[3] Lebeau, *Ann. Chim. Phys.*, 1899, [7], 16, 457.
[4] Awdejew, *Pogg. Annalen*, 1842, 56, 100.
[5] Biltz, *Zeitsch. anorg. Chem.*, 1913, 82, 438.
[6] Helmolt, *ibid.*, 1893, 3, 115.
[7] Atterberg, *Ber.*, 1874, 7, 472.
[8] Atterberg, *Bull. Soc. chim.*, 1873, 19, 497.
[9] Neumann, *Annalen*, 1888, 244, 335.
[10] Welkow, *Ber.*, 1874, 7, 803.
[11] Welkow, *ibid.*, 38.
[12] Nilson, *J. prakt. Chem.*, 1876, 16, 264.
[13] Welkow, *Ber.*, 1873, 6, 1288.
[14] Mosmier, *Ann. Chim. Phys.*, 1897, [7], 12, 415.
[15] Lebeau, *ibid.*, 1899, [7], 16, 457.
[16] Fichter and Brunner, *Zeitsch. anorg. Chem.*, 1915, 93, 84.
[17] Mallard, *Zeitsch. Kryst. Min.*, 1887, 14, 605; 15, 650.
[18] Ebelmen, *Compt. rend.*, 1851, 33, 526.
[19] Nilson and Pettersson, *Ber.*, 1880, 13, 1459 (density of BeO=3·01).
[20] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721 (density of BeO=2·9640).

Parsons [3] was unable to obtain the blue oxide from the ignition of the hexahydrated sulphate reported by Levi-Malvano.[4]

Beryllium Hydroxide, $Be(OH)_2$, is precipitated as a white gelatinous precipitate from dissolved beryllium salts by ammonia, ammonium sulphide, or caustic alkalies. It dissolves in ammonium carbonate or excess of alkali solution, and separates from any of these solutions on boiling. Vauquelin first observed, during an examination of the emerald, that the earth deposited from a boiling potassium hydroxide solution was not alumina. The similarities between the hydroxides of aluminium and beryllium had prevented their distinction, and still make it difficult to identify, isolate, or estimate beryllia. Vauquelin noted a number of differences between beryllia and alumina, and realised that the former was more basic.[5] The properties established for beryllium and its compounds indicate quite clearly that it is more basic than aluminium and less basic than magnesium.[6] Beryllium hydroxide is amphoteric; its acid properties are slightly stronger than those of zinc, but are very weak.[7]

The carbonates of the alkalies precipitate a product containing some carbon dioxide. Boiling expels the carbon dioxide, but the precipitate usually occludes about 2 per cent. of alkali. Beryllium hydroxide dissolves readily in dilute acids and caustic alkalies, slowly in concentrated solutions of sodium bicarbonate or ammonium carbonate, and immediately in a saturated, boiling solution of the bicarbonate.[8] Dilution precipitates it from its solution in alkalies—slowly in the cold, rapidly at 100° C. When washed with cold water it goes slowly into colloidal solution; washing with ammonium acetate solution prevents this.[1]

Beryllium hydroxide is more reactive when freshly precipitated than after standing or heating in contact with water,[9] and it seems to lose its colloidal character rapidly after being precipitated.[10] Three forms of beryllium hydroxide have been described;[11] and when precipitated from boiling dilute alkali hydroxide solutions it is granular, perhaps crystalline, and not adsorbent.[12]

The following heats of reaction of the hydroxide with dilute acids have been obtained:—

$$[Be(OH)_2]+H_2SO_4.Aq.=BeSO_4.Aq.+16{\cdot}1\ Cal.^{13}$$
$$[Be(OH)_2]+2HCl.Aq.=BeCl_2.Aq.+13{\cdot}64\ Cal.^{13}$$
$$[Be(OH)_2]+2HF.Aq.=BeF_2.Aq.+19{\cdot}683\ Cal.^{14}$$

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[1] Parsons and Barnes, *J. Amer. Chem. Soc.*, 1906, **28**, 1589.

[2] Crookes, *Ann. Chim. Phys.*, 1881, [5], **23**, 555.

[3] Parsons, *The Chemistry and Literature of Beryllium* (The Chemical Publishing Co., Easton, Pa.; Williams & Norgate, London), 1909.

[4] Levi-Malvano, *Atti R. Accad. Lincei*, 1905, [5], **14**, ii, 502.

[5] Vauquelin, *Ann. Chim.*, 1798, [1], **26**, 155, 170, 259.

[6] Ley, *Zeitsch. physikal. Chem.*, 1899, **30**, 218.

[7] Hantzsch, *Zeitsch. anorg. Chem.*, 1902, **30**, 289.

[8] Parsons and Barnes, *Science*, 1906, **24**, 240.

[9] Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1904, **38**, 377.

[10] Bleyer and Muller, *Arch. Pharm.*, 1913, **251**, 304.

[11] Bleyer and Kaufman, *Zeitsch. anorg. Chem.*, 1913, **82**, 71; Brinton, *J. Amer. Chem Soc.*, 1916, **38**, 2361.

[12] Britton, *Analyst*, 1919, **46**, 437.

[13] Thomsen, *Pogg. Annalen*, 1871, **143**, 488.

[14] Peterson, *Zeitsch. physikal. Chem.*, 1890, **5**, 259.

Potassium Beryllate.—Potassium beryllate, $Be(OK)_2$, has been described as a snow-white mass with a silky lustre. It was prepared by dissolving beryllia in aqueous or alcoholic potassium hydroxide, but contained some potassium carbonate. It is very hygroscopic and easily hydrolysed by water. There is a similar compound with sodium.[1]

Beryllium Peroxide.—The basic peroxide $2BeO_2.3BeO+8\frac{1}{2}H_2O$ has been prepared by acting on a basic beryllium carbonate with hydrogen peroxide. It has all the usual properties of peroxides, and is moderately stable.[2]

BERYLLIUM AND SULPHUR.

Beryllium Sulphide is a white amorphous solid. It can be prepared by heating the anhydrous chloride with sulphur or hydrogen sulphide. It is also obtained when beryllium carbide is heated at a high temperature with sulphur.[3, 4]

Wöhler said it dissolved with difficulty in water, without disengaging hydrogen sulphide.[5] Lebeau said it was decomposed by water,[3] but Mieleitner and Steinmetz found that even boiling water only decomposed it slightly, though acids, including carbonic acid, acted on it readily.[4] In contact with concentrated nitric acid it burns brightly and sulphur separates.[4]

Crude beryllium sulphide, prepared from the metal and sulphur vapour,[5] is strongly phosphorescent.[6]

Beryllium Sulphate.—Beryllium oxide dissolves in hot concentrated sulphuric acid, and anhydrous beryllium sulphate remains after driving off the excess of acid.[3] According to Taboury, the anhydrous sulphate is stable up to 530°-540° C., and can be used for estimating beryllium.[7] Beryllium sulphate requires strong, continuous heating to convert it into beryllium oxide.[8] It is unchanged in dry air, and requires prolonged contact, or boiling, with water to dissolve it. The *tetrahydrate*, $BeSO_4.4H_2O$, crystallises out when the concentrated solution is poured into 95 per cent. alcohol; it can be recrystallised from dilute alcohol or water.[3, 9, 10] Beryllium sulphate has been recently prepared by treating a concentrated solution of the nitrate with sulphuric acid, pouring into alcohol, washing the crystals free from acid and recrystallising.[8]

The tetrahydrate forms tetragonal tetrahedra which are doubly refracting, negative, uniaxial, and have a density of 1·713 [11] or 1·7125.[12] It dissolves in its own weight of water and is insoluble in alcohol. Its aqueous solution is strongly acid, and, when concentrated, dissolves zinc with the evolution of hydrogen. The aqueous solution is sweet as well as acid, and comparison of sulphate with chloride solutions shows that sweetness depends on cation concentration.[1] $N/_4$ to $N/_{10}$ solutions hydrolyse from 0·52–0·68 per cent.[2] Its heat of solution is 85·603 Cal.[3]

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[1] Krüss and Moraht, *Ber.*, 1890, 23, 727.

[2] Kornarovoski, *J. Russ. Phys. Chem. Soc.*, 1913, 45, 608.

[3] Lebeau, *Ann. Chim. Phys.*, 1899, [7], 16, 457.

[4] Mieleitner and Steinmetz, *Zeitsch. anorg. Chem.*, 1913, 82, 92.

[5] Wöhler, *Ann. Chim. Phys.*, 1828, 39, 77.

[6] Biltz, *Zeitsch. anorg. Chem.*, 1913, 82, 438.

[7] Taboury, *Compt. rend.*, 1913, 159, 180.

[8] Britton and Allmand, *Trans. Chem. Soc.*, 1921, 119, 1463.

[9] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 1433.

[10] Britton, *Analyst*, 1919, 46, 359.

[11] Topsöe, *Chem. Zentr.*, 1873, 76; Topsöe and Christiansen, *Ann. Chim. Phys.*, 1874, [5], 1, 5; Wulff, *Zeitsch. Kryst. Min.*, 1890, 17, 592.

[12] Krüss and Moraht, *Annalen*, 1891, 262, 38.

Powdered beryllium sulphate tetrahydrate is stable in air if the aqueous vapour pressure is not less than the pressure of its own water of crystallisation. It slowly loses water over phosphorous pentoxide,[4] and, on heating to 100° C., readily converts into the *dihydrate*, $BeSO_4.2H_2O$.[5] This dihydrate resembles the tetrahydrate in appearance and properties, is stable in dry air at ordinary temperatures, but slowly and continuously loses water if the temperature is raised to between 100° C. and 110° C.[6] According to Levi-Malvano it melts at 158° C., loses 1 molecule of water, and forms the *monohydrate*.[7] Taboury confirmed the mono- and di-hydrates, and suggested the possibility of obtaining a *hemihydrate* at 150°–160° C.[8]

Marignac obtained a *hexahydrate*, and Levi-Malvano also prepared it from a supersaturated solution of the sulphate.[7, 9] Levi-Malvano thought, on the evidence of its cryohydrate, that no higher hydrate can exist.[7]

Parsons could discover no evidence for Klatzo's *heptahydrate*.[6]

Many basic sulphates of beryllium have been described, but they are, apparently, solid solutions of the sulphate in the hydroxide, and not definite compounds.[6]

Double Sulphates of Beryllium.—Beryllium forms no alum, and this fact intimates a difference between beryllium and aluminium which was considered by many to indicate that beryllium, like magnesium, is divalent.[10]

The double sulphate, $K_2SO_4.BeSO_4.2H_2O$, crystallises out at 25° C. from supersaturated solutions containing potassium and beryllium sulphates, if the proportion of the latter in the solute lies between 37·2 and 84·8 per cent.[11] Awdejew, during an attempt to prepare a beryllium alum, discovered this salt in 1842 by a simple evaporation of its constituents in appropriate proportions.[12] The crystals are very small,[11] white,[13] slightly soluble in cold water and much more soluble in hot.[10] Marignac also described them as opaque, hard, and mamillated.[13] Their form has not been determined.[11, 13]

$(NH_4)_2SO_4.BeSO_4.2H_2O$ has been obtained from mixed solutions of beryllium and ammonium sulphates. Atterberg originally concentrated a solution containing molecular proportions of the two sulphates over sulphuric acid. The salt is very deliquescent.[11]

Atterberg reported $BeSO_4.K_2SO_4.2KHSO.4H_2O$ as needle-shaped prisms, and $3BeSO_4.2Na_2SO_4.12H_2O$ as needle-like crystals which radiated in star-shaped groups. Both salts were prepared by evaporating the constituent salts in mixed solution—the former solution being strongly acid.[1]

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[1] Höber and Kiesow, *Zeitsch. physikal. Chem.*, 1898, 27, 601.
[2] Bruner, *ibid.*, 1900, 32, 133.
[3] Pollok, *Trans. Chem. Soc.*, 1904, 85, 603.
[4] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721.
[5] Atterberg, *Bull. Soc. chim.*, 1873, 19, 497.
[6] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 1433.
[7] Levi-Malvano, *Atti R. Accad. Lincei*, [5], 14, ii, 502.
[8] Taboury, *Compt. rend.*, 1913, 159, 180.
[9] Levi-Malvano, *Gazzetta*, 1909, 39, ii, 438.
[10] Debray, *Ann. Chim. Phys.*, 1855, [3], 44, 5.
[11] Britton and Allmand, *Trans. Chem. Soc.*, 1921, 119, 1463.
[12] Awdejew, *Pogg. Annalen*, 1842, 56, 100.
[13] Marignac, *Ann. Chim. Phys.*, 1873, [4], 30, 45.

Beryllium Sulphite, $BeSO_3$, is obtained as colourless, hexagonal plates when the freshly precipitated hydroxide is added to a saturated alcoholic solution of sulphur dioxide, and the resulting solution evaporated *in vacuo* over sulphuric acid and alkali. It is decomposed by both alcohol and water.

If the hydroxide is dissolved in aqueous sulphurous acid, evaporation leaves a gummy mass of $BeSO_3.BeO$.[2]

Beryllium Thiosulphate, $BeS_2O_3.11H_2O$, is said to result from the action of sodium thiosulphate on beryllium sulphate.[3] Parsons could not confirm it.[4]

BERYLLIUM AND SELENIUM.

Beryllium Selenate, $BeSeO_4.4H_2O$, is isomorphous with the sulphate, prepared similarly to it, and resembles it in properties. Its density is 2·03, and it is converted into the dihydrate at 100° C.[5]

BERYLLIUM AND CHROMIUM.

Glassmann claimed to have obtained the **normal chromate,** $BeCrO_4.H_2O$, in reddish-yellow, monoclinic crystals by dissolving the carbonate in concentrated chromic acid, and the **yellow basic chromate,** $BeCrO_4.6Be(OH)_2$, by decomposing this with water.[6] Bleyer and Moorman [7] failed to obtain them, though solutions were obtained containing Be and Cr in the ratio 1 : 1. They state that $15BeO.CrO_3.12H_2O$ is precipitated by potassium chromate from solutions of beryllium chloride, however the proportions of these are varied.

Mallard describes **beryllium chromite,** $BeO.Cr_2O_3$, as a deep green powder crystallising like alexandrite. It was prepared by fusing chromic oxide with beryllia and boric anhydride.[8]

BERYLLIUM AND MOLYBDENUM.

Atterberg boiled beryllium hydroxide with molybdic acid and obtained $BeMoO_4.Be(OH)_2.2H_2O$ in fine, almost insoluble needles.[9]

Rosenheim and Woge, by a similar method, obtained the **normal molybdate,** $BeMoO_4.2H_2O$, as an oily liquid which solidified into slender needles. They also described some complex molybdates containing beryllium.[10]

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[1] Atterberg, *Bull. Soc. chim.*, 1873, 19, 497.

[2] Joy, *Chem. News*, 1863, 8, 183, 197; Atterberg, *Bull. Soc. chim.*, 1873, 19, 497; Krüss and Moraht, *Ber.*, 1890, 23, 727.

[3] Faktor, *Chem. Zentr.*, 1901, [2], 878.

[4] Parsons, *The Chemistry and Literature of Beryllium* (Williams & Norgate, London, The Chemical Publishing Co., Easton, Pa.), 1909.

[5] Atterberg, *Bull. Soc. chim.*, 1873, 19, 497; Topsöe and Christiansen, *Ann. Chim. Phys.*, 1874, [5], 1, 5; Roozeboom, *Zeitsch. physikal. Chem.*, 1891, 8, 504.

[6] Glassmann, *Ber.*, 1907, 40, 2602.

[7] Bleyer and Moorman, *Zeitsch. anorg. Chem.*, 1912, 76, 70.

[8] Mallard, *Compt. rend.*, 1887, 105, 1260.

[9] Atterberg, *Bull. Soc. chim.*, 1873, 19, 497.

[10] Rosenheim and Woge, *Zeitsch. anorg. Chem.*, 1897, 15, 283.

BERYLLIUM AND NITROGEN.

Beryllium Nitride, Be_3N_2, is similar chemically to aluminium nitride. The amorphous powder obtained by heating the metal in nitrogen above 900° C., fuses at 2200° C. under atmospheric pressure, and solidifies to colourless crystals which scratch glass. It dissociates at 2400° C., is stable in air, slowly decomposed by boiling water, and decomposed more readily than aluminium nitride by dilute acids and hot concentrated alkali hydroxides. Ammonia and beryllium hydroxide result from these reactions.

Heating in ammonia secures a more complete conversion to nitride than heating in nitrogen. A mixture of beryllia and carbon also yields the nitride at 1900° C. in nitrogen: beryllium carbide reacts with nitrogen at 1250° C., or with ammonia at 950°–1000° C. –

$$3Be_2C + 2N_2 = 2Be_3N_2 + 3C.^{1}$$

The direct action of cyanogen on metallic beryllium at 800° C. also produces the nitride.[2]

Beryllium Azide, $Be(N_3)_2$, appears to be formed when an aqueous solution of beryllium sulphate is treated with barium azide, but it is easily decomposed by water.[3]

Beryllium Nitrate, $Be(NO_3)_2.4H_2O$, was the second salt of beryllium prepared by Vauquelin, who used it as one means of distinguishing between the new earth and alumina. He discovered that it was very deliquescent, and had a sweet taste followed by astringency.[4] It forms a crystalline, deliquescent mass, which melts in its water at 60·5° C. It is only stable in contact with nitric acid or its vapour, since it readily loses oxides of nitrogen. It is most easily prepared by saturating nitric acid with beryllium carbonate, evaporating, and adding concentrated nitric acid. It is soluble in alcohol and acetone, and can be recrystallised from concentrated nitric acid.[5]

Since aluminium nitrate is insoluble in amyl alcohol, beryllium nitrate can be freed from it by this solvent.[6]

Small quantities of beryllium nitrate are often used in solutions for impregnating incandescent mantles.[7]

BERYLLIUM AND THE PHOSPHORUS GROUP.

Beryllium Phosphates, Phosphite, and Hypophosphite.—Monoberyllium orthophosphate, $BeH_4(PO_4)_2$, is similar to the corresponding arsenate. Triberyllium orthophosphate, $Be_3P_2O_8.6H_2O$, is precipitated from beryllium sulphate by disodium phosphate in the presence of acetic acid. Sodium pyrophosphate precipitates beryllium pyrophosphate, $Be_2P_2O_7.9H_2O$, from solutions of beryllium salts. Colourless crystals of beryllium metaphosphate, $Be(PO_3)_2$, can be prepared if water is absent.[8]

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[1] Fichter and Brunner, *Zeitsch. anorg. Chem.*, 1912, 93, 84.

[2] Vournasos, *Bull. Soc. chim.*, 1917, [4], 21, 282.

[3] Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 292.

[4] Vauquelin, *Ann. Chim.*, 1798, [1], 26, 155, 170, 259.

[5] Ordway, *Amer. J. Sci.*, 1858, [2], 26, 197; Parsons, *Science*, 1906, 25, 402.

[6] Browning and Kuzirian, *Internat. Cong. App. Chem.*, 1912, 1, 87.

[7] Martin, *Industrial and Manufacturing Chemistry* (*Inorganic*) (Crosby, Lockwood & Son), 1917, ii, 307–8.

[8] Mallard, *Zeitsch. Kryst. Min.*, 1887, 14, 605.

Ouvrard obtained some double phosphates of beryllium with alkali metals.[1]

Beryllium phosphite (basic), $4BeHPO_3.BeO.7H_2O$, and hypophosphite, $BeH_4P_2O_4$, have been prepared.[2]

Beryllium Hypophosphate.—Sodium hypophosphate is said to precipitate beryllium hypophosphate, $2BePO_3.3H_2O$, from hot solutions of beryllium sulphate.[1]

Beryllium Arsenates.—Monoberyllium arsenate, $BeH_4(AsO_4)_2$, is obtained as colourless, hygroscopic leaflets after preparation in concentrated solution and evaporation *in vacuo*. Triberyllium arsenate, $Be_3(AsO_4)_2.15H_2O$, has been prepared from arsenic oxide and beryllium hydroxide as an amorphous powder. Other arsenates and double arsenates with alkali metals are unstable.[3]

Beryllium Arsenite.—Definite compounds of beryllium with arsenious acid cannot be prepared.[4]

Beryllium Antimonate, $Be(SbO_3)_2.6H_2O$, was prepared by adding a soluble salt of beryllium to a hot solution of sodium metantimonate.[5]

Beryllium Vanadates.—Beryllium metavanadate, $Be(VO_3)_2.4H_2O$, is obtained as yellow crystals by boiling equimolecular quantities of beryllium hydroxide and vanadium pentoxide with water, filtering, concentrating, and pouring into a large volume of 95 per cent. alcohol. It dissolves readily in hot water and in pyridine. One thousand parts of cold water dissolve 1 part of it, and it is practically insoluble in chloroform, ether, and absolute alcohol. It crystallises in cubes modified by octahedra.

No other definite vanadates have been prepared.[6]

Beryllium Columbate. By fusing the precipitate from beryllium chloride and potassium columbate with boric anhydride, Larsson obtained a crystalline product containing 6·24 per cent. BeO and 89·60 per cent. Cb_2O_5.[7]

BERYLLIUM AND CARBON.

Beryllium Carbide, Be_2C, was described by Lebeau as transparent, yellowish-brown, microscopic crystals which scratch quartz and have a density of 1·9 at 15° C. He prepared it by heating beryllia and carbon in an electric furnace. This compound is attacked in the heat by chlorine, bromine, hydrogen fluoride, hydrogen chloride, concentrated sulphuric acid, fused potassium hydroxide, potassium permanganate, lead peroxide, slowly by concentrated nitric and hydrochloric acids, and superficially by oxygen. Contact with water or dilute acids slowly liberates methane.

Lebeau originally assigned to it the formula Be_4C_3, emphasised its similarity to aluminium carbide, and noted that it pointed to an atomic weight of 13·8 for beryllium.[8] Henry's formula, Be_2C,[9] is now accepted.

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[1] Ouvrard, *Compt. rend.*, 1890, 110, 1333.
[2] Bleyer and Muller, *Zeitsch. anorg. Chem.*, 1913, 79, 263.
[3] Bleyer and Muller, *ibid.*, 1912, 75, 285.
[4] Bleyer and Muller, *Arch. Pharm.*, 1913, 251, 304.
[5] Ebel, *Ber.*, 1889, 22, 3044.
[6] Brinton, *J. Amer. Chem. Soc.*, 1916, 38, 2361.
[7] Larsson, *Zeitsch. anorg. Chem.*, 1896, 12, 188.
[8] Lebeau, *Compt. rend.*, 1895, 121, 496.
[9] Henry, *ibid.*, 1895, 121, 600.

It reacts with nitrogen at 1250° C. and with ammonia at about 1000° C.—

$$3Be_2C+2N_2=2Be_3N_2+3C.^{1}$$

Beryllium Borocarbide.—Lebeau described a compound, $C_4B_6Be_6$, obtained by heating beryllia and boron in a carbon crucible in the electric furnace. It forms crystals with a metallic lustre, which have a density of 2·4 and dissolve readily in mineral acids. It oxidises superficially at a red heat, and burns in chlorine at about 450° C.[2]

Beryllium Carbonate.—Indefinite basic carbonates of beryllium are precipitated from boiling solutions of the hydroxide in alkali carbonates. When the precipitate from boiling ammonium carbonate solution is kept over sulphuric acid, it tends to the composition $BeCO_3.3Be(OH)_2.2H_2O$.[3] The basic carbonates, though they are probably very indefinite in composition, are useful for preparing other compounds of beryllium.[4] It is said that if a current of carbon dioxide is passed through a basic carbonate, suspended in water, and the solution evaporated in an atmosphere of carbon dioxide, crystals of normal beryllium carbonate, $BeCO_3.4H_4O$, separate out. This salt is also said to become anhydrous at 100° C., and to lose carbon dioxide at higher temperatures.[5] The existence of a definite carbonate of beryllium is, however, very doubtful.[6]

Sestini found that beryllia dissolved in water charged with carbon dioxide at ordinary pressures, and ascribed its solubility to the formation of beryllium hydrogen carbonate.[7]

A double carbonate of beryllium and potassium is said to crystallise out when beryllium hydroxide is digested with potassium carbonate solution and treated with alcohol.[8]

Basic Beryllium Acetate, $3Be(C_2H_3O_2)_2.BeO$, is too important for the isolation and purification of beryllium to be unnoticed.[9] Its composition and vapour density also favour a divalent beryllium with an atomic weight of about 9, and it is specially suitable for the accurate determination of the latter.

Urbain and Lacombe, in 1901, obtained it in small octahedral crystals by evaporating down a solution of beryllium hydroxide in dilute acetic acid, dissolving the residue in boiling anhydrous acetic acid and cooling.[10] Parsons dissolved basic beryllium carbonate in glacial acetic acid, boiled off the excess of acid, and obtained the same crystals by cooling a solution of the residue in boiling glacial acetic acid.[3]

It melts to a clear liquid at 283°–284° C., and boils without decomposition at 330°–331° C. Since the vapour can be heated to 360° C. in

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[1] Fichter and Brunner, *Zeitsch. anorg. Chem.*, 1915, 93, 84.

[2] Lebeau, *Compt. rend.*, 1898, 126, 1347.

[3] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721.

[4] Parsons and Robinson, *ibid.*, 1906, 28, 555.

[5] Weeren, *Pogg. Annalen*, 1853, 92, 101; Joy, *Amer. J. Sci.*, 1863, [2], 36, 83.

[6] Cameron and Robinson, *J. Physical Chem.*, 1908, 12, 562; Parsons, *The Chemistry and Literature of Beryllium* (The Chemical Publishing Co., Easton, Pa.; Williams & Norgate, London), 1909.

[7] Sestini, *Gazzetta*, 1890, 20, 313.

[8] Debray, *Ann. Chim. Phys.*, 1855, [3], 44, 5.

[9] Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1904, 40, 465.

[10] Urbain and Lacombe, *Compt. rend.*, 1901, 133, 874.

the presence of air without any alteration, its vapour density can be readily determined.

Its density, referred to water at 4° C., is 1·362. It is readily soluble in chloroform and other organic solvents, though only slightly so in alcohol or ether. Water hydrolyses it: slowly in the cold, rapidly when hot. It becomes soluble after complete hydrolysis. Dry air has no action upon it. Ordinary acids free acetic acid from it. The water they contain is probably the agent of their action, for it is remarkable that, though it is a basic compound, its solution in glacial acetic acid is unchanged by saturation with hydrogen chloride.[1]

By heating in a sealed tube at 150° C. with glacial acetic acid and acetic anhydride, the basic acetate is converted into the normal acetate. When the normal acetate is heated above 300° C. it melts with decomposition and the basic acetate sublimes.[2]

The corresponding basic formate, basic propionate, basic isobutyrate, basic butyrate, and basic isovalerate are also well defined and relatively stable.[3, 4, 5]

Tanatar assigned the general formula Be_2OR_6 (instead of Be_4OR_6) to the above salts—ascribing tetravalency to beryllium.[5]

Beryllium Oxalates.—*Beryllium oxalate trihydrate*, $BeC_2O_4.3H_2O$, can be prepared by dissolving basic beryllium carbonate in rather more than an equivalent amount of oxalic acid. On crystallising, oxalic acid crystals separate first, then crystals of beryllium oxalate. Even after nine recrystallisations the latter contain occluded oxalic acid. In the sufficiently recrystallised product the neutralisation of the occluded acid by exactly enough basic beryllium carbonate produces the pure normal oxalate. It crystallises in orthorhombic crystals, is stable at room temperature, very soluble in water, acid in reaction, sharp and sweet in taste, and readily decomposed by heat.[6] 100 c.c. water at 25° C. dissolve 63·2 grm.; oxalic acid dissolves it more readily.[7]

At 100°–105° C. the trihydrate passes into the monohydrate, which is stable in dry air. It loses water slowly above 105° C. and rapidly towards 220° C. Decomposition begins near the latter temperature, and at 350° C. the salt is completely converted into the oxide.

Other oxalates, basic and acid, which have been described, apparently do not exist.[6]

Beryllium Cyanide.—When cyanogen decomposes beryllium iodide below a red heat, a white, less volatile substance is produced which dissolves in water. The solution has the properties of a cyanide solution.[8]

Beryllium Platinocyanide, $BePtCy_4$, is obtained as a golden product by decomposing barium platinocyanide with beryllium sulphate and purifying with alcohol and ether. It goes orange at 30° C.

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[1] Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721.

[2] Steinmetz, *Zeitsch. anorg. Chem.*, 1907, 54, 217.

[3] Urbain and Lacombe, *Compt. rend.*, 1901, 133, 874.

[4] Lacombe, *ibid.*, 1902, 134, 772.

[5] Tanatar, *Ber.*, 1910, 43, 1230.

[6] Parsons and Robinson, *J. Amer. Chem. Soc.*, 1906, 28, 555.

[7] Wirth, *Zeitsch. anorg. Chem.*, 1914, 87, 7.

[8] Lebeau, *Compt. rend.*, 1898, 126, 1272.

and red or green at higher temperatures. Below 30° C. it contains water.

The compound $BeMg_2Pt_3Cy_{12}+16H_2O$ was also obtained.[1]

BERYLLIUM AND SILICON.

Beryllium Silicates.—Williams prepared *beryl*, $Be_3Al_2(SiO_3)_6$, artificially in 1873.[2] In 1894 Traube precipitated a solution containing 3 molecules of beryllium sulphate and 1 molecule of aluminium sulphate with sodium silicate. The precipitate was transformed into beryl by heating for three days at 1700° C. with one quarter of its weight of boric anhydride.[3]

Hautefille and Perrey obtained *emerald*, which has the same composition as beryl, by heating a mixture of silica, alumina, beryllia, and lithium hydrogen molybdate. At temperatures above 800° C. emerald is converted into *phenacite*, Be_2SiO_4. They also obtained phenacite by heating a mixture of silica, beryllia, lithium vanadate, and lithium carbonate.[4]

Stein obtained an orthosilicate, Be_2SiO_4, and a metasilicate, $BeSiO_3$, by fusing beryllia and silica in proper proportions.[5]

Duboin prepared some complex silicates containing beryllia and potassium oxide.[6]

Beryllium Silicotungstate, $Be_4(W_{12}SiO_{40})_3$, is said to crystallise below 45° C. as a cubic hydrate containing $93H_2O$, above 45° C. as a rhombohedral hydrate containing $87H_2O$, and as a hydrate with $45H_2O$ in presence of nitric acid at 30° C.[7]

BERYLLIUM AND BORON.

Beryllium Borate.—Krüss and Moraht described a borate, $5BeO.B_2O_3$, resembling beryllia in appearance, which they prepared by precipitating beryllium chloride with borax, or by neutralising it in presence of much boric acid with sodium carbonate.[8] It is probably a solid solution of boric acid in beryllium hydroxide.[9]

BERYLLIUM AND ALUMINIUM.

Beryllium Aluminate.—Ebelmen prepared artificial *cymophane* (chrysoberyl), $Be(AlO_2)_2$, by fusing the constituent oxides with boric anhydride and calcium carbonate.[10]

Crystals indistinguishable from cymophane result from the solution of alumina and beryllia in fused alkaline sulphides. Hautefeuille and Perrey used a mixture of alumina, beryllia, potassium sulphate, and carbon.[11]

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[1] Toczynski, *Zeitsch. Chem.*, 1871, [2], 7, 275.

[2] Williams, *Phil. Mag.*, 1873, [4], 46, 314.

[3] Traube, *Jahrb. Min.*, 1894, I, Mem., 275.

[4] Hautefille and Perrey, *Compt. rend.*, 1888, 106, 1800; *Ann. Chim. Phys.*, 1890, [6], 20, 447.

[5] Stein, *Zeitsch. anorg. Chem.*, 1907, 55, 159.

[6] Duboin, *Compt. rend.*, 1896, 123, 698.

[7] Wyrouboff, *Bull. Soc. franç. Min.*, 1896, 19, 219.

[8] Krüss and Moraht, *Ber.*, 1890, 23, 727.

[9] Bleyer and Paczuski, *Kolloid Zeitsch.*, 1914, 14, 295.

[10] Ebelmen, *Ann. Chim. Phys.*, 1851, [3], 33, 34.

[11] Hautefille and Perrey, *Compt. rend.*, 1888, 106, 487.

DETECTION AND ESTIMATION.

Beryllium is detected and estimated through its precipitation as hydroxide. A systematic procedure for detecting beryllium in the presence of other elements has been tabulated by Noyes, Bray, and Spear.[1] Parsons and Barnes also gave a useful summary of the methods, as used up to 1906, for estimating beryllium,[2] and Britton gave another summary in 1921.[3]

In the usual schemes of analysis, beryllium hydroxide is precipitated when ammonia is added to precipitate Group IIIA. Beryllium and ferric hydroxides are easily and completely separated by wet treatment with sodium peroxide: ferric hydroxide remains undissolved, and beryllium hydroxide dissolves as sodium beryllate, Na_2BeO_2.[1] The separation of beryllium and aluminium hydroxides is a serious difficulty which has greatly influenced the history and fortunes of beryllium. Since beryllium is easily separated by ordinary methods, both qualitatively and quantitatively, from all elements except aluminium, its analytical discussion centres on its separation from co-precipitated beryllium and aluminium hydroxides.[2]

The traditional method of dissolving out the beryllium hydroxide from the aluminium hydroxide with concentrated ammonium carbonate is untrustworthy.[4] The deposition of beryllium hydroxide by boiling the suitably diluted solution of the two hydroxides in potassium or sodium hydroxide has been used, following Vauquelin's original method,[5] up to recent times for separating aluminium from beryllium.[4] But this method is apparently too inaccurate to be applicable quantitatively.[2] Britton, however, has obtained good results by concentrating the solution containing aluminium and beryllium, treating with just enough sodium hydroxide to redissolve the precipitate, boiling at considerable dilution, and immediate filtration.[3]

Wunder and Wenger fused the mixed oxides of aluminium and beryllium with sodium carbonate, and precipitated the alumina by boiling with excess of ammonium nitrate.[6]

Beryllium hydroxide can be separated quantitatively from aluminium (and ferric) hydroxide by its solubility in a hot 10 per cent. solution of sodium hydrogen carbonate. The hydroxides are dissolved in hydrochloric acid, and the boiling hot mixture of the chlorides added to a nearly boiling solution of sodium hydrogen carbonate containing enough reagent to make the mixed liquid an approximately 10 per cent. solution. Less beryllium is mechanically retained in the precipitated aluminium hydroxide by this method than by adding solid sodium hydrogen carbonate to the solution of the chlorides after nearly neutralising with ammonia and then boiling. The precipitated aluminium hydroxide should be redissolved and the separation repeated. The beryllium in the filtrate from the double precipitation can be precipitated as hydroxide by ammonia and ignited to the oxide.[2]

If concentrated solutions of aluminium and beryllium salts are shaken with ethylamine, all the aluminium passes into solution and the beryllium is precipitated.[1]

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[1] Noyes, Bray, and Spear, *J. Amer. Chem. Soc.*, 1908, **30**, 481.
[2] Parsons and Barnes, *ibid.*, 1906, **28**, 1589.
[3] Britton, *Analyst*, 1921, **46**, 359.
[4] Wunder and Chéladzé, *Ann. Chim. anal.*, 1911, **16**, 205.
[5] Vauquelin, *Ann. Chim.*, 1798, **26**, 155, 170, 259.
[6] Wunder and Wenger, *Zeitsch. anal. Chem.*, 1912, **51**, 470.

Beryllium is said to be completely precipitated by ammonia in the cold if ammonium chloride is present, by ammonium sulphide if time is allowed, and by potassium iodide and iodate.[2]

Some effective methods depend upon the separation of beryllium and aluminium in the form of chlorides. The solubility of beryllium chloride and the insolubility of aluminium chloride in concentrated hydrochloric acid and ether allows an effective separation. The mixed hydroxides are dissolved in concentrated hydrochloric acid. This solution is mixed with ether and saturated with hydrogen chloride—keeping down the temperature to about 15° C. After standing, the aluminium is completely precipitated as white crystalline $AlCl_3.6H_2O$. This method is equally effective with all proportions of the two hydroxides.[3, 4, 5, 6] The beryllium can be finally isolated and estimated, if necessary, by precipitation with ammonia or by treatment with nitric acid and ignition.

A mixture of acetone and acetyl chloride dissolves beryllium chloride and leaves aluminium chloride undissolved.[7]

Another very effective route of separation lies through the basic acetate. Haber and van Oordt dissolved the mixed hydroxides in glacial acetic acid and separated the basic beryllium acetate by its solubility in chloroform.[8] Beryllium basic acetate can also be separated from other acetates by its ready solubility in hot glacial acetic acid and comparative insolubility when cold.[5, 9] Kling and Gelin convert iron, aluminium, and beryllium into their basic acetates, and distil off the last under reduced pressure.[10]

Some volumetric methods have been suggested. An acidimetric process depends on the behaviour of beryllium salts as acids towards phenolphthalein. The neutralised solution, which should contain the beryllium as chloride, is titrated with decinormal sodium hydroxide, using phenolphthalein as indicator. Aliquot parts of this are then titrated with decinormal acid, using, in one case, methyl orange as indicator, and, in the other, phenolphthalein. The difference between these two titrations represents beryllium.[11]

In an iodometric process an approximately decinormal solution of the normal salt is heated with potassium iodate and iodide in a current of hydrogen. The liberated iodine is collected in a solution of potassium iodide and titrated with sodium thiosulphate.[11]

Taboury suggests the dehydrated sulphate as a convenient form for estimating beryllium.[12]

Copaux estimates beryllium in beryl by heating the powdered mineral with sodium silicofluoride. Boiling water extracts the soluble sodium beryllium fluoride and leaves the insoluble double fluoride of aluminium, silica, etc. An aliquot part of the aqueous extract is evaporated with excess of sulphuric acid till white fumes appear. The residue is precipitated, after solution, as hydroxide and weighed as oxide. Silica and alumina may contaminate the final residue and require removal by suitable methods.[1]

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[1] Renz, *Ber.*, 1903, 36, 2751.
[2] Bleyer and Boshart, *Zeitsch. anal. Chem.*, 1912, 51, 748.
[3] Havens, *Amer. J. Sci.*, 1897, [4], 3, 111.
[4] Havens, *Zeitsch. anorg. Chem.*, 1898, 16, 15.
[5] Parsons and Barnes, *J. Amer. Chem. Soc.*, 1906, 28, 1589.
[6] Noyes, Bray, and Spear, *ibid.*, 1908, 30, 481.
[7] Minnig, *Amer. J. Sci.*, 1915, [4], 40, 482.
[8] Haber and van Oordt, *Zeitsch. anorg. Chem.*, 1904, 40, 465.
[9] Parsons and Robinson, *J. Amer. Chem. Soc.*, 1906, 28, 555.
[10] Kling and Gelin, *Bull. Soc. chim.*, 1914, [4], 15, 205.
[11] Bleyer and Moorman, *Zeitsch. anal. Chem.*, 1912, 51, 360.
[12] Taboury, *Compt. rend.*, 1913, 159, 180.

Amyl alcohol dissolves beryllium nitrate and does not dissolve aluminium nitrate.[2]

Beryllium hydroxide dissolves colloidally in pure water, and must be washed with water containing an electrolyte—ammonium acetate solution is convenient. Beryllium oxide obtained by igniting the hydroxide is very hygroscopic.[3]

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[1] Copaux, *Compt. rend.*, 1919, **168**, 610.

[2] Browning and Kuzirian, *Inter. Cong. Appl. Chem.*, 1912, **1**, 87.

[3] Parsons and Barnes, *J. Amer. Chem. Soc.*, 1906, **28**, 1589.

CHAPTER III.

MAGNESIUM AND ITS COMPOUNDS.

MAGNESIUM.

Symbol, Mg. Atomic Weight, 24·32 (O=16).

Occurrence.—Meteorites, which are samples of extra-terrestrial origin, often contain combined magnesium. It is, after iron, their most important metallic constituent.[1] Magnesium has been spectroscopically discovered in the sun,[2] and in the earth's crust the number of its atoms has been estimated as 1·67 per cent. of the total of elementary atoms.[3]

Magnesium compounds are widely distributed over the earth. *Magnesium chloride*, $MgCl_2$, and, to a lesser extent, *magnesium bromide*, $MgBr_2$, and *magnesium iodide*, MgI_2, occur in natural waters including sea-water. The slightly soluble *magnesium fluoride*, MgF_2, occurs as the mineral *sellaïte*. Sea-water and most mineral springs contain more salts of magnesium than of calcium, but in river-water calcium salts preponderate.[4] *Magnesium sulphate* is a prevalent magnesium salt in natural water, and *Epsom salts*, $MgSO_4.7H_2O$, derive their name from their occurrence in the famous mineral spring at Epsom. $MgSO_4.7H_2O$ occurs as the mineral *epsomite* or, as it is called when found in the Stassfurt deposits, *reichardtite*.

The Stassfurt deposits had a marine origin, and consist of narrow bands of anhydrous calcium sulphate, interspersed, at fairly regular intervals, through a mass of rock salt. Beds rich in magnesium and potassium salts cap the narrow seams of calcium sulphate. The deposits divide roughly into four regions—

1. *Anhydrite*, $CaSO_4$.
2. *Polyhalite*, $2CaSO_4.MgSO_4.K_2SO_4.2H_2O$, about 60 metres.
3. *Kieserite*, $MgSO_4.H_2O$, about 30 metres.
4. *Carnallite*, $MgCl_2.KCl_4.6H_2O$, about 23 metres.[5]

These deposits are the most important commercial source of magnesium and its salts. They contain also the following salts: *tachhydrite*,

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[1] Farrington, *Meteorites* (Chicago), 1915, p. 114.

[2] Tacchini, *Compt. rend.*, 1876, 82, 1385.

[3] Fersmann, *Bull. Acad. Sci. St. Pétersbourg*, 1912, [vi], 367.

[4] Lubavin, *J. Russ. Phys. Chem. Soc.*, 1892, 24, 389.

[5] Armstrong, *Brit. Assoc. Report*, 1901, 262.

For a discussion of the production of magnesium salts in the Stassfurt and other deposits, see Rózsa, *Zeitsch. Elektrochem.*, 1913, 19, 109, and a series of papers in *Zeitsch. anorg. Chem.*, 1914 to 1919 inclusive.

$CaCl_2.2MgCl_2.12H_2O$, *krugite*, $K_2SO_4.4CaSO_4.MgSO_4.2H_2O$, *bischoffite*, $MgCl_2.6H_2O$, *kainite*, $KCl.MgSO_4.3H_2O$, *schönite* or *picromerite*, $K_2SO_4.MgSO_4.6H_2O$, *leonite*, $K_2SO_4.MgSO_4.4H_2O$, *langbeinite*, $K_2SO_4.2MgSO_4$, *blödite* or *astrakanite*, $Na_2SO_4.MgSO_4.4H_2O$, *loewite*, $Na_2SO_4.MgSO_4.2H_2O$, and *vanthoffite*, $3Na_2SO_4.MgSO_4$.

The double sulphate, $(NH_4)_2SO_4.MgSO_4.6H_2O$, occurs as *boussingaultite*.

Many natural waters contain *magnesium bicarbonate*, $Mg(HCO_3)_2$: normal *carbonates* are represented in many mineral species. $MgCO_3$ occurs as *magnesite*; *breunnerite*, $(Mg,Fe)CO_3$, occurs in meteorites.[1] *Nesquehonite* is $MgCO_3.3H_2O$, and *dolomite*, $(Ca,Mg)CO_3$, is widely distributed. Many mountain ranges consist largely of this important mineral species. *Ankerite* is $(Mg,Fe)CO_3.CaCO_3$.

Basic carbonates occur as *hydromagnesite*, $3MgCO_3.Mg(OH)_2.3H_2O$, *landsfordite*, $4MgO.3CO_2 22H_2O$, and *hydrogioberite*, $[(Mg.OH).CO_3.2H_2O]$.

Northupite is $Na_2CO_3.MgCO_3.NaCl$.

Magnesium oxide, MgO, occurs as *periclase* and, hydrated, in *brucite*, $Mg(OH)_2$. In conjunction with other oxides it occurs as *magnoferrite*, $MgO.Fe_2O_3$, and *jacobsite*, $(Mn,Mg)O.(Fe,Mn)_2O_3$.

Magnesium molybdate occurs as *belonesite*, $MgMoO_4$.

Magnesium phosphate occurs as *bobierrite*, $Mg_3(PO_4)_2.8H_2O$, in *wagnerite*, $Mg_3(PO_4)_2.MgF_2$, in *struvite*, $(NH_4)MgPO_4.6H_2O$, and in *lüneburgite*, $Mg_3(PO_4)_2.B_2O_3.8H_2O$.

Among the *arsenates* are: *hoernesite*, $Mg_3(AsO_4)_2.8H_2O$, *cabrerite*, $(Ni,Mg)_3(AsO_4)_2.8H_2O$, *adelite*, $Ca(MgOH)AsO_4$, and *tilasite*, $Ca(MgF)AsO_4$.

The following *silicates* have been identified in meteorites:[2] *enstatite* and *clinoenstatite*, $MgSiO_3$, *diopside*, $MgCa(SiO_3)_2$, *hedenbergite*, $(Mg,Fe)Ca(SiO_3)_2$, *forsterite*, Mg_2SiO_4, *chrysolite*, $(Mg,Fe)SiO_4$, and some *augites*. Magnesium also occurs as silicate in *talc* or *steatite*, $H_2Mg_3(SiO_3)_4$, *meerschaum*, $H_2Mg_2(SiO_3)_3$, *olivine*, $(Mg,Fe)_2SiO_4$, and *serpentine*, $Mg_3Si_2O_7.2H_2O$.

Phlogopite or *magnesia mica* is $K_2O.2H_2O.6MgO.Al_2O_3.6SiO_2$, and *asbestos*, which is very important industrially, is $CaMg_3(SiO_3)_4$.

Geikielite is $MgTiO_3$, and among the *borates* are: *pinnoite*, $MgO.B_2O_3.3H_2O$, *boracite*, $2Mg_3B_8O_{15}.MgCl_2$, and *kaliborite*, $KMg_2B_{11}O_{19}.9H_2O$.

Magnesium occurs also in *spinel*, $MgO.Al_2O_3$, *hydrotalcite*, $Mg_3Al(OH)_6.3H_2O$, and *kornerupine*, $Mg(AlO)_2SiO_4$.

Animals and plants contain small quantities of magnesium: in blood, chlorophyll, seeds, milk, and bones, for example.

History.—In 1695 Nehemiah Grew, a London physician, published an account of a medicinal salt obtained from the well-known mineral spring at Epsom. "Epsom salts" soon became famous, and are still used in medicine. George and Francis Moult established a factory in 1700 to obtain the salt from a spring at Shooter's Hill, near London. It was soon afterwards discovered by Friedrich Hoffmann in Seidlitz mineral water, and crystallised by Hoy from the mother-liquors of sea-water. The history of magnesium thus began with its sulphate, $MgSO_4.7H_2O$.

"Magnesia alba" was discovered, and its medicinal value observed, early in the eighteenth century. Since pyrolusite was then called

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[1] Farrington, *Meteorites* (Chicago), 1915, p. 117.

[2] Farrington, *ibid.*, pp. 117–8.

magnesia nigra, the new substance was apparently named to contrast with it. Valentini in 1707, and Slevogt in 1709, prepared it from saltpetre mother-liquors. Partly because these preparations contained calcium carbonate, magnesia and lime were constantly confused till Black, in 1755, clearly distinguished them. He showed that magnesia alba was a compound of " fixed air " with a peculiar earth, which had a soluble sulphate.[1] When Davy, in 1808, showed that magnesia was the oxide of a metal, he named the metal *magnium*.[2] Finally, the name *magnesium* was adopted for the metal in magnesia, and *manganese* for the metal in pyrolusite. The latter had been known both as *magnesium* and *manganesium*.

" Magnesia " is derived from " magnesian stone," an alchemistic designation of the loadstone, and a stone shining like silver, which may have been talc. A confusion of pyrolusite with the loadstone may have led to the terms magnesia alba and magnesia nigra.[3]

The metal was first prepared in mass by Bussy in 1829.[4] He decomposed magnesium chloride with potassium; electrolytic methods are now used in industry.

Preparation of Metallic Magnesium.—Magnesium was first prepared by acting on its chloride with potassium.[5] Later, a mixture of magnesium chloride, calcium fluoride, sodium chloride, and potassium chloride,[6] or of carnallite and fluorspar,[7] was used—sodium being substituted for potassium.

Proposals have been made to reduce the sulphate with iron or hydrocarbons;[8] to reduce magnesium minerals, such as magnesite or dolomite, with coal and ferric oxide;[9] and to reduce the double cyanide of sodium and magnesium with zinc.[10]

The direct reduction of fused magnesia by carbon is violent at 2030° C.,[11] and potassium vapour at a strong red heat will also reduce it.

Magnesium is now prepared by electrolysis. Sir Humphrey Davy obtained an amalgam of magnesium by electrolysing a mixture of magnesia and red mercuric oxide between a platinum anode and a mercury cathode.[12] Subsequent experimenters electrolysed solutions of magnesium salts : Becquerel obtained the metal from a concentrated solution of the chloride,[13] and a solution of the double sulphate of ammonium and magnesium was electrolysed at 70°–100° C.[14]

An attempt was made to electrolyse molten double sulphides of magnesium and the alkalies.[1] In 1852 Bunsen electrolysed the molten anhydrous chloride;[2] Matthiessen mixed three equivalents of potassium chloride with every four of magnesium chloride,[3] and Fischer took the natural step of employing carnallite—the naturally occurring double chloride of magnesium and potassium.[4] Magnesium is now chiefly manufactured by electrolysing this fused salt. Carnallite is less volatile than magnesium chloride, and more easily dehydrated without formation of magnesia.

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[1] Black, *Experiments upon Magnesia Alba, Quicklime, and other Alkaline Substances* (Alembic Club Reprint, No. 1; Clay, Edinburgh; Simpkin, Marshall, Hamilton, Kent & Co., London), 1893.

[2] Davy, *The Decomposition of the Fixed Alkalies and Alkaline Earths* (Alembic Club Reprint, No. 6), 1894.

[3] *New Oxford Dictionary.*

[4] Bussy, *J. Pharm. Chim.*, 1829, **15**, 30.

[5] Bussy, *ibid.*, 1829, **15**, 30; 1830, **16**, 142; Liebig, *Pogg. Annalen*, 1830, **19**, 137.

[6] Deville and Caron, *Ann. Chim. Phys.*, 1863, [3], **67**, 340.

[7] Reichardt, *Jahresber.*, 1864, 192.

[8] Petitjean, *Dingl. poly. J.*, 1858, **148**, 371.

[9] Püttner, *ibid.*, 1885, **256**, 567.

[10] Lauterbraun, German Patent, 39915 (1886).

[11] Kowalke and Grenfell, *Trans. Amer. Electrochem. Soc.*, 1916, **27**, 221.

[12] Davy, Alembic Club Reprint, No. 6, 1894.

[13] Becquerel, *Ann. Chim. Phys.*, 1831, [2], **48**, 337.

[14] English Patent, 16651 (1884).

The electrolysis is performed in an iron pot which acts as cathode. The anode is of carbon, and holes in the porcelain pot surrounding it permit communication between the anodic and cathodic compartments. To maintain the molten condition of the liberated magnesium the cell is placed in a furnace. A number of such cells is usually connected in series with a source of current, so that the P.D. between each pair of electrodes is about 8 volts. A usual current density is about 1000 amp. per sq. metre. The chlorine is carried off by a side pipe, and the molten magnesium collects in the cathodic compartment on the surface of the molten electrolyte. It is protected from oxidation by an atmosphere of inert gas. The holes between the anodic and cathodic compartments are arranged to avoid any passage of the upper layer of magnesium into the anode compartment. The working temperature is apparently between 700° C. and 800° C.[5, 6]

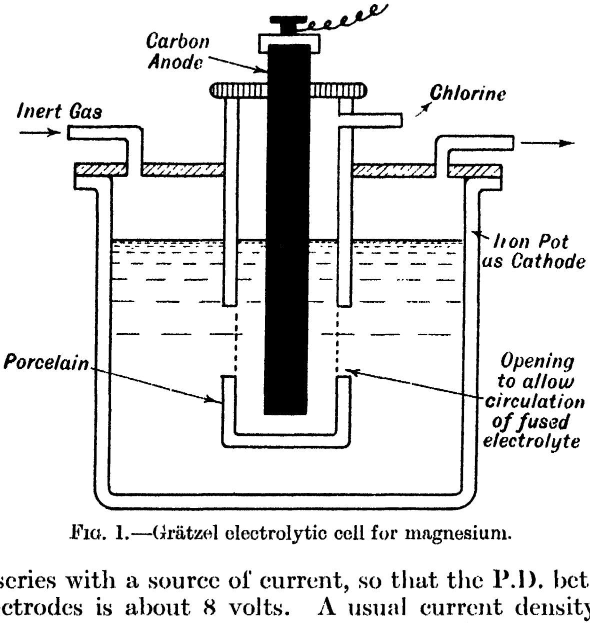

FIG. 1.—Grätzel electrolytic cell for magnesium.

The globules of magnesium do not coalesce in the presence of magnesium oxide or magnesium sulphate. The addition of ammonium chloride during the fusion of the magnesium chloride prevents the formation of oxide. Any sulphate is decomposed by adding enough carbon to the fused chlorides: the oxide thus produced is converted into chloride by ammonium chloride. Oettel found that the addition of calcium fluoride removed the disinclination of the magnesium globules to coalesce.[1]

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[1] Jaennigen, *Zeitsch. angew. Chem.*, 1895, **8**, 317.
[2] Bunsen, *Annalen*, 1852, **82**, 137.
[3] Matthiessen, *Ann. Chim. Phys.*, 1855, [3], **45**, 347.
[4] Fischer, *Jahresber.*, 1885, ii, 2013.
[5] Borchers, *Zeitsch. Elektrochem.*, 1895, **1**, 361.
[6] Oettel, *ibid.*, 1895, **2**, 394.

Swan could say in 1901 that the only company known to be manufacturing metallic magnesium was the Aluminium und Magnesium Gesellschaft, Hemelingen.[2] Their electrolyte contained equimolecular proportions of magnesium, potassium, and sodium chlorides. It was prepared from carnallite by adding sodium chloride. Anhydrous magnesium chloride was continuously added during the process (which was continuous) to keep the bath composition constant. The electrolyte was kept basic and contained calcium fluoride.[3]

Molinari says that, prior to the Great European War, the world's consumption of metallic magnesium approached 100 tons. American companies are now producing considerable quantities.[4]

Magnesium can be purified by distillation,[5] but it is more usually purified by remelting with pure carnallite in an iron crucible. The floating metal is ladled off and poured into ingots. It is usually converted into wire by squeezing the semifluid metal through dies, and is then commonly rolled into ribbon. It is also handled commercially as powder.

Magnesium metal may contain from 6–17·5 c.c. of occluded hydrogen, and from 1·2–4·1 c.c. of occluded carbon monoxide, in every 20 grm.[6] From 0·05–0·07 per cent. of silica, and about 0·08 per cent. of iron and aluminium, have been found in it.[7] Samples containing small amounts of alumina and ferric oxide have been found to be free from carbon, alkali metals, and alkaline earth metals.[8]

Physical Properties of Magnesium.—Magnesium ribbon is brilliant and white, resembling silver. When sublimed *in vacuo* the cooled metallic deposit consists of beautiful silver-white crystals[9] which are usually regular hexagonal prisms.[10] Similar crystals crystallise from a solution of magnesium in molten sodium.[11]

Its density is very close to Deville and Caron's original figure of 1·75:[5] a more modern figure is 1·74.[12] It melts at 650±2° C.,[11, 12, 13] and boils at about 1100° C.:[14] the actual boiling-point may be nearer 1120° C.[15] Its specific heat has been given as 0·2456 at 0° C., 0·2519 at 50° C.,[16] and 0·223 between −185° C. and +20° C.[17] Its electrical conductivity compared with mercury at 0° C. is 22·84 at 0° C. and 16·34 at 100° C.[1] Its absolute conductivity for heat from 0° C.–100° C. is 37·6,[1] its atomic refraction is 6·9, its atomic volume is about 13·3, and it is diamagnetic.[2]

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[1] Oettel, *Zeitsch. Elektrochem.*, 1895, **2**, 394.
[2] Swan, *J. Soc. Chem. Ind.*, 1901, **20**, 666.
[3] *Zeitsch. Elektrochem.*, 1901, **7**, 408.
[4] Molinari, *Treatise on General and Industrial Inorganic Chemistry* (translated by Pope) (Churchill), 1920, p. 670.
[5] Deville and Caron, *Ann. Chim. Phys.*, 1863, [3], **67**, 340.
[6] Dumas, *Compt. rend.*, 1880, **90**, 1027; Delachanal, *ibid.*, 1909, **148**, 561.
[7] Zemczuznys, *Zeitsch. anorg. Chem.*, 1906, **49**, 400.
[8] Kahlenberg, *J. Amer. Chem. Soc.*, 1903, **25**, 380.
[9] Dumas, *Compt. rend.*, 1880, **90**, 1027.
[10] Des Cloizeaux, *ibid.*, 1880, **90**, 1101.
[11] Mathewson, *Zeitsch. anorg. Chem.*, 1906, **48**, 191.
[12] Zemczuznys, *ibid.*, 1906, **49**, 400.
[13] Sahmen, *ibid.*, 1908, **57**, 1; Vogel, *ibid.*, 1909, **63**, 169.
[14] Ditte, *Compt. rend.*, 1871, **73**, 108.
[15] Greenwood, *Proc. Roy. Soc.*, 1909, **A82**, 396.
[16] Lorenz, *Wied. Annalen*, 1881, **13**, 422, 582.
[17] Nordmeyer and Bernoulli, *Ber.*, 1907, **5**, 175.

Magnesium is a relatively strong metal : its ultimate tensile stress is 23·2 kilos per sq. mm., its bending strength 17·4 kilos, and its specific resistance to compression 27·2 kilos per sq. mm.[3] The compressibility of the metal is about $2·7 \times 10^{-6}$ per atmosphere.[2]

Magnesium is malleable, but ductile only at high temperatures. At 450° C. the metal can be rolled, pressed, and readily worked.[3]

Magnesium, condensed from vapour on cooled platinum sheets, exhibits photo-electric activity when exposed to light rays in an exhausted tube.[4]

The stronger lines in the *spectrum* of magnesium, in decreasing order of wave-length (Rowland), are—

Spark : 5711·6, 5528·7, 5183·8, 5172·9, 5167·6, 4703·3, 4481·3, 4352·4, 3838·4, 3832·5, 3829·5, 3336·8, 3332·3, 3330·1, 3097·1, 3093·1, 3091·2, 2942·2, 2937·9, 2928·7, 2915·6, 2852·2, 2802·8, 2798·2, 2795·6, 2790·9, 2783·1, 2781·5, 2779·9, 2778·4, 2776·8.

Arc : 8807·0, 5711·6, 5528·7, 5183·8, 5172·9, 5167·6, 4703·3, 4352·4, 3838·4, 3832·5, 3829·5, 3336·8, 3332·3, 3330·1, 3097·1, 3093·1, 3091·2, 2942·2, 2938·7, 2937·9, 2928·7, 2915·6, 2852·2, 2848·5, 2846·9, 2802·8, 2798·2, 2795·6, 2790·9, 2783·1, 2781·5, 2779·9, 2778·4, 2776·8.[5]

Chemical Properties.—Magnesium ribbon burns with a bright light in air to the oxide and nitride : [6] Winkler says no nitride is formed unless inactive substances which absorb heat are present.[7] The great brightness of this light [8] makes magnesium useful in flashlights, signalling, and pyrotechny. Burning magnesium gives a continuous spectrum.[9]

Heated magnesium decomposes carbon dioxide [10, 11] (the formation of magnesium carbide may interfere with the reaction),[12] carbon monoxide [13] (this has been denied),[11] sulphur dioxide,[11, 14] hydrogen sulphide, nitrous oxide, nitric oxide,[11] all oxides except those of the alkalies and alkaline earths,[15] some sulphides,[16] and combines directly with the halogens, sulphur, nitrogen, phosphorus, and other elements.

Magnesium does not tarnish in dry air, but in moist air becomes covered lightly with oxide. Distilled water acts on it very slowly,[17] and though it has been suggested that perfectly pure water attacks magnesium until the action is stopped by a coating of oxide,[1] there seems to be no action if dissolved gases are entirely absent.[2] The heated metal reacts readily with steam—

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[1] Lorenz, *loc. cit.*

[2] Richards, Stull, Brink, and Bonnet, *J. Amer. Chem. Soc.*, 1909, 31, 154.

[3] *J. Soc. Chem. Ind.*, 1887, 6, 730.

[4] Pohl and Pringsheim, *Ber. Deut. physikal. Ges.*, 1912, 14, 546.

[5] Watts, *Index of Spectra*, Appendix U (1911) (Wesley & Son, London ; Heywood & Son, Manchester).

[6] Deville and Caron, *Ann. Chim. Phys.*, 1863, [3], 67, 340.

[7] Winkler, *Ber.*, 1890, 23, 120. See also Magnesium Nitride.

[8] Bunsen and Roscoe, *Phil. Trans.*, 1859, 149, 920.

[9] Simmler, *Pogg. Annalen*, 1862, 115, 242, 425.

[10] Phipson, *Proc. Roy. Soc.*, 1864, 13, 217 ; Wartha, *Ber.*, 1871, 4, 94.

[11] Kessler, *Ber.*, 1869, 2, 369.

[12] Winkler, *ibid.*, 1890, 23, 2642.

[13] Martignon, *Bull. Soc. chim.*, 1909, [iv], 5, 269.

[14] Uhl, *Ber.*, 1890, 23, 2151.

[15] Warren, *Chem. News*, 1889, 60, 187 ; Winkler, *Ber.*, 1890, 23, 44, 120, 772, 2642 ; Weston and Ellis, *Trans. Faraday Soc.*, 1908, 4, 130.

[16] Pertusi, *Ann. Chim. anal.*, 1915, 20, 229.

[17] Kahlenberg, *J. Amer. Chem. Soc.*, 1903, 25, 380.

$$\mathrm{Mg+H_2O=MgO+H_2}.$$ [3]

Magnesium amalgam decomposes water violently,[4] and many magnesium alloys act similarly.[5]

In general, action occurs in systems containing magnesium, water, and an electrolyte. Powdered magnesium reacts with the water of crystallisation of many substances,[6] and the metal decomposes water rapidly in the presence of a drop of platinic chloride[4, 7, 8] or of a little palladious chloride.[9] Magnesium reduces solutions of nitrates, nitrites,[6, 10] and chlorates.[11] It liberates its equivalent of hydrogen from dilute hydrochloric or sulphuric acid;[12] it also evolves hydrogen, more slowly and at very different rates,[13] from solutions of many salts —including its own.[14, 15, 16, 17]

Getman concluded that the reaction

$$\mathrm{Mg+2H_2O=Mg(OH)_2+H_2}$$

is catalytically accelerated by dissolved potassium chloride[18] and other dissolved salts: the reaction is equally rapid with impure and perfectly pure metal. In solutions of hydrolysed salts, the evolution of hydrogen is accelerated if the base is weak, and retarded if it is strong.[13]

Magnesium, according to Getman,[13] acts in four distinguishable ways on aqueous solutions of salts—

(A) Neutral salts function solely as catalysts, and the magnesium forms hydrogen and magnesium hydroxide with the water. A basic salt may result.[14, 19]

(B) When the base is weak, the magnesium reacts first with the acid from the hydrolysis and then with the solvent. In the latter reaction the saline constituents act as catalytic stimulants.

(C) When the acid is weak, the hydrogen-ion concentration is depressed, and the magnesium reacts very slightly, if at all, with the solvent.

(D) When the cation is less electro-positive than the magnesium, the metal of the salt is replaced by the latter. Since such salts usually have an acid reaction, the magnesium generally directly displaces the hydrogen of the acid as well.[1]

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[1] Bryant, *Chem. News*, 1899, 80, 211.
[2] Roberts and Brown, *J. Amer. Chem. Soc.*, 1903, 25, 801.
[3] Kessler, *Ber.*, 1869, 2, 369.
[4] Hartley, *Chem. News*, 1866, 14, 73.
[5] See Magnesium Alloys.
[6] Michailenko and Mustinsky, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 181.
[7] Kern, *Chem. News*, 1876, 33, 112, 236.
[8] Ballo, *Ber.*, 1883, 16, 694.
[9] Knapp, *Chem. News*, 1912, 105, 253.
[10] Kahlenberg, *J. Amer. Chem. Soc.*, 1903, 25, 380.
[11] Kippenberger, *Chem. Zeit.*, 1895, 19, 1269.
[12] For rate of solution in acids, see Kajander, *Bull. Soc. chim.*, 1880, [2], 34, 325.
[13] Getman, *J. Amer. Chem. Soc.*, 1917, 39, 596.
[14] Tommasi, *Bull. Soc. chim.*, 1899, [3], 21, 885.
[15] Mouraour, *Compt. rend.*, 1900, 130, 140.
[16] Roberts and Brown, *J. Amer. Chem. Soc.*, 1903, 25, 801.
[17] Hughes, *Trans. Chem. Soc.*, 1919, 115, 272.
[18] Getman, *J. Amer. Chem. Soc.*, 1916, 38, 2594.
[19] Lemoine, *Compt. rend.*, 1899, 129, 291.

Magnesium precipitates its equivalent of pure copper, gold, or platinum from solutions containing no other metals than the alkalies or alkaline earths. Many other metals alloy with the magnesium.[2] Tellurium can be estimated by precipitating it with magnesium,[3] and zinc is also quantitatively precipitated from its acetate in the presence of alkaline earth metals.[4]

The formation of oxides or hydroxides of metals has been noted during their displacement from their salts by magnesium,[5, 6] and it has been suggested that the action of magnesium on salts primarily converts their metal into its oxide or hydroxide.[7]

Nitric oxide, nitrous oxide, and nitrogen are evolved, according to Acworth and Armstrong, when nitric acid acts upon magnesium. When the acid is mixed with an equal volume of water these gases correspond to 64·23 per cent. of the metal dissolved. They correspond to 44·51 per cent. when the acid is mixed with 12 parts of water. Nitric oxide predominates.[8] If some hydrochloric acid is present hydroxylamine is formed, but it decomposes rapidly.[9] Ammonium nitrate is also produced during the action.[10] Much hydrogen is also said to be evolved, and the proportion of ammonia increases with the concentration of the nitric acid till the latter reaches 40 per cent., and then decreases.[11]

Alkaline hydroxides do not act on magnesium;[6, 12, 13] sodium carbonate solution acts on it slightly, and borax solution with considerable vigour.[13]

Concentrated sulphuric acid begins to attack magnesium at 215° C. with the evolution of sulphur dioxide and a trace of hydrogen sulphide.[14] Sulphurous acid converts the metal into its sulphite.[15]

Potassium dichromate inhibits the solution of magnesium in acetic acid: the addition of an alkali or of a magnesium salt of a strong acid destroys the "passivity."[16]

The metal acts on methyl alcohol to form magnesium methoxide,[17] and enters into many important reactions in organic chemistry.[18]

A green unstable colloidal solution of magnesium has been prepared by the electrical method.[19]

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[1] Bryant, *Chem. News*, 1899, **79**, 75.
[2] Villiers and Borg, *Compt. rend.*, 1893, **116**, 1524.
[3] Crane, *Amer. Chem. J.*, 1900, **23**, 408.
[4] Warren, *Chem. News*, 1889, **60**, 187.
[5] Kern, *Chem. News*, 1875, **32**, 309; Clowes, *ibid.*, 1898, **78**, 155; Bryant, *ibid.*, 1899, **80**, 211; Tommasi, *Bull. Soc. chim.*, 1899, [3], **21**, 885.
[6] Phipson, *Proc. Roy. Soc.*, 1864, **13**, 217.
[7] Kern, *Chem. News*, 1876, **112**, 236.
[8] Acworth and Armstrong, *J. Chem. Soc.*, 1877, **32**, 77.
[9] Divers, *Trans. Chem. Soc.*, 1883, **43**, 453.
[10] Bijlert, *Zeitsch. physikal. Chem.*, 1899, **31**, 103.
[11] Montemartini, *Gazzetta*, 1892, **22**, 384, 397, 426.
[12] Kahlenberg, *J. Amer. Chem. Soc.*, 1903, **25**, 380.
[13] Getman, *ibid.*, 1917, **39**, 596.
[14] Adie, *Proc. Chem. Soc.*, 1899, **15**, 132.
[15] Schweizer, *Amer. Chem. J.*, 1871, **1**, 296.
[16] Holroyd, *Proc. Chem. Soc.*, 1904, **20**, 38.
[17] Szarvasy, *Ber.*, 1897, **30**, 806.
[18] Hepworth, *J. Soc. Chem. Ind.*, 1922, **41**, 7T.
[19] Svedberg, *Ber.*, 1905, **38**, 3616.

Magnesium apparently consists of three isotopes of atomic weights, 24, 25, and 26.[1]

Uses of Magnesium.—Magnesium is used for various forms of illumination—in signalling, flashlights, and pyrotechny. It is a valuable reducing agent in the laboratory, and Warren[2] suggested its use in Marsh's test because it contains no arsenic, and in reducing ferric salts because of its freedom from iron.

Metallic magnesium prevents blowholes in brass or copper, makes nickel castings sound, and is a constituent of the important alloy magnalium, which is an alloy of aluminium and magnesium.

Grignard's discovery of magnesium alkyl and aryl halides in 1900[3] provided the organic chemist with an important reagent. Hepworth[4] has summarised the applications of magnesium to synthetic organic chemistry.

Magnesium oxide is used medicinally, as a refractory material, in cements and hydraulic mortars, as the basis of the filament in the Nernst lamp, and has been used instead of lime in the oxyhydrogen lantern. Magnesium oxide and chloride are constituents of various "Sorel cements." The peroxide is used as an antiseptic and for bleaching.

The sulphate, basic carbonates (magnesia alba), the bicarbonate, and the citrate are used medicinally. Magnesium sulphate and chloride are used for finishing cotton fabrics and also for weighting silk or paper.

Meerschaum is used for making tobacco pipes, and asbestos, because of its non-inflammability and low heat conductivity, has extensive industrial uses.

Atomic Weight.—The atomic weight of magnesium, which has always been recognised as a divalent element, has been determined by the following methods:—

(A) The conversion of the oxide into the sulphate.[5]
(B) The ignition of the sulphate to the oxide.[6]
(C) The precipitation of magnesium sulphate with barium chloride.[7]
(D) The precipitation of magnesium chloride with silver nitrate.[8]
(E) The ignition of the oxalate into the oxide.[9]
(F) The ignition of the carbonate into the oxide.[10]
(G) The conversion of the metal into the oxide.[11]

In 1884 Marignac[12] critically reviewed the determinations of the atomic weight of magnesium, and obtained the ratio

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[1] Aston, *Isotopes* (Arnold & Co.), 1922, pp. 80–83.

[2] Warren, *Chem. News*, 1889, 60, 187.

[3] Grignard, *Compt. rend.*, 1900, 130, 1322.

[4] Hepworth, *J. Soc. Chem. Ind.*, 1922, 41, 7T.

[5] Berzelius, *Ann. Chim. Phys.*, 1820, 14, 373; Svanberg and Nordenfeldt, *J. prakt. Chem.*, 1848, 45, 473; Bahr, *ibid.*, 1852, 56, 489; Marignac, *Ann. Chim. Phys.*, 1884, [6], 1, 321.

[6] Jacquelain, *Ann. Chim. Phys.*, 1851, [3], 32, 195; Marignac, *loc. cit.*

[7] Gay-Lussac, *ibid.*, 1820, [2], 13, 308; Scheerer, *Pogg. Annalen*, 1846, 69, 535; 1847, 70, 407; Jacquelain, *loc. cit.*

[8] Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 187 ($MgCl_2 : 2Ag$); Richards and Parker, *Zeitsch. anorg. Chem.*, 1897, 13, 81 ($MgCl_2 : 2Ag$ and $MgCl_2 : 2AgCl$).

[9] Svanberg and Nordenfeldt, *J. prakt. Chem.*, 1848, 45, 473.

[10] Marchand and Scheerer, *ibid.*, 1850, 50, 385 (later corrections in Scheerer, *Annalen*, 1858, 110, 236); Jacquelain, *Ann. Chim. Phys.*, 1851, [3], 32, 195.

[11] Burton and Vorce, *Amer. Chem. J.*, 1890, 12, 219.

[12] Marignac, *Ann. Chim. Phys.*, 1884, [6], 1, 321.

$$MgO : MgSO_4 = 100 : 298{\cdot}27$$

as the mean of ten conversions of the pure oxide into the sulphate, and the ratio

$$MgO : MgSO_4 = 100 : 298{\cdot}31$$

as the mean of twelve ignitions of the sulphate into the oxide.

Using the atomic weights O=16 and S=32·065, these results calculate to atomic weights for magnesium of 24·38 and 24·37 respectively.

Burton and Vorce, in 1890,[1] obtained the ratio

$$Mg : MgO = 100 : 165{\cdot}877$$

by converting the carefully purified metal into the nitrate and igniting to the oxide. This result, which is the mean of ten determinations, gives an atomic weight of 24·287 for magnesium, if O=16.

Dumas, in 1859,[2] as the mean of eleven determinations, obtained the ratio

$$MgCl_2 : 2Ag = 100 : 225{\cdot}91$$

by estimating the silver after precipitating magnesium chloride with silver nitrate. Using atomic weights Cl=35·457 and Ag=107·880, this result gives 24·59 for the atomic weight of magnesium. Dumas was not very confident in his result, since he found it difficult to ensure the purity of his magnesium chloride, but he decided that it was probably better to retain 12 as the equivalent of magnesium instead of the 12·5 of Berzelius, pending further investigation.

Richards and Parker, in 1897,[3] obtained the following results. Both their atomic weights for magnesium, calculated by using O=16, Cl=35·456, and Ag=107·930, and atomic weights calculated from the fundamental data used in this series, namely, Ag=107·880 and Cl=35·457, are given.

Ratio.	No. of Determinations	Atomic Weight (Richards and Parker).	Atomic Weight (Recalculated).
$MgCl_2 : 2AgCl = 100 : 300{\cdot}975$	5	24·369	24·334
$MgCl_2 : 2Ag = 100 : 226{\cdot}566$	6	24·365	24·321
$MgCl_2 : 2Ag = 100 : 226{\cdot}559$	6	24·362	24·319

In 1909 the International Commission on Atomic Weights altered the value from the 24·36 then in use to 24·32, and this value was retained in 1925.[4]

ALLOYS OF MAGNESIUM.

Alloys of magnesium and zinc resist oxidation more than either of the metals separately.[5] Many other magnesium alloys are very chemically reactive. Le Bon found that magnesium acted much more vigorously on water when it was amalgamated with very small quantities of mercury.[1] In 1864 Phipson described a hard, brittle, lavender-coloured alloy containing 85 parts of tin and 15 of magnesium, which decomposed water at ordinary temperatures and took fire if air were admitted during its preparation.[2] This was a forerunner of a series of very chemically active alloys which contain magnesium.

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[1] Burton and Vorce, *Amer. Chem. J.*, 1890, **12**, 219.

[2] Dumas, *Ann. Chim. Phys.*, 1859, [3], **55**, 187.

[3] Richards and Parker, *Zeitsch. anorg. Chem.*, 1897, **13**, 81.

[4] *Proc. Chem. Soc.*, 1908, **24**, 5; 1909, **25**, 8; *J. Amer. Chem. Soc.*, 1925, **47**, 597.

[5] Ashcroft, *Trans. Faraday Soc.*, 1919, **14**, 271.

Alloys containing 5–50 per cent. magnesium and 95–50 per cent. *lead* rapidly absorb oxygen from moist air. The alloy consisting of the compound Mg_2Pb is the most reactive: heat is required when the magnesium exceeds 35 per cent. The oxidation crumbles the alloy to a black powder of $Mg(OH)_2$ and $Pb_2(OH)_2$. In presence of water the $Pb_2(OH)_2$ oxidises to $Pb(OH)_2$. Free hydrogen is liberated when the alloys are boiled with water; digestion with water under pressure at about 150° C. completely oxidises the lead to lead oxide and liberates the theoretical quantity of hydrogen.[3, 4] Mg_2Pb is the only known definite compound of magnesium and lead.[4, 5]

The pyrophoric alloys, such as are used in cigarette-lighters, etc., which produce sparks when struck with hardened steel, contain cerium alloyed with other metals—usually iron. These alloys spark easily, because cerium combines energetically with oxygen at a low temperature. A surface film of black cerium suboxide may be an important agent in the process.[6] According to Hirsch, alloys of magnesium with 75–85 per cent. of *cerium* are highly pyrophoric.[6] The compound CeMg contains approximately 85 per cent. of cerium, and Vogel[7] says that the alloy corresponding with this compound is pyrophoric. He says the same of the alloy corresponding to Ce_4Mg, which contains about 96 per cent. of cerium. Since the combination between magnesium and cerium is endothermic, their alloys are very effective in thermal reduction processes.[6]

The industrially important alloys of magnesium and *aluminium*, known as *magnalium*, were originally prepared by making molten aluminium the cathode in a fused salt of magnesium.[8] The earlier magnaliums appear to have contained less than 2 per cent. of magnesium.[9] Magnesium compounds, such as carnallite, are now commonly electrolysed below a red heat and aluminium added during the process.[10]

The tensile strength and elastic limit of the alloys show a maximum at about 8 per cent. of magnesium. They increase in hardness and decrease in density with the magnesium content.[11] The alloys containing 10–30 per cent. of magnesium are malleable, have a density between 2·0 and 2·5, are suitable for castings, easily worked without softening, polish well, and do not fracture easily. They polish better and become more

[1] Le Bon, *Compt. rend.*, 1900, **131**, 706.
[2] Phipson, *Proc. Roy. Soc.*, 1864, **13**, 217.
[3] Ashcroft, *Trans. Faraday Soc.*, 1919, **14**, 271.
[4] Grube, *Zeitsch. anorg. Chem.*, 1905, **44**, 117.
[5] Kurnakoff and Stepanoff, *ibid.*, 1905, **46**, 177.
[6] Hirsch, *Met. and Chem. Eng.*, 1911, **9**, 540.
[7] Vogel, *Zeitsch. anorg. Chem.*, 1915, **91**, 277.
[8] English Patent, 14582 (15th July 1899).
[9] Barnet, *J. Soc. Chem. Ind.*, 1905, **24**, 832.
[10] Blücher, *Modern Industrial Chemistry* (translated by Millington) (Gresham Publishing Co., London), 1914.
[11] B. Ohtani, Kōgyō-Kwagaku Zasshi, *J. Chem. Ind.* (Japan), 1922, **25**, 36.

brittle with increase in the magnesium content.[1] Magnalium does not easily corrode.[2]

The common magnalium, containing 10 per cent. of magnesium, can be soldered[3] and plated with gold or nickel.[1]

Since magnalium retains a silvery lustre it is useful for making certain parts of optical instruments,[4] such as mirrors, and is used in parts of various machines and scientific instruments.

The compound Mg_4Al_3 consists of silver-white, hard, brittle crystals.[5] There is probably a compound MgAl, and there may be Mg_3Al_2. Mg_2Al and $MgAl_4$ are doubtful.[6]

Lithium and magnesium appear to form solid solutions.[7]

Sodium, according to Phipson, forms malleable alloys with magnesium that readily decompose water.[8] According to Mathewson sodium will dissolve about 1·6 per cent. of magnesium at 657° C., but the latter separates out in hexagonal crystals as the temperature falls. Magnesium will dissolve about 2 per cent. of sodium.[9]

Potassium appears not to mix with fused magnesium,[10] though Phipson said it formed malleable alloys that decomposed water.[8]

Copper forms Mg_2Cu and $MgCu_2$, indicated by the freezing-point curve, that are brittle, crystalline, and coloured like magnesium.[11] Boudouard found an indication of MgCu on the curve, and claimed to have isolated this compound.[12]

Silver.—Alloys of silver and magnesium are harder than their components, brittle, and more easily oxidised or decomposed by water than magnesium itself. Freezing-point and conductivity curves indicate the compounds MgAg and Mg_3Ag.[13]

Gold forms alloys with magnesium that are stable in air at ordinary temperatures. They are yellow when the percentage of magnesium is not over 18 and silver-grey when it is.

Mg_3Au (m.-pt. 83° C.), Mg_2Au (m.-pt. 796° C.), and MgAu (m.-pt. 1160° C.) are indicated on the freezing-point curve. Mg_3Au separates from its alloys with magnesium in large regular crystals. The action between gold and molten magnesium is violent.[14]

Calcium alloys with magnesium in all proportions. The alloys with 10 per cent. and over of calcium are brittle.[15] Ca_3Mg_4, indicated on the freezing-point curve, is silvery, brittle, stable in air, and only slowly acted upon by water.[16]

Zinc.—The compound Mg_4Zn has been described,[17] but $MgZn_2$ seems to be the only known compound of zinc with magnesium.[1] It has been isolated by distilling off, *in vacuo*, the excess of zinc from a mixture of its constituents, and can be distilled *in vacuo* without change.[2]

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[1] Blücher, *loc. cit.*

[2] Barnet, *loc. cit.*

[3] *J. Soc. Chem. Ind.*, 1901, 20, 815.

[4] *Ibid.*, 1900, 19, 557.

[5] Grube, *Zeitsch. anorg. Chem.*, 1905, 45, 225; Vogel, *ibid.*, 1919, 107, 265.

[6] Boudouard, *Compt. rend.*, 1901, 132, 1325; Broniewski, *ibid.*, 1911, 152, 85.

[7] Masing and Tammann, *Zeitsch. anorg. Chem.*, 1910, 67, 183.

[8] Phipson, *Proc. Roy. Soc.*, 1864, 13, 217.

[9] Mathewson, *Zeitsch. anorg. Chem.*, 1906, 48, 191.

[10] Smith, *ibid.*, 1907, 56, 109.

[11] Urazoff, *J. Russ. Phys. Chem. Soc.*, 1907, 39, 1566; Sahmen, *Zeitsch. anorg. Chem.*, 1908, 57, 1.

[12] Boudouard, *Compt. rend.*, 1902, 135, 794; 1903, 136, 1327.

[13] Schemtschuschny, *Zeitsch. anorg. Chem.*, 1906, 49, 400; Smirnoff and Kurnakoff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 108; *Zeitsch. anorg. Chem.*, 1911, 72, 31.

[14] Vogel, *Zeitsch. anorg. Chem.*, 1909, 63, 169.

[15] Stockem, *Metallurgie*, 1906, 3, 147.

[16] Baar, *Zeitsch. anorg. Chem.*, 1911, 70, 352.

[17] Boudouard, *Compt. rend.*, 1904, 139, 424.

Cadmium and magnesium form a single compound, MgCd, which is greyish white, slightly harder than cadmium, oxidised in moist air, and acted upon readily by water.[1] Two forms of MgCd, differing in hardness, are indicated by electrical conductivity experiments.[3] It melts at 427° C. and dissolves in all proportions in either metal. Magnesium and cadmium form a continuous series of solid solutions.[4]

Mercury.—Magnesium does not amalgamate easily,[5] but amalgams have been made by introducing magnesium ribbon into nearly boiling mercury, and by acting on crystalline magnesium sulphate with potassium amalgam. Silvery crystals of an amalgam have been prepared by rubbing small quantities of magnesium at a time into mercury contained in a warm mortar. The product dulled in air. The immediate product is a thick fluid which cools to a hard crystalline mass. One part of magnesium and 18 parts of mercury (practically $MgHg_2$) give the most satisfactory product. These amalgams reduce many organic compounds.[6]

Cambi and Speroni affirm the existence of $MgHg_2$ and suggest that of MgHg.[7]

Magnesium amalgams decompose water.[8]

Thallium alloys with magnesium blacken in air, especially if the air is moist, through oxidation. The melting-point curve indicates the compounds Mg_8Tl_3, Mg_3Tl, and Mg_3Tl_2.[9]

Tin forms the compound Mg_2Sn when it is melted with magnesium in hydrogen at 700°–800° C. The combination develops heat, and the compound is brittle and easily tarnished in air.[9] It crystallises in regular octahedra.[10]

Antimony forms Mg_3Sb_2 in steel-grey needles that slowly oxidise in air.[1]

Bismuth forms Mg_3Bi_2, a steel-grey brittle compound that slowly oxidises in moist air.[1]

Nickel and magnesium are quite miscible in the fused state. The freezing-point curve indicates the compounds $MgNi_2$ and Mg_2Ni.[11]

COMPOUNDS OF MAGNESIUM.

MAGNESIUM AND HYDROGEN.

Magnesium Hydride.—Winkler observed an absorption of gas when magnesium and magnesium oxide were heated in a current of hydrogen. The solid product had an unpleasant odour, evolved hydrogen slowly in contact with water, and produced water when it was heated in oxygen.[1] Jolibois, by a different method, obtained a grey powder which much more certainly contained magnesium hydride than Winkler's product. It decomposed at 280° C. with evolution of hydrogen, and 1 molecule of hydrogen was expelled for every atom of magnesium—corresponding to the formula MgH_2. Jolibois obtained his product by heating magnesium ethyl iodide (electrically) to 175° C. Dry ether washed practically all the iodine out of it, and it then, in contact with water, gave off hydrogen which took fire.[2]

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[1] Grube, *Zeitsch. anorg. Chem.*, 1906, 49, 72.

[2] Berry, *Proc. Roy. Soc.*, 1911, 86, 67.

[3] Urazoff, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 752.

[4] Guillet, *Rev. Mét.*, 1922, 19, 359.

[5] Phipson, *Proc. Roy. Soc.*, 1864, 13, 217.

[6] Evans and Fetsch, *J. Amer. Chem. Soc.*, 1904, 26, 1158.

[7] Cambi and Speroni, *Atti R. Accad. Lincei*, 1915, [v], 24, i, 734.

[8] Hartley, *Chem. News*, 1866, 14, 73.

[9] Grube, *Zeitsch. anorg. Chem.*, 1905, 46, 76.

[10] Sustschinsky, *Zeitsch. Kryst. Min.*, 1903, 38, 264.

[11] Voss, *Zeitsch. anorg. Chem.*, 1908, 57, 34.

A characteristic spectrum, obtained by high-frequency discharge between magnesium electrodes in hydrogen[3] and observed in sun-spot spectra,[4] has been attributed to magnesium hydride.

MAGNESIUM AND THE HALOGENS.

Magnesium Fluoride, MgF_2, unlike other magnesium halides, is very sparingly soluble in water: 7·6 mgm. of the amorphous variety dissolve in 1 litre of pure water.[5] It is precipitated in a gelatinous form from magnesium sulphate solution by alkali fluorides. Cossa advises dissolving pure magnesia in hydrofluoric acid and expelling the excess of acid by heat.[6] The white amorphous fluoride is converted by fusion, either with [7] or without [6] salt, into a crystalline variety which is identical with the mineral sellaïte.[8] *Sellaïte* occurs as small, transparent tetragonal crystals, with a density of 2·95–3·10 and a hardness of 5.[9]

Crystalline magnesium fluoride is very infusible, only slightly attacked by all acids except sulphuric, and can be made to fluoresce or phosphoresce.[6, 7] It forms readily fusible compounds with barium, strontium, and calcium sulphates, and interacts with aluminium sulphate to form aluminium fluoride.[6]

A process has been patented for preparing magnesium fluoride by heating, in a dry or wet way, calcium fluoride with magnesium chloride, or with a double chloride of magnesium and potassium.[8]

$NaF.2MgF_2$ is obtained by boiling magnesia with a solution of sodium fluoride,[10] or crystalline by fusing magnesium chloride with excess of sodium fluoride and sodium chloride.[11]

When a fusion of magnesia and potassium fluoride (or potassium hydrogen fluoride) is cooled, flattened quadratic prisms of $MgF_2.3KF$ result. Crystalline, $MgF_2.2KF$, is simultaneously produced by increasing the proportion of magnesia in the melt. Both compounds are attacked by sulphuric and hydrochloric acids.[12]

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[1] Winkler, *Ber.*, 1891, 24, 1966.

[2] Jolibois, *Compt. rend.*, 1912, 154, 116.

[3] Brooks, *Proc. Roy. Soc.*, 1908, 80A, 218.

[4] Fowler, *Phil. Trans.*, 1909, 209A, 447.

[5] Kohlrausch, *Zeitsch. physikal. Chem.*, 1905, 50, 356.

[6] Cossa, *Gazzetta*, 1877, 7, 212.

[7] Röder, *Dissertation* (Göttingen), 1863; Dammer, *Handbuch der anorganischen chemie* (Enke, Stuttgart), 1894, II, 2, 423.

[8] Feldmann, *J. Soc. Chem. Ind.*, 1888, 7, 122.

[9] Strüver, *Jahresber.*, 1868, 1020.

[10] Tissier, *ibid.*, 1863, 158.

[11] Geuther, *ibid.*, 1865, 173.

[12] Duboin, *Compt. rend.*, 1895, 120, 678.

The following *double fluorides* have been reported: $MgTiF_6.6H_2O$,[1] $MgZrF_6.5H_2O$,[2] $MgSnF_6.6H_2O$.[1]

Magnesium Chloride. Anhydrous $MgCl_2$ is white, deliquescent, and soluble in water with great evolution of heat. It is formed by the action of chlorine on the metal[3] or on heated magnesium oxide,[4] or, more easily, on a heated mixture of magnesium oxide and carbon.[5]

It has also been prepared by heating $NH_4Cl.MgCl_2.6H_2O$,[6] by heating the hydroxide in hydrogen chloride,[7] and by heating the hexahydrate *in vacuo* at 175° C.[8]

It is easily distilled in a current of hydrogen, and the cooled product crystallises into shining laminated crystals that have a density of 2·177[9] and melt at 708° C.[10]

Between 580° C. and 700° C. the reaction

$$2MgCl_2+O_2\rightleftharpoons 2MgO+2Cl_2$$

is endothermic.[11, 12]

Between 350° C. and 505° C. the reaction

$$MgCl_2+H_2O\rightleftharpoons MgCl(HO)+HCl$$

is exothermic. The oxychloride decomposes from 505°–510° C., and above the latter temperature the reaction

$$MgCl_2+H_2O\rightleftharpoons MgO+2HCl$$

is endothermic.[12] Hydrogen chloride has been prepared by this last reaction.[13]

The monoetherate, $MgCl_2.Et_2O$, has been obtained in white acicular crystals.[14]

$MgCl_2.4NH_3$ has been prepared as an easily decomposable compound,[15] and $MgCl_2.6NH_3$ has also been reported.[16]

When a solution of oxide or carbonate of magnesium in hydrochloric acid is crystallised, the hexahydrate, $MgCl_2.6H_2O$, separates as colourless monoclinic crystals with a density of 1·56 and a bitter taste. The hexahydrate is stable in contact with the saturated solution of magnesium chloride from −3·4° to 116·7° C. From 116·7° to 181° C. the tetrahydrate is the stable form and the dihydrate above 181° C. From −3·4° to −16·8° C. the α-octahydrate is stable. Between −9·6° C. and −17·4° C. a labile solution may be in equilibrium with the labile β-octahydrate. The dodecahydrate is the stable form from −16·8° to −33·6° C. : the crystals are lighter than their mother-liquor.[1]

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[1] Marignac, *Ann. Mines*, 1859, [5], 15, 256.

[2] Marignac, *J. prakt. Chem.*, 1861, 83, 202.

[3] Ohmann, *Ber.*, 1920, 53B, 1429.

[4] Gay-Lussac and Thénard, *Recherches*, 1811, 2, 143.

[5] Bussy, *J. Ch. méd.*, 1830, 6, 142.

[6] Döbereiner, *Schweigger's J.*, 1820, 2, 90; Liebig, *Pogg. Annalen*, 1830, 19, 137.

[7] Hempel, *Ber.*, 1888, 21, 897.

[8] German Patent, 161662 (1903).

[9] Deville and Caron, *Ann. Chim. Phys.*, 1863, [3], 67, 340.

[10] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 273.

[11] Haber and Fleischmann, *Zeitsch. anorg. Chem.*, 1906, 51, 336.

[12] Moldenhauer, *ibid.*, 1906, 51, 369.

[13] German Patent, 51084 (1889).

[14] Domanicki, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 1790.

[15] Clark, *Annalen*, 1851, 78, 369.

[16] Isambert, *Jahresber.*, 1868, 182.

A monohydrate has been prepared by heating the tetrahydrate above 111° C. in hydrogen chloride,[2] and a dihydrate has been obtained as small, white, deliquescent crystals from a solution of the chloride in hydrochloric acid.[3]

The hexahydrate is obtained as a by-product in the preparation of potassium chloride from carnallite, in the Weldon process, and in the Solvay alkali process.

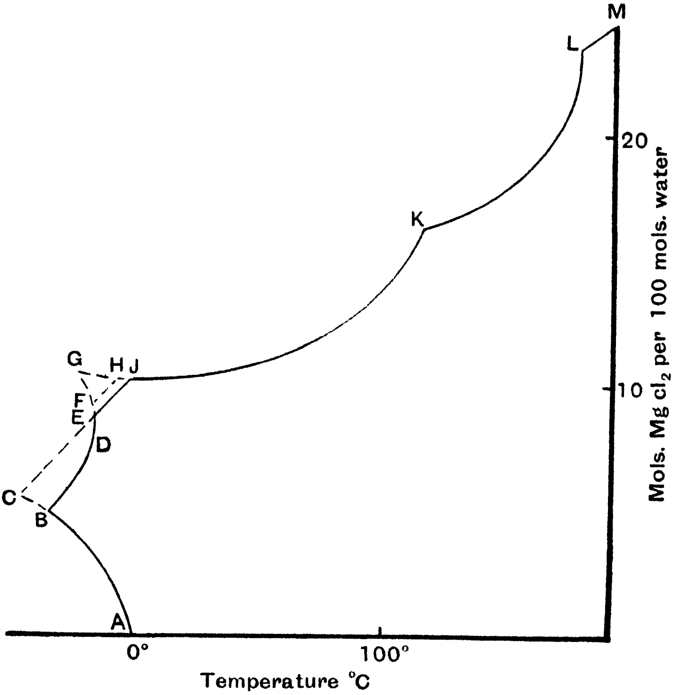

FIG. 2.

A. Stable solutions in contact with ice, curve AB.
B. Stable solutions in contact with the following hydrates: $MgCl_2.12H_2O$, curve BDE; $MgCl_2.8\alpha H_2O$, curve EJ; $MgCl_2.6H_2O$, curve JK; $MgCl_2.4H_2O$, curve KL; $MgCl_2.2H_2O$, curve LM.
C. Labile solutions in contact with $MgCl_2.8\beta H_2O$, curve FH; $MgCl_2.12H_2O$, curve EG; $MgCl_2.8\alpha H_2O$, curve EC; $MgCl_2.6H_2O$, curve JG; Ice, curve BC.

Concentrated solutions of magnesium chloride dissolve oxide or carbonate of lead, lead sulphate, and small amounts of zinc oxide.[4]

One hundred parts of water dissolve 52·2 parts of $MgCl_2$ at 0° C., and the density of the saturated solution at 15° C. is 1·3619.[5]

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[1] Bogorodusky, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 735; van 't Hoff and Meyerhoffer, *Zeitsch. physikal. Chem.*, 1898, **27**, 75.
[2] Moldenhauer, *Zeitsch. anorg. Chem.*, 1906, **51**, 369.
[3] Ditte, *Ann. Chim. Phys.*, 1881, [5], **22**, 560.
[4] Hof, *Chem. Zeit.*, 1909, **33**, 1077.
[5] Engel, *Bull. Soc. chim.*, 1887, [2], **47**, 318.

The solubility of $MgCl_2.6H_2O$ in parts of $MgCl_2$ per 100 parts solution is—

Temperature, ° C.	22	62	68·2	79·7	116·67
Solution	35·5	38·0	38·3	39·5	46·1 [1]

$MgCl_2$ and $MgCl_2.6H_2O$ are soluble in alcohol.

$$[Mg]+(Cl_2) = [MgCl_2]+151·01 \text{ Cal.}$$
$$[MgCl_2]+Aq. = MgCl_2.Aq.+35·92 \text{ Cal.}$$
$$[MgCl_2.6H_2O]+Aq. = MgCl_2.Aq.+2·937 \text{ Cal.}[2]$$

Basic Chlorides.—Magnesium chloride has a corrosive action on steam boilers,[3] and when its solution is evaporated it begins to give off hydrogen chloride when the $MgCl_2$ and H_2O are in about the proportion of 1 molecule to 6.[4]

Sorel found that a mixture of calcined magnesia with concentrated magnesium chloride solution set in a few hours to a solid mass.[5] Magnesia or Sorel cements are now prepared by heating slightly burned dolomite with solutions of magnesium chloride. Gelatinous liquids, such as glue solutions, are added to secure effective mixing. Magnesia cements are useful for cementing metallic objects, but the atmosphere acts upon them.[6]

Various compounds corresponding to the general formula $MgCl_2.xMgO.yH_2O$ have been described.[7] These magnesium oxychlorides are probably solid solutions and not definite compounds.[8] According to Robinson and Waggaman,[9] the solid substance in equilibrium with solutions containing less than 10 per cent. of $MgCl_2$ is an indefinite solid solution, and $MgCl_2.3MgO.10H_2O$ is the solid in contact with more concentrated solutions.

The compact products of the action of magnesium chloride on the oxide will polish. They absorb carbon dioxide, and water dissolves magnesium chloride out of them. The crystallised preparations are also attacked by water.[10] Prolonged treatment with water leaves a compact solid as hard as sandstone, which will polish.[11] This residue is a hydrated magnesium oxide, $2MgO.3H_2O$, and resembles the mineral brucite, $Mg(OH)_2$.

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[1] van 't Hoff and Meyerhoffer, *Zeitsch. physikal. Chem.*, 1898, 27, 75. For densities of solutions, see Kremers, *Pogg. Annalen*, 1858, 104, 155; Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 281, 283; Oudemans, *Zeitsch. anal. Chem.*, 1868, 7, 420; Wagner, *Zeitsch. physikal. Chem.*, 1890, 5, 31. For freezing-points of solutions, see Loomis, *Ann. Phys. Chem.*, 1896, [2], 57, 495; Jones and Chambers, *Amer. Chem. J.*, 1900, 23, 89. For boiling-points of solutions, see Gerlach, *Zeitsch. anal. Chem.*, 1887, 26, 440; Skinner, *Trans. Chem. Soc.*, 1892, 61, 341. For transference ratios, see Becie, *Zeitsch. physikal. Chem.*, 1898, 27, 1. For heat of dilution, see Dunnington and Hoggard, *Amer. Chem. J.*, 1899, 22, 207.

[2] Thomsen, *J. prakt. Chem.*, 1875, [2], 11, 233. See also Berthelot and Ilosvay, *Ann. Chim. Phys.*, 1883, [5], 29, 304.

[3] Feld, *Chem. Zeit.*, 1902, 26, 1099.

[4] Casaseca, *Compt. rend.*, 1853, 37, 350; Hof, *Chem. Zeit.*, 1915, 39, 470.

[5] Sorel, *Compt. rend.*, 1867, 65, 102.

[6] Blücher, *Modern Industrial Chemistry* (translated by Millington) (Gresham Publishing Co., London), 1914.

[7] Bender, *Annalen*, 1871, 159, 341; Davis, *Chem. News*, 1872, 25, 258; Krause, *Annalen*, 1873, 165, 38; André, *Compt. rend.*, 1887, 94, 444; Robinson and Waggaman, *J. Physical Chem.*, 1909, 13, 673.

[8] Kallauner, *Chem. Zeit.*, 1909, 33, 871.

[9] Robinson and Waggaman, *loc. cit.* See Hof, *Chem. Zeit.*, 1908, 32, 993.

[10] Krause, *loc. cit.*; André, *loc. cit.*

[11] Bender, *loc. cit.*

Double Chlorides.—A double chloride of sodium and magnesium, namely, $NaCl.MgCl_2$, is indicated on the freezing-point curve,[1] and is said to have been prepared crystalline.[2] The potassium salts, $KCl.MgCl_2$ and $2KCl.MgCl_2$,[3] are indicated on the freezing-point curve.[1] On raising a cool solution of potassium and magnesium chlorides to $-21°$ C., *carnallite*, $KCl.MgCl_2.6H_2O$,[4] which is unstable at lower temperatures, is formed according to the equation—

$$KCl + MgCl_2.12H_2O \rightleftharpoons KCl.MgCl_2.6H_2O + 6H_2O.$$

Above 167·5° C. the carnallite is again completely decomposed, and at all intermediate temperatures it is partially decomposed by water. At these intermediate temperatures carnallite can only exist in contact with a solution containing excess of potassium or magnesium chloride.[5]

Carnallite is concentrated commercially until the bulk of the potassium chloride is deposited. Magnesium chloride is obtained from the mother-liquor and used for preparing other magnesium salts.

Carnallite occurs at Stassfurt in large masses, which are usually tinged red with iron.[6] It also occurs in some salt lakes.[7]

Pure carnallite crystallises in colourless rhombic prisms which have a hardness of 1, a density of 1·6, and deliquesce in air, leaving a residue of solid potassium chloride. One hundred parts of water at 18° C. dissolve 64·5 parts of carnallite with lowering of temperature. Natural carnallite contains rubidium and cæsium.[8]

$RbCl.MgCl_2.6H_2O$ [8] and $CsCl.MgCl_2.6H_2O$ [9] have been described.

Ammonium magnesium chloride, $NH_4.MgCl_2.6H_2O$,[10] crystallises from a solution of its constituent salts in small, colourless, deliquescent crystals which dissolve in 6 parts of water and have a density of 1·456.

Smaller crystals deposit from a solution containing the sulphates of magnesium and ammonium together with magnesium chloride.[11]

Magnesium chloride free from oxide is obtained by igniting the double chloride.

$2MgCl_2.CaCl_2.12H_2O$ crystallises, above 22° C., from a solution of its constituent salts in appropriate proportions.[12] It occurs in the Stassfurt deposits as transparent deliquescent masses, which are frequently yellow, and is known as *tachhydrite*.[13] It crystallises in the hexagonal rhombohedral system, and has a hardness of 2·5. At 15° C. the density of the mineral is 1·671, and of the artificial crystals prepared by reaction between the component salts 1·666.[14]

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[1] Menge, *Zeitsch. anorg. Chem.*, 1911, **72**, 162.

[2] Poggiale, *Compt. rend.*, 1870, **20**, 1130; de Schulten, *Bull. Soc. franç. Min.*, 1898, **21**, 87.

[3] Produced analogously to the corresponding double fluoride (Duboin, *Compt. rend.*, 1895, **120**, 678).

[4] Rose, *Pogg. Annalen*, 1856, **98**, 161.

[5] van 't Hoff and Meyerhoffer, *Zeitsch. physikal. Chem.*, 1899, **30**, 64.

[6] Hake, *J. Soc. Chem. Ind.*, 1883, **2**, 146.

[7] Merle, *Bull. Soc. chim.*, 1868, [2], **10**, 63; Schröker, *Jahresber.*, 1862, 767.

[8] Feit and Kubiersky, *Chem. Zeit.*, 1892, **16**, 335.

[9] Wells and Campbell, *Zeitsch. anorg. Chem.*, 1893, **5**, 273.

[10] Kittel, *Jahresber.*, 1857, 150.

[11] de Schulten, *Bull. Soc. chim.*, 1897, [3], **17**, 165.

[12] van 't Hoff, *Zeitsch. anorg. Chem.*, 1905, **47**, 245.

[13] Rammelsberg, *Pogg. Annalen*, 1856, **98**, 261.

[14] de Schulten, *Compt. rend.*, 1890, **111**, 929.

$MgCl_2.ZnCl_2.6H_2O$,[1] $MgCl_2.CdCl_2.12H_2O$,[2] $MgCl_2.HgCl_2.6H_2O$ and $MgCl_2.3HgCl_2.5H_2O$,[3] $MgCl_2.2TlCl_3.6H_2O$,[4] $2MgCl_2.PbCl_2.13H_2O$,[5] $MgCl_2.Mg(Cl.OH).2SbCl_5.17H_2O$,[6] and $MgCl_2.2MnCl_2.12H_2O$ [7] have been described.

Magnesium Bromide.—Anhydrous $MgBr_2$ has been prepared by the action of bromine on a heated mixture of carbon and magnesium oxide, or on the heated metal, by melting the anhydrous chloride with ammonium bromide, and by heating a mixture of ammonium bromide and hydrated magnesium bromide. It is a white crystalline mass, resembling magnesium chloride, which is hygroscopic, easily oxidised in air, and not volatile.[8] It melts at 695° C.[9]

It dissolves freely in water with the evolution of heat,[10, 11, 12] and crystallises, under ordinary conditions, from its aqueous solutions as $MgBr_2.6H_2O$.[8, 13] This hexahydrate occurs naturally in the upper layers of the Stassfurt deposits, and can be prepared by dissolving magnesium in hydrobromic acid and crystallising over sulphuric acid,[14] or by the action of bromine on magnesium dust and water.[8] The pure product from the decomposition of the dietherate melts at 164° C.[11] $MgBr_2.10H_2O$ crystallises at lower temperatures: it melts and loses water at 12° C.[15]

The hexahydrate loses 2 molecules of water on heating, and at higher temperatures both hydrogen bromide and water are liberated. An atmosphere of hydrogen bromide inhibits the decomposition.[14]

The heat of combination of $MgBr_2$ is 21·700 Cal., and its heat of solution is 43·300 Cal.[16]

Magnesium bromide occurs in sea-water and in saline springs.

Magnesium Oxybromides.—$MgBr_2.3MgO.12H_2O$ has been prepared in small acicular crystals by dissolving calcined magnesia in magnesium bromide solution. It loses 6 molecules of water at 120° C., and is decomposed by water or alcohol.[17]

$MgBr(OH).MgBr_2.2(C_2H_5)_2O$ has been prepared as colourless hygroscopic crystals which are decomposed by water.[18]

Double Bromides of Magnesium.—The following have been described: $KBr . MgBr_2 . 6H_2O$, $NH_4Br . MgBr_2 . 6H_2O$,[19, 8]

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[1] Warner, *Chem. News*, 1873, **27**, 271.

[2] Rimbach, *Ber.*, 1897, **30**, 3073.

[3] Bonsdorff, *Pogg. Annalen*, 1829, **17**, 133.

[4] Gewecke, *Annalen*, 1909, **366**, 217.

[5] Otto and Drewes, *Arch. Pharm.*, 1890. **228**, 495.

[6] Wanland and Schlegelmilch, *Ber.*, 1901, **34**, 2633.

[7] Saunders, *Amer. Chem. J.*, 1892, **14**, 148.

[8] Lerch, *J. prakt. Chem.*, 1883, [2], **28**, 338. For action of bromine on magnesium, also see Gautier and Sharpy, *Compt. rend.*, 1891, **113**, 597.

[9] Carnelley, *Trans. Chem. Soc.*, 1878. **33**, 273.

[10] Mylius and Funk, *Ber.*, 1897, **30**, [2], 1716.

[11] Menschutkin, *Zeitsch. anorg. Chem.*, 1907, **52**, 152.

[12] For densities of solutions, see Gerlach, *Zeitsch. anal. Chem.*, 1869, **8**, 285.

[13] van 't Hoff and Dawson, *Zeitsch. physikal. Chem.*, 1897, **22**, 598.

[14] Kreider, *Amer. J. Sci.*, 1905, [iv], **20**, 97.

[15] Panfilow, *J. Russ. Phys. Chem. Soc.*, 1894, **26**, 231.

[16] Beketoff, *Chem. Zentr.*, 1892, **1**, 11.

[17] Tassilly, *Compt. rend.*, 1897, **125**, 605.

[18] Holroyd, *Proc. Chem. Soc.*, 1904, **20**, 38.

[19] Feit, *J. prakt. Chem.*, 1889, [2], **39**, 373, de Schulten, *Bull. Soc. chim.*, 1897, [iii], **17**, 167.

$MgBr_2.SnBr_4.10H_2O$,[1] $2MgBr_2.PbBr_2.16H_2O$,[2] $MgBr_2.HgBr_2$, $MgBr_2.2HgBr_2$, $MgBr_2.2MnBr_2.12H_2O$.[3]

Magnesium Iodide.—Anhydrous MgI_2 is similar to $MgBr_2$, though it is more easily oxidised and melts at a higher temperature. It has not been prepared, apparently, by passing iodine vapour over a heated mixture of carbon and magnesium oxide, but its methods of preparation are similar to those of the bromide.[4]

A saturated solution contains 148 parts of MgI_2 in every 100 parts of water.[5, 6] $MgI_2.8H_2O$ separates at ordinary temperatures from a solution either of the anhydrous salt in water or of magnesia in hydriodic acid,[7] or, in colourless prismatic needles, from the product of the action of iodine on magnesium powder and water.[4] At lower temperatures $MgI_2.10H_2O$ separates.[5]

Magnesium iodide occurs in sea-water and saline springs; it forms double salts with mercuric chloride.[8]

The heat of combination of MgI_2 is 84·800 Cal., and the heat of solution 49·800 Cal.[9]

Double Iodides, $KI.MgI_2.6H_2O$ and $NH_4I.MgI_2.6H_2O$, have been prepared by evaporating solutions of the mixed salts over sulphuric acid in a vacuum. They crystallise in flattened prisms of densities 2·547 and 2·346 at 15° C.[10] $MgI_2.2BiI_3.12H_2O$ has been obtained.[11]

Oxyhalogen Compounds of Magnesium. When magnesium oxide or hydroxide is dissolved in *hypochlorous* or *hypobromous* acid,[12] or its suspension in water treated with chlorine or bromine,[13] or when bleaching-powder suspension in water is heated with magnesium sulphate, the resulting solutions have bleaching properties. These solutions decompose slowly in the cold, and rapidly on heating, to halide and halate. They are often preferred to bleaching powder for bleaching because they are less caustic.[14] Magnesium hypobromite and bromate are produced by electrolysing potassium bromide solution.[15] Magnesium metal dissolves in hypochlorous acid to a relatively stable hypochlorite solution.[16]

Magnesium Chlorate, $Mg(ClO_3)_2.6H_2O$, occurs in deliquescent crystals which are soluble in water and in alcohol, melt in their own water at 40° C., and decompose at 120° C. into water, chlorine, oxygen, and magnesium oxide.

It is prepared by passing chlorine into a hot suspension of magnesium hydroxide in water, or by decomposing barium chlorate with magnesium sulphate.[1, 2]

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[1] Leteur, *Compt. rend.*, 1891, 113, 540.

[2] Otto and Drewes, *Arch. Pharm.*, 1891, 229, 585.

[3] Saunders, *Amer. Chem. J.*, 1892, 14, 150.

[4] Lerch, *J. prakt. Chem.*, 1883, [2], 28, 338.

[5] Mylius and Funk, *Ber.*, 1897, 30, [2], 1716.

[6] Menschutkin, *Zeitsch. anorg. Chem.*, 1907, 52, 152.

[7] Panfilow, *J. Russ. Phys. Chem. Soc.*, 1894, 26, 231.

[8] Duboin, *Compt. rend.*, 1906, 142, 1338.

[9] Beketoff, *Chem. Zentr.*, 1892, I, 11.

[10] de Schulten, *Bull. Soc. chim.*, 1900, [3], 23, 158.

[11] Lineau, *Pogg. Annalen*, 1860, III, 240.

[12] Balard, *Ann. Chim. Phys.*, 1834, 57, 225.

[13] Grouvelle, *ibid.*, 1821, 17, 37; Lunge and Landolt, *Dingl. poly J.*, 1886, 259, 47.

[14] Bolley and Jokisch, *Bull. Soc. chim.*, 1866, [2], 7, 524.

[15] Sarghel, *Zeitsch. Elektrochem.*, 1899, 6, 149, 173.

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

According to Meusser, the hexahydrate loses 2 molecules of water at 35° C. and other 2 at 65° C. The tetrahydrate crystallises in hygroscopic rhombohedra and the dihydrate decomposes at 80° C.[3]

Magnesium Bromate, $Mg(BrO_3)_2.6H_2O$, occurs in colourless, efflorescent, regular octahedra. It dissolves in 1·4 parts of water, melts in its own water, and is dehydrated by heating to 200° C. Above that temperature it decomposes into magnesium oxide, bromine, and oxygen. It is prepared by dissolving magnesium oxide or carbonate in bromic acid, or by heating magnesium fluosilicate with potassium bromate.[4, 5] It is also produced, along with hypobromite, during the electrolysis of potassium bromide solution.[6]

Magnesium Iodate, $Mg(IO_3)_2.4H_2O$, is more stable than the chlorate or bromate. The monoclinic crystals lose three molecules of water at 150° C. and the fourth at 210° C. At higher temperatures the anhydrous salt decomposes. It is prepared by the double decomposition of magnesium nitrate and an alkaline iodate, or by dissolving magnesia in iodic acid. It dissolves in 9·4 parts of water at 15° C. and in 3·14 parts at 100° C.[7]

A supersaturated solution of magnesium iodate, cooled to 0° C. and stirred, deposits rhombic plates of the dodecahydrate which melts at 50° C. and passes into the tetrahydrate.[2]

Magnesium Perchlorate, $Mg(ClO_4)_2$, occurs in deliquescent needles which were said to be very soluble in either water or alcohol. It is prepared by dissolving magnesia in aqueous perchloric acid,[8] and has been described as a hexa-aquo-salt with the formula $[Mg(H_2O)_6](ClO_4)_2$.[9]

The *hexahydrate* has been obtained by drying over the anhydrous perchlorate. It melts between 145° C. and 147° C., and the crystallised salt does not deliquesce though the fused material does.[10] It becomes the *trihydrate* when kept over phosphorus pentoxide at 20°–25° C., and *anhydrous* when heated in dry air up to 250° C. The anhydrous salt hisses in water, and compares favourably with phosphorus pentoxide as a drying agent. The trihydrate is less efficient than the anhydrous at temperatures above 0° C. The densities of the three salts, at 25°/4° C. and corrected to a vacuum, are respectively 1·970, 2·044, and 2·60.[11]

Magnesium Periodates. Langlois[12] obtained small prismatic crystals of magnesium dimesoperiodate, $Mg_2I_2O_9$, with 12 molecules of water, by dissolving magnesium carbonate in periodic acid. A residue of the trihydrate remained after heating the crystals to 100° C.

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[1] Wächter, *J. prakt. Chem.*, 1843, 30, 325.

[2] Mylius and Funk, *Ber.*, 1897, 30, [2], 1716.

[3] Meusser, *ibid.*, 1902, 35, [2], 1414.

[4] Rammelsberg, *Pogg. Annalen*, 1841, 52, 89.

[5] Löwig, *Arch. Pharm.*, 1830, 33, 6.

[6] Sarghel, *Zeitsch. Elektrochem.*, 1899, 6, 149, 173.

[7] Millon, *Ann. Chim. Phys.*, 1843, [3], 9, 422; Marignac, *Jahresber.*, 1857, 150; Ditte, *Recherches sur l'acide Iodique*, 1870, 69.

[8] Sérullas, *Ann. Chim. Phys.*, 1830, 45, 270.

[9] Weinland and Ensgraber, *Zeitsch. anorg. Chem.*, 1913, 84, 368.

[10] See Sérullas, *Ann. Chim. Phys.*, 1831, [2], 46, 304.

[11] Willard and Smith, *J. Amer. Chem. Soc.*, 1922, 44, 2255.

[12] Langlois, *Ann. Chim. Phys.*, 1852, [3], 34, 257.

Rammelsberg obtained the metaperiodate, $Mg(IO_4)_2.10H_2O$, from the mother-liquor.[1]

Rammelsberg also described some other periodates.[2]

MAGNESIUM AND MANGANESE.

Magnesium Permanganate.—Michael and Garner describe $Mg(MnO_4)_2$ as a crystalline salt with a bluish-grey metallic lustre which desiccation *in vacuo* at 100° C. alters to a purple tint. Mitscherlich and Aschoff originally described it as a deliquescent substance with 6 molecules of water of crystallisation. Mitscherlich's original method of preparation, reaction between solutions of barium permanganate and magnesium sulphate, is still the best.

In aqueous solution magnesium permanganate is rapidly decomposed at water-bath heat, giving off oxygen and ozone. It is apparently liable to explode in the solid condition.

Magnesium permanganate is a very vigorous oxidising agent. This vigour may be partly connected with the tendency of magnesium salts to hydrolyse to magnesium hydroxide.[3] Since strong alkali is produced when potassium permanganate oxidises substances in aqueous solution, magnesium permanganate is often a preferable oxidising agent, apart from its vigour, because it only involves the formation of the relatively inert magnesium hydroxide.

A solution of the salt in glacial acetic acid is an extremely powerful oxidising agent; in pyridine its oxidising powers are much less.[4]

MAGNESIUM AND OXYGEN.

Magnesium Suboxide.—During the electrolysis of magnesium and potassium chlorides in a graphite crucible, Frary and Berman obtained a dark substance which oxidised rapidly and evolved hydrogen from water.[5] Beetz had noted a similar compound on the positive pole when sodium chloride solution was electrolysed between magnesium electrodes,[6] and Gore had observed a black deposit when magnesium was in contact with palladium, water, and carbon tetrachloride vapour, and under other conditions. The powder went white on heating, dissolved in dilute acids, and probably dissolved in alkaline sulphides.[7]

Baborovsky concluded that the electrolytically produced "suboxide" was a mixture of hydroxide and finely divided metal.[8]

Magnesium Oxide.—The mineral *periclase*, MgO, crystallises in transparent regular octahedra which have a density of 3·7–3·9 and a hardness of 5·5–6. When the amorphous variety of the oxide is volatilised in an electric furnace it deposits in the crystalline form.[9] Amorphous magnesia remains as a residue when magnesium salts of oxyacids are heated in air or when magnesium burns in air or oxygen.[1]

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[1] Rammelsberg, *Pogg. Annalen*, 1841, **52**, 89; 1844, **55**, 239.

[2] Rammelsberg, *ibid.*, 1868, **134**, 499, 503, 510.

[3] Hauser (*Chem. Zeit.*, 1913, **37**, 58) found that magnesium ions accelerate some oxidations by potassium permanganate.

[4] Michael and Garner, *Amer. Chem. J.*, 1906, **35**, 267.

[5] Frary and Berman, *Trans. Amer. Electrochem. Soc.*, 1915, **27**, 209.

[6] Beetz, *Phil. Mag.*, 1866, [4], **32**, 269.

[7] Gore, *Chem. News*, 1884, **50**, 157.

[8] Baborovsky, *Ber.*, 1903, **36**, 2719; *Zeitsch Elektrochem.*, 1905, **11**, 465.

[9] Heusler, *Zeitsch. anorg. Chem.*, 1896, **11**, 293.

Amorphous magnesium oxide has been most commonly prepared by gentle prolonged heating of the carbonate or hydroxide, and the natural carbonate has long been used for this purpose.[2] The denser the original carbonate and the higher the temperature of production, the denser the resulting oxide.

Since waste magnesium chloride liquors remain after the preparation of potassium chloride from carnallite, magnesium chloride has often been used as a starting-point for preparing magnesium oxide. Magnesium chloride has been (*a*) heated with steam,[3, 4] (*b*) converted into hydroxide by lime,[3, 5] (*c*) converted into oxychloride by heating with magnesite and decomposed by water into hydroxide and chloride,[6] (*d*) precipitated as hydroxide by calcium oxychloride solution,[7] (*e*) treated with calcined dolomite.[3, 8]

Magnesium sulphate has also been treated with calcined dolomite.[9]

Ordinary magnesium oxide is a white, tasteless, odourless powder. Its density is 3·1932 after being heated to 350° C,[10] and 3·654 after fusion in an electric furnace.[11] Between these temperatures its density rises as it is heated more strongly. Ordinary commercial magnesia is a fine, very bulky powder, of density 3·07–3·2. The volume occupied by a given weight may vary from 1 to 3·5, according to the carbonate from which it is prepared, and it is commonly classed as "heavy" and "light."[12] "Heavy" carbonates require a higher temperature than "light" to decompose them, and the resulting oxide is denser.[13]

Moist magnesium oxide is alkaline to litmus. The higher the temperature to which it has been raised the more slowly it dissolves in water, and the rate of solution also varies with the source: oxide prepared from magnesite at a white heat appears to be practically insoluble.[13, 14]

Polymerisation probably accounts for the increased density of magnesium oxide with increased temperature, and for its correspondingly increased resistance to the action of water.[13, 15]

The influence of preliminary treatment on the solution of magnesium oxide probably explains the variation from 500 mgm. to 5 mgm. per litre obtained by different observers for its solubility.[13, 16] Magnesia absorbs water and carbon dioxide in contact with air, and is soluble in acids.[17]

The oxide obtained by gently heating the native carbonate "sets" to a firm mass with a little water, and the oxide from the nitrate prepared by treating artificial carbonates with nitric acid behaves similarly. The product of the ignition of artificial carbonates does not "set."[1]

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[1] Winkler, *Ber.*, 1890, **23**, 120; Matignon and Lassieur, *Compt. rend.*, 1912, **154**, 63.

[2] Planche, *Bull. Pharm.*, 1810, **2**, 71.

[3] *Chem. News*, 1881, **44**, 76.

[4] See Magnesium Chloride.

[5] Schloesing, *Compt. rend.*, 1881, **93**, 156, 215.

[6] German Patent, 19259 (September 1881).

[7] German Patent, 20277 (February 1882).

[8] Clossen, *Jahresber.*, 1881, 1262.

[9] Scheibler, German Patent, 16575 (1881).

[10] Ditte, *Compt. rend.*, 1861, **53**, 111.

[11] Moissan, *ibid.*, 1894, **118**, 506.

[12] *British Pharmacopœia.*

[13] Anderson, *Trans. Chem. Soc.*, 1905, **87**, 257.

[14] Campbell, *J. Ind. Eng. Chem.*, 1918, **10**, 595.

[15] Moissan, *Compt. rend.*, 1894, **118**, 506.

[16] Fyfe, *Edinburgh Phil. J.*, 1821, **5**, 305; Fresenius, *Annalen*, 1846, **59**, 123; Bineau, *Compt. rend.*, 1855, **41**, 570; Kohlrausch and Rose, *Zeitsch. physikal. Chem.*, 1893, **12**, 241; Dupré and Bialas, *Zeitsch. angew. Chem.*, 1903, **16**, 54.

[17] See also Magnesium Hydrogen Sulphates.

It melts at about 2250° C. and then vaporises freely; its boiling-point is near its melting-point. Carbon seems to reduce it at temperatures as low as 1700° C. In the electric furnace the reaction

$$CO + Mg = C + MgO$$

must be prevented, either by removing the carbon monoxide or alloying the magnesium with copper, to obtain the metal.[2] Otherwise deposits of magnesia are obtained.[3]

Crystalline magnesium oxide sublimes when the amorphous oxide is heated either in an electric furnace[4] or strongly with hydrochloric acid.[5] It also crystallises out of a fusion of potassium and magnesium hydroxides,[6] and Debray obtained it by heating magnesium sulphate strongly with an alkali sulphate.[7] Artificially prepared crystalline magnesium oxide is usually octahedral and corresponds to natural periclase, though Houdard, by heating the amorphous variety with magnesium sulphide, obtained cubical crystals with a density of 3·5692 3·5705.[8]

Crystalline magnesium oxide dissolves slowly in warm hydrochloric or nitric acid, rapidly in sulphuric acid, and is scarcely attacked by water.[9]

Thomsen's value of 143·4 Cal. for the heat of formation of magnesium oxide is probably too low.[10] Its molecular heat at 2780° C. is about 11·6 Cal.[11]

Magnesium oxide emits a bright white light at a red heat, and has been used instead of lime in the oxyhydrogen lantern. Since it is very refractory it is used for making crucibles, firebricks, furnace linings, etc. It conducts heat rather well, but it can easily be moulded and fired without any addition of other substances. In medicine it is used as a purgative, and as an antidote to poisoning by arsenious acid, copper sulphate, and acids. Magnesia is also an important constituent of cements and hydraulic mortars. It has a brilliant red fluorescence when mixed with a little chromic oxide,[12] and phosphoresces under certain conditions.[13]

Magnesium Hydroxide, $Mg(OH)_2$, occurs naturally as *brucite* in colourless rhombohedra, similarly to calcite, though it sometimes has a bluish or greenish colour. A residue of $2MgO.3H_2O$, resembling brucite, is obtained by prolonged treatment of the compact products of the action of magnesium chloride on magnesia with hot water.[14]

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[1] Anderson, *Trans. Chem. Soc.*, 1905, 87, 257.

[2] Slade, *ibid.*, 1908, 93, 327.

[3] Lebeau, *Compt. rend.*, 1907, 144, 799.

[4] Heusler, *Zeitsch. anorg. Chem.*, 1896, 11, 293.

[5] Deville, *Compt. rend.*, 1861, 53, 199, 1267; Otto and Kloos, *Ber.*, 1891, 24, 1480; Meunier, *Bull. Soc. chim.*, 1919, [iv], 25, 560.

[6] de Schulten, *Bull. Soc. Min.*, 1898, 21, 87.

[7] Debray, *Compt. rend.*, 1861, 52, 985.

[8] Houdard, *ibid.*, 1907, 144, 1349.

[9] Houdard, *ibid.* See also Magnesium Hydrogen Sulphates.

[10] Moissan, *ibid.*, 1899, 128, 384.

[11] Wartenberg and Witzel, *Zeitsch. Elektrochem.*, 1919, 25, 209.

[12] de Boisbaudran, *Compt. rend.*, 1887, 104, 330.

[13] Crookes, *Proc. Roy. Soc.*, 1887, 42, 111.

[14] Bender, *Annalen*, 1871, 159, 341.

Flattened, hexagonal, prismatic crystals of $Mg(OH)_2$ have been obtained by heating magnesium chloride with a large excess of potassium hydroxide in the presence of water to 210°–220° C., cooling and extracting the alkali. Their density is 2·36 at 15° C., and they dissolve easily in acids or in warm concentrated ammonium chloride solution.[1]

$Mg(HO)_2$ precipitates when sodium or potassium hydroxide is added to a solution of a magnesium salt,[2] or when alkali salts are electrolysed with a platinum cathode and a magnesium anode.[3] After washing and drying at 100° C. it is a white tasteless powder. One litre of water dissolves 9 mgm. at 18° C.[4]

Ammonium salts prevent the precipitation of magnesium hydroxide by ammonia by diminishing the dissociation of the ammonium hydroxide.[5] The decreased concentration of hydroxyl ions decreases the formation of magnesium hydroxide below the precipitation point.[6] Ammonium sulphate is more effective than ammonium chloride in preventing precipitation—though it is less completely dissociated. According to the equation

$$2MgSO_4 \rightleftharpoons Mg^{\cdot\cdot} + [Mg(SO_4)_2]'',$$

magnesium sulphate gives fewer magnesium ions than the chloride. The presence of ammonium sulphate still further depresses the dissociation, and the formation of magnesium hydroxide is thus further kept below the precipitation point.[7]

The moist hydroxide has an alkaline reaction, dissolves in acids, including carbonic acid,[8] and decomposes into water and oxide at a dull red heat.

Magnesium Peroxide.—Hydrogen peroxide precipitates from ammoniacal solutions of magnesium salts a substance with peroxide properties.[9] The dried product from the action of sodium hydroxide on magnesium sulphate in the presence of hydrogen peroxide corresponds roughly with $MgO_2.3MgO.Aq.$[10] More highly peroxidised products result when magnesium chloride solution is electrolysed in the presence of hydrogen peroxide. The electrolytic cell is divided into two parts by a porous diaphragm, and the cathodic compartment contains the hydrogen peroxide. The anodes are platinum or carbon, and the cathodes platinum or tin. The reaction is represented by the equation

$$Mg+O_2+2H_2O=Mg(OH)_4.$$ [11]

A substance containing 42 per cent. magnesium peroxide is obtained by treating ignited magnesia with pure hydrogen peroxide.[12]

Commercial magnesium peroxide is a white amorphous powder which is apparently a compound consisting of magnesium peroxide, magnesium hydroxide, and constitutional water. The ordinary product contains 8 per cent. available oxygen, and has a density of 0·615. One part dissolves in 14,550 parts of water at 20° C. It is stable in dry air, even up to 160° C., but is sensitive to the carbon dioxide in moist air.[1]

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[1] de Schulten, *Compt. rend.*, 1885, **101**, 72.

[2] Patten, *J. Amer. Chem. Soc.*, 1903, **25**, 186.

[3] Glaser, *Zeitsch. anorg. Chem.*, 1898, **4**, 427.

[4] Kohlrausch and Rose, *Ann. Phys. Chem.*, 1894, [2], **50**, 127.

[5] Lovén, *Zeitsch. anorg. Chem.*, 1896, **11**, 404.

[6] Treadwell, *ibid.*, 1903, **37**, 326; Herz and Muhs, *ibid.*, 1904, **38**, 138.

[7] Brunner, *Helv. Chim. Acta*, 1919, **2**, 277.

[8] Monhaupt, *Chem. Zeit.*, 1904, **28**, 868.

[9] Haas, *Ber.*, 1884, **17**, 2249; Gibson and Morrison, *Proc. Roy. Soc. Edin.*, 1885, **13**, 146.

[10] Ruff and Geisel, *Ber.*, 1904, **37**, 3683.

[11] Hinz, German Patent, 151129 (1904).

[12] Merck, German Patent, 171372 (1906).

Compounds with the general formula $x\text{MgO}.y\text{MgO}_2.z\text{H}_2\text{O}$ result when ethereal solutions of nearly anhydrous hydrogen peroxide act on magnesium oxide. They are light white powders which decompose violently when heated, and are decomposed by water. The compound $2\text{MgO}.2\text{MgO}_2.3\text{H}_2\text{O}$, which is stable at 30° C., passes, by gradual heating, into $3\text{MgO}.2\text{MgO}_2.3\text{H}_2\text{O}$ at 50° C. and into $4\text{MgO}.2\text{MgO}_2.3\text{H}_2\text{O}$ at 70° C.[2]

$\text{KCl}.\text{MgO(OH)}_2$ results from the action of an ethereal solution of hydrogen peroxide on MgO and KCl, and $\text{MgCl}_2.2\text{MgO}_2.\text{Aq}.$ when the potassium chloride is replaced by magnesium chloride.[2]

Many methods for preparing magnesium peroxide have been patented—the action of sodium peroxide on magnesium salts being often applied. It is used as a bleaching or sterilising agent, and, medicinally, as a wash for wounds.[3]

Weltzien[4] obtained an alkaline solution by acting on magnesium with hydrogen peroxide. A white mass, soluble in water, remained after evaporation. He attributed the formula MgO_2H_2 to it, but Prud'homme, who found that it lost oxygen at about 300° C., formulated it as $3\text{Mg(OH)}_2 + \text{MgO(OH)}_2$.[5]

MAGNESIUM AND SULPHUR.

Magnesium Sulphide.—Crude MgS has been prepared by the action of hydrogen sulphide on magnesium nitride[6] or heated magnesium,[7] or heated magnesium filings and sulphur.[8] Reichel heated magnesium in sulphur vapour.[9] The crude product obtained by heating magnesium in a current of hydrogen and then in hydrogen and sulphur vapour can be purified by heating it in a highly evacuated quartz tube to 600°–700° C. for two hours (the excess of metal is thus volatilised), or by dissolving out the excess of magnesium in ethyl iodide, which is mixed with ether and contains a crystal of iodine. The purified sulphide is then washed with ether and dried in a vacuum desiccator placed in a water-bath.[10] Pure magnesium sulphide has also been prepared by igniting the oxide or anhydrous sulphate in nitrogen containing carbon disulphide vapour.[11]

Pure magnesium sulphide is a reddish-white amorphous powder.[10] It is converted into cubical crystals by heating in an electric furnace, and the same crystals are obtained by substituting a mixture of magnesium chloride and stannous sulphide for the magnesium sulphide.[8]

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[1] Foregger and Phillip, *J. Soc. Chem. Ind.*, 1906, **25**, 298.

[2] Carrasco, *Gazzetta*, 1909, **39**, ii, 47.

[3] Blücher, *Modern Industrial Chemistry* (translated by Millington) (Gresham Publishing Co., London), 1914.

[4] Weltzien, *Annalen*, 1866, **138**, 132.

[5] Prud'homme, *Compt. rend.*, 1891, **112**, 1374.

[6] Briegleb and Geuther, *Annalen*, 1862, **123**, 228.

[7] Kessler, *Ber.*, 1869, **2**, 369.

[8] Mourlot, *Compt. rend.*, 1898, **127**, 180.

[9] Reichel, *J. prakt. Chem.*, 1875, **12**, 55.

[10] Tiede, *Ber.*, 1916, **49**, 1745.

[11] Tiede and Richter, *ibid.*, 1922, **55**, 69.

Mg_4S_5 is said to have been obtained by heating magnesia to redness in carbon disulphide vapour.[1]

The heat of formation of MgS is 79·600 Cal.[2]

Magnesium sulphide is reduced by calcium carbide in an electric furnace—magnesium volatilises and calcium sulphide remains.[3]

Pure magnesium sulphide becomes phosphorescent by the addition of small amounts of manganese, bismuth, or antimony.[4] The crystalline form is scarcely attacked by water at ordinary temperatures, and steam is needed for the reaction

$$MgS+H_2O=MgO+H_2S.$$

The amorphous form reacts readily with water or moist air—

$$2MgS+2H_2O=Mg(SH)_2+Mg(OH)_2.^5$$

Magnesium Hydrogen Sulphide is only known in aqueous solution. Since it is strongly hydrolysed the solution readily loses hydrogen sulphide, and, if it is concentrated, produces a steady stream of gas at 60° C.[6]

Solutions have been prepared by passing hydrogen sulphide through magnesium hydroxide suspended in water,[7] or by decomposing magnesium sulphate with barium hydrogen sulphide.[8]

A dark yellow polysulphide solution, which is decomposed by heat into magnesium hydroxide, hydrogen sulphide, and sulphur, results when $Mg(HS)_2$ is digested with sulphur, or MgS with sulphur and water.[9] A similar solution is obtained by heating magnesium chloride with polysulphides of calcium.[10]

Magnesium Sulphite.—Crystals of $MgSO_3.6H_2O$ are obtained by the action of sulphurous acid on magnesium,[11] magnesium oxide,[12] or magnesium carbonate,[13] or by the double decomposition of magnesium sulphate and sodium sulphite.[13, 14] They dissolve in 80 parts of cold water and in 120 parts of hot,[12] though the action of hot water apparently produces a basic salt.[14] Basic magnesium sulphite, $MgSO_3+2Mg(OH)_2$, prepared by passing sulphur dioxide into water containing magnesia in suspension, has been used in sugar refining.[15] The acid sulphite could not be prepared in the crystalline form.[16] Evaporation at high temperature of the product of the reaction between sulphurous acid and magnesium hydroxide is said to yield crystals of $MgSO_3.3H_2O$.[17] Rhombic crystals of $MgSO_3.7H_2O$ were reported, which lost 1 molecule of water at 52° C.[13]

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[1] Frémy, *Ann. Chim. Phys.*, 1853, [3], 38, 324.

[2] Sabatier, *ibid.*, 1881, [5], 22, 86.

[3] Geelmuyden, *Compt. rend.*, 1900, 130, 1026.

[4] Tiede and Richter, *Ber.*, 1922, 55, 69.

[5] Mourlot, *Compt. rend.*, 1898, 127, 180.

[6] Divers and Shimidzu, *Trans. Chem. Soc.*, 1884, 45, 699. A current of hydrogen removes all the hydrogen sulphide and leaves magnesium hydroxide (Béchamp, *Ann. Chim. Phys.*, 1869, [4], 16, 245).

[7] Pelouze, *Ann. Chim. Phys.*, 1866, [4], 7, 179.

[8] Thomsen, *Pogg. Annalen*, 1870, 140, 526.

[9] Reichel, *J. prakt. Chem.*, 1875, 12, 55.

[10] Stingl and Morenski, *ibid.*, 1879, [2], 20, 81.

[11] Schweizer, *Amer. Chem. J.*, 1871, 1, 296.

[12] Hager, *J. Chem. Soc.*, 1875, 28, 1239.

[13] Rother, *ibid.*, 1875, 28, 423.

[14] Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 44.

[15] Bergreen and Licht, *Bied. Centr.*, 1884, 201.

[16] Davies, *Pharm. J. Trans.*, 1872, [3], 2, 965.

[17] Hartog, *Compt. rend.*, 1887, 104, 1793.

The hexagonal crystals of the hexahydrate oxidise slowly to sulphate in air, lose their water above 200° C., decompose into oxide and sulphur dioxide when heated strongly, and become the *monohydrate* at 100° C.[1] Sulphur dioxide slowly converts magnesia into the sulphite at about 326° C., which then decomposes at a slightly higher temperature.[2]

The following **double sulphites of magnesium and ammonium** have been prepared: $3MgSO_3.(NH_4)_2SO_3.18H_2O$,[3,4] $MgSO_3.(NH_4)_2SO_3.12H_2O$,[5] and $MgSO_3.(NH_4)_2SO_3.6H_2O$.[4]

Double Dithionate of Magnesium, $BaS_2O_6.MgS_2O_6.4H_2O$, was prepared by precipitating half the barium from barium dithionate by sulphuric acid and saturating the solution with magnesia.[6]

Magnesium Sulphate, $MgSO_4$, is known anhydrous, and with 12, 8, 7, 6, 5, 4, 2, 5/4, and 1 molecules of water.

Rhombic prisms of the *heptahydrate* separate from solutions containing magnesium sulphate at ordinary temperatures.[7] It is the principal magnesium salt of commerce, and is known as Bittersalz, from its bitter taste, or as Englisches Salz or Epsom salts, from its occurrence in the mineral spring at Epsom. It frequently forms a fibrous efflorescence in dry mines,[8] occurs in crystals in the Kentucky caves, and is being deposited in the Gulf of Kara-Boghaz, in the Eastern Caspian.[9] The naturally occurring solid heptahydrate is known as *epsomite*, or, in the Stassfurt deposits, as *reichardtite*.[10]

It was formerly prepared by crystallisation from natural waters, as Grew obtained it, in 1695, from the Epsom mineral spring. Dolomite was also frequently decomposed with sulphuric acid: the soluble magnesium sulphate being separated from the sparingly soluble calcium sulphate. Crude kieserite, $MgSO_4.H_2O$, was also converted into epsomite. It is now commonly prepared from the mother-liquor remaining after the preparation of magnesium chloride. Magnesium hydroxide is precipitated by adding milk of lime and dissolved in sulphuric acid. The salt can be purified by crystallisation.

The density of the crystals is 1·676,[7] and they have an appreciable vapour pressure.[8] Pickering[11] says the pure crystals are stable in air, though they seem to lose water in dry air or over calcium chloride.[12]

$MgSO_4.7H_2O$ is soluble in dilute alcohol and insoluble in absolute.[13] Its solubility in water has been expressed by 0·47816t° + 25·76,[14] by 20·5 + 0·2276t° from 0°–123° C., and by 48·5 — 0·4403t° from 123°–190° C.:[15] in parts $MgSO_4$ per 100 parts water.

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[1] Archbold, *Jahresber.*, 1872, 240. [2] Birnbaum and Wittich, *Ber.*, 1880, 13, 651.

[3] Rother, *J. Chem. Soc.*, 1875, 28, 423. [4] Hartog, *loc. cit.*

[5] Ladenberg, *Pogg. Annalen*, 1826, 7, 14. [6] Schiff, *Annalen*, 1858, 105, 239.

[7] Thorpe and Watts, *Trans. Chem. Soc.*, 1880, 37, 102.

[8] Frowein, *Zeitsch. physikal. Chem.*, 1887, 1, 5.

[9] *Nature*, 1904, 69, 281. [10] Krause, *Arch. Pharm.*, 1875, [3], vi, 41.

[11] Pickering, *Trans. Chem. Soc.*, 1885, 47, 100; 1886, 49, 260.

[12] Johnson, *Centr. Min.*, 1915, 289. [13] Schiff, *Annalen*, 1861, 118, 362.

[14] Gay-Lussac, *Ann. Chim. Phys.*, 1819, 11, 296.

[15] Étard, *Compt. rend.*, 1888, 106, 740. See also Tobler, *Annalen*, 1855, 95, 193. The following determinations have been made on solutions of magnesium sulphate:—Densities: Schiff, *Annalen*, 1858, 108, 336; 1860, 113, 183; Oudemans, *Zeitsch. anal. Chem.*, 1868, 7, 419; Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 287; Kohlrausch and Hallwachs, *Ann. Phys. Chem.*, 1894, [2], 53, 14; Barnes and Scott, *J. Physical Chem.*, 1898, 2, 536. Freezing-points: Guthrie, *Phil. Mag.*, 1876, [5], 1, 365. Conductivities: Kohlrausch, Holborn, and Diesselhorst, *Ann. Phys. Chem.*, 1898, [2], 64, 417. Refraction: Glad-

A labile variety of the heptahydrate sometimes crystallises from cold supersaturated solutions in monoclinic tablets that are more soluble than the ordinary salt.[1] This β-salt is isomorphous with $FeSO_4.7H_2O$, and sometimes forms when crystals of the hexahydrate are in contact with their mother-liquor at 0°–10° C.[2]

At 100° C. $MgSO_4.7H_2O$ becomes the dihydrate, at 130°–140° C. the monohydrate, and anhydrous at 280° C.[3] When strongly ignited it obstinately retains traces of sulphuric acid.[4] Its heat of solution is —3·863 Cals.[5]

The *dodecahydrate* separates in large crystals from concentrated solutions of the sulphate when cooled below 0° C. : it is stable only between its cryohydric point—3·9° C., and 1·8° C. when it decomposes into the heptahydrate.[6]

The *octahydrate* separates at 25° C. from solutions of magnesium sulphate containing some sodium sulphate. At 30° C., if the proportion of sodium sulphate is increased to about 32 molecules per cent., the octahydrate transforms into the heptahydrate. Air drying results in the same change.[7]

The *hexahydrate* occurs dimorphically as tetragonal crystals that change readily into monoclinic prisms. The former, or α-variety, was obtained by inoculating a concentrated solution of the sulphate with a small tetragonal crystal of copper and zinc sulphates.[8] The latter, or β-variety, crystallises from warm solutions of magnesium sulphate. It is more soluble than the heptahydrate.[2] It has been obtained by crystallisation above 40° C.,[3] and even at temperatures as low as 25° C.,[2] though the transition temperature from hepta- to hexa-hydrate is 48·2° C.[9] The presence of sodium chloride lowers this temperature.[10] Its density is 1·751.[3]

The heptahydrate when kept over sulphuric acid in air passes into the *pentahydrate*, which has a density of 1·869.[3] The pentahydrate, however, is apparently unstable, like the *tetrahydrate*. The heptahydrate passes into the former at 77·5° C. and into the latter at a similar temperature. These two salts begin to transform into the *monohydrate* at 67°–68° C.[9]

The *dihydrate* has a density of 2·373 when prepared by boiling the heptahydrate with absolute alcohol. It also results from heating the heptahydrate to 100° C.[11] It separates in bundles of slender needles

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stone and Hibbert, *Trans. Chem. Soc.*, 1897, 71, 822. Transport Numbers: Huybrechts, *Ann. Chim. Phys.*, 1907, [8], 11, 68. Transference Ratios: Bein, *Zeitsch. physikal. Chem.*, 1898, 27, 1. Thermal Expansion: Lannoy, *Zeitsch. physikal. Chem.*, 1895, 18, 442. Thermal Effects of Dilution: Pollok, *Proc. Chem. Soc.*, 1899, 15, 8. The vapour tension of a saturated solution at 20° C. is 14·5 mm. mercury (Lescœur, *Ann. Chim. Phys.*, 1896, [7], 7, 416).

[1] Lœwel, *Ann. Chim. Phys.*, 1855, [3], 43, 405.

[2] Pickering, *Trans. Chem. Soc.*, 1885, 47, 100.

[3] Thorpe and Watts, *ibid.*, 1880, 37, 102. See Merwin, *J. Washington Acad. Sci.*, 1914, 4, 494.

[4] Bailey, *Trans. Chem. Soc.*, 1887, 51, 676.

[5] Pickering, *ibid.*, 1886, 49, 260; Thomsen, *J. prakt. Chem.*, 1878, [2], 17, 165.

[6] Fritsche, *Pogg. Annalen*, 1837, 42, 577.

[7] Takegami, *Mem. Coll. Sci. Kyoto*, 1921, 5, 191. See also Sodium Magnesium Sulphates.

[8] de Boisbaudran, *Ann. Chim. Phys.*, 1869, [4], 18, 246.

[9] van 't Hoff, Meyerhoffer, and Smith, *Jahresber.*, 1901, 1, 374; Wiedemann, *ibid.*, 1882, 39.

[10] van 't Hoff and Meyerhoffer, *J. Chem. Soc.*, 1903, 84, Abs. ii, 555.

[11] Thorpe and Watts, *Trans. Chem. Soc.*, 1880, 37, 102.

when magnesium sulphate solution containing magnesium chloride is concentrated at 65° C. These soon alter to transparent crystalline masses of $MgSO_4.5/4H_2O$.[1]

From solutions containing different proportions of magnesium sulphate and chloride at 25° C. the series of hydrates from the hepta to the tetra separate.[2]

The heptahydrate decomposes into the *monohydrate* at 130°–140° C. Its density is 2·478. Bischof assigned a density of 2·517 to the naturally occurring *kieserite.*[3] Kieserite occurs, as an essential constituent of Abraumsalz, in the upper layers of the Stassfurt deposits, most frequently in white granular masses and less frequently in monoclinic crystals. It is only slightly soluble in water, which, however, slowly converts it into the heptahydrate. The partially hydrated substance is hard like stone—" kieseritsteine." Boiling water more rapidly completes the hydration, and the heptahydrate can then be crystallised from the solution.[4] Kieserite is formed when a concentrated solution of magnesium sulphate is poured into a hot, saturated solution of magnesium chloride.[5] The monohydrate will only separate from solutions of magnesium sulphate above 67° C., but in presence of other substances it may separate at 25° C.[6]

Kieserite is separated from the more soluble portion of the Abraumsalz by water, and sent into commerce as block kieserite that has been partially converted into the heptahydrate.[7]

The heat of solution of $MgSO_4.H_2O$ has been given as 13·300 Cal. and as 12·131 Cal.[8]

Anhydrous magnesium sulphate prepared by heating the heptahydrate to 200° C. has a density of 2·709, though a value as low as 2·628 has been found.[3] It melts at 1124° C. but decomposes considerably below that temperature,[9] and retains traces of sulphuric acid after strong ignition.[10] Its heat of solution is 20·425 Cal.,[11] its heat of formation is 302·300 Cal., and it is nearly insoluble in concentrated hydrochloric acid.[12]

It cakes in water, but dissolves rapidly when pounded up in it.[8]

The residue contains MgS and MgO when carbon reduces magnesium sulphate at lower temperatures ; at higher temperatures and with less carbon the products are oxide, sulphur dioxide, and sulphur. Above 700° C. hydrogen sulphide reduces it to oxide, and carbon monoxide to oxide, sulphur dioxide, and sulphur.[13]

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[1] van 't Hoff and Dawson, *Chem. Zentr.*, 1899, i, 1137.

[2] van 't Hoff and Escheicher, *Jahresber.*, 1898, i, 204.

[3] Thorpe and Watts, *loc. cit.*

[4] Grüneberg, *Bull. Soc. chim.*, 1869, [2], 11, 424.

[5] Precht and Wittjen, *Ber.*, 1881, 14, 2131.

[6] van 't Hoff and Meyerhoffer, *J. Chem. Soc.*, 1903, 84, Abs. ii, 555.

[7] Grüneberg, *Ber.*, 1872, 5, 840.

[8] Pickering, *Trans. Chem. Soc.*, 1885, 47, 100.

[9] Nacken, *Chem. Zentr.*, 1908, i, 1850 ; Gay-Lussac (*Ann. Chim. Phys.*, 1820, [2], 13, 310) noted that it lost sulphur trioxide on heating, and Boussingault (*Ann. Chim. Phys.*, 1867, [4], 12, 421), that a red heat fused it and left magnesia.

[10] Bailey, *Trans. Chem. Soc.*, 1887, 51, 676.

[11] Pickering, *ibid.*, 1886, 49, 260.

[12] Heusgen, *Ber.*, 1877, 10, 259.

[13] Zawadzki, Kossak, and Narbut, *Chem. Zentr.*, 1922, 93, iii, 32. According to Jacquemain (*Jahresber.*, 1858, 86), MgS is produced by the action of carbon monoxide at a red heat. Béchamp (*Ann. Chim. Phys.*, 1869, [4], 16, 245) noted that in the decomposition of magnesium sulphate by carbon the proportion of sulphide to oxide was small.

Magnesium Hydrogen Sulphates.—Magnesia dissolves more readily in sulphuric acid of density 1·7 than in more concentrated acid. By cooling the former solution or evaporating it at boiling-point, prismatic crystals of $Mg(HSO_4)_2$ separate. $MgSO_4.3H_2SO_4$ crystallises in small shining tables from the latter solution on cooling. These latter crystals, on heating, melt with decomposition.[1] Prismatic doubly refracting crystals of $KHMg(SO_4)_2.2H_2O$ are obtained by treating a solution of leonite, $K_2SO_4.MgSO_4.4H_2O$, with 85 per cent. nitric acid. Water converts them into schönite, $K_2SO_4.MgSO_4.6H_2O$.[2]

Sodium Magnesium Sulphates.—$Na_2SO_4.3MgSO_4$, melting with decomposition at 814° C., $3Na_2SO_4.MgSO_4$, corresponding to *vant-hoffite*, and $Na_2SO_4.MgSO_4$, existing in three modifications and corresponding to anhydrous *blödite*, are indicated on the freezing-point curve.[3, 4]

Blödite is formed at 22° C. according to the equation

$$MgSO_4.7H_2O + Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4.MgSO_4.4H_2O + 13H_2O.$$

The double salt crystallises from the mixed solution between 25° C. and 71° C., and below 22° C. a mixture of Epsom and Glauber's salts crystallises.[5] *Blödite* is identical with *simonite* from Hallstadt,[6] and has been called *astrakanite* from its occurrence in the salt lakes of the Astrakan Steppe.[6, 7, 8] It is associated with carnallite and kainite in the Stassfurt deposits. Monoclinic crystals of blödite occur at Monte Sambuco in Sicily,[8] and isolated crystals, weighing up to 652 grm., have been found in the crust on Soda Lake, California.[9]

Blödite transforms into *loewite* at 71° C.,[10] and at 59° C. in the presence of sodium chloride [11] or of magnesium sulphate.[12] *Loewite* has the formula $2Na_2SO_4.2MgSO_4.5H_2O$, and occurs naturally in the Magdeburg-Hallerstadt salt district.[13]

The double salt $Na_2SO_4.2MgSO_4$, analogous to langbeinite, apparently cannot exist, at any rate below 90° C.[12] *Vanthoffite*, $3Na_2SO_4.MgSO_4$, occurs naturally in the same district as loewite, and has been prepared by the transformation of blödite at higher temperatures than its transition-point into loewite.[12, 13] Natural vanthoffite has the same $D^{25}=2·6955$ as the artificial,[4] and shows an alteration in refraction at 489° C.[4]

Prismatic crystals of $Na_2SO_4.MgSO_4.8H_2O$ have been reported as a saline efflorescence in Toledo.[14]

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[1] Schultz, *Pogg. Annalen*, 1868, **133**, 137.

[2] Meyerhoffer and Cottrell, *Zeitsch. anorg. Chem.*, 1901, **27**, 442.

[3] Ginsberg, *ibid.*, 1909, **61**, 122.

[4] Nacken, *Chem. Zentr.*, 1908, i, 1850.

[5] van 't Hoff and Deventer, *Zeitsch. physikal. Chem.*, 1887, **1**, 165; Roozeboom, *Zeitsch. physikal. Chem.*, 1888, **2**, 513. According to Takegami (*Mem. Coll. Sci. Kyoto*, 1921, **5**, 191), $MgSO_4.8H_2O$ separates at 25° C., and blödite when the proportion of sodium sulphate is increased. At 30° C. the heptahydrate forms if the proportion of sodium sulphate is increased to about 32 molecules per cent.

[6] Geinitz and Zincken, *J. Chem. Soc.*, 1872, **25**, Abs. 125.

[7] Koechlin, *ibid.*, 1901, **80**, Abs. ii, 64.

[8] Millosevich, *Atti R. Accad. Lincei*, 1920, [v], **29**, i, 344.

[9] Schaller, *J. Washington Acad. Sci.*, 1913, **3**, 75.

[10] van 't Hoff and O'Farelly, *Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 370.

[11] van 't Hoff and Meyerhoffer, *J. Chem. Soc.*, 1903, **84**, Abs. ii, 555.

[12] Denison, *Trans. Faraday Soc.*, 1905, **1**, 136.

[13] Kubierschky and van 't Hoff, *Sitzungsber. Akad. Wiss. Berlin*, 1902, 404.

[14] Munos Y Luna, *Jahresber.*, 1854, 893.

Blödite crystallises in the monoclinic system with a hardness of 2·5 and a density of 2·2–2·3;[1] *loewite* crystallises in the tetragonal system with a density of 2·376 and a hardness of 2·5–3.[2]

Potassium Magnesium Sulphates.—*Schönite*, or *picromerite*, $K_2SO_4.MgSO_4.6H_2O$, occurs in the Stassfurt deposits, and crystallises in transparent monoclinic prisms from a solution of the mixed salts in equimolecular proportions at ordinary temperatures.[3] Their density at 20°/4° is 2·0277.[4] Since schönite is produced at −3° C. according to the equation

$$K_2SO_4 + MgSO_4.7H_2O \rightleftharpoons K_2SO_4.MgSO_4.6H_2O + H_2O,^5$$

and since $MgSO_4.12H_2O$ is the stable hydrate between 3·9° C. and 1·8° C.,[6] the system should become labile at the latter temperature.

One hundred parts of water dissolve 25 parts at 25° C. and 59·8 parts at 75° C.[7]

Schönite passes into *leonite*, $K_2SO_4.MgSO_4.4H_2O$, at 47·5° C.,[8] and at lower temperatures in the presence of sodium chloride.[9] Nitric acid effects the reverse change.[10] It crystallises in tables, and has been prepared by evaporating a solution of schönite and sodium chloride at 60° C.[11] Leonite occurs naturally at Leopoldshall, near Stassfurt, in thick, tabular crystals which usually have a yellowish tinge and are soluble in water.[12]

Leonite in solution is transformed into *langbeinite*, $K_2SO_4.2MgSO_4$, at 89° C., and at lower temperatures in the presence of other salts.[9] Langbeinite has been prepared by treating schönite with superheated steam, or kainite with water under pressure, or kainite with magnesium chloride solution from 120°–145° C.,[13] and by melting its component salts together.[14] It occurs in the Prussian salt deposits and elsewhere in isometric crystals. The mineral has a glassy lustre, a conchoidal fracture, a hardness of 3–4, and a density of 2·83. It is hygroscopic and slowly decomposed by water. It occurs rarely in cubical crystals,[15] and the artificial crystals are usually octahedral.[14] It melts at 930° C. and shows simple refraction ($D^{25} = 2·629$).[16]

Artificial *langbeinite*, produced by fusing $MgSO_4$ and K_2SO_4 in molecular proportions, is converted by exposure to air into schönite and epsomite—

$$K_2SO_4.2MgSO_4 + 13H_2O = K_2SO_4.MgSO_4.6H_2O + MgSO_4.7H_2O.^{17}$$

$$\begin{array}{ll}[K_2SO_4.MgSO_4] & + Aq. = K_2SO_4.MgSO_4.Aq. + 10·60 \text{ Cal.}\\ [K_2SO_4.MgSO_4.6H_2O] & + Aq. = K_2SO_4.MgSO_4.Aq. - 10·024 \text{ Cal.}\\ [K_2SO_4.MgSO_4.4H_2O] & + Aq. = K_2SO_4.MgSO_4.Aq. - 5·16 \text{ Cal.}^{18}\end{array}$$

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[1] Munos Y Luna, *loc. cit.*; Hauer, *Jahresber.*, 1856, 875.

[2] Hauer, *loc. cit.*

[3] Schwarz, *Dingl. poly. J.*, 1870, **198**, 159; Schröder, *Ber.*, 1874, **7**, 1117; Tutton, *Trans. Chem. Soc.*, 1893, **63**, 337.

[4] Tutton, *ibid.*, 1896, **69**, 344.

[5] Heide, *Zeitsch. physikal. Chem.*, 1893, **12**, 416.

[6] Fritsche, *Pogg. Annalen*, 1837, **42**, 577.

[7] Tobler, *Annalen*, 1855, **95**, 193.

[8] van 't Hoff and Williams, *Jahresber.*, 1898, 205.

[9] van 't Hoff and Meyerhoffer, *J. Chem. Soc.*, 1903, **84**, Abs. ii, 555.

[10] Meyerhoffer and Cottrell, *Zeitsch. anorg. Chem.*, 1901, **27**, 442.

[11] Heide, *Ber.*, 1893, **26**, 414.

[12] Tenne, *J. Chem. Soc.*, 1897, **72**, Abs. ii, 268.

[13] Precht, *Chemische Industrie*, 1880, **3**, 418.

[14] Mallet, *Min. Mag.*, 1899, **12**, 159.

[15] Luedecke, *Zeitsch. Kryst. Min.*, 1899, **29**, 255.

[16] Nacken, *Chem. Zentr.*, 1908, i, 1850.

[17] Mallet, *Trans. Chem. Soc.*, 1900, **77**, 216.

[18] Thomsen, *J. prakt. Chem.*, 1878, [2], **18**, 1–63.

Rubidium Magnesium Sulphate, $Rb_2SO_4.MgSO_4.6H_2O$, and Cæsium Magnesium Sulphate, $Cs_2SO_4.MgSO_4.6H_2O$, crystallise from mixed solutions of their constituent salts in molecular proportions.[1]

Ammonium Magnesium Sulphate, $(NH_4)_2SO_4.MgSO_4.6H_2O$, occurs as *cerbolite* in the fumaroles of Mount Cerboli in Tuscany,[2] and is a by-product of the Tuscan boric acid industry.[3] It is also known as boussingaultite.[4] Yellowish-white transparent masses of this salt were formed at the Riga gasworks because the lime used for purifying contained much magnesia.[5]

It crystallises from the mixed solutions of its constituent salts in transparent monoclinic prisms with a density of 1·723 at 20°/4° C.[6] Its solubility in parts per 100 of solution has been represented by

$$10{\cdot}55+0{\cdot}2215t+0{\cdot}000668t^2$$

from 0°–100° C., within 1 per cent.,[3] though there are discrepancies among the various determinations.[7] No transition-point was found between 0° C. and 100° C.[3]

The crystals can apparently be dehydrated by heating without losing their form.[8]

Potassium Calcium Magnesium Sulphates.—*Polyhalite*, $K_2SO_4.2CaSO_4.MgSO_4.2H_2O$, is a characteristic member of the Stassfurt deposits. By boiling gypsum with suitably concentrated solutions of other two sulphates, the series of salts represented by the general formula $M_2SO_4.2CaSO_4.M'SO_4.2H_2O$ can be prepared: M′ being copper, cadmium, nickel, or zinc, and M being potassium or ammonium. Polyhalite itself results when gypsum is boiled with a concentrated solution of magnesium sulphate containing about 4 per cent. of potassium sulphate.[9] *Syngenite*, $K_2SO_4.CaSO_4.H_2O$, is converted into polyhalite by warming at 56° C. with a solution containing sodium, potassium, and magnesium chlorides, and magnesium sulphate, or with crystalline magnesium sulphate and chloride.[10]

Polyhalite crystallises in the monoclinic system, with a density of 2·77, and hot water dissolves away the sulphates of magnesium and potassium from it.[11]

Krugite, $K_2SO_4.4CaSO_4.MgSO_4.2H_2O$, occurring also at Stassfurt, could not be obtained by the interaction of polyhalite and gypsum, though crystals, apparently orthorhombic, were obtained by the prolonged heating of gypsum with a solution containing magnesium chloride and potassium sulphate.[12]

Krugite is crystalline, its density is 2·801, hot water acts on it to produce gypsum, and cold water leaves the insoluble salt $K_2SO_4.CaSO_4.H_2O$.[11]

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[1] Tutton, *Trans. Chem. Soc.*, 1893, 63, 337; 1896, 69, 344.

[2] Schmidt, *Annalen*, 1856, 98, 273.

[3] Porlezza, *Atti R. Accad. Lincei*, 1914, [v], 23, ii, 509.

[4] Bechi, *Jahresber.*, 1864, 857.

[5] Glasenapp, *Dingl. poly. J.*, 1878, 227, 192.

[6] Tutton, *Trans. Chem. Soc.*, 1905, 87, 1123.

[7] Tobler, *Annalen*, 1855, 95, 193; Lothian, *Pharm. J.*, 1910, [iv], 30, 546; Seidell, *Pharm. J.*, 1911, [iv], 33, 846. For conductivities of solutions, see Lindsay, *Amer. Chem. J.*, 1901, 25, 62; Jones and Caldwell, *ibid.*, 349.

[8] Warington, *Proc. Chem. Soc.*, 1885, 65.

[9] d'Ans, *Ber.*, 1908, 41, 1777.

[10] Basch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1900, 48, 1084.

[11] Precht, *Ber.*, 1881, 14, 2138.

[12] Geiger, *Chem. Zentr.*, 1904, i, 604.

Double Sulphates of Magnesium.—The following have been described: $(Mg,Cu)SO_4.Aq.$,[1] $MgSO_4.ZnSO_4.14H_2O$ and $MgSO_4.ZnSO_4.10H_2O$,[2] $5MgSO_4.3ZnSO_4.56H_2O$, $MgSO_4.TlSO_4.6H_2O$,[3] $MgSO_4.UO_2SO_4.5H_2O$,[4] $MgSO_4.2MnSO_4.15H_2O$ (mineral fauserite), $MgSO_4.NiSO_4.28H_2O$, $2K_2SO_4.MgSO_4.ZnSO_4.12H_2O$ and $2K_2SO_4.MgSO_4.NiSO_4.12H_2O$,[5] $MgSO_4.ZnSO_4.MnSO_4.21H_2O$.[6]

Kainite occurs in the Stassfurt beds,[7] and at Kalusz in Eastern Galicia.[8] Meyerhoffer,[9] from its polytherms (equilibrium relationships at different temperatures), concluded that its formula is $MgSO_4.KCl.3H_2O$,[10] not $MgSO_4.K_2SO_4.MgCl_2.6H_2O$,[11] and that its temperatures of formation lie between 76° C. and 85° C. In the presence of sodium chloride it cannot exist above 83° C.[12] An interaction between carnallite and magnesium sulphate may account for its association with carnallite at Stassfurt.[13]

It is monoclinic,[14, 15] but is usually found in massive granular condition with a reddish, grey, or white colour. Its hardness is about 2·5 and its density about 2·1.[15] It does not deliquesce, and its potash content makes it a valuable and widely used fertiliser.

One hundred parts of water dissolve 79·56 parts at 18° C.[16] Schönite, $K_2SO_4.MgSO_4.6H_2O$, crystallises first from the saturated solution,[10] and this and other reactions have been used in working up kainite for potassium and magnesium salts.[17]

Magnesium Thiosulphate, $MgS_2O_3.6H_2O$, crystallises in rhombic prisms which are stable in air, readily soluble in water, and precipitated from a concentrated solution by alcohol.[18] It has been prepared by digesting a solution of magnesium sulphite with sulphur,[18] and by decomposing magnesium sulphate in solution with barium thiosulphate.[19]

The *double salts* $MgS_2O_3.K_2S_2O_3.6H_2O$ and $MgS_2O_3.(NH_4)_2S_2O_3.6H_2O$ have been prepared.[20]

MAGNESIUM AND SELENIUM.

Magnesium Selenide.—The direct combination of magnesium with selenium is too vigorous to be practically applicable. An impure product is obtained by heating magnesium in nitrogen containing selenium vapour, or by reducing magnesium selenate with carbon in an electric furnace. Fonzes-Diacon prepared it by acting with hydrogen selenide on anhydrous magnesium chloride heated to redness.

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[1] Scott, *Trans. Chem. Soc.*, 1897, **71**, 567.

[2] Pierre, *Ann. Chim. Phys.*, 1846, [3], **16**, 244.

[3] Werther, *Jahresber.*, 1864, 249.

[4] Coninck and Chauvenet, *Bull. Acad. roy. Belg.*, 1905, 151, 182.

[5] Vohl, *Annalen*, 1855, **94**, 57.

[6] Vohl, *ibid.*, 1856, **99**, 124.

[7] Zincken, *Jahrb. Miner.*, 1865, 310.

[8] Kolski, *Chem. Zentr.*, 1915, i, 271.

[9] Meyerhoffer, *Zeitsch. anorg. Chem.*, 1903, **34**, 145.

[10] Rammelsberg, *Jahresber.*, 1866, 951.

[11] Frank, *Ber.*, 1868, **1**, 121.

[12] van 't Hoff and Meyerhoffer, *J. Chem. Soc.*, 1903, **84**, Abs. ii, 555.

[13] Löwenherz (*Zeitsch. physikal. Chem.*, 1894, **13**, 459; 1897, **23**. 95) has studied saturated solutions containing K_2SO_4, $MgSO_4$, KCl, and $MgCl_2$ in all proportions.

[14] Groth, *Pogg. Annalen*, 1869, **137**, 442.

[15] Zepharovich, *Zeitsch. Kryst. Min.*, 1882, **6**, 234. According to de Schulten (*Compt. rend.*, 1890, **111**, 929), the density at 15° C. of artificial kainite is 2·120, and of the colourless crystalline mineral 2·151.

[16] Krause, *Arch. Pharm.*, 1875, [3], **6**, 326.

[17] See Dupré and Hake, *Dingl. poly. J.*, 1879, **233**, 492; *Jahresber.*, 1880, 1174; 1882, 1397.

[18] Rammelsberg, *Pogg. Annalen*, 1842, **56**, 303. See *Jahresber.*, 1855, 345.

[19] Hager, *Jahresber.*, 1863, 191.

[20] Kessler, *Pogg. Annalen*, 1848, **74**, 282; Fock and Kluss, *Ber.*, 1890, **23**, 534.

MgSe is whitish yellow, crystalline, and decomposed rapidly in moist air, evolving hydrogen selenide. Excess of water appears to form a soluble hydrated selenide.[1]

Magnesium Selenite.—Cubic crystals of $MgSeO_3.6H_2O$ separate on adding sodium carbonate solution to a solution of a magnesium salt and selenious acid. It is insoluble in water, soluble in acids (including selenious acid), forms a *monohydrate* at 100° C., becomes anhydrous between 150° C. and 200° C., and leaves a residue of magnesia at higher temperatures. When treated with water under pressure at 150° C. it transforms into a rhombic *dihydrate*, which has similar properties to the hexahydrate.[2, 3] A *heptahydrate* has been precipitated from selenite and magnesium-salt solutions by ammonia,[4] and Berzelius[5] described a *trihydrate* from the neutralisation of selenious acid with magnesium carbonate.

The *acid salts* $MgSeO_3.H_2SeO_3.3H_2O$ and $MgSeO_3.2H_2SeO_3.3H_2O$ were obtained by evaporating solutions containing MgO and SeO_2 in suitable proportions,[3] and rhombohedral $MgO.2SeO_2$ by heating a solution of the neutral salt in selenious acid under pressure at 200° C. The last is also insoluble in water and soluble in acids.[2]

Magnesium Selenate, $MgSeO_4$, crystallises with 6 or 7 molecules of water, and the two hydrates are isomorphous with the corresponding hydrates of magnesium sulphate. The double salts $R_2SeO_4.MgSeO_4.6H_2O$ are also isomorphous with the corresponding sulphates.[6]

MAGNESIUM AND TELLURIUM.

Magnesium Telluride, MgTe, is obtained by heating magnesium in tellurium vapour and a current of hydrogen. The direct union of the two elements is very vigorous. It is a white substance that is decomposed, with evolution of hydrogen telluride, by acidulated water. It crackles in air or water and apparently decomposes.[7]

Magnesium Tellurite.—A solution of sodium tellurite precipitates a white, flocculent precipitate of $5MgTeO_3.9H_2O$ from magnesium chloride solution. It is slightly soluble in water.

There is evidence for the existence of the hydrate $10MgTeO_3.9H_2O$.[8]

Magnesium Tellurate.—$MgTeO_4$ and $MgH_2(TeO_4)_2$ are obtained as white flocculent precipitates by precipitation of a magnesium salt with normal or acid potassium tellurate. The latter salt is the more soluble.[9]

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[1] Moissan, *Traité de Chimie Minérale* (Masson et Cie), Paris, 1904, vol. iii, p. 938; Berzelius, *Traité de Chimie*, 1831.

[2] Boutzoureano, *Ann. Chim. Phys.*, 1889, [vi], 18, 289.

[3] Nilson, *Bull. Soc. chim.*, 1874, [2], 21, 253.

[4] Hilger and Gerichten, *Zeitsch. anal. Chem.*, 1874, 13, 132, 394.

[5] Berzelius, *Traité de Chimie*, 1831.

[6] Mitscherlich, *Pogg. Annalen*, 1827, 11, 327. See *Jahresber.*, 1873, 143.

[7] Berthelot and Fabre, *Ann. Chim. Phys.*, 1888, [6], 14, 104.

[8] Lenher and Wolesensky, *J. Amer. Chem. Soc.*, 1913, 35, 723; Berzelius, *Traité de Chimie*, 1831.

[9] Berzelius, *loc. cit.*

MAGNESIUM AND CHROMIUM.

Magnesium Chromite.—The compounds $2MgO.Cr_2O_3$ and $3MgO.2Cr_2O_3$, and finally, at a red heat, $MgO.Cr_2O_3$, result from the calcination of magnesium chromate. Amorphous $MgO.Cr_2O_3$ is also obtained by calcining either the double chromate of magnesium and potassium,[1] or magnesium chloride with potassium dichromate.[2]

Dark green octahedral crystals of $MgO.Cr_2O_3$ are formed when magnesia and green chromium trioxide, in appropriate proportions, are heated strongly with boric acid,[3] or, alone, in the electric furnace. Their physical properties seem to vary with their mode of production : they scratch glass and not quartz, and have a density of 4·415 at 16° C. when prepared by the boric acid method ; the furnace product is harder than quartz, and its density is 4·6 at 20° C. Sulphuric acid attacks them readily ; they resist boiling nitric acid and are slowly attacked by hydrochloric and hydrofluoric acids. They are very resistant to oxidising agents in general.[4]

Magnesium Chromate, $MgCrO_4.7H_2O$, crystallises in large transparent prisms isomorphous with Epsom salts.[5, 6, 7] It becomes $MgCrO_4.H_2O$ at 130° C.[8] Yellow crystals of $MgCrO_4.5H_2O$, isomorphous with copper sulphate, were obtained by crystallisation above 30° C. Water partly decomposed them.[9]

Potassium Magnesium Chromate, $K_2CrO_4.MgCrO_4.6H_2O$, crystallises from the mixed solutions of its constituent salts at −10° C. It deposits as small, lemon-yellow crystals which effloresce[10] and are monoclinic.[11] It can be crystallised out up to 15° C., but is apparently unstable even at 10° C. and changes slowly into the *dihydrate.* The change is more rapid at 120° C.[11] The dihydrate forms light yellow prismatic crystals which dissolve in water without decomposition ; it can be crystallised from very concentrated solutions.[12]

Rubidium Magnesium Chromate and Cæsium Magnesium Chromate are isomorphous. Monoclinic crystals of $Rb_2CrO_4.MgCrO_4.6H_2O$ or $Cs_2CrO_4.MgCrO_4.6H_2O$ crystallise out from solutions of the constituent chromates in appropriate proportions.[10, 13, 14]

Ammonium Magnesium Chromate, $(NH_4)_2CrO_4.MgCrO_4.6H_2O$, crystallises in large monoclinic prisms isomorphous with the corresponding double sulphate.[5, 8, 14] The *dihydrate* has been precipitated in yellow crystals, which are stable in water, by adding a 2*N* solution of $MgCrO_4$ to a 2*N* solution of $(NH_4)_2CrO_4$.[15]

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[1] Schweitzer, *J. prakt. Chem.*, 1846, 39, 259.
[2] Gerber, *Bull. Soc. chim.*, 1877, 2, 437.
[3] Ebelmen, *Ann. Chim. Phys.*, 1848, [3], 22, 211.
[4] Dufau, *Compt. rend.*, 1896, 123, 886.
[5] Grailich, *Jahresber.*, 1858, 164.
[6] Topsöe and Christiansen, *ibid.*, 1873, 142.
[7] Fock, *Zeitsch. Kryst. Min.*, 1879, 4, 583.
[8] Abott, *Jahresber.*, 1877, 44.
[9] Wyrouboff, *Bull. Soc. chim.*, 1889, [3], 2, 500.
[10] Briggs, *Trans. Chem. Soc.*, 1904, 85, 679.
[11] Duffour, *Compt. rend.*, 1919, 169, 73.
[12] Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185.
[13] Barker, *Trans. Chem. Soc.*, 1911, 99, 1326.
[14] Tutton and Porter, *Min. Mag.*, 1912, 16, 169.
[15] Gröger, *Zeitsch. anorg. Chem.*, 1908, 58, 412.

MAGNESIUM AND MOLYBDENUM.

Magnesium Molybdate, $MgMoO_4.7H_2O$, is obtained in slender, glancing prisms, which resemble Epsom salts, by crystallisation after heating magnesia with molybdic acid and water. It is unstable in air, easily soluble in water, and dehydrates without melting when heated.[1] The *pentahydrate* separates from more concentrated solutions; it becomes the *dihydrate* at 100° C.[2] Some complex molybdates,[1] and the double molybdates $K_2MoO_4.MgMoO_4.2H_2O$ and $(NH_4)_2MoO_4.MgMoO_4.2H_2O$,[3] have been described.

$MgMoO_4$ occurs naturally as *belonesite* in colourless, white, tetragonal crystals.

MAGNESIUM AND TUNGSTEN.

Magnesium Tungstates.—Large, colourless, octahedral and columnar crystals of $MgWO_4$ are obtained by fusing sodium tungstate with excess of magnesium chloride and salt.[4] Ullik obtained a *heptahydrate* by acting on magnesium carbonate with tungstic acid.[5] The metatungstate, $MgO.4WO_3.8H_2O$, and the paratungstate, $3MgO.7WO_3.24H_2O$,[6] have been prepared. Various double tungstates have also been reported.[5, 6, 7]

MAGNESIUM AND NITROGEN.

Magnesium Nitride.—When magnesium is heated in air it begins to combine with oxygen at 600° C., and a volume of air can be deprived of its oxygen by keeping the temperature well below 670° C. At the latter temperature the metal combines with nitrogen to form magnesium nitride.[8] Magnesium nitride is an amorphous powder, greenish grey or greenish yellow in colour, and corresponding to the formula Mg_3N_2.[9] It is stable in dry air, but water converts it into ammonia and magnesium hydroxide—

$$Mg_3N_2+6H_2O=2NH_3+3Mg(OH)_2.$$

Dilute acids decompose it similarly. It is said to dissociate completely at 1500° C., and to react when heated in carbon dioxide according to the equation—

$$Mg_3N_2+3CO_2=3MgO+3CO+N_2.$$

Carbon monoxide acts less readily and a much higher temperature is needed—

$$Mg_3N_2+3CO=3MgO+N_2+3C.^{10}$$

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[1] Ullik, *Annalen*, 1867, **144**, 204.

[2] Struve, *J. prakt. Chem.*, 1854, **61**, 453.

[3] Ullik, *Annalen*, 1867, **144**, 320.

[4] Geuther and Forsberg, *ibid*, 1861, **120**, 270.

[5] Ullik, *Jahresber.*, 1867, 222.

[6] Knorre, *Ber.*, 1886, **19**, 819.

[7] Lotz, *Annalen*, 1854, **91**, 49; Marignac, *Ann. Chim. Phys.*, 1863, [3], **69**, 58.

[8] Matignon and Lassieur, *Compt. rend.*, 1912, **154**, 63.

[9] Smits, *Rec. Trav. chim.*, 1893, **12**, 198.

[10] Fichter and Schölly, *Helv. Chim. Acta*, 1920, **3**, 298. Briegleb and Gautier stated that, in both instances, cyanogen was produced (*Annalen*, 1862, **123**, 228). See also under Magnesium Cyanide.

When it is warmed with anhydrous nickel chloride, nickel nitride is formed, and other metallic chlorides react similarly.[1]

It was first prepared by heating magnesia in nitrogen,[2] and finally, much purer and more readily, by heating the metal in ammonia.[3] In some methods of preparation the metal was heated in mass with a slight exposure of surface: the outer rind was oxidised and the inner core converted into nitride.[4]

Borchers and Beck electrolysed with an anode liquid of magnesium oxide and alkali fluoride, and a cathode liquid of fused zinc. The liberated magnesium alloyed with the zinc and combined with the nitrogen of air which was blown into it.[5]

Its heat of formation has been given as +119·7 Cal.[3]

Magnesium Azide, $Mg(N_3)_2$.—Magnesium dissolves easily in dilute hydrazoic acid, and a readily soluble salt is obtained by decomposing barium azide with magnesium sulphate. This salt explodes on heating, is decomposed by hot water, and has not been obtained pure.[6]

Magnesium Nitrite is usually prepared by interaction between barium nitrite and magnesium sulphate,[7, 8] and has also been obtained by treating silver nitrite with magnesia[9] or with magnesium chloride.[10]

The *trihydrate*, $Mg(NO_2)_2.3H_2O$, crystallises in deliquescent leaflets[10, 11] which are yellowish[8] or snow-white.[7] It slowly decomposes in a stoppered bottle,[8] and its solution decomposes, evolving nitric oxide when evaporated on the water-bath.[7, 8, 10]

Careful concentration under diminished pressure, or under diminished pressure over sulphuric acid, results finally in the *dihydrate*.[7, 8, 12] This has also been obtained by digesting magnesium sulphate and sodium nitrite with 94 per cent. alcohol and evaporating under reduced pressure.[13] It occurs as a hard, efflorescent, white mass[8] or as clear crystals,[13] and is much more stable than the trihydrate. It does not usually dissolve to a clear solution, and may partially decompose on continued dehydration.[7, 8]

Magnesium Nitrate.—Metallic magnesium, magnesia, and magnesium carbonate dissolve easily in nitric acid to magnesium nitrate. From neutral solutions at ordinary temperatures the *hexahydrate*, $Mg(NO_3)_2.6H_2O$, crystallises in monoclinic prisms and needles which do not effloresce over sulphuric acid.[14] $Mg(NO_3)_2.9H_2O$ forms when the solution is cooled to −20° C.; at −17° C. it reverts to the hexahydrate.[15]

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[1] Smits, *Rec. Trav. chim.*, 1896, 15, 135.

[2] Deville and Caron, *Annalen*, 1857, 101, 359.

[3] Matignon, *Compt. rend.*, 1912, 154, 135.

[4] Eidmann and Moeser, *Ber.*, 1901, 34, 390; Kirchner, *Chem. Zeit.*, 1901, 25, 395; Matignon and Lassieur, *loc. cit.*

[5] German Patent, 196323, 1906.

[6] Curtis and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 291.

[7] Vogel, *Zeitsch. anorg. Chem.*, 1903, 35, 385.

[8] Rây, *Trans. Chem. Soc.*, 1905, 87, 178.

[9] Fischer, *Pogg. Annalen*, 1848, 74, 115.

[10] Lang, *ibid.*, 1863, 118, 282.

[11] Fischer, *ibid.*, 1848, 74, 115.

[12] Hampe, *Annalen*, 1863, 125, 334.

[13] Matuschek, *Chem. Ind.*, 1902, 20.

[14] Lescœur, *Ann. Chim. Phys.*, 1896, [7], 7, 416. According to Chodnew (*Annalen*, 1849, 71, 241), a dihydrate is formed by long standing over sulphuric acid, and a monohydrate by heating to 210°-245° C.

[15] Funk, *Ber.*, 1899, 32, i, 96.

The heat of solution of the *hexahydrate* is −4·200 Cal.; it melts in its water of crystallisation, and with rising temperature loses water and, apparently, nitric acid.[1, 2] The basic salts $3MgO.2N_2O_5.5H_2O$[3] and $4MgO.N_2O_5$[2] have been said to result from this double loss.

According to Lescœur, the *hexahydrate* gradually dissociates into the *trihydrate* at 65° C., and the latter also results when a saturated, neutral solution of magnesium nitrate is mixed with an equal volume of fuming nitric acid.[1] Ditte, by heating the hexahydrate, obtained a syrupy mass which suddenly solidified into the *trihydrate.* He also obtained transparent prisms of the *dihydrate* by heating the nitrate till nitric oxide began to come off, dissolving in nitric acid, and crystallising. The crystals were very deliquescent.[4]

Magnesia is the final product of heat upon magnesium nitrate:[2] according to Graham, the *monohydrate* is formed at the temperature of melting lead.[1]

A nearly saturated solution of magnesium nitrate evolves heat on dilution.[5] A saturated aqueous solution of magnesium nitrate at 0° C. contains 39·96 per cent. of the anhydrous salt.[6]

$$Mg(OH)_2 + 2HNO_3Aq. = Mg(NO_3)_2Aq. + 27{\cdot}600 \text{ Cal.}$$

Didier[7] obtained $3MgO.N_2O_5.5H_2O$ in slender, white, microscopic needles, which were optically active, by treating a solution of magnesium nitrate at 100° C. with small quantities of magnesium at a time, heating to 150° C., filtering through cloth, and allowing to stand in a closed vessel. It was decomposed by water and alcohol.

Double Nitrates of Magnesium have been obtained with potassium,[8, 9] with ammonium,[9] and with calcium.[10] Meyer and Jacoby prepared $MgCe(NO_3)_6.8H_2O$,[11] and $MgO.La_2O_3.2N_2O_5.8H_2O$ has been reported.[12]

MAGNESIUM AND PHOSPHORUS.

Magnesium Phosphide.—When calcium phosphate and magnesium are heated together, the action is violent and magnesium phosphide is apparently produced.[13] It was also obtained by heating magnesium with various substances, organic or inorganic, containing phosphorus.[14]

It has been more effectively prepared by heating magnesium in phosphorus vapour and carbon dioxide,[15] and by the direct union of magnesium and phosphorus.[16] Gautier heated magnesium in phosphorus vapour and hydrogen, and obtained small, brilliant, dark green-grey crystals corresponding to Mg_3P_2. Magnesium phosphide is stable in dry air,[1] but readily decomposed by moisture into magnesium hydroxide and pure hydrogen phosphide. The halogens and ordinary mineral acids also decompose it, and it burns at a dull red heat in oxygen to magnesium phosphate.[2]

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[1] Lescœur, *Ann. Chim. Phys.*, 1896, [7], 7, 416.
[2] Ditte, *Compt. rend.*, 1879, 89, 641.
[3] Millon, *Ann. Chim. Phys.*, 1845, [3], 13, 134.
[4] Ditte, *loc. cit.*; Funk (*Ber.*, 1899, 32, 96) could not confirm the di- or tri-hydrate.
[5] Dunnington and Hoggard, *Amer. Chem. J.*, 1899, 22, 207.
[6] Funk, *loc. cit.*
[7] Didier, *Compt. rend.*, 1896, 122, 935.
[8] Lang, *J. prakt. Chem.*, 1862, 86, 295.
[9] Graham, *Annalen*, 1839, 29, 18.
[10] Moissan, *Traité de Chimie Minérale*, 1904, iii, 982.
[11] Meyer and Jacoby, *Ber.*, 1900, 33, 2137.
[12] Holzmann, *Jahresber.*, 1858, 135; Carus, *ibid.*
[13] Duboin, *Compt. rend.*, 1901, 132, 826.
[14] Bunsen, *Annalen*, 1866, 138, 292; Schönn, *Zeitsch. anal. Chem.*, 1869, 8, 53.
[15] Blunt, *J. Chem. Soc.*, 1865, 18, 106.
[16] Parkinson, *ibid.*, 1867, 20, 127, 309.

Magnesium Hypophosphite.—Octahedral crystals of $Mg(H_2PO_2).6H_2O$ [3] are obtained by boiling magnesium oxalate with calcium hypophosphite.[4]

Magnesium Phosphite, $MgHPO_3$, has been obtained in small crystals by dissolving magnesium oxide or carbonate in phosphorus acid. It contains some water of crystallisation.[5]

Magnesium Hypophosphate, $MgPO_3.6H_2O$, is precipitated by normal sodium hypophosphate from a solution of magnesium sulphate as a sparingly soluble, fine, crystalline precipitate. It dissolves in acetic acid containing a little hydrochloric acid, and $MgPO_3.12H_2O$ is obtained by concentrating the solution. It becomes the hexahydrate at 200° C.[6]

Magnesium Orthophosphate occurs as bobierrite, $Mg_3(PO_4)_2.8H_2O$, in wagnerite, $2Mg_3(PO_4)_2.MgF_2$, and in the parts and products of animals or plants—in bones, for example, and in guano.[7]

When a magnesium salt is precipitated cold by trisodium phosphate, colloidal, gelatinous magnesium orthophosphate first forms which slowly becomes crystalline.[8] $Mg_3(PO_4)_2.22H_2O$ separates at 10° C. from mixed solutions of magnesium sulphate, disodium hydrogen phosphate, and sodium bicarbonate: the precipitate from more concentrated solutions is amorphous, but crystals of density 1·640 separate at greater dilutions. A crystalline *octahydrate* separates from still more dilute solutions at 20°–25° C., and larger monoclinic crystals with a density of 2·195, resembling bobierrite, result when dilute ammonia is dropped into a solution containing magnesium chloride, disodium hydrogen phosphate, and hydrochloric acid.[9] It loses water over sulphuric acid or at 100° C., and becomes anhydrous at a red heat.[10]

The *heptahydrate* occurs in guano,[11] and has been prepared in small hexagonal crystals by boiling acid magnesium phosphate with magnesium carbonate.[12]

The *pentahydrate* has been prepared by the action of water at 120° C. on $MgHPO_4$,[13] and is precipitated as a white, amorphous, tasteless powder when trisodium phosphate is boiled with excess of magnesium sulphate.[14]

One part of freshly precipitated magnesium orthophosphate dissolves in about 5000 parts of water and in about 10,000 parts after ignition.[1] The solubility is increased by sodium chloride and some other salts.[2] The precipitate dissolves readily in mineral acids, very much less readily in acetic acid, and when dehydrated by calcination becomes phosphorescent.[3]

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[1] Emmerling (*Ber.*, 1879, **12**, 153) said it oxidised to phosphate.

[2] Gautier, *Compt. rend.*, 1899, **128**, 1167.

[3] Rammelsberg, *J. Chem. Soc.*, 1873, **26**, 9; Beckenkamp (*Zeitsch. Kryst. Min.*, 1903, **37**, 618) places them in the tetragonal system.

[4] Rose, *Pogg. Annalen*, 1828, **12**, 85.

[5] Rose, *ibid.*, 1827, **9**, 28; Rammelsberg, *ibid.*, 1867, **131**, 359.

[6] Rammelsberg, *Chem. Zentr.*, 1891, ii, 790. See Salzer, *Annalen*, 1877, **187**, 329.

[7] Stein and Tollens, *Annalen*, 1877, **187**, 79.

[8] Berthelot, *Ann. Chim. Phys.*, 1887, [6], **11**, 353.

[9] de Schulten, *Bull. Soc. franç. Min.*, 1903, **26**, 81.

[10] Stein and Tollens, *loc. cit.*, 87.

[11] Bobierre, *Jahresber.*, 1868, 949.

[12] Debray, *Ann. Chim. Phys.*, 1861, [3], **61**, 431.

[13] Schaffner, *Annalen*, 1844, **50**, 145; Debray, *loc. cit.*

[14] Rose, *Pogg. Annalen*, 1849, **76**, 20.

Natural *bobierrite* crystallises in the monoclinic system with a hardness of 2·5 and a density of 2·43. *Wagnerite* is monoclinic, and has a hardness of 5 5·5; its density is 3·06.

Acid Magnesium Phosphates. $MgHPO_4.14H_2O$ separates from cold, dilute mixed solutions of magnesium sulphate and sodium phosphate in insoluble, tasteless, silky needles.[4] The disodium salt precipitates it from magnesium acetate solution;[5] it also precipitates an acid phosphate from magnesium sulphate,[6] which has been said to be the *pentahydrate*.[7] Crystalline $MgHPO_4.9H_2O$ has been obtained by digesting phosphoric acid in the cold with magnesium carbonate.[8]

$MgHPO_4.14H_2O$ becomes the *hexahydrate* at 100° C., and, at ordinary temperatures, dries gradually into a mixture of the *hexa-* and *tri-hydrate*.[9] The *trihydrate* is said to be the stable salt in equilibrium with relatively dilute solutions of phosphoric acid.[10]

A *dihydrate* has been said to result when ammonium magnesium phosphate is heated with alcohol—

$$NH_4MgPO_4.6H_2O \rightleftharpoons MgHPO_4.2(H_2O)+4H_2O+NH_3.$$[11]

A *monohydrate* was obtained by heating a solution of magnesium carbonate in excess of phosphoric acid at 225° C. in sealed tubes. Its microscopic, hexagonal, lamellated crystals dissolve in dilute acids and do not change at 100° C.[12]

Hot water decomposes the *hexahydrate* into insoluble $Mg_3(PO_4)_2.5H_2O$ and soluble $Mg(H_2PO_4)$.[8] The *dihydrate* of the latter is obtained by heating magnesia on the water-bath with concentrated phosphoric acid, and cooling. It dissolves readily in water without decomposition.[13]

Magnesium Metaphosphate, $Mg(PO_3)_2$, is obtained, by heating magnesium carbonate at 316° C. with excess of phosphoric acid, as an anhydrous powder which is insoluble in water, little soluble in dilute acids, and soluble in concentrated sulphuric acid.[14] The *tetrahydrate* was obtained by adding alcohol to a solution of a magnesium salt and ammonium metaphosphate.[15]

Other metaphosphates have been described.[16]

Magnesium Pyrophosphate.—Sodium pyrophosphate precipitates amorphous $Mg_2P_2O_7.3H_2O$ from magnesium sulphate solutions, which becomes the crystalline *trihydrate* when dissolved in sulphurous acid and heated. A gelatinous trihydrate separates from a heated solution of acidified sodium pyrophosphate in which magnesia has been dissolved. It is slightly soluble in water, but is soluble in nitric, hydrochloric, and pyrophosphoric acids.[1] According to Popp,[2] the amorphous precipitate spontaneously changes to a crystalline *pentahydrate*.

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[1] Völcker, *Jahresber.*, 1862, 131.
[2] Liebig, *Annalen*, 1858, 106, 193.
[3] Schaffner, *Annalen*, 1844, 50, 146.
[4] Schaffner, *loc. cit.*, 145; Graham, *Annalen*, 1839, 29, 24.
[5] Graham, *loc. cit.*
[6] Berthelot, *Ann. Chim. Phys.*, 1887, [6], 11, 353.
[7] Ladenburg, *Handwörterbuch*, 1889, 7, 23.
[8] Debray, *Ann. Chim. Phys.*, 1861, [3], 61, 431.
[9] Reischauer, *Jahresber.*, 1865, 175.
[10] Cameron and Bell, *J. Physical Chem.*, 1907, 11, 363.
[11] Dehn and Heuse, *J. Amer. Chem. Soc.*, 1907, 29, 1159.
[12] de Schulten, *Compt. rend.*, 1885, 100, 877.
[13] Stoklasa, *Zeitsch. anorg. Chem.*, 1892, 1, 302.
[14] Maddrell, *Annalen*, 1847, 61, 53.
[15] Ladenburg, *Handwörterbuch*, 1889, 7, 24.
[16] Fleitmann and Henneberg, *Jahresber.*, 1847–48, 361; 1849, 238.

$2MgO.P_2O_5.7H_2O$, and two modifications of $2MgO.P_2O_5.15H_2O$, have been prepared from magnesium sulphate and sodium phosphate under different conditions.[3] Ammonium magnesium phosphate is converted into the first by soaking in glycerol.[4]

These hydrates, $MgHPO_4$, and the double phosphate of ammonium and magnesium, ignite to the *anhydrous* pyrophosphate. Popp[2] referred the incandescence which sometimes accompanies the last ignition to a passage from the crystalline to the amorphous condition. When there is no incandescence, the pyrophosphate is white and loose in texture; when there is, it is dark, lava-like, and more resistant to acids. Since the dark colour is due to enclosed and unburnt carbon, incandescence can be prevented by excluding organic matter. Slow precipitation at boiling temperature, evaporation before ignition with an ammonium salt, or very slow ignition also prevents it.[5] Phosphides may occur during ignition if organic matter is present.[6]

At the temperature of the electric furnace the pyrophosphate decomposes with the formation of phosphorus and magnesia.[7] It also loses weight when heated in a blast.[8]

Nitric acid liberates pyrophosphoric acid from magnesium pyrophosphate and forms magnesium nitrate.[9]

Digestion with concentrated sulphuric acid converts it into orthophosphate.[10] It dissolves in acids and does not combine with ammonia.[11]

It has been crystallised from the molten condition.[12]

Double Phosphates of Magnesium.—Microscopic prisms of $NaMgPO_4.9H_2O$ were obtained by crystallising a solution of magnesium oxide in sodium dihydrogen phosphate. It becomes the *monohydrate* at 110° C. Rhombic plates of $KMgPO_4.6H_2O$ are prepared analogously. It becomes the *monohydrate* at 110° C. and anhydrous on calcination. Water decomposes it.[13]

Ouvrard obtained the double metaphosphate $KMg(PO_3)_3$ in prisms of density 2·4 at 20° C. and soluble in acids.[14] Various other double phosphates with the alkali metals have been described [15]—including

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[1] Schwarzenberg, *Annalen*, 1848, 65, 146.
[2] Popp, *Bull. Soc. chim.*, 1870, [2], 14, 195.
[3] Struve, *Zeitsch. anal. Chem.*, 1897, 36, 289.
[4] Struve, *ibid.*, 1898, 37, 485.
[5] Karaoglanow and Dimitrow, *ibid.*, 1918, 57, 353. See Balareff, *Zeitsch. anorg. Chem.*, 1916, 97, 149.
[6] Pereira, *Trans. Chem. Soc.*, 1914, 106, 816.
[7] Moissan, *Ann. Chim. Phys.*, 1896, [7], 9, 134.
[8] Järvinen, *Zeitsch. anal. Chem.*, 1905, 44, 333.
[9] Campbell, *Phil. Mag.*, 1862, [4], 24, 580; Luck, *Zeitsch. anal. Chem.*, 1874, 13, 255; Handy, *J. Amer. Chem. Soc.*, 1900, 22, 31.
[10] Weber, *Jahresber.*, 1847–48, 947.
[11] Pavesi and Rotondi, *Ber.*, 1874, 7, 818.
[12] Anderson, *J. Washington Acad. Sci.*, 1914, 4, 318.
[13] Shröcker and Violet, *Annalen*, 1866, 140, 229.
[14] Ouvrard, *Ann. Chim. Phys.*, 1889, [6], 16, 310.
[15] Chevron and Droixhe, *Jahresber.*, 1888, 523.

$RbMgPO_4.6H_2O$, which was obtained by precipitating mixed solutions of magnesium and rubidium chlorides with disodium hydrogen phosphate. Unlike the corresponding potassium salt, it is stable to water.[1]

Ammonium Magnesium Orthophosphate.—Fourcroy precipitated a solution of a magnesium salt with ammonium phosphate or with sodium phosphate in the presence of an ammonium salt and ammonia.[2] Precipitation is incomplete without excess of the alkaline phosphate and of ammonia to neutralise the acid liberated during the reaction—

$$MgCl_2 + NH_4Cl + Na_2HPO_4 = NH_4MgPO_4 + 2NaCl + HCl.$$[3]

The salt is also less soluble in ammonia than in water: between 20·5° C. and 22·5° C., 1 part of the double phosphate dissolves in 13,497 parts of water and in 60,883 parts of ammonia solution of density 0·961.[4] Precipitation is only complete on standing or after vigorous shaking.[5]

The *hexahydrate* usually precipitates in the cold, but is transformed into the *monohydrate* at 47°–48° C. in contact with water, and the degree of hydration of the precipitate varies with the temperature and the composition of the liquid.[6]

Rhombic crystals of the *hexahydrate* occur as *struvite*, with a hardness of 2·1 and a density of 1·65. It also occurs in guano,[7] in urinary calculi, in gallstones, and crystallises from alkaline urine.

The *hexahydrate* crystallises in various forms of the cubic system,[8] has an alkaline reaction and an insipid taste.[9]

Cubical crystals of the *monohydrate*, stable at 100° C., have been obtained by the action of neutral ammonium phosphate on magnesium sulphate.[10] The *hexahydrate* does not alter in air up to 30° C.,[11] and, though Graham said it dried to the *monohydrate*,[12] does not seem to dry to definite composition at 100° C.[13]

Ammonium magnesium phosphate ignites to the pyrophosphate of magnesium with the evolution of ammonia and water.

MAGNESIUM AND ARSENIC.

Magnesium Arsenide, Mg_3As_2, is prepared as a brown mass with metallic lustre by heating magnesium powder and arsenic in hydrogen. It fuses with difficulty, falls to a powder in air, and reacts with water or dilute acids to form arsine.[14]

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[1] Erdmann and Koethner, *Annalen*, 1897, 294, 71.

[2] Riffault, *Ann. Chim. Phys.*, 1821, 19, 90; Graham, *Annalen*, 1839, 29, 24.

[3] Berzelius, *Pogg. Annalen*, 1825, 4, 275; Lesieur, *Compt. rend.*, 1864, 59, 191.

[4] Ebermayer, *J. prakt. Chem.*, 1853, 60, 41. For solubilities in water and ammonia, see also Fresenius, *Annalen*, 1845, 55, 109; Völcker, *Jahresber.*, 1862, 131; Kubel, *Zeitsch. anal. Chem.*, 1869, 8, 125; Kissel, *ibid.*, 173. For solubilities in various acids and salts, see Liebig, *Annalen*, 1858, 106, 185; Millot, *Bull. Soc. chim.*, 1872, [2], 18, 20; Ville, *Compt. rend.*, 1872, 75, 544; Lindo, *Chem. News*, 1883, 48, 217.

[5] For further details of precipitation, see Detection and Estimation.

[6] Bube, *Zeitsch. anal. Chem.*, 1910, 49, 525.

[7] de la Provostaye, *Compt. rend.*, 1861, 53, 442.

[8] Millot and Maquenne, *Bull. Soc. chim.*, 1875, [2], 23, 238; Stein and Tollens, *Annalen*, 1877, 187, 87.

[9] Stolba, *Chem. Zentr.*, 1876, 727.

[10] Millot and Maquenne, *loc. cit.*

[11] Struve, *Zeitsch. anal. Chem.*, 1898, 37, 485.

[12] Graham, *Annalen*, 1839, 29, 1.

[13] Dehn and Heuse, *J. Amer. Chem. Soc.*, 1907, 29, ii, 1137.

[14] Parkinson, *Trans. Chem. Soc.*, 1867, 20, 125, 309.

Magnesium Arsenites.—Magnesium *orthoarsenite*, $Mg_3(AsO_3)_2$, is obtained as a white precipitate, easily soluble in water and dilute acids, by adding to a solution of magnesium chloride in 50 per cent. alcohol a solution of potassium orthoarsenite made just neutral with acetic acid.[1] The *pyroarsenite*, $Mg_2As_2O_5.4H_2O$, is produced by double decomposition between barium pyroarsenite and magnesium sulphate. It is a white, granular, hygroscopic, amorphous powder, soluble in dilute acids and water, which readily darkens on heating.[2] Bloxam[3] obtained a pyroarsenite by precipitating magnesium sulphate with ammonium arsenite and heating the precipitate.

Magnesium Arsenates.—Crystallised $Mg_3(AsO_4)_2.22H_2O$ (density 1·788) and $Mg_3(AsO_4)_2.8H_2O$ (corresponding to *hoernesite*, of density 2·609) were prepared analogously to the corresponding phosphates.[4]

Prismatic crystals of $2MgHAsO_4.H_2O$ are obtained by heating a solution of magnesium carbonate in excess of arsenic acid at 225° C. in sealed tubes.[5] The pyroarsenate, $Mg_2As_2O_7$, results from the ignition of the double arsenate of ammonium and magnesium.[6]

These arsenates are insoluble in water but soluble in acids. $Mg(H_2AsO_4)_2$ is deliquescent, and soluble in water.

Ammonium Magnesium Arsenate resembles the corresponding phosphate, is formed under analogous conditions, and ignites to the pyroarsenate.[7] The *hexahydrate*, $NH_4MgAsO_4.6H_2O$, precipitates under ordinary conditions, and, when heated between 40° C. and 235° C., loses ammonia and water.[8] It is therefore doubtful whether either the *monohydrate* or $NH_4MgAsO_4.\frac{1}{2}H_2O$ [9] is produced at 100° C.

One part of NH_4MgAsO_4 dissolves in 2788 parts of water at 15° C., and in 15,786 parts of ammonia solution containing 1 part of 0·96 ammonia to 3 parts of water.[10]

Magnesium can be estimated by precipitation as this double arsenate, which is then ignited or titrated.[11]

Thioarsenic Salts of Magnesium.—A suspension of arsenic trisulphide in water is decolorised by the addition of magnesia—soluble magnesium thioarsenite and insoluble magnesium hydrogen arsenite being formed—

$$2As_2S_3+5MgO+H_2O=Mg_3(AsS_3)_2+2MgHAsO_3.$$

On boiling the solution of magnesium thioarsenite, decomposition occurs according to the equation—

$$Mg_3(AsS_3)_2+7H_2O=2MgHAsO_3+6H_2S+MgO.^{12}$$

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[1] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 19. See Stein, *Annalen*, 1850, 74, 221.

[2] Stavenhagen, *loc. cit.*, 20.

[3] Bloxam, *J. prakt. Chem.*, 1862, 87, 118.

[4] de Schulten, *Bull. Soc. franç. Min.*, 1903, 26, 81.

[5] de Schulten, *Compt. rend.*, 1885, 100, 877.

[6] See Ammonium Magnesium Arsenate.

[7] Levol, *Ann. Chim. Phys.*, 1846, [3], 17, 501.

[8] Lefèvre, *ibid.*, 1892, [6], 27, 55; Dehn and Heuse, *J. Amer. Chem. Soc.*, 1907, 29, 1137.

[9] Field, *Jahresber.*, 1858, 176; Puller, *Zeitsch. anal. Chem.*, 1871, 10, 52.

[10] Fresenius, *ibid.*, 1864, 3, 207.

[11] See under Detection and Estimation. Also Puller, *Zeitsch. anal. Chem.*, 1871, 10, 52; Wood, *Trans. Chem. Soc.*, 1874, 27, 1100; Brauner, *Zeitsch. anal. Chem.*, 1877, 16, 57; Reichel, *ibid.*, 1881, 20, 89; Austin, *Zeitsch. anorg. Chem.*, 1900, 23, 146.

[12] Clermont and Frommel, *Ann. Chim. Phys.*, 1879, [5], 18, 201.

Nilson[1] obtained a brown mass of $MgS.As_2S_3.5H_2O$ by evaporating a solution of arsenic trisulphide in calcium hydrosulphide. He also obtained $2MgS.As_2S_3.8H_2O$ as a yellow crystalline difficultly soluble salt, $3MgS.As_2S_3.9H_2O$ as a pure yellow crystalline salt, and $5MgS.2As_2S_3.30H_2O$ as a yellow crystalline salt.[1]

MAGNESIUM AND VANADIUM.

Magnesium Vanadates.—$MgO.2V_2O_5.8H_2O$ is obtained as a sparingly soluble yellow salt, decomposed by hot water with separation of vanadic acid, by interaction between ammonium divanadate and magnesium chloride.[2] Red and brown varieties of $3MgO.5V_2O_5.28H_2O$ were prepared by treating the product of the action of amorphous vanadic acid on magnesia alba and water with acetic acid. This dimorphous salt crystallises in the triclinic system.[3] Manasse obtained it by diluting the concentrated solution of the *normal vanadate*, $MgO.V_2O_5.6H_2O$, with acetic acid. Small, radiating, colourless prismatic crystals of the *normal salt* were obtained by boiling vanadic acid with magnesia alba and water, evaporating and crystallising. A yellowish-red crystalline crust of $4MgO.6V_2O_5.19H_2O$ settles out of a hot solution containing potassium divanadate and excess of magnesium sulphate. It loses its water at 200° C.[4]

MAGNESIUM AND COLUMBIUM.

Magnesium Columbates.—Hexagonal tablets and prisms of $4MgO.Cb_2O_5$ (density 4·43) are obtained by adding magnesium chloride to potassium columbate solution, fusing the precipitate with anhydrous magnesium chloride, and lixiviating with water and hydrochloric acid. If the precipitated salt is fused with borax and lixiviated, $MgO.Cb_2O_5$ is obtained in small prismatic crystals. Joly's $3MgO.Cb_2O_5$ [5] could not be confirmed.[6]

White, flocculent $MgO.Cb_2O_5.7H_2O$ precipitates from mixed solutions of magnesium chloride and sodium columbate.[7]

MAGNESIUM AND TANTALUM.

Magnesium Tantalates.—Rose precipitated $MgO.2TaO_2.2\frac{1}{2}H_2O$ from solutions of sodium tantalate and magnesium sulphate.[8] Joly obtained $4MgO.Ta_2O_5$, isomorphous with the corresponding columbate, by fusing tantalic acid with excess of magnesium chloride.[9]

Some double magnesium tantalates have been prepared.[10]

MAGNESIUM AND CARBON.

Magnesium Carbide.—Moissan thought that magnesium carbide could not exist at electric-furnace temperature,[11] but Lebeau obtained acetylene by the action of water on his product.[1] Similar products have been obtained by heating magnesium in benzol vapour[2] or in a current of acetylene.[3] Lebeau thought that the vapours of carbon and magnesium reacted, but carbon reduces magnesia at 1700° C., if reoxidation is prevented, and, since hydrogen from water is usually present in furnaces,[4] magnesium carbide probably results from an interaction between acetylene (produced by a union between carbon and hydrogen) and magnesium.[5]

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[1] Nilson, *Jahresber.*, 1876, 211 ; *Trans. Chem. Soc.*, 1876, 30, 482.

[2] Hauer, *J. prakt. Chem.*, 1860, [1], 80, 329.

[3] Sugiura and Baker, *Trans. Chem. Soc.*, 1879, 35, 713.

[4] Manasse, *Annalen*, 1887, 240, 48.

[5] Joly, *Compt. rend.*, 1875, 81, 266.

[6] Larsson, *Zeitsch. anorg. Chem.*, 1896, 12, 195.

[7] Balke and Smith, *J. Amer. Chem. Soc.*, 1908, 30, 1651.

[8] Rose, *J. prakt. Chem.*, 1857, [1], 72, 43.

[9] Joly, *loc. cit.*, 1266.

[10] Balke and Smith, *loc. cit.*, 1667.

[11] Moissan, *Ann. Chim. Phys.*, 1899, [7], 16, 151.

When acetylene is passed over heated magnesium, MgC_2, Mg_2C_3, and C are produced in varying proportions according to the temperature. The decomposition

$$2MgC_2 = Mg_2C_3 + C$$

is rapid between 570° C. and 610° C. Above 610° C. the reaction

$$Mg_2C_3 = 2Mg + C$$

predominates. Mg_2C_3 predominates over MgC_2 when paraffin or aromatic hydrocarbons are passed over the heated metal.

Both carbides are decomposed by water—

$$MgC_2 + 2H_2O = Mg(OH)_2 + C_2H_2;$$
$$Mg_2C_3 + 4H_2O = 2Mg(OH)_2 + C_3H_4 \text{ (allylene).}$$

The products of the acetylene reaction between 465° C. and 515° C. are hard, compact, steel-grey masses which decompose water slowly ; those obtained above 550° C. are grey, brittle, and rapidly decomposed by water.[6]

Magnesium Cyanide.—Scheele treated magnesium hydroxide with hydrocyanic acid,[7] and Schulz[8] heated the double ferrocyanide of potassium and magnesium to redness, treated with water and evaporated, to obtain $Mg(CN)_2$. It is perhaps produced, in small quantities and very easily decomposed by moisture, by the action of carbon monoxide on heated magnesium.[9]

The colourless solution of magnesium in hydrocyanic acid soon goes brown, and $Mg(CN)_2$ is so soluble and so easily hydrolysed that Schulz's "crystals" were probably magnesium hydroxide. Magnesium cyanide is also very soluble in alcohol.

When magnesium ferrocyanide is heated, the reaction

$$Mg_2[Fe(CN)_6] = 2Mg(CN)_2 + FeC_2 + N_2$$

occurs at about 200° C. At 400° C. only 3·30 per cent. of the cyanide is produced, and none at 800° C.—magnesium nitride resulting in greater and greater proportion as the temperature rises.[10]

$$[Mg(OH)_2] + 2HCN.Aq. = Mg(CN)_2.Aq. + 112{\cdot}000 \text{ Cal.}^{11}$$

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[1] Lebeau, *Compt. rend.*, 1907, 144, 799.

[2] Parkinson, *Ann. Chim. Phys.*, 1886, [6], 9, 385.

[3] Berthelot, *ibid.*, 1866, [4], 9, 406.

[4] Slade, *Trans. Chem. Soc.*, 1908, 93, 327.

[5] Pring and Hutton, *ibid.*, 1906, 89, 1591.

[6] Novák, *Ber.*, 1909, 42, 4209 ; *Zeitsch. physikal. Chem.*, 1910, 73, 513.

[7] Scheele, *Opusc.*, 1782, 2, 148.

[8] Schulz, *J. prakt. Chem.*, 1856, [1], 68, 257.

[9] Fichter and Schölly, *Helv. Chim. Acta*, 1920, 3, 303. See also Briegleb and Geuther, *Annalen*, 1862, 123, 228, and under Magnesium Nitrate.

[10] Fichter and Suter, *Helv. Chim. Acta*, 1922, 5, 396. See Eidmann *J. prakt. Chem.*, 1899, [2], 59, 1.

[11] Varet, *Compt. rend.*, 1895, 121, 598.

Magnesium Thiocyanate.—The crystals of $Mg(CNS)_2.4H_2O$ are very soluble in alcohol and water. To prepare them a solution of magnesia in thiocyanic acid is evaporated over sulphuric acid.[1]

Magnesium Carbonate.—If a solution containing magnesium sulphate and sodium bicarbonate is supersaturated with carbon dioxide and heated so that the gas can only escape slowly, microscopic rhombohedra of $MgCO_3$ separate.[2] Similar colourless transparent crystals occur naturally as *magnesite*, which also occurs amorphous in compact masses. The naturally occurring crystals, which are often yellow, grey, or brown, are isomorphous with calcite, have a density of 3·0–3·1 and a hardness of 3·5–4·5. If a solution of magnesium carbonate in carbonic acid is evaporated to dryness at atmospheric pressure, the small residual crystals are isomorphous with orthorhombic aragonite[3]—magnesium carbonate is thus isodimorphous with calcium carbonate. Rhombohedral magnesite is also prepared by heating precipitated magnesium carbonate with water and solid carbon dioxide at 185° C. at a pressure of 20–30 atmospheres.[4]

Many mountain chains consist largely of *dolomite*, a double carbonate of magnesium and calcium, which is widely distributed, similar in form to magnesite, with a density of 2·85 and a hardness of 3·5–4. Dissolved magnesium carbonate occurs in natural waters containing carbon dioxide—including sea-water.[5] It is prepared *amorphous* by precipitating magnesium sulphate with sodium carbonate and calcining,[6] by decomposing calcium carbonate with magnesium chloride, or by heating sodium carbonate and magnesium sulphate from 160°–175° C. in sealed tubes.[7]

A litre of water at 19·5° C. dissolves 0·970 grm. $MgCO_3$ when pure, 26·5 grm. when charged with carbon dioxide at 1 atmosphere, and 50·6 grm. when charged with carbon dioxide at 6 atmospheres.[8] The solubility diminishes as the temperature rises—becoming *nil* at 100° C. under a pressure of 765 mm.[9] According to Treadwell and Reuter,[10] magnesium hydrogen carbonate is only stable when free carbonic acid is present, and at 15° C. and 760 mm. a solution in which the partial pressure of carbon dioxide is 0 contains 0·7156 grm. $MgCO_3$ per litre. In solutions of magnesium carbonate in carbonated water some magnesium carbonate remains dissolved even after prolonged boiling, and deposition appears to proceed slowly.[11]

The solubility of magnesium carbonate in carbonated water is increased by various salts[12]—including cold alkaline borates.[13]

Magnesium carbonate has an alkaline reaction, is rapidly decomposed by acids, and dissociates into MgO and CO_2 when heated. At 825° C.

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[1] Meitzendorff, *Pogg. Annalen*, 1842, 56, 71.
[2] Sénarmont, *Ann. Chim. Phys.*, 1851, [3], 32, 148.
[3] Rose, *Pogg. Annalen*, 1837, 42, 366.
[4] Marc and Simek, *Zeitsch. anorg. Chem.*, 1913, 82, 17.
[5] Jacobsen, *Annalen*, 1875, 167, 29.
[6] Jacquelain, *Ann. Chim. Phys.*, 1851, [3], 32, 195; Bineau, *ibid.*, 1857, [3], 51, 299.
[7] Moissan, *Traité de Chimie Minérale*, 1904, iii, 954.
[8] Engel, *Ann. Chim. Phys.*, 1888, [6], 13, 344.
[9] Engel and Ville, *Compt. rend.*, 1881, 93, 340; Engel, *ibid.*, 1885, 100, 352.
[10] Treadwell and Reuter, *Zeitsch. anorg. Chem.*, 1898, 17, 170.
[11] Rinne, *Chem. Zeit.*, 1907, 31, 125.
[12] Hunt, *Amer. J. Sci.*, 1866, [2], 42, 49; Engel, *Compt. rend.*, 1885, 100, 352; Cameron and Seidell, *J. Physical Chem.*, 1903, 7, 578.
[13] Wittstein, *Arch. Pharm.*, 1875, [3], 6, 40.

the pressure of the dissociation products is 1 atmosphere,[1] and CO_2 is apparently retained on heating to redness.[2] Magnesite is more resistant than the artificial carbonate to acids and heat.

$KHCO_3.MgCO_3.4H_4O$, when carefully heated up to 150° or 200° C., leaves a transparent residue of crystals with the original form. Water dissolves out potassium carbonate and leaves crystalline anhydrous magnesium carbonate.[3] Magnesium carbonate is obtained anhydrous and dry by heating the double carbonate of ammonium and magnesium. This carbonate is very unlike the natural mineral and Sénarmont's [4] artificial magnesite. It retains the crystalline form of the original carbonate, abstracts water from the air as vigorously as lime, absorbs ammonia gas, and sets like plaster in contact with a little water. A litre of water dissolves about 2 grm. of this carbonate, though it only dissolves about 1 grm. in the hydrated condition. When suspended in water the anhydrous carbonate is gradually transformed into the crystalline *trihydrate*.[5]

$MgCO_3.3H_2O$ is produced by the action of sodium or potassium bicarbonate on magnesium sulphate solutions at ordinary temperatures; [6] by deposition at 60° C. from a solution of magnesium carbonate or hydroxide in carbonic acid; [7] by the addition of alcohol to the solution of magnesium bicarbonate,[8] or by exposing the latter to air; [9] by leaving the precipitate in contact with the liquid when sodium carbonate precipitates a magnesium salt; [10] by precipitating magnesium sulphate with ammonium carbonate; [11] and by warming the pentahydrate with water.[12]

It is flocculent when first precipitated by alcohol, but soon becomes crystalline,[13] and its habit of crystallising in rhombic needles may identify it with *nesquéhonite*,[14] which has the same composition. The finely divided salt effloresces in air, and its density at 18° C. is 1·808.[15] It becomes the *monohydrate* at 100° C., which also separates from solutions of magnesium bicarbonate at a fairly high temperature.[16] The trihydrate loses its third molecule of water, with partial decomposition, at much higher temperatures.

Its constitution may be $OH.MgCO_3H.2H_2O$, and its decomposition by boiling water may be represented by

$$OH.MgCO_3H.2H_2O=2H_2O+OH.MgCO_3H$$

and

$$OH.MgCO_3H+H_2O=Mg(OH)_2+H_2O+CO_2.$$ [16]

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[1] Brill, *Zeitsch. anorg. Chem.*, 1905, **45**, 275. Moisture seems to accelerate dissociation (Marc and Simek, *Zeitsch. anorg. Chem.*, 1913, **82**, 17).

[2] Marchand and Scheerer, *J. prakt. Chem.*, 1850, [1], **50**, 585.

[3] Engel, *Compt. rend.*, 1885, **101**, 814.

[4] Sénarmont, *Ann. Chim. Phys.*, 1851, [3], **32**, 148.

[5] Engel, *Compt. rend.*, 1899, **129**, 598.

[6] Boussingoult, *Ann. Chim. Phys.*, 1825, **29**, 285; Favre, *Ann. Chim. Phys.*, 1844, [3], **10**, 474; Knorre, *Zeitsch. anorg. Chem.*, 1903, **34**, 260. See also $KHCO_3.MgCO_3.4H_2O$.

[7] Monhaupt, *Chem. Zeit.*, 1904, 868; Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 788.

[8] Monhaupt, *loc. cit.*

[9] Knorre, *loc. cit.*

[10] Knorre, *loc. cit.* See Jacquelain, *Ann. Chim. Phys.*, 1851, [3], **32**, 195.

[11] Fichter and Osterwalder, *Zeitsch. anal. Chem.*, 1915, **55**, 389.

[12] Knorre, *loc. cit.*; Cesaro, *Bull. Acad. roy. Belg.*, 1910, **37**, 151.

[13] Monhaupt, *Chem. Zeit.*, 1904, 868.

[14] Cesaro, *Bull. Acad. roy. Belg.*, 1910, **37**, 151.

[15] Knorre, *loc. cit.*, 1903, **34**, 260.

[16] Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 788.

Crystallised $MgCO_3.3H_2O$ has apparently no definite solubility in water, and over a wide range of temperature its reaction with water approximates to

$$5MgCO_3+2H_2O=Mg(OH)_2.3MgCO_3+Mg(HCO_3)_2.^1$$

Natural *nesquéhonite* has a hardness of 2·5 and a density of 1·84.

At lower temperatures than about 15° C. the *pentahydrate* separates instead of the trihydrate.[2, 3, 4] The crystals deposited from solutions of magnesia in carbonic acid are monoclinic, usually hexagonal prisms, and are practically identical with *landsfordite*, though Dana assigned to this the composition $4MgO.3CO_2.22H_2O$.[5] They are said to be soluble in 267 parts of cold water, and in solution they apparently, especially on warming, transform into the trihydrate.[3, 5]

According to Leitmeier,[6] when hydrated magnesium carbonates deposit from the water of the mineral springs at Rohitsch, the pentahydrate does not form above 6° C., and it loses water in the air at 20° C.

Natural *landsfordite* has a hardness of 2·5 and a density of 1·5–1·7.

Various other hydrates, including a *dihydrate*,[7] a *tetrahydrate*,[8] and others,[9] have been reported, but are doubtful.

Basic Carbonates of Magnesium.—When $MgCO_3$ is heated, basic carbonates result from a progressive loss of CO_2.[10]

Magnesia alba is commercially prepared as a white powder by precipitating magnesium sulphate or chloride with sodium carbonate. Magnesia alba levis results from precipitation in the cold, and magnesia alba ponderosa from precipitation in the heat. Both the light, bulky form and the heavier variety are used as laxatives in medicine, in dentistry, and for toilet purposes. They ignite respectively to the light and heavy oxides of magnesium. The light carbonate, "when examined under the microscope, is found to consist of amorphous particles with numerous slender prisms intermixed."[11]

Various other processes have been patented or proposed for preparing magnesia alba. Pattinson carefully ignited dolomite, dissolved out the magnesium carbonate by carbon dioxide under 5–6 atmospheres pressure, and, after separating calcium carbonate, injected steam.[12] Magnesia has been agitated with alkaline bicarbonate,[13] and magnesium hydroxide, precipitated by milk of lime from the "bittern" obtained by extracting salt from sea-water, has been dissolved in carbonic acid, heated rapidly to 70° C., and then slowly to the boiling-point.[14]

Magnesia alba is only slightly soluble in water (the solution has an alkaline reaction), but is soluble in acids and in solutions of ammonium salts.

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[1] Seyler and Lloyd, *Trans. Chem. Soc.*, 1917, 111, 994.
[2] Fritsche, *Pogg. Annalen*, 1836, 37, 306; Engel, *Compt. rend.*, 1885, 100, 911.
[3] Knorre, *Zeitsch. anorg. Chem.*, 1903, 34, 260.
[4] Auerbach, *Zeitsch. Elektrochem.*, 1904, 10, 161.
[5] Cesaro, *Bull. Acad. roy. Belg.*, 1910, 37, 151.
[6] Leitmeier, *Zeitsch. Kryst. Min.*, 1909, 47, 104.
[7] Engel, *Compt. rend.*, 1885, 100, 911.
[8] Damour, *ibid.*, 1857, 44, 561; Marignac, *Jahresber.*, 1855, 344.
[9] Kippenberger, *Zeitsch. anorg. Chem.*, 1894, 6, 177.
[10] Brill, *ibid.*, 1905, 45, 275.
[11] *British Pharmacopœia*, 1914.
[12] Pattinson, *Dingl. poly. J.*, 1873, 209, 467.
[13] German Patent, 13762 (October 1886).
[14] Gutzkow, *Dingl. poly. J.*, 1888, 270, 30.

Its composition is usually said to approximate to that of *hydromagnesite*, $Mg(OH)_2.3MgCO_3.3H_2O$,[1] but analyses of its composition were never very consistent, and it seems quite certain that its composition is very variable.[2,3]

The product of the decomposition of $MgCO_3.3H_2O$ by water has been said to approximate to the composition usually ascribed to magnesia alba.[4] The precipitation of basic carbonates by sodium carbonate from magnesium salts has, following Rose, been usually ascribed to hydrolytic decomposition of the normal carbonate, but Davis suggests that the numerous basic carbonates of magnesium, as they have been described, are varying mixtures of different substances. Some of them may be solid solutions of MgO and $MgCO_3$.[3]

The naturally occurring *hydromagnesite*, $3MgCO_3.Mg(OH)_2.3H_2O$, crystallises in the monoclinic system with a hardness of 3·5 and a density of 2·15. *Hydrogioberite*, $(Mg.OH)_2CO_3.2H_2O$, occurs in light grey compact masses of density 2·16.

Magnesium Hydrogen Carbonate.[5]—When magnesium carbonate dissolves in water containing carbon dioxide, the reaction

$$MgCO_3+H_2O+CO_2=Mg(HCO_3)_2$$

presumably occurs.[6] To obtain a pure solution, magnesia alba can be dissolved in carbonated water and magnesium carbonate precipitated by boiling. The precipitate, thus freed from sodium carbonate, is redissolved in carbonated water, and the process, if necessary, repeated.[7] Carbon dioxide can also be passed through distilled water containing pure magnesia in suspension.[8]

Double Carbonates of Magnesium.—Knorre[9] obtained octahedral crystals of $Na_2CO_3MgCO_3$, belonging to the tetragonal system, by digesting precipitated magnesium carbonate with excess of sodium bicarbonate solution. The crystals are isometric and doubly refractive. De Schulten[10] obtained flat rhombohedra, with a density of 2·729 at 15° C., by heating mixed solutions of magnesium nitrate and sodium carbonate in a closed flask at 100° C. Na_2CO_3 is said to precipitate $Na_2CO_3.MgCO_3.15H_2O$ from magnesium sulphate solution at temperatures below 10° C.[11] Knorre could not confirm Deville's[12] quartz-like crystals obtained by digesting magnesia alba with sodium bicarbonate at 60°–70° C.

$K_2CO_3.MgCO_3.4H_4O$ is produced in rhombic prisms by digesting $MgCO_3.3H_2O$ with potassium bicarbonate solution, or by the action of excess of concentrated potassium carbonate solution on a solution of magnesium chloride. Cold water slowly decomposes it into $MgCO_3.3H_2O$, and hot water into magnesia alba.[13]

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[1] The composition of the light magnesia alba used in the rubber industry is said to approximate to $11MgCO_3.3Mg(OH)_2.11H_2O$ (Greider, *J. Ind. Eng. Chem.*, 1922, **14**, 385).

[2] Anderson, *Trans. Chem. Soc.*, 1905, **87**, 257.

[3] Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 788.

[4] Seyler and Lloyd, *Trans. Chem. Soc.*, 1917, **111**, 994.

[5] See also Carbonates and Basic Carbonates of Magnesium.

[6] Bodländer, *Zeitsch. physikal. Chem.*, 1900, **35**, 23.

[7] Davis, *loc. cit.*

[8] Rinne, *Chem. Zeit.*, 1907, **31**, 125.

[9] Knorre, *Zeitsch. anorg. Chem.*, 1903, **34**, 260.

[10] de Schulten, *Compt. rend.*, 1896, **122**, 1427.

[11] Norgaard, see Moissan, *Traité de Chimie Minérale*, 1904, iii, 981.

[12] Deville, *Ann. Chim. Phys.*, 1851, [3], **33**, 75.

[13] Knorre, *loc. cit.* See Bonsdorf, *Ann. Chim. Phys.*, 1822, [2], **20**, 12; Deville, *loc. cit.*

$KHCO_3.MgCO_3.4H_2O$ separates from the reaction

$$3(MgCO_3.3H_2O)+2KCl+CO_2=2(KHCO_3.MgCO_3.4H_2O)+MgCl_2$$

in triclinic crystals,[1] which have a density of 1·984 [2] and do not alter in air.[3] Potassium carbonate is obtained from the double salt by extracting with water after ignition or under pressure at 140° C.[4]

It was first prepared by the reaction

$$MgCl_2+3KHCO_3+3H_2O=KHCO_3.MgCO_3.4H_2O+2KCl+CO_2.$$

The double salt crystallises out slowly [5] in snow-white crystals.[2] $MgCO_3.3H_2O$ precipitates sometimes in this reaction [3] and at other times succeeds the double salt.[6] The proportionate concentrations of $KHCO_3$ and $MgCl_2$ determine precipitation. The reversible reaction

$$KHCO_3.MgCO_3.4H_2O \rightleftharpoons MgCO_3.3H_2O+KHCO_3+H_2O$$

is related to these observations, and indicates that the double salt can be prepared by acting with potassium bicarbonate on $MgCO_3.3H_2O$ suspended in water.[7]

Efflorescent crystals of $RbHCO_3.MgCO_3.4H_2O$ were obtained by warming a solution of rubidium bicarbonate with magnesium carbonate in a current of carbon dioxide at 60° C.[8]

$(NH_4)_2CO_3.MgCO_3.4H_2O$ was obtained in rectangular prisms by the action of ammonium carbonate on magnesia or magnesium carbonate suspended in water.[9] Deville obtained unstable $(NH_4)HCO_3.MgCO_3.4H_2O$ by acting on magnesium salts with a large excess of ammonium bicarbonate, and at a low temperature unstable $2(NH_4HCO_3.MgCO)_3.11H_2O$.[10] The former loses ammonia, water, and carbon dioxide in the air, and is decomposed by water with the formation of $MgCO_3.3H_2O$.[11] Engel only obtained $(NH_4)_2CO_3.MgCO_3.4H_2O$ by saturating a mixture of ammonium and magnesium bicarbonates with carbon dioxide in the absence of air.[12] $(NH_4)_2CO_3.MgCO_3.6H_2O$ precipitates from a magnesium salt and normal ammonium carbonate when the solution contains half its volume of alcohol.[13]

Dolomite,[14] $MgCO_3.CaCO_3$,[15] is widely distributed in nature.

One thousand parts of water at 18° C., charged with carbon dioxide at 750 mm., dissolve 0·310 parts of normal dolomite, but the solubility in carbonated water varies with the condition of the mineral.[16] Strong acids dissolve it, and its resistance to attack by dilute acids seems to increase with its iron content.[1] When heated to 400° C. and treated with water it acts like a cement,[2] though the loss of carbon dioxide is said to begin at 500° C.[3]

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[1] Kittel, *Jahresber.*, 1857, 150.

[2] Knorre, *Zeitsch. anorg. Chem.*, 1903, 34, 260.

[3] Engel, *Ann. Chim. Phys.*, 1886, [6], 7, 260.

[4] See $MgCO_3.3H_2O$.

[5] Berzelius, *Ann. Chim. Phys.*, 1820, [2], 14, 370.

[6] Nanty, *Compt. rend.*, 1910, 152, 605.

[7] Auerbach, *Zeitsch. Elektrochem.*, 1904, 10, 161 ; Buchner, *ibid.*, 1908, 14, 63.

[8] Erdmann and Koethner, *Annalen*, 1896, 294, 73.

[9] Favre, *Ann. Chim. Phys.*, 1844, [3], 10, 474. See Schaffgotsch, *Pogg. Annalen*, 1858, 104, 482.

[10] Deville, *Ann. Chim. Phys.*, 1852, [3], 35, 454.

[11] Knorre, *Zeitsch. anorg. Chem.*, 1903, 34, 260.

[12] Engel, *Compt. rend.*, 1899, 129, 598.

[13] Gooch and Eddy, *Zeitsch. anorg. Chem.*, 1908, 58, 427.

[14] See Magnesium Carbonate.

[15] For some analyses, see *Jahresber.*, 1849, 813 ; Knight, *Chem. News*, 1914, 109, 193 ; Rothrock and Shumaker, *ibid.*, 1920, 120, 29.

[16] Cossa, *Jahresber.*, 1869, 1242, 1257 ; Gorup-Besanez, *ibid.*, 1871, 1214.

Artificial dolomite has been prepared by the action of magnesium chloride and sodium carbonate solutions on calcium carbonate (vaterite) at 180°–200° C. in carbon dioxide at 50 atmospheres,[4] and by many other methods.[5]

Northupite, $Na_2CO_3.MgCO_3.NaCl$, occurs naturally, crystallised in the isometric system, in colourless, white, or brown crystals, with a hardness of 3·5–4 and a density of 2·38.

It has been prepared artificially by heating sodium chloride, sodium carbonate, magnesium chloride, and water in a closed flask for eight hours at 100° C. The octahedral crystals had a density of 2·377 at 15° C.; cold water decomposed them, and they melted with decomposition at a red heat.[6]

Magnesium Thiocarbonate, $MgCS_3$.—Berzelius mixed solutions of magnesium sulphate and barium thiocarbonate. The evaporated solution left an amorphous, pale yellow mass that was partly decomposed by boiling water into magnesium carbonate.[7]

Yellow aqueous solutions result when magnesium hydroxide is shaken with water and carbon disulphide,[8] or magnesium is immersed partly in carbon disulphide and partly in water.[9]

MAGNESIUM AND SILICON.

Magnesium Silicide.[10]—Crude silicides are obtained by heating magnesium strongly with silica or silicates.[11, 12] Silicon and magnesium unite directly when they are heated in a current of hydrogen,[12] and their freezing-point curve indicates the compound Mg_2Si.[13]

Mg_2Si is left as brilliant slate-blue octahedra when magnesium is dissolved away from an alloy containing 25 per cent. of silicon by ethyl iodide and ether. The alloy is prepared by heating together fragments of magnesium, magnesium filings, and potassium silicofluoride. Other alloys of silicon and magnesium also contain crystals of the silicide.[14]

It slowly decomposes water at ordinary temperatures—evolving hydrogen. Cold hydrochloric acid attacks it violently with the evolution of hydrogen and spontaneously inflammable silicon hydride.[14] Concentrated sulphuric or nitric acid attacks it slowly; the dilute acid acts more rapidly.[1] It dissociates completely at 1100°–1200° C. *in vacuo* or in hydrogen.[2] It precipitates many heavy metals from their salts, and even decomposes solutions of chlorides of the alkalies.[3]

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[1] Gaubert, *Compt. rend.*, 1914, 159, 486.

[2] Deville, *Jahresber.*, 1865, 798; Crace-Calvert, *ibid.*, 1865, 798–799.

[3] Grünberg, *Zeitsch. anorg. Chem.*, 1913, 80, 337; Kallauner, *Chem. Zeit.*, 1913, 37, 1317.

[4] Spangenberg, *Zeitsch. Kryst. Min.*, 1913, 52, 529.

[5] See Morlot, *Pogg. Annalen*, 1848, 74, 591; Pfatt, *Jahrb. Miner.*, 1907, Beil.-Bd., 23, 529; *Centr. Min.*, 1903, 659; Linck, *J. Chem. Soc.*, 1911, 100, Abs. ii, 294.

[6] de Schulten, *Compt. rend.*, 1896, 122, 1427.

[7] Berzelius, *Traité de Chimie*, 1831.

[8] Walker, *Chem. News*, 1874, 30, 28.

[9] Taylor, *ibid.*, 1882, 45, 125.

[10] Vigouroux (*Ann. Chim. Phys.*, 1897, [7], 12, 171) has given a short history of magnesium silicide up to 1897.

[11] Phipson, *Proc. Roy. Soc.*, 1864, 13, 217; Gattermann, *Ber.*, 1889, 22, 186; Besson, *Compt. rend.*, 1912, 154, 116.

[12] Winkler, *Ber.*, 1890, 23, 2642.

[13] Vogel, *Zeitsch. anorg. Chem.*, 1909, 61, 46.

[14] Lebeau and Bossuet, *Compt. rend.*, 1908, 146, 282.

Magnesium Silicates. The heating curve of magnesia and precipitated silica shows no arrest between 500° C. and 1450° C.[4] Ebelmen[5] obtained Mg_2SiO_4 and $MgSiO_3$ by heating magnesia and boric acid with appropriate proportions of silica. The artificial crystals of the former were identical with *forsterite* from Vesuvius, and the latter was obtained both as asbestos-like fibres and as rhombic crystals of *enstatite.* Enstatite has also been prepared by heating silica with magnesium chloride, and, together with crystals of the orthosilicate, Mg_2SiO_4 (olivine), by heating silica with magnesia and magnesium chloride.[6] Enstatite and olivine, structurally similar to the meteoric varieties, were obtained together by heating to redness magnesium, steam, and silicon chloride.[7]

Alkaline silicates precipitate gelatinous magnesium silicate from magnesium salts ; the precipitate is apparently $MgO.2SiO_2.2H_2O$.[8]

The natural magnesium silicates have an alkaline reaction.[9] The *orthosilicate,* $(Mg,Fe)_2SiO_4$, occurs as *olivine* or *peridotite* in rhombic crystals or compact masses. Its hardness is 6–7 and its density 3·1–3·5. *Forsterite,* Mg_2SiO_4, has a hardness of 6–7 and a density of about 3·24. The *metasilicate,* $MgSiO_3$, occurs as *enstatite* in fibrous or lamellated masses with a density of 3·19 and a hardness of 5·5. *Talc* and *steatite,* $Mg_3H_2(SiO_3)_4$, are an acid salt of metasilicic acid. When pure they are white, unctuous powders : steatite being less distinctly crystalline than talc. They are used for polishing and other purposes. *Serpentine* can be represented as a basic orthosilicate, $Mg_2(MgHO)H_3(SiO_4)_2$. The serpentines vary in colour - green or red (due to iron) predominating. The natural masses of serpentine are much sought after for making ornaments. *Meerschaum,* $2MgO.3SiO_2.2H_2O$, occurs in compact masses which are white or grey. Its density is 0·99–1·28 and its hardness is 2–2·5. Tobacco-pipes, cigarette-holders, etc., are made from it.[10]

MAGNESIUM AND BORON.

Magnesium Boride.—Dark, impure magnesium borides were obtained by heating boron trioxide and magnesium in appropriate proportions,[11] or with the oxide in excess,[12] by heating magnesium in boron trichloride vapour, and by heating magnesium and boron in a current of hydrogen[13] or alone.[14] Hydrochloric and nitric acids liberated impure boron hydride from them.

According to Winkler,[15] Mg_9B_2 was produced when magnesium was heated with boron trioxide in hydrogen, and Mg_2B_5 when magnesium and borax were heated together. Moissan[1] distinguished an unstable boride, decomposed by water, from a stable form that resisted the action of water, hydrochloric acid, and nitric acid. He obtained the latter in crystalline form by heating magnesium with excess of boron trioxide.

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[1] Vogel, *Zeitsch. anorg. Chem.*, 1909, 61, 46.

[2] Lebeau and Bossuet, *Compt. rend.*, 1908, 146, 282.

[3] Winkler, *Ber.*, 1890, 23, 2642.

[4] Hedvall, *Zeitsch. anorg. Chem.*, 1916, 98, 69.

[5] Ebelmen, *Ann. Chim. Phys.*, 1851, [3], 33, 56.

[6] Hautefeuille, *ibid.*, 1865, [4], 4, 175.

[7] Meunier, *Compt. rend.*, 1881, 93, 737.

[8] Heldt, *J. prakt. Chem.*, 1865, [1], 94, 157.

[9] Pichard, *Compt. rend.*, 1878, 87, 797.

[10] Jakob (*Helv. Chim. Acta*, 1920, 3, 669) has indicated structural formulæ for the natural silicates of magnesium.

[11] Jones, *Trans. Chem. Soc.*, 1879, 35, 41.

[12] Moissan, *Compt. rend.*, 1892, 114, 392.

[13] Jones and Taylor, *Trans. Chem. Soc.*, 1881, 39, 213.

[14] Moissan, *loc. cit.*, 619.

[15] Winkler, *Ber.*, 1890, 23, 772.

According to Rây,[2] only Mg_3B_2 is produced at a red heat and under normal pressure. It is produced by heating magnesium with *amorphous* boron, or by heating magnesium and boron trioxide in a current of hydrogen. It dissolves in dilute hydrochloric acid and decomposes when heated.

Magnesium Borates.—Only two borates can be prepared by heating magnesia with boron trioxide.[3] The *orthoborate*, $Mg_3(BO_3)_2$, is obtained by heating boric anhydride strongly with boron trioxide with or without potassium hydrogen fluoride. The crystals are nacreous, difficultly fusible, with a density of 2·987 at 21° C., or transparent prisms. Boiling water and dilute acetic acid do not dissolve them, but they are soluble in mineral acids. Magnesium *pyroborate*, $2MgO.B_2O_3$, results with a larger excess of boron trioxide.[4]

Rammelsberg[5] prepared the hydrated orthoborate, $B_2O_3.3MgO.9H_2O$, and, by crystallising from a filtered solution of magnesium hydroxide in excess of boric acid solution, the compound $MgO.3B_2O_3.8H_2O$. The *heptahydrate* has been obtained similarly to the octahydrate. The hydrated *metaborate*, $MgO.B_2O_3.8H_2O$, separates as a white amorphous precipitate on warming mixed solutions of magnesium chloride and borax. Small crystals of $3MgO.4B_2O_3.11H_2O$ were obtained from the filtrate. Fine needles of $MgO.B_2O_3.3H_2O$, corresponding to the mineral *pinnoite*, are obtained by heating the octahydrate with a warm concentrated solution of magnesium chloride. When a solution of magnesium oxide in boric acid is concentrated and kept stirred at 100° C. after the addition of a solution containing potassium hydroxide and boric acid, $KMg_2B_{11}O_{19}.9H_2O$ finally separates. It corresponds to the mineral *kaliborite*.[6]

Boracite, $2Mg_3B_8O_{15}.MgCl_2$, results from heating a mixture of magnesium borate, boric acid, magnesium chloride, and sodium chloride, or from heating 1 part of sodium borate with 2 parts of magnesium chloride and a little water in sealed tubes at 275°-280° C. The cubic crystals of artificial boracite have a density of 2·89 : the density of the mineral is about 2·9. Boracite, pinnoite, and kaliborite occur in the Stassfurt deposits.[7]

Pinnoite crystallises in the tetragonal system with a hardness of 3·4 and a density of 3·3.

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[1] Moissan, *loc. cit.*

[2] Rây, *Trans. Chem. Soc.*, 1914, 105, 2162.

[3] Guertler, *Zeitsch. anorg. Chem.*, 1904, 40, 236. See Heinz and Richter, *Pogg. Annalen*, 1860, 110, 613; Le Roux, *Compt. rend.*, 1867, 64, 126; Ditte, *ibid.*, 1873, 77, 785, 893; 1875, 80, 490, 561.

[4] Ebelmen, *Ann. Chim. Phys.*, 1851, [3], 33, 50; Le Chatelier, *Compt. rend.*, 1891, 113, 1034; Ouvrard, *ibid.*, 1901, 132, 257; Guertler, *Zeitsch. anorg. Chem.*, 1904, 40, 236.

[5] Rammelsberg, *Pogg. Annalen*, 1840, 49, 451.

[6] van 't Hoff and Bruni, *Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 805; van 't Hoff, *ibid.*, 1008.

[7] de Gramont, *Compt. rend.*, 1890, 111, 43.

MAGNESIUM AND ALUMINIUM.

Magnesium Aluminate, $MgO.Al_2O_3$.—Natural *spinel* crystals belong to the cubic system, have a density of 3·60–3·63 and a hardness of 8. Colourless, octahedral crystals of spinel are easily prepared by heating alumina and magnesia for a few minutes in an electric furnace. Their density at 15° C. is 3·57, and they are very resistant to ordinary chemical reagents.[1]

Ebelmen obtained rose-coloured crystals by heating a mixture of alumina, magnesia, potassium chromate, and boric acid. He obtained other colours by adding suitable oxides.[2]

DETECTION AND ESTIMATION.

Detection.—The solutions used for estimating or detecting magnesium should contain no cations other than the alkali metals. Since the chloride of magnesium is soluble, since its sulphide[3] does not precipitate in either acid or alkaline solution, and since neither its hydroxide[4] nor its carbonate[5] is precipitated by ammonia in the presence of ammonium salts, it is most usual to detect and estimate magnesium through its precipitation as $Mg(NH_4)PO_4$[6] by sodium phosphate (or another soluble phosphate) in the presence of ammonia and ammonium chloride. The estimation is usually completed by ignition to the pyrophosphate,[7] though the original precipitate is sometimes titrated according to the equation

$$Mg(NH_4)PO_4 + 2HCl = MgCl_2 + (NH_4)H_2PO_4.$$

An excess of decinormal acid is added and the residual acid titrated, using methyl orange as indicator, with decinormal alkali. Winkler[8] suggests weighing the original precipitate (as $Mg(NH_4)PO_4.6H_2O$) after drying over calcium chloride, and Jones[9] after drying in air on a tarred filter paper. The precipitate has also been dissolved in a known quantity of sulphuric acid and determined by the Zeiss refractometer.[10] A microchemical test depends on the precipitation of magnesium ammonium phosphate as shining prisms united into rosettes.[11]

A precipitate of pure (hydrated) $Mg(NH_4)PO_4$ can only be obtained by careful attention to conditions. Some $Mg[(NH_4)_2(PO_4)]_2$ probably contaminates it when a magnesium salt is precipitated with excess of phosphate solution in the presence of ammonia and ammonium chloride.[12, 13, 14] Some magnesium metaphosphate, $Mg(PO_3)_2$, is then formed on ignition as well as $Mg_2P_2O_7$, and the result is too high. The metaphosphate in the calcined precipitate is indicated by its insolubility in hydrochloric acid.[1] It may be formed by the reaction

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[1] Dufau, *Bull. Soc. chim.*, 1901, [iii], 25, 669.

[2] Ebelmen, *Ann. Chim. Phys.*, 1851, [3], 23, 36.

[3] See Magnesium Sulphide.

[4] See Magnesium Hydroxide.

[5] See Magnesium Carbonates.

[6] For properties, see Ammonium Magnesium Phosphate.

[7] See Magnesium Pyrophosphate.

[8] Winkler, *Zeitsch. angew. Chem.*, 1918, 31, 211.

[9] Jones, *J. Biol. Chem.*, 1916, 25, 87.

[10] Wagner and Schultze, *Zeitsch. anal. Chem.*, 1907, 46, 501.

[11] Kunz-Krause, *Ber.*, 1920, 53, [B], 1672.

[12] Balareff, *Zeitsch. anorg. Chem.*, 1918, 103, 73.

[13] Gooch and Austin, *ibid.*, 1899, 20, 121.

[14] Nebauer, *ibid.*, 1892, 2, 45.

$$Mg[(NH_4)_2(PO_4)]_2 = Mg(PO_3)_2 + 4NH_3 + 2H_2O,^2$$

or as a consequence of the reaction

$$Mg[(NH_4)_2(PO_4)]_2 = Mg(NH_4)PO_4 + (NH_4)_3PO_4.$$

The dissociation of the ammonium phosphate results partly in the loss of P_2O_5, which can be usually observed,[3] and partly in metaphosphate by reaction between the escaping P_2O_5 and $Mg_2P_2O_7$.[1] Excess of ammonium salts favours the formation of $Mg[(NH_4)_2.(PO_4)]_2$ and alkalinity of $Mg_3(PO_4)_2$.[4]

Estimation.—The precipitation of ammonium magnesium phosphate has been applied volumetrically by precipitating with a known quantity of phosphate and estimating the excess.[5] Stolba's method of titrating the precipitate with acid is more generally used.[6] The precipitate can be prepared for titration by washing away the ammonia with alcohol, which has been criticised as tedious,[7] by washing with alcohol and ether,[8] or by drying off the ammonia on filter paper exposed to air at ordinary temperatures or at 50°–60° C.[9] Bruckmiller [10] sucks the precipitate dry on the filter, washes with alcohol and then with hot water into the precipitation beaker. A known excess of decinormal acid is added and titrated back, using methyl orange as indicator, with decinormal alkali. This method has been applied to the estimation of small quantities of magnesium—using methyl red as indicator.[11]

Brandis [8] has suggested the determination of the ammonia in the precipitate by alkaline hypobromite: the process resolves into a titration of iodine by thiosulphate.

The corresponding double arsenate of magnesium and ammonium, $Mg(NH_4)AsO_4.6H_2O$, is also employed for estimating magnesium. It is precipitated by adding ammonium arsenate to a distinctly ammoniacal solution of the magnesium salt. Cooling by a freezing mixture or adding alcohol hastens precipitation. The precipitate is treated similarly to the double phosphate and ignited to the pyroarsenate.[12]

The double arsenate is liable to contamination very similarly to the double phosphate [13] and to reduction on ignition.[14]

A volumetric method has been applied to this precipitate by dissolving it in hydrochloric acid, adding potassium iodide, and titrating the liberated iodine. For this purpose an ammoniated solution of a magnesium salt has been precipitated with sodium arsenate,[7] and the solution containing magnesium has been treated with potassium arsenate and then with ammonia.[1]

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[1] Balareff, *loc. cit.* [2] Gooch and Austin, *loc. cit.* [3] Nebauer, *loc. cit.*

[4] Järvinen, *Zeitsch. anal. Chem.*, 1904, **43**, 279; Bruckmiller, *J. Amer. Chem. Soc.*, 1917, **39**, 610.

[5] Raffa, *Gazzetta*, 1908, **38**, 556; Repiton, *Chem. Zentr.*, 1908, **i**, 1329.

[6] Stolba, *Chem. Zentr.*, 1876, 727.

[7] Meade, *J. Amer. Chem. Soc.*, 1899, **21**, 146.

[8] Brandis, *Zeitsch. anal. Chem.*, 1910, **49**, 152.

[9] Handy, *J. Amer. Chem. Soc.*, 1900, **22**, 31.

[10] Bruckmiller, *loc. cit.*

[11] Hibbard, *J. Ind. Eng. Chem.*, 1919, **11**, 753.

[12] Browning and Drushel, *Amer. J. Sci.*, 1907, [iv], **23**, 293. See also under Ammonium Magnesium Arsenate.

[13] Raffa, *Gazzetta*, 1909, **39**, i, 154.

[14] Virgili, *Zeitsch. anal. Chem.*, 1905, **44**, 492.

The titration should be done in strongly acid solution.[2] This precipitate can also be titrated acidimetrically, similarly to the double phosphate.[3]

To secure a pure precipitate of ammonium magnesium phosphate the solution should be as free as possible from ammonium salts and neutral[4] or just alkaline.[5] The phosphate should be added first and then strong ammonia in excess.[6] If any acid phosphate of magnesium is precipitated, the ammonia converts it into the double phosphate.

Gibbs[7] advised microcosmic salt as a precipitant: he precipitated from a boiling solution containing some ammonium chloride and added ammonia to the cooled liquid. Jörgenson[8] also advised hot precipitation. Schmitz[9] acidified the solution containing magnesium salt and phosphate with hydrochloric acid, heated to boiling, alkalinised with ammonia, cooled, and added one-fifth volume of concentrated ammonia. Slightly ammoniacal diammonium phosphate has also been recommended as a precipitant.[10] Raffa[11] added the magnesium solution rapidly to an excess of disodium ammonium phosphate.

Accurate results are obtained by settling the original precipitate, decanting, dissolving in hydrochloric acid, and precipitating with a slight excess of ammonia.[12]

Precipitation is only complete after long standing unless the liquid is shaken continuously. The precipitate is washed with 2·5 per cent. ammonia and ignited to whiteness. It seems advisable, to avoid loss of P_2O_5, to ignite over a Bunsen flame and not over a blast.[10] Fresenius treated the ignited residue with nitric acid, evaporated, and re-ignited to obtain a perfectly white pyrophosphate. This has been said to give low results.[13] The precipitate should be kept free from organic matter and raised slowly in temperature during ignition to avoid a dark residue.[14]

Schaffgotsch[15] precipitated magnesium as the double carbonate of ammonium and magnesium, $(NH_4)_2CO_3.MgCO_3.4H_2O$. Gooch and Eddy[16] add to the solution of the magnesium salt half its volume of absolute alcohol, precipitate with normal ammonium carbonate solution containing 50 per cent. of alcohol, wash the precipitate of $(NH_4)_2CO_3.MgCO_3.6H_2O$ with ammonium carbonate solution and ignite it to magnesium oxide.

In the absence of alkali metals magnesium can be estimated in its salts of volatile acids by evaporation with concentrated sulphuric acid, heating to redness, and weighing as $MgSO_4$.[1] Neutral solutions of magnesium chloride can be treated with a slight excess of ammonium fluoride, evaporated to a syrup, finally ignited to MgF_2, and weighed.[2]

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[1] Rosenthaler, *Zeitsch. anal. Chem.*, 1907, 46, 714.
[2] Kolthoff, *Pharm. Weekblad*, 1919, 56, 1322.
[3] Bailley, *J. Pharm. Chim.*, 1919, [vii], 20, 55.
[4] Nebauer, *Zeitsch. anorg. Chem.*, 1893, 4, 251; Dumas, *Chem. Eng.*, 1910, 12, 185.
[5] Bruckmiller, *J. Amer. Chem. Soc.*, 1917, 39, 610.
[6] Nebauer, *Zeitsch. anorg. Chem.*, 1892, 2, 45.
[7] Gibbs, *Chem. News*, 1873, 28, 51.
[8] Jörgenson, *Zeitsch. anal. Chem.*, 1906, 45, 273. See Magnesium Pyrophosphate.
[9] Schmitz, *ibid.*, 1906, 45, 512.
[10] Järvinen, *ibid.*, 1905, 44, 333. See Magnesium Pyrophosphate.
[11] Raffa, *Gazzetta*, 1908, 38, 556.
[12] Gooch and Austin, *Zeitsch. anorg. Chem.*, 1899, 20, 121.
[13] Handy, *J. Amer. Chem. Soc.*, 1900, 22, 31. See Magnesium Pyrophosphate.
[14] Balareff, *Zeitsch. anorg. Chem.*, 1916, 97, 149; Karaoglanow and Dimitrow, *Zeitsch. anal. Chem.*, 1918, 57, 353. See Magnesium Pyrophosphate.
[15] Schaffgotsch, *Pogg. Annalen*, 1858, 104, 482.
[16] Gooch and Eddy, *Zeitsch. anorg. Chem.*, 1908, 58, 427.

The Schaffgotsch method has been used to separate magnesium from the alkali metals (though lithium must be absent). Magnesium chloride can be converted into oxide by ignition with mercuric oxide. Mercuric chloride and the excess of mercuric oxide volatilise, and magnesium oxide remains. The operation should be repeated several times.[3] This reaction serves to separate magnesium from the alkali metals, and a separation can also be effected by precipitating magnesium hydroxide with an aqueous solution of dimethylamine or a solution of guanidine.[4] Barium hydroxide and calcium hydroxide are used for the same purpose.

Nicolardot and Dandurand [2] consider that precipitation as ammonium magnesium phosphate is the most trustworthy method of estimating magnesium when alkali metals are present, though double phosphates of alkali and magnesium are liable to form in solutions containing alkali cations.[5]

Palkin [6] dissolves out magnesium chloride from admixed potassium and sodium chlorides with alcohol and ether.

Magnesium is liable to be occluded when calcium is previously separated as oxalate. Methods of separating magnesium and calcium adequately are discussed under Calcium.

Colorimetric Estimation.—An approximate method for estimating small quantities of magnesium depends upon separation as ammonium magnesium phosphate, followed by solution in hydrochloric acid and addition of molybdic acid in the presence of hydroquinone or other reducing agents. The yellow colour is compared with the colour of a standard solution that has been similarly treated.[7]

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[1] Magnesium sulphate is said to retain traces of sulphuric acids at high temperatures (Bailey, *Trans. Chem. Soc.*, 1887, 51, 676).

[2] Nicolardot and Dandurand, *Rev. Mét.*, 1919, 16, 193.

[3] Kallauner, *Chem. Zeit.*, 1911, 35, 1165.

[4] Herz and Drucker, *Zeitsch. anorg. Chem.*, 1901, 26, 347.

[5] Balareff, *ibid.*, 1918, 102, 241.

[6] Palkin, *J. Amer. Chem. Soc.*, 1920, 42, 1618.

[7] Briggs, *J. Biol. Chem.*, 1922, 52, 349; Hammett and Adams, *ibid*, 1922, 52, 211; Kramer and Tisdall, *ibid.*, 1921, 48, 223; Bell and Doisy, *ibid.*, 1920, 44, 55.

CHAPTER IV.

ZINC AND ITS COMPOUNDS.

ZINC.

Symbol, Zn. Atomic Weight, 65·38 (O = 16).

Occurrence.—Native zinc has been found in Australia, at Melbourne,[1] but the uncombined metal occurs very rarely. The principal ore of the metal is the sulphide, ZnS, which occurs as *zinc blende* (*sphalerite* and *wurtzite*).

Zinc also occurs as the oxide in *zincite* or red zinc ore, ZnO, as the normal carbonate *calamine*,[2] $ZnCO_3$, or *smithsonite*, which is also known as *zinc spar*,[2] and as the basic carbonate *hydrozincite*. The oxysulphide, 4ZnS.ZnO, occurs as *voltzite*.

Goslarite is hydrated zinc sulphate, $ZnSO_4.7H_2O$, and the anhydrous salt, $ZnSO_4$, occurs as *zincosite*.

Other zinc minerals are: *hopeite*, $Zn_3(PO_4)_2.4H_2O$, some basic phosphates, including *tarbuttite*, $Zn_3(PO_4)_2.Zn(OH)_2$, and *hibbenite*, $2Zn_3(PO_4)_2.Zn(OH)_2.6\frac{1}{2}H_2O$, *kottigite*, $Zn_3(AsO_4)_2.8H_2O$, *adamine*, $ZnHAsO_4.H_2O$, *calamine*[2] or *hemimorphite*, often formulated as $(Zn.OH)_2SiO_3$, *willemite*, $2ZnO.SiO_2$, *gahnite*, $ZnO.Al_2O_3$.

Zinc is associated with other metals in minerals, such as *franklinite*, $(Fe,Zn,Mn)O.(Fe,Mn)_2O_3$, and *aurichalcite*, $2(Zn,Cu)CO_3.3(Zn,Cu)(OH)_2$.

Small quantities of zinc are dispersed widely through the older rocks, the sea,[3] and the tissues and organs of animals[4]—including the human body.[5] Zinc also seems to be a normal constituent of marine organisms,[6] and has been observed in wood ashes.[7]

History.[8]—Pliny and Dioscorides refer to a peculiar earth called "cadmia" with which copper was melted to prepare brass. This alloy of copper and zinc was used by the ancients. The name "zinken" was apparently first used by Paracelsus, though it was applied for long after indifferently to the metal and its ore. The term "spelter," commercially applied to zinc, is apparently connected with the German *Spiauter* or *Spialter*, and dates from Boyle.[9]

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[1] Becker, *Jahrb. Miner.*, 1857, 312, 698; Phipson, *Compt. rend.*, 1862, 55, 218.

[2] The name "calamine" is applied by English mineralogists to the natural carbonates, but by American to natural silicates of zinc.

[3] Dieulafait, *Ann. Chim. Phys.*, 1880, [5], 21, 256; *Compt. rend.*, 1883, 96, 70.

[4] Bertrand and Vladesco, *Bull. Soc. chim.*, 1922, [4], 31, 268.

[5] Rost, *Med. Klin.*, 1921, 17, 123.

[6] Bodansky, *J. Biol. Chem.*, 1920, 44, 399.

[7] Braun, *Pogg. Annalen*, 1854, 92, 175; Demarcay, *Compt. rend.*, 1900, 130, 91.

[8] For a history of zinc, see Hommel, *Chem. Zeit.*, 1912, 36, 905, 918. For its history in India and China, see Hommel, *Zeitsch. angew. Chem.*, 1912, 25, i, 97.

[9] New English Dictionary.

The metal itself was probably first prepared in India, and China subsequently became sole producer until the middle of the eighteenth century. During the seventeenth century the nature of zinc and its ores was misunderstood, and there was frequent confusion between zinc and bismuth. Homberg, in 1695, identified zinc as the metal from blende, and Kunkel, about 1700, recognised that calamine contained a metal that alloyed with copper during the manufacture of brass.

Champion erected a zinc factory at Bristol in 1743, and the first continental zinc works was established at Liége in 1807.

Zinc oxide was known to the ancients from its production, during the manufacture of brass, when zinc vapour burned in air : it was often called " philosopher's wool " (*nix alba*). The " white vitriol " of the alchemists was ordinary zinc sulphate, and Glauber first obtained zinc chloride by dissolving calamine in spirits of salt.

Preparation of Zinc.—I. *Dry Process of Extraction.*—The ore is concentrated by washing, roasted to the oxide, and heated to a white heat with carbon. The reduced metal distils over and is collected in receivers.

The *roasting* is usually performed on the sulphide (zinc blende) or the carbonate (calamine, zinc spar, smithsonite), but zinc silicates are sometimes dehydrated by heating and reduced by carbon. The roasting must be sufficient to convert the sulphide completely into oxide. If the temperature is too low some zinc sulphate is formed that is converted into sulphide during the reduction with carbon. This sulphide is very difficult to reduce.

Zinc blende is usually roasted in multiple-bedded reverberatory furnaces that are frequently heated by waste gases from the smelting furnaces. The sulphur dioxide evolved by the roasting blende may be used in the manufacture of sulphuric acid.

The *reduction* is effected by heating the roasted oxide with ground coal in fireclay retorts. The English and Carinthian methods of conducting the process have been abandoned. In the Belgian process the retorts have a circular or elliptical section, and are set in the furnace in tiers. In the Silesian process the retorts have a section resembling a narrow window with an arched top, and are usually arranged in a single row, though there may be two tiers. There are various other differences of detail between the two methods. It is now usual to fire by gas, and the regenerative principle is almost universal. Electric smelting has been successfully practised in British Columbia, Sweden, and other places.[1] In the Rhenish process the retorts are somewhat larger than in the Silesian, and are muffle-shaped or elliptical.

The *distillation* of the volatilised zinc secures the metal. The condensers should be hot enough to keep the condensed metal in a liquid state. If the retorts are kept well filled with carbon monoxide, no zinc oxide is produced to distil over with the metal. If carbon dioxide is present, oxidation of the metal occurs. The formation of zinc oxide in an oxidising atmosphere has prevented the successful smelting of zinc in blast furnaces.

II. *Wet-extraction* processes have been studied and recommended for commercial application. In these processes the zinc is converted into a soluble salt which is then dissolved out. Thus zinc blende has been calcined to zinc sulphate and extracted with dilute sulphuric acid,[1] or roasted with sodium chloride and extracted with water.[2] These and similar processes have been variously combined with the dry-distillation process. The Leadville ores are roasted to zinc sulphate and extracted with water. The extraction of the zinc is completed by chlorination.[3]

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[1] For action of carbon on zinc oxide, see under Zinc Oxide. For review of electrothermal metallurgy of zinc, see *U.S. Bureau of Mines*, Bull. 208, 1923. Also see Ingalls, *Trans. Amer. Electrochem. Soc.*, 1921, 40, 245.

III. The *electrolytic preparation* of zinc is employed by Messrs. Brunner Mond, Ltd. The calcium-chloride liquors obtained in the ammonia-soda process are treated with crude zinc oxide and carbon dioxide. Zinc chloride and calcium carbonate are thus formed. The zinc-chloride liquors are electrolysed in a cell with carbon anodes and rotating disc-shaped iron cathodes. The chlorine produced is used for making bleach, and the zinc is stripped from the cathodes and melted down. The metal is guaranteed to contain 99·96 per cent. of zinc, and is valuable for making ductile brasses.[4]

Zinc of 99·9 per cent. purity can be obtained by electrolysing zinc sulphate solution. The metal thus prepared is sometimes brittle, and the brittleness is probably due to occluded hydrogen.[5]

Gallo [6] proposes the electrolysis of a mixture of zinc fluoride and sodium chloride. The admixture of salt, by lowering the melting-point to 500° C., permits the electrolytic decomposition of the fused fluoride without risk of previous decomposition by water-vapour. Better results are obtained by this use of the fluoride than by electrolysing the fused chloride. The latter process is difficult to apply.[7]

In an electrolytic method recently described, the solution obtained by treating the ore is purified and then freed from lead, copper, and cadmium by zinc dust. It is then electrolysed between an anode of lead and a cathode of aluminium. The current density at the cathode is 2·6 amp. per sq. dcm. The zinc deposit is easily removed.[8]

Purification of Zinc.—Spelter, as commercial zinc is commonly called, is often refined by liquation when the crude material contains about 3 per cent. of lead. By keeping the metal molten for some days the heavier lead collects at the bottom. The top layers, in which the lead content has diminished to about 1 per cent., representing the solubility of lead in zinc at the temperature employed, are then removed.[9] Cadmium and iron are also separated during this process.

Spelter usually contains lead, iron, and cadmium,[9] and traces of arsenic, antimony, tin, sulphur, and carbon.[10] Copper and silver [11] may be present, and occluded gases.[12] Small quantities of various other elements, including phosphorus, may be present.

Zinc of 99·7–99·9 per cent. purity can be obtained by passing the volatilised products from the retorts through "fume filters." The zinc-vapour, being less dense than the "lead fume," etc., passes more readily through the incandescent carbon or other porous material, such as fireclay, constituting the filter, and condenses very free from impurities. If the zinc-vapour is led from the fume filters into the condensers through nozzles packed with carbon to exclude the action of air, the formation of "fume" is prevented.[1] *Zinc fume* or "blue powder" is a mixture of finely divided zinc and zinc oxide.[2]

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[1] Parnell, *Brit. Assoc. Rep.*, 1880, 544.

[2] Swindells, *Chem. Gazette*, 1851, 9, 420.

[3] *J. Soc. Chem. Ind.*, 1888, 7, 572.

[4] For electrolysis of zinc, see under Electrodeposition.

[5] Schwarz, *Zeitsch. Elektrochem.*, 1923, 29, 198.

[6] Gallo, *Gazzetta*, 1913, 43, i, 361.

[7] See Lorenz, *Zeitsch. anorg. Chem.*, 1895, 10, 78; 1896, 12, 272; Grünauer, *ibid.*, 1904, 39, 389; Vogel, *Trans. Faraday Soc.*, 1906, 2, 56.

[8] Palmer and Wejnarth, *Zeitsch. Elektrochem.*, 1923, 29, 557.

[9] Mylius and Fromm, *Ber.*, 1895, 28, 1563.

[10] Elliot and Storer, *Jahresber.*, 1860, 180; Funk, *Ber.*, 1895, 28, 3129; Scholl, *Chem. and Met. Eng.*, 1922, 26, 595.

[11] Friedrich, *Zeitsch. angew. Chem.*, 1904, 17, 1636.

[12] Morley, *Amer. Chem. J.*, 1890, 12, 460; Schwarz, *loc. cit.*

Zinc can be refined electrolytically by using zinc sheet as cathode and impure zinc as anode. By distilling electrolytic zinc, obtained by repetitions of this process, metal of 99·999 per cent. purity can be obtained.[3]

Zinc can be prepared free from arsenic by melting it with sodium,[4] and spectroscopically pure by repeated distillation *in vacuo.*[5]

Zinc of 99·95 per cent. purity is said to be obtained by treating a saturated solution of pure zinc sulphate with sodium amalgam at 81° C., washing the crystals, drying them, and removing the mercury by distillation in a vacuum slowly at 400° C.[6]

Uses of Zinc.—Zinc is a constituent of many important alloys.[7] Some pyrophoric alloys consist of zinc with small quantities of copper and aluminium.[8] The *zinc dust* condensed during the distillation (known as "blue powder" or "zinc fume") is used in the dyeing industry as a reducing agent. A zinc-copper couple, copper deposited on zinc, is a very effective reducing agent: it will decompose water with the evolution of hydrogen even at 2° C.[9] Rods of zinc are used in batteries, and rolled zinc plates are used in the manufacture of many articles. A small percentage of lead is desirable in spelter intended for rolling. When zinc is granulated by pouring it into hot water it forms small globules, known as bean-shot, and flakes when it is poured into cold water, known as feathered-shot metal.[10] Granulated zinc is a common laboratory reagent, and the arsenic-free metal has an important use in applying the Marsh test and its modifications for small quantities of arsenic.

Zinc is extensively used for *galvanising* iron to protect it from rust. The name is derived from the original method of galvanic deposition. This method was superseded by dipping the iron in molten zinc.[11] In the *sherardising* process iron (or steel) articles are heated with zinc dust in closed vessels to a temperature somewhat below the melting-point of the zinc. The coating thus obtained resists atmospheric corrosion very effectively.[12] The zinc can also be sprayed on to the surface to be coated.[13]

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[1] Primrose, *Inst. of Metals*, 1909, ii, 231; Bannister, *ibid.*, 1910, i, 213.

[2] Smith, *The Zinc Industry* (Longmans, Green & Co., London), 1918, p. 118.

[3] Mylius and Fromm, *loc. cit.*

[4] Thorne and Jeffers, *Analyst*, 1906, **31**, 101. See Hehner, *ibid.*, 1902, **27**, 261.

[5] Morse and Arbuckle, *Amer. Chem. J.*, 1898, **20**, 195.

[6] Drescher, *J. Soc. Chem. Ind.*, 1924, **43**, 178B.

[7] See under Alloys.

[8] Guertler, *Chem. Zeit.*, 1919, **43**, Rep. 260; Czochralski and Lohrke, *Chem. Zentr.*, 1920, iv, 252.

[9] Gladstone and Tribe, *Proc. Roy. Soc.*, 1871–72, **20**, 218; *J. Chem. Soc.*, 1877, **31**, 561; 1879, **35**, 567; Stock, *J. Soc. Chem. Ind.*, 1897, **16**, 107.

[10] Smith, *The Zinc Industry* (Longmans, Green & Co., London), 1918, p. 138.

[11] Cranfurd, British Patent, 7355 (1837).

[12] Hinchley, *Trans. Faraday Soc.*, 1911, **6**, 133.

[13] Schoop, *J. Soc. Chem. Ind.*, 1911, **30**, 291.

Since zinc can now be electrolytically deposited effectively, and the coating is more resistant than when it is obtained by the dipping process, the original galvanic method may, in its turn, supersede the method of dipping the iron into molten zinc.[1] Cyanide-plating solutions for electrolytic deposition are very effective.[2]

Zinc is also used for precipitating gold or silver in the cyanide process.

Physical Properties of Zinc.—Zinc is a greyish-white or bluish-white metal. It has a metallic lustre, can take a high polish, and tarnishes quickly in ordinary air.

Zinc is said to undergo *allotropic modification* from an α-variety to a β-variety at 174° C., and from the β-variety to a γ-variety at 322° C.[3] According to Cohen and Heldermann, ordinary zinc is a metastable mixture of several allotropic modifications, and "atomised" zinc is also a mixture of two or more allotropic forms.[4]

Zinc sublimes in a crystalline form when it is distilled in hydrogen or *in vacuo*.[5] The crystals were supposed to occur dimorphically in the regular and hexagonal systems,[6] but crystalline zinc is, however, apparently hexagonal and probably holohedral.[7]

When zinc is crushed its micro-structure becomes homogeneous and its hardness increases. Annealing restores the crystalline structure.[8] The cast metal " cries " more feebly than tin.

It is brittle at ordinary temperatures, but becomes malleable and ductile at 100°–150° C. The metal is rolled hot on the large scale, but it remains sufficiently malleable after heating to be rolled or drawn into wire. Above 205° C. the metal again becomes brittle enough to be pulverised in a mortar.[8]

Zinc is distinctly plastic at 200°–400° C.,[9] and the warm metal can be pressed through an opening.[10]

The modulus of elasticity, or Young's modulus of zinc, has been given as varying between 7670 and 10,550, or an average of 9300 kgm. per sq. mm.:[11] it varies with the nature and purity of the metal.

In determinations of the tensile strength the breaking load of thin rolled zinc was found to be about 24,000 lb. per sq. inch, and the tension modulus of elasticity 11,500,000 lb. per sq. inch.[12]

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[1] See Pring and Tainton, *Trans. Chem. Soc.*, 1914, 105, 710.

[2] Horsch and Fuwa, *Trans. Amer. Electrochem. Soc.*, 1922, 41, 211; Wernlund, *ibid.*, 1921, 40, 257.

[3] Losana, *Gazzetta*, 1923, 53, 539. Le Chatelier (*Compt. rend.*, 1890, 111, 454) and Mönkemeyer (*Zeitsch. anorg. Chem.*, 1905, 43, 182) confirmed the β to γ transformation, and Benedicks (*Métallurgie*, 1910, 7, 531) the α to β transformation, though Werner (*Zeitsch. anorg. Chem.*, 1913, 83, 301) did not confirm the latter.

[4] Cohen and Heldermann, *J. Chem. Soc.*, 1914, 106, Abs. ii, 127, 652; 1915, 108, Abs. ii, 52. Benedicks and Arpy (*Zeitsch. anorg. Chem.*, 1914, 88, 237) criticised their conclusions.

[5] *Jahresber.*, 1847–48, 434; 1889, i, 504.

[6] Nicklès, *Ann. Chim. Phys.*, 1848, [3], 22, 37; Rose, *Pogg. Annalen*, 1859, 107, 448; *Jahresber.*, 1859, 195.

[7] Brögger and Flinck, *Zeitsch. Kryst. Min.*, 1884, 9, 236; Williams and Burton, *Amer. Chem. J.*, 1889, 11, 225. It may be rhombohedral (Williams, *Amer. Chem. J.*, 1892, 14, 275).

[8] For micro-structure of zinc, see Smith, *The Zinc Industry* (Longmans, Green & Co., London), 1918, p. 140. See Masing, *Zeitsch. Metallk.*, 1921, 13, 425, for recrystallisation of cold-worked zinc.

[9] Spring, *Zeitsch. physikal. Chem.*, 1894, 15, 65.

[10] Lenkojeff and Tammann, *Ann. Physik*, 1903, [4], 10, 647.

[11] Sutherland, *Phil. Mag.*, 1891, [5], 32, 224.

[12] Moore, *J. Inst. Metals*, 1915, 14, 230.

The average compressibility of zinc, the fractional change of volume produced by one megabar pressure, is $1 \cdot 5 \times 10^{-6}$ per unit volume per megabar, between 100 and 500 megabars.[1]

The hardness of zinc seems to be 2·5 on Mohs' scale, but it varies with the purity of the metal, and perfectly pure zinc seems to be softer than silver.

The density of distilled zinc at 20°/24° C. is 6·9225, which rises to 7·12722 after compression under 10,000 atmospheres,[2] but it varies with the history of the metal and usually diminishes on "working."[3]

Schiff[4] found that the density of granulated zinc at 12° C. varied from 6·966 to 6·975, and recorded determinations by other observers from 6·861 to 7·1908. According to Kalischer,[5] a specimen of rolled zinc of density 7·1812 had a density of 7·1841 when it became crystalline by heating to 130°–300° C. (Water at 0° C. = 1.)

The density of zinc decreases on melting. One grm. of zinc was found to expand by 0·010 c.c. on melting,[6] the corresponding densities have been estimated at 7·2 and 6·48,[7] and the density of molten zinc is expressed by the formula

$$D = 6 \cdot 59 - 0 \cdot 00097\ (t - 419)$$

at any temperature t.[8] The slight contraction during solidification adapts the metal for castings.[9]

The vapour density of zinc corresponds to a monatomic molecule.[10] When zinc dissolves in mercury it depresses the vapour pressure as if its molecule were monatomic.[11]

Zinc melts at 419·4° C.[12] There has been a gradual convergence on this figure during the progress of research.[13]

The latent heat of fusion of zinc is about 1·730 Cal.[14]

Berthelot found 920° C. for the boiling-point of zinc.[15] Higher temperatures had been found by earlier investigators.[16] More recently 918° C. has been assigned as the boiling-point.[17]

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

[2] Kahlbaum, Roth, and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 284.

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

[4] Schiff, *Annalen*, 1858, 107, 62.

[5] Kalischer, *Ber.*, 1881, 14, 2750.

[6] Toepler, *Ann. Phys. Chem.*, 1894, [2], 53, 343. See also Johnston and Adams, *Zeitsch. anorg. Chem.*, 1911, 72, 11.

[7] Roberts and Wrightson, *Jahresber.*, 1881, 36–37; 1883, 50.

[8] Hogners, *J. Amer. Chem. Soc.*, 1921, 43, 1624.

[9] Smith, *The Zinc Industry* (Longmans, Green & Co., London), 1918, p. 139.

[10] Mensching and Meyer, *Ber.*, 1886, 19, 3298; Biltz, *Chem. Zentr.*, 1895, i, 770; Cooke, *Proc. Roy. Soc.*, 1906, 77A, 148.

[11] Ramsay, *Trans. Chem. Soc.*, 1889, 55, 533; Beckmann and Liesche, *Zeitsch. anorg. Chem.*, 1914, 89, 190. According to Hildebrande (*8th Inter. Cong. Appl. Chem.*, 1912, 22, 147), zinc dissolved in mercury is partly associated thus: $2Zn = Zn_2$.

[12] Dana and Foote, *Trans. Faraday Soc.*, 1920, 15, 186; Scheel, *Zeitsch. angew. Chem.*, 1919, 32, i, 348; Guertler and Pirani, *Chem. Zentr.*, 1919, iii, 910.

[13] Egerton, *Phil. Mag.*, 1917, [6], 33, 47 (418° C.); Lewkonja, *Zeitsch. anorg. Chem.*, 1908, 59, 320 (419° C.); Donski, *ibid.*, 1908, 57, 188 (420° C.); Hindrichs, *ibid.*, 1907, 55, 416 (419° C.); Petrenko, *ibid.*, 1906, 48, 350 (419° C.).

[14] Laschtschenk, *J. Russ. Phys. Chem. Soc.*, 1913, 45, 552. 1·820 Cal. according to Egerton, *Phil. Mag.*, 1917, [6], 33, 33.

[15] Berthelot, *Compt. rend.*, 1900, 131, 381.

[16] Becquerel, *Ann. Chim. Phys.*, 1863, [3], 68, 73 (932° C.); Deville, *Compt. rend.*, 1880, 90, 773 (916°–954° C.); Troost, *ibid.*, 1882, 94, 788 (942° C.); Violle, *ibid.*, 1882, 94, 720 (930° C.); Barus, *U.S. Geol. Survey*, 1889, No. 54 (929° C.).

[17] Egerton, *loc. cit.*, [6], 33, 471. See Greenwood, *Proc. Roy. Soc.*, 1909, 10, 83A, 490. According to Heycock and Lamplough (*Proc. Chem. Soc.*, 1912, 28, 3), zinc boils at 905·7° C.

In vacuo zinc volatilises slowly at 184° C.[1] and boils at 550° C.[2] According to Heycock and Lamplough, the boiling-point alters by 0·133° C. per mm. difference from normal pressure.[3]

The latent heat of vaporisation at boiling-point is 31·430 Cal.[4]

The specific heat varies from 0·08421 at —127·5° C. to 0·09570 at 123·5° C.[5] From the mean of determinations by Naccari, Bede, and Schlübel, the specific heat of zinc is 0·0929 between 18° C. and 100° C., 0·0957 between 18° C. and 200° C., and 0·0978 between 18° C. and 300° C.[6] According to Kahlbaum, Roth, and Siedler,[7] the specific heat of distilled zinc is 0·0939, which becomes 0·0940 after compression.

The thermal conductivity decreases with the temperature up to the melting-point. Then there is a sharp drop, succeeded by another gradual rise.[8] According to Lees,[9] the thermal conductivity of pure, redistilled cast zinc varies from 0·20 at —170° C. to 0·268 at 18° C. According to Jäger and Diesselhorst it is 0·265 at 18° C. for pure cast zinc and 0·262 at 100° C.[10]

The electrical conductivity in reciprocal ohms per cm. cube varies from $19·5 \times 10^4$ at —170° C. to $16·9 \times 10^4$ at 18° C.[11] The conductivity has been expressed as $5·45\ (1 + 0·0039t + 0·0000017t^2)$ microhms at any temperature t between 15° C. and 300° C.[12]

Breaks in the thermal and electrical conductivity curves have been connected with allotropic modifications of zinc.[13]

The coefficient of linear expansion is $10·06 \times 10^{-6}$ between —183° C. and 12·6° C., and $17·11 \times 10^{-6}$ between 19·3° C. and 100·2° C.[14]

The most important lines in the arc spectrum of zinc, in Ångström (10^{-8} cm.) units, are: 3036, 3072, 3345, 4630·06, 4680·138, 4722·164, 4810·535, 4912, 4925, 6103, 6362·345.

Colloidal Zinc.—A fairly stable colloidal solution of zinc in ether has been obtained by sparking between zinc electrodes immersed in the liquid.[15]

Colloidal solutions can be prepared by electrical discharge between zinc electrodes under water, but they are more unstable than corresponding cadmium solutions.[16]

The colloidal solution of zinc in isobutyl alcohol, obtained by an electrical method, is stable. It is brownish red by transmitted light and greyish black by reflected.[17]

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[1] Demarcay, *Compt. rend.*, 1882, 94, 184.

[2] Kraft, *Ber.*, 1905, 38, 262; Hansen, *ibid.*, 1909, 42, 211 (b.-pt. at 760 mm.=920° C.).

[3] Heycock and Lamplough (*Proc. Chem. Soc.*, 1912, 28, 4). *Cf.* Greenwood, *Proc. Roy. Soc.*, 1909, 10, 83A, 490; Barus, *Phil. Mag.*, 1890, [5], 29, 141.

[4] van Liempt, *Zeitsch. anorg. Chem.*, 1920, 114, 105.

[5] Griffiths and Griffiths, *Phil. Trans.*, 1914, 214A, 335.

[6] Schlübel, *Zeitsch. anorg. Chem.*, 1914, 86, 94.

[7] Kahlbaum, Roth, and Siedler, *ibid.*, 1902, 29, 284.

[8] Konno, *J. Chem. Soc.*, 1920, 118, Abs. ii, 223.

[9] Lees, *Phil. Trans.*, 1908, 208A, 426.

[10] Jäger and Diesselhorst. See Lees, *loc. cit.*

[11] Lees, *loc. cit.*, 437.

[12] Benedicks and Arpy, *Zeitsch. anorg. Chem.*, 1914, 88, 252.

[13] *Cf.* allotropy of zinc, *ante.*

[14] Gruneisen, *Ann. Physik*, 1910, [4], 33, 50.

[15] Svedberg, *Ber.*, 1905, 38, 3618.

[16] Billitzer, *ibid.*, 1902, 35, 1933; Bredig, *Zeitsch. physikal. Chem.*, 1900, 32, 128; *Zeitsch. angew. Chem.*, 1898, 11, 953; Tichomirow and Lidow, *Ber.*, 1883, 16, 2276.

[17] Svedberg, *ibid.*, 1906, 39, 1712.

Chemical Properties of Zinc.—Zinc tarnishes rapidly in air. It burns to the oxide when heated, and zinc wool burns with a brilliant flame when lighted with a Bunsen burner—forming a coherent mass of oxide.[1]

In dry oxygen oxidation virtually ceases below 150° C. when the surface film has formed. As the temperature rises above this, moist oxygen begins to act more vigorously than dry.[2] Ozone attacks the metal somewhat more actively than oxygen.[3]

Basic carbonates are formed by atmospheric action upon zinc,[4] and hydrogen peroxide can be detected during the rusting.[5]

Steam acts readily on the metal at a red heat,[6] but the reaction

$$ZnO+H_2O \rightleftharpoons ZnO_2+H_2$$

is reversible.[7] Potable waters dissolve zinc, and distilled or rain water dissolves it more readily than harder water,[8] though purified water has been said to have no action on the metal.[9]

Ground waters may take up 5 parts of zinc per million when they pass through galvanised iron pipes.[10]

According to Davies,[11] all waters attack zinc when air is present. Coating the zinc, he adds, does not stop the action, and zinc is found in the viscera of people who have drunk water containing zinc compounds. Moderate hardness in the water favours the action, he also says, extreme hardness does not prevent it, and rain-water has the least action.

The corrosion of zinc by acidic reagents is greater when the metal contains lead, cadmium, or iron than in the refined product. Minute traces of arsenic, antimony, copper, or tin also favour corrosion.[12]

Aqueous halogen acids dissolve zinc to the halide with evolution of hydrogen.[13] The rate of dissolution in hydrochloric acid depends upon the condition of the metal,[14] also upon the impurities present,[15] and the action is very slow if the metal is pure.[16] Dry hydrogen chloride has a solvent action in the following solvents: chloroform, ethyl chloride,[17] amyl alcohol, methyl alcohol, ethyl alcohol, acetone, ethyl ether,[1] and benzene.[2]

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[1] Ohmann, *Ber.*, 1912, **45**, 2973.

[2] Jordis and Rosenhaupt, *Chem. Zeit.*, 1908, **32**, 19.

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

[4] Pettenkofer, *Jahresber.*, 1856, 788; Bolzano, *Dingl. poly. J.*, 1864, **173**, 107; Moody, *Proc. Chem. Soc.*, 1903, **19**, 273.

[5] Dunstan, *Proc. Chem. Soc.*, 1903, **19**, 152. See Traube, *Ber.*, 1882, **15**, 667, 2421, 2434.

[6] Regnault, *Ann. Chim. Phys.*, 1836, [2], **62**, 350.

[7] Deville, *ibid.*, 1855, [3], **43**, 477; Ditte, *Compt. rend.*, 1871, **73**, 108; Glaser, *Zeitsch. anorg. Chem.*, 1903, **36**, 25; Gillet, *Bull. Soc. chim. Belg.*, 1912, **26**, 106.

[8] Venable, *J. Amer. Chem. Soc.*, 1884, **6**, 214.

[9] Bonsdorff, *Pogg. Annalen*, 1837, **41**, 293; **42**, 325.

[10] Howard, *J. Amer. Water Works Assoc.*, 1923, **10**, 411.

[11] Davies, *J. Soc. Chem. Ind.*, 1899, **18**, 102.

[12] Prost, *Bull. Soc. chim. Belg.*, 1914, **28**, 94.

[13] Spring and Aubel, *Ann. Chim. Phys.*, 1887, [6], **11**, 524.

[14] The passivity and velocity of solution in acids has been studied by Centnerszwer and Sachs, *Zeitsch. physikal. Chem.*, 1914, **87**, 692; Centnerszwer and Drukker, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 439, 528; Centnerszwer, *ibid.*, 1916, **48**, 470.

[15] Prost, *Bull. Soc. chim. Belg.*, 1914, **28**, 94.

[16] Reynolds and Ramsay, *Trans. Chem. Soc.*, 1887, **51**, 857; Falk and Waters, *Amer. Chem. J.*, 1904, **31**, 407.

[17] Patten, *J. Physical Chem.*, 1903, **7**, 153.

$$Zn+2HCl.200H_2O=ZnCl_2.400H_2O+H_2+36.320 \text{ Cal.}$$

if the hydrogen is dry. The corresponding figure for moist hydrogen at the same temperature, 20° C., is 36·070 Cal.[3]

Zinc reacts with dilute aqueous sulphuric acid to form hydrogen and zinc sulphate, but if the metal is very pure there is scarcely any action.[4] There is probably no action at all if both acid and metal are exceedingly pure, and the rate of solution varies with the condition of the zinc and the impurities present.[5] Solution proceeds more slowly at first, and this preliminary " induction period " is probably due to a layer of hydrogen bubbles that prevents contact between the metal and the acid. Rise of temperature increases the rate of solution, and its effect increases with the acid concentration, though it has no appreciable effect when the acid is very dilute.[6] Amalgamation protects zinc from attack by acids, because the discharge potential of hydrogen on mercury exceeds the potential of zinc.[7]

Small quantities of sulphur dioxide and hydrogen sulphide are often produced during the action of dilute sulphuric acid on ordinary zinc, though they are not produced if the acid and metal are nearly pure. Sulphur dioxide is the chief gaseous product when the sulphuric acid is concentrated, but hydrogen sulphide is also produced at higher temperatures, and both compounds are formed when the temperature is fairly high (160° C.).[8]

When zinc is heated in a stream of sulphur dioxide some sulphide seems to be formed.[9] When aqueous sulphurous acid acts on zinc the sulphite and salts of other sulphur acids are produced in the solution. If the action occurs at 200° C. in sealed tubes, amorphous zinc sulphide, sulphur, and zinc sulphate result.[10] Zinc hydrosulphite or hyposulphite is formed if dry sulphur dioxide is passed through a suspension of zinc in absolute alcohol,[11] and, according to Bernsthen,[12] the reaction

$$Zn+2SO_2=ZnS_2O_4$$

first occurs when aqueous sulphurous acid acts upon zinc. Secondary reactions then occur. According to Schutzenberger,[13] zinc sulphite and zinc hydrosulphite are the primary products, and no hydrogen is produced.

According to Fordos and Gélis,[14] zinc sulphite and hydrogen are produced first. Then the nascent hydrogen reduces some sulphurous acid to hydrogen sulphide. This may precipitate part of the sulphite (this occurs to a considerable extent with cadmium) as sulphide, and it also interacts with sulphur dioxide to form sulphur. The sulphur finally reacts with some zinc sulphite to produce zinc thiosulphate. Since zinc sulphide reacts with excess of sulphurous acid according to the equation

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[1] Zecchini, *Gazzetta*, 1897, **27**, i, 466.

[2] Kahlenberg, *J. Physical Chem.*, 1902, 6, 1. See Falk and Waters, *Amer. Chem. J.*, 1904, **31**, 407.

[3] Richards and Thorvaldsen, *J. Amer. Chem. Soc.*, 1922, **44**, 1060.

[4] de la Rive, *Ann. Chim. Phys.*, 1830, [2], **43**, 425; Reynolds and Ramsay, *Trans. Chem. Soc.*, 1887, **51**, 854.

[5] Pullinger, *ibid.*, 1890, **57**, 815.

[6] Ericson-Auren, *Zeitsch. anorg. Chem.*, 1901, **27**, 209.

[7] Watts and Whipple, *Trans. Amer. Electrochem. Soc.*, 1917, **32**, 279.

[8] Muir and Adie, *Trans. Chem. Soc.*, 1888, **53**, 58. For action of H_2SO_4 on Zn, also see Berthelot, *Ann. Chim. Phys.*, 1898, [7], **14**, 186.

[9] Uhl, *Ber.*, 1890, **23**, 2154.

[10] Geitner, *Annalen*, 1864, **129**, 350.

[11] Nabl, *Monatsh.*, 1899, **20**, 679.

[12] Bernsthen, *Annalen*, 1880, **208**, 176.

[13] Schutzenberger, *Compt. rend.*, 1869, **69**, 196.

[14] Fordos and Gélis, *Ann. Chim. Phys.*, 1843, [3], 8, 352.

$$2ZnS+3SO_2=2ZnS_2O_3+S,$$

as Henderson and Weiser[1] point out, Fordos and Gélis obtained a solution of zinc sulphite and thiosulphate when they acted upon the metal with an excess of sulphurous acid. They noted that the decomposition

$$2ZnS_2O_3=ZnS+ZnS_3O_6$$

readily occurs.

The reaction between zinc and sulphurous acid may apparently vary with the conditions, but the formation of various thionic acids has usually been explained by the primary formation of zinc sulphite and nascent hydrogen.[2] Zinc sulphide has a tendency to precipitate from solutions resulting from the action of sulphurous acid on zinc from the decomposition of zinc thiosulphate, etc.

According to Schweitzer,[3] zinc sulphite and thiosulphate are first formed, and the liquid also ultimately contains sulphur, zinc sulphide, and trithionate. Nascent hydrogen, he adds, is not produced, and is not responsible for any reactions.

According to Acworth and Armstrong,[4] nitric oxide, nitrous oxide, and nitrogen are always evolved by the action of nitric acid on zinc. Montemartini says that hyponitrous acid, nitric oxide, nitrous oxide, nitrogen, and ammonia are formed at a low temperature with a large excess of acid. Nitrous acid is also formed if the solution does not contain more than 30 per cent. of acid, and nitrogen peroxide if it does. A maximum of ammonia is produced with acid of concentration 40–45 at a temperature of 3°–8° C., a maximum of nitrous oxide at a concentration of 40 and a minimum at 80, a maximum of nitrogen peroxide at a concentration of 80, which then remains constant, and nitrogen is never formed in more than very small quantities.[5] Hydroxylamine is said to be produced during the action of nitric acid on zinc, and to be easily observable if sulphuric or another acid is present.[6] Bijlert[7] detected no hydroxylamine when $N/20$ to $N/10$ nitric acid acted upon zinc--ammonia was formed. Nitrous acid has been said to be the primary product of the reaction.[8]

Zinc dissolves slowly in caustic alkalies, forming hydrogen and zincates.

Zinc apparently forms no compound with hydrogen,[9] though the spectrum of an arc between zinc poles in hydrogen has been said to indicate *zinc hydride*,[1] and the existence of zinc hydride has been affirmed.[2] The metal, however, is apt to occlude hydrogen,[3] and zinc dust has been said to contain thirty-nine times its volume of this gas.[4]

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[1] Henderson and Weiser, *J. Amer. Chem. Soc.*, 1913, **35**, 240.

[2] Risler-Beunet, *Pogg. Annalen*, 1862, **96**, 470. See Berthelot, *Ann. Chim. Phys.*, 1898, [7], **14**, 189.

[3] Schweitzer, *Chem. News*, 1871, **23**, 293.

[4] Acworth and Armstrong, *J. Chem. Soc.*, 1877, **32**, 73.

[5] Montemartini, *Gazzetta*, 1892, **22**, i, 277.

[6] Divers, *Trans. Chem. Soc.*, 1883, **43**, 447.

[7] Bijlert, *Zeitsch. physikal. Chem.*, 1899, **31**, 103.

[8] By both Armstrong and Veley. See *J. Soc. Chem. Ind.*, 1891, **10**, 206.

[9] Cameron, *Chem. News*, 1860, **2**, 181; Paneth, Matthies, and Schmidt-Hebbel, *Ber.*, 1922, **55B**, 787.

It decomposes nitric oxide slowly but completely at 600° C.,[5] and unites directly with most of the negative elements.

Zinc displaces less electropositive metals from solutions of their salts, and a *zinc-copper couple*, prepared by depositing copper on zinc, decomposes water at ordinary temperatures. This evolution of hydrogen accounts, it seems probable, for the production of this gas when zinc displaces copper and other metals from their solutions.[6] The zinc-copper couple is an effective reducing agent,[7] and will decompose water even at 2° C.[8] A properly prepared couple is suitable for estimating nitrogen (by reducing it to ammonia) in water.[9]

There is a period of induction when metals are replaced in solutions of their salts by zinc,[10] and they may be precipitated partly in the form of hydroxide, nickel, and cobalt, for example.[11] If asbestos is wrapped round a zinc rod that is dipped in a solution of lead acetate, or copper sulphate, or antimony chloride and tartaric acid, a spongy mass of metal settles out on the asbestos. A black deposit of antimony also drops to the bottom of the vessel, that explodes when heated (explosive antimony).[12]

Zinc and copper have been said to be reciprocally replaceable by one another to some extent under appropriate conditions,[13] and a solution of an iron salt was said to be produced by acting on the solution of a normal zinc salt with powdered iron.[14]

Hydrogen is evolved when magnesium is immersed in a solution of zinc chloride, and zinc containing some hydroxide is precipitated.[15] Magnesium will only precipitate 50 per cent. of the zinc from a solution of zinc sulphate, and the precipitated zinc contains some oxides of magnesium and zinc.[16] Aluminium reacts with solutions of zinc salts.[17]

Electrodeposition of Zinc. It is difficult both to deposit zinc completely by electrolysis and to obtain good deposits. The frequent sponginess, looseness, or porosity of electrolytically deposited zinc has been ascribed to the presence of oxide [18] or hydride.[19] Occluded hydrogen may make the deposit brittle,[1] and if the temperature rises to about 80° C. the zinc adheres badly to the cathode.[2] Zinc is usually prepared electrolytically from sulphate solutions.

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[1] Fowler and Payn, *Proc. Roy. Soc.*, 1903, **72**, 256.

[2] Leeds, *Ber.*, 1876, **9**, 1456; Siemens and Halske, *Dingl. poly. J.*, 1893, **288**, 258.

[3] Delachanal, *Compt. rend.*, 1909, **148**, 561; Schwarz, *Zeitsch. Elektrochem.*, 1923, **29**, 198.

[4] Williams, *Chem. News*, 1885, **51**, 146.

[5] Müller and Barck, *Zeitsch. anorg. Chem.*, 1923, **129**, 309.

[6] Gladstone and Tribe, *Proc. Roy. Soc.*, 1871–72, **20**, 218.

[7] Gladstone and Tribe, *J. Chem. Soc.*, 1877, **31**, 561.

[8] Gladstone and Tribe, *ibid.*, 1879, **35**, 567.

[9] Stock, *J. Soc. Chem. Ind.*, 1897, **16**, 107.

[10] Centnerszwer and Drukker, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 528.

[11] Kreman, Angelberger, Bakalow, Röhrich, and Stöger, *Zeitsch. anorg. Chem.*, 1923, **127**, 316.

[12] Warren, *Chem. News*, 1890, **61**, 183.

[13] Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 540.

[14] Raikow and Goworuchui-Georgiew, *Chem. Zeit.*, 1903, **27**, 1192.

[15] Kern, *Chem. News*, 1875, **31**, 76.

[16] Bryant, *ibid.*, 1899, **79**, 75.

[17] Formenti and Levi, *Chem. Zentr.*, 1901, ii, 1298.

[18] Mylius and Fromm, *Zeitsch. anorg. Chem.*, 1895, **9**, 158; Spear, *J. Amer. Chem. Soc.*, 1910, **32**, 533.

[19] Siemens and Halske, *Dingl. poly. J.*, 1893, **288**, 258; Sand, *Trans. Chem. Soc.*, 1907, **91**, 406.

To obtain satisfactory deposits by electrolysis the current density at the cathode should be uniform and the acidity should be constant.[3] High-current densities promote efficient deposition : investigation has steadily raised the suitable current density from about 1 amp. per sq. dcm.[4, 5] to about 20 amp.,[2] and up to 50.[6] More positive metals than zinc should be absent.[7] Copper and cadmium, if present in the electrolyte, are deposited with the zinc.[8] The presence of iron is said to contaminate the zinc very little under efficient conditions for electrolysis,[6] though McIntosh mentions a low iron content in the electrolyte as one condition for good deposition.[7] McIntosh also says that colloids should not be present, but they increase the efficiency according to Hansen,[8] and Pring and Tainton say that a little colloidal matter favours the electrolysis by producing bright, adherent deposits and permitting a higher current density which secures greater current efficiency.[6] Neutral solutions, or solutions as neutral as possible, have been advocated,[5] but acid solutions seem to be effective if the other conditions are good.[6]

Zinc can be deposited from commercial solutions, according to Pring and Tainton,[6] with an efficiency of 95 per cent. if the concentration of sulphuric acid is about 15 grm. per 100 c.c., the current density is 20–50 amp. per sq. dcm., and the P.D. is 5 volts between platinum electrodes or 3 volts between electrodes of zinc. According to McIntosh,[7] the zinc concentration should be high.

Palmer and Wejnarth have recently described an electrolytic method of extracting the zinc from solutions prepared from the ore by using a current density of 2·6 amp. per sq. dcm. at the cathode. The anode is lead and the cathode aluminium.[9]

The American electrolytic methods,[10] which are in extensive use, are similar to this method. Since high-current densities of upwards of 100 amp. per sq. foot are required for efficient deposition,[11] they only attempt to deposit a portion of the zinc in the electrolyte, and the residual liquid is then again enriched from fresh ore. The electrolyte contains from 5–7·5 per cent. of zinc, a current density of about 25 amp. to the sq. foot is employed, and, though the optimum acidity is 25–30 grm. sulphuric acid per 100 c.c.,[11] the electrolyte is acidified with from 2–2·5 per cent. The temperature may be 30°–45° C., and a little glue is sometimes added, though the electrolyte must be otherwise very pure.[12] The colloidal matter raises the over-voltage of hydrogen, and, by making the hydrogen bubbles more readily detachable, keeps the deposit smooth.[1] The lead anodes and aluminium cathodes must also be very pure. Between 3 and 4 volts is a usual P.D.

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[1] Schwarz, *Zeitsch. Elecktrochem.*, 1923, **29**, 198. See Spear, *loc. cit.*

[2] Fedotieff and Stender, *Zeitsch. anorg. Chem.*, 1923, **130**, 51.

[3] Chancel, *Bull. Soc. chim.*, 1916, [4], **19**, 59.

[4] Mylius and Fromm, *loc. cit.*

[5] Burgess, *Electrochem. Met. Ind.*, 1905, **3**, 17.

[6] Pring and Tainton, *Trans. Chem. Soc.*, 1914, **105**, 710.

[7] McIntosh, *Trans. Roy. Soc. Canada*, 1917–18, [3], **11**, 113.

[8] Hansen, *Met. and Chem. Eng.*, 1918, **18**, 481 ; *J. Soc. Chem. Ind.*, 1919, **38**, 259A.

[9] Palmer and Wejnarth, *Zeitsch. Elektrochem.*, 1923, **29**, 557. The zinc deposit is easily removed and unaffected by the presence of glue in the electrolyte.

[10] Liddell, *Handbook of Chemical Engineering* (McGraw Hill Book Co., New York and London), 1922, ii, 745, 801.

[11] Tainton, *Trans. Amer. Electrochem. Soc.*, 1922, **41**, 189.

[12] According to Scholl (*Chem. Met. Eng.*, 1922, **26**, 595), arsenic, antimony, nickel, cobalt, and copper, when present in a few parts per million, cause a re-solution of the zinc after the first fifteen to twenty hours.

Cyanide-plating solutions are the most effective, and zinc deposited from these provides a better rust-proof coating than the deposit from sulphate solutions.[2] Good results are obtained with a current density of 2 amp. per sq. dcm., a temperature of 40° C., and moderate agitation of the electrolyte.[3]

Rotating cathodes are not much used in the electrolytic preparation of zinc, but they are commonly used, to secure effectiveness, in its *electrolytic estimation*. Though zinc is a difficult metal to estimate by electrolytic methods, the estimation can be performed by using an electrolyte containing 2 grm. sodium sulphate and 1 grm. sodium acetate for every gram of zinc sulphate.[4]

According to Engelenberg,[5] zinc and cadmium can be separated quantitatively by electrolysis in hydrochloric acid solution containing hydroxylamine or hydrazine sulphate.

Accurate results can be secured by depositing the zinc on a weighed mercury cathode.[6] The atomic weight of zinc has been determined by thus estimating the zinc in zinc chloride[7] and zinc bromide.[8]

Attempts have been made to estimate zinc by electrolysis in solutions containing (*a*) oxalate and free oxalic or tartaric acid;[9] (*b*) acetate and free acetic acid;[10] (*c*) caustic alkali or ammonia;[11] (*d*) cyanide.[12] But if the difficulty of depositing all the zinc is surmounted, the results then, according to Spear,[13] tend to be too high through the inclusion of zinc oxide or hydroxide with the deposited metal. The difficulty of complete precipitation also increases, he adds, with the concentration of the hydroxyl ions.

Atomic Weight of Zinc.—On the International List of Atomic Weights zinc is given as 65·38.[14] It has apparently four *isotopes*, with atomic weights of 64, 66, 68, and 70.[15] They can be partially separated by distillation in a high vacuum.[16] The atomic number is 30.

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[1] Tainton, *Trans. Amer. Electrochem. Soc.*, 1922, 41, 189.

[2] Wernlund, *Trans. Amer. Electrochem. Soc.*, 1921, 40, 257.

[3] Horsch and Fuwa, *ibid.*, 1922, 41, 211.

[4] Price, *Trans. Faraday Soc.*, 1907, 3, 88. Rotating anodes have been tried. See Ingham, *J. Amer. Chem. Soc.*, 1904, 26, 1269.

[5] Engelenberg, *Zeitsch. anal. Chem.*, 1923, 62, 257.

[6] For description of the cell, see Baxter and Hartmann, *J. Amer. Chem. Soc.*, 1915, 37, 123, and for a discussion of it, see Baxter and Wilson, *ibid.*, 1921, 43, 1230.

[7] Baxter and Hodges, *ibid.*, 1921, 43, 1242.

[8] Baxter and Grose, *ibid.*, 1916, 38, 868.

[9] Classen, *Quant. Chem. Anal. by Elect.* (Wiley & Sons, New York; Chapman & Hall, London; translated by Boltwood), 1903, 164.

[10] Smith, *J. Amer. Chem. Soc.*, 1902, 24, 1073; Exner, *ibid.*, 1903, 25, 899; Price and Humphreys, *J. Soc. Chem. Ind.*, 1909, 28, 117.

[11] Amberg, *Ber.*, 1903, 36, 2489; Exner, *J. Amer. Chem. Soc.*, 1903, 25, 899; Spitzer, *Zeitsch. Elektrochem.*, 1905, 11, 401; Frary, *J. Amer. Chem. Soc.*, 1907, 29, 1596; Snowdon, *J. Physical Chem.*, 1907, 11, 369; Price, *Trans. Faraday Soc.*, 1907, 3, 88; Breisch, *Zeitsch. anal. Chem.*, 1924, 64, 13.

[12] Luckow, *ibid.*, 1880, 19, 1.

[13] Spear, *J. Amer. Chem. Soc.*, 1910, 32, 533. For studies of the electro-analysis of zinc, see also Ingham, *J. Amer. Chem. Soc.*, 1904, 26, 1269; Sand, *Trans. Chem. Soc.*, 1907, 91, 403.

[14] *J. Amer. Chem. Soc.*, 1925, 47, 597.

[15] Dempster, *Phys. Review*, 1922, 20, 631; Aston, *J. Soc. Chem. Ind.*, 1923, 42, 935. See also Aston, *Isotopes* (Edward Arnold, London), 1922, p. 146.

[16] Egerton, *Nature*, 1922, 110, 773.

The following determinations have been made of the atomic weight of zinc[1]:—

(A) In 1814 Wollaston gave the ratio Zn : O = 100 : 24·41.[2] Somewhat higher values than the atomic weight for zinc of 64·73, which this ratio gives, had been previously obtained.[3]

Jacquelaine obtained the ratio Zn : O = 100 : 24·169 by two conversions of the metal into the nitrate and ignition to oxide. He found no occluded gases in his oxides, Zn = 66·201.[4]

Erdmann,[5] by the same method, obtained the ratio Zn : O = 100 : 24·6. The atomic weight of zinc is 65·04.

Morse and Burton made fifteen determinations by this method, and tested in all cases their zinc oxide for nitrogen oxides.[6] According to their ratio Zn : O = 100 : 24·5139, the atomic weight of zinc is 65·269.

Morse and Arbuckle[7] corrected this investigation by eight determinations, in which allowance was made for occluded gases. Their corrected value for the atomic weight of zinc was 65·457.

(B) Several experimenters ignited the sulphate into the oxide. The oxalate[8] and the lactate[9] have also been ignited.

Jacquelaine obtained the ratio Zn : O = 100 : 24·147 by converting a known weight of metal into sulphate and igniting to oxide.[10] From this ratio, which is the sum of two determinations, zinc is 66·26.

Erdmann[11] gave the ratio $ZnSO_4 : ZnO = 100 : 50{\cdot}26$. The sum of two ignitions of the sulphate by Baubigny[12] gave the ratio $ZnSO_4 : ZnO = 100 : 50{\cdot}414$. The atomic weight of zinc is 65·40 from the latter ratio.

(C) Some of the earlier investigators determined the hydrogen evolved by dissolving known quantities of zinc in dilute acid.[13] Van der Plaats,[14] from three determinations, obtained Zn = 65·68.

Reynolds and Ramsay,[15] as the mean of five determinations, obtained Zn = 65·4787 ± 0·016135. This figure, which was calculated on the assumption that H = 1·0, makes Zn = 65·9776 if H = 1·00762.

(D) Gladstone and Hibbert[16] obtained the ratio 2Ag : Zn = 3·2980 : 1 by the simultaneous electrolytic deposition of silver and zinc. Their result, obtained from six experiments, makes the atomic weight of zinc 65·421.

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[1] The following atomic weight values have been used in calculating the atomic weights in this section :—

H = 1·00762 O = 16·000 S = 32·065
Cl = 35·457 Br = 79·916 Ag = 107·880

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

[2] Wollaston, *Phil. Trans.*, 1814, 21.

[3] Gay-Lussac, *Mém. d'arcœuil*, 1811, 2, 174; Berzelius, *Pogg. Annalen*, 1811, 8, 126, 134.

[4] Jacquelaine, *Ann. Chim. Phys.*, 1843, [3], 7, 189.

[5] Erdmann, *Annalen*, 1844, 50, 435.

[6] Morse and Burton, *Amer. Chem. J.*, 1888, 10, 311. See *Jahresber.*, 1888, ii, 103.

[7] Morse and Arbuckle, *Amer. Chem. J.*, 1898, 20, 195. Their uncorrected value was 65·328.

[8] Favre, *Ann. Chim. Phys.*, 1844, [3], 10, 163.

[9] Pelouze. See Richards and Rogers, *Zeitsch. anorg. Chem.*, 1895, 10, 2.

[10] Jacquelaine, *loc. cit.*

[11] Erdmann, *Annalen*, 1844, 50, 435.

[12] Baubigny, *Chem. News*, 1883, 48, 244.

[13] Jacquelaine, *loc. cit.*; Favre, *loc. cit.*

[14] van der Plaats, *Compt. rend.*, 1885, 100, 52.

[15] Reynolds and Ramsay, *Trans. Chem. Soc.*, 1887, 51, 854.

[16] Gladstone and Hibbert, *ibid.*, 1889, 55, 443. They regarded their similarly obtained ratio Cu : Zn = 1 : 1·0322 (from five results) as containing a probable error of 1 in 1000.

(E) Marignac[1] analysed the double salt $ZnCl_2.2KCl$. Baxter and Hodges[2] determined the percentage of zinc in the chloride by estimating the metal electrolytically. Their ratio Zn : Cl_2=0·92195 : 1, obtained as an average of seven determinations, gave Zn=65·379.

Baxter and Grose[3] operated similarly on the bromide and obtained the ratio Zn : Br_2=0·409103 : 1. They made eight determinations, and calculated an atomic weight of 65·388 for zinc.

Richards and Rogers[4] determined the ratios $ZnBr_2$: 2Ag and $ZnBr_2$: 2AgBr by analysing the bromide. Their paper also contained the following determinations by Richards alone. The ratio $ZnBr_2$: 2Ag=104·379 : 100 was obtained from three experiments. This makes Zn=65·376. From his ratio $ZnBr_2$: 2AgBr=0·599611 : 1, obtained from three determinations, Zn=65·377.

The International Committee on Atomic Weights for 1925 have adopted the value

Zn=65·38.

Alloys of Zinc.—*Sodium* is only partially miscible with zinc, and a saturated solution of sodium in zinc contains about 3 per cent. of the former metal. These two metals form a compound that is grey, harder, and more brittle than zinc, and slowly acted upon by water. Its formula approximates to $NaZn_{11}$ or $NaZn_{12}$.[5]

Potassium forms a compound with zinc that apparently occurs in several physical modifications. Its formula is probably KZn_{12}.[6]

Copper.—The alloys of zinc with copper have great commercial importance. The addition of zinc to copper at first increases both the ductility and tenacity. The ductility begins to decrease when the zinc is more than 30 per cent., and the tenacity falls off rapidly when it is more than 40 per cent.[7]

Brass contains from about 30–33 per cent. of zinc and 70–67 per cent. of copper. *Muntz metal*, containing 40 per cent. zinc and 60 per cent. copper, can be rolled either hot or cold, while brass can only be rolled cold. *Brazing solder* contains equal proportions of the two metals, though the proportions are sometimes varied: it is harder than brass, more ductile, and cannot be rolled. Various other alloys, such as *pinchbeck*, contain 90 per cent. and upwards of copper. The alloys containing less than 50 per cent. of copper are white and brittle: their commercial importance is slight.[8]

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[1] Marignac, *Ann. Chim. Phys.*, 1884, [6], **1**, 309.

[2] Baxter and Hodges, *J. Amer. Chem. Soc.*, 1921, **43**, 1242.

[3] Baxter and Grose, *ibid.*, 1916, **38**, 868.

[4] Richards and Rogers, *Zeitsch. anorg. Chem.*, 1895, **10**, 1. See Clarke, *J. Amer. Chem. Soc.*, 1896, **18**, 203.

[5] Mathewson, *Zeitsch. anorg. Chem.*, 1906, **48**, 195. Gay-Lussac and Thénard (*Recherches physico-chimiques* (Paris), 1811, **1**, 243) described a compound of sodium with zinc. See also Rieth and Beilstein, *Annalen*, 1862, **123**, 254; 1863, **126**, 248.

[6] Smith, *Zeitsch. anorg. Chem.*, 1908, **56**, 114.

[7] For studies of the system Cu–Zn, see Shepherd, *J. Physical Chem.*, 1904, **8**, 421; Carpenter and Edwards, *Int. Zeitsch. Metallographie*, 1912, **2**, 209; Carpenter, *Int. Zeitsch. Metallographie*, 1912, **3**, 170; *J. Inst. Metals*, 1912, **3**, 170; **7**, 70; **8**, 51, 59; Guillet, *Rev. de Métallurgie*, 1906, **3**, 243.

[8] For chemical and electrochemical properties of zinc alloys, see Sauerwald, *Zeitsch. anorg. Chem.*, 1920, **111**, 243. For mechanical properties, Guillet, *Compt. rend.*, 1918, **166**,

Norsa concluded that the compounds CuZn, $CuZn_2$, and $CuZn_6$ exist;[1] Cu_2Zn_3 may also exist,[2] and possibly Cu_2Zn.[3]

Silver.—A silver-zinc alloy is obtained by adding a solution of silver sulphate to water containing a zinc plate.[4] Liquid silver and zinc alloy in all proportions.[5] The alloys are fairly malleable up to 34·3 atomic per cent. of zinc, but become brittle and tough with increasing quantities.[6] Their brittleness and hardness attain a maximum between 47·6 and 60 per cent. of zinc.[7]

The compounds Ag_2Zn_3 and Ag_2Zn_5 seem to exist.[8] Various other compounds have been indicated by equilibrium studies, but the results are not very concordant.[9]

Gold.—The addition of gold to zinc raises the freezing-point.[10] Molten gold absorbs zinc vapour, and its ductility is destroyed by alloying with zinc.[11] Small quantities of zinc slightly increase the tensile strength.[12]

Alloys rich in gold are about as hard as the latter, but not quite so tenacious. Alloys containing between 31 and 61 per cent. of zinc are hard and brittle, and these qualities gradually diminish as the proportion of zinc increases.[13]

The compound AuZn seems to exist, but the evidence for other compounds is conflicting.[14]

Calcium.—Alloys of zinc containing 6 per cent. of calcium are rather harder than zinc and are fairly stable towards air and water. As the proportion of calcium increases they darken in air and act more on

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735; Shepherd, Carpenter, Edwards, and Parravano, *Gazzetta*, 1914, **44**, ii, 475; Hudson, *J. Inst. Metals*, 1914, **12**, 89; *J. Chem. Soc.*, 1915, **108**, Abs. ii, 261; Lohr, *J. Physical Chem.*, 1913, **17**, 1. For annealing, Stead and Stedman, *J. Inst. Metals*, 1914, **11**, 119; Portevin, *Compt. rend.*, 1914, **158**, 1174. For heating *in vacuo*, Thorneycroft and Turner, *J. Inst. Metals*, 1914, **12**, 214. For rate of solution in acids, Centnerszwer and Sachs, *Zeitsch. physikal. Chem.*, 1914, **89**, 213. For corrosion, Whyte, *J. Inst. Metals*, 1915, **13**, 80. For vapour pressures, see Guillet and Ballay, *Compt. rend.*, 1922, **175**, 1057.

[1] Norsa, *Compt. rend.*, 1912, **155**, 348; Sackur, *Ber.*, 1905, **38**, 2186; Puschin, *Zeitsch. anorg. Chem.*, 1908, **56**, 30; Puschin and Rjashski, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1905.

[2] Carpenter, *Int. Zeitsch. Metallographie*, 1912, **3**, 170.

[3] Puschin, *Zeitsch. anorg. Chem.*, 1908, **56**, 30.

[4] Mylius and Fromm, *Ber.*, 1894, **27**, 630.

[5] Wright, *J. Soc. Chem. Ind.*, 1894, **13**, 1014.

[6] Heycock and Neville (*Trans. Chem. Soc.*, 1897, **71**, 414) have studied the freezing-point curve. For electromotive behaviour, see Kremann and Ruderer, *Chem. Zentr.*, 1920, iii, 684.

[7] Petrenko, *Zeitsch. anorg. Chem.*, 1906, **48**, 347.

[8] Bornemann, *Métallurgie*, 1909, **6**, 336; Kremann and Hofmeier, *Monatsh.*, 1911, **32**, 563; Carpenter and Whiteley, *Int. Zeitsch. Metallographie*, 1912, **3**, 145; Carpenter, *ibid.*, 1912, **3**, 170.

[9] Petrenko, *loc. cit.* (AgZn, Ag_2Zn_3, Ag_2Zn_5, Ag_3Zn_2); Pushin, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 353 ($AgZn_2$, $AgZn_4$, $AgZn_6$, Ag_2Zn); Pushin and Maximenko, *ibid.*, 1909, **41**, 500 (AgZn, $AgZn_6$, Ag_2Zn_3, and, doubtfully, Ag_2Zn, AgZn, $AgZn_{10}$). Groves and Turner (*Trans. Chem. Soc.*, 1912, **101**, 591) suggest the possibility of Ag_3Zn.

[10] Heycock and Neville, *loc. cit.*, 419.

[11] Hatchett, *Phil. Trans.*, 1803, **93**, 57.

[12] Roberts-Austen, *ibid.*, 1888, **179**, 344.

[13] Vogel, *Zeitsch. anorg. Chem.*, 1906, **48**, 319.

[14] Groves and Turner, *Trans. Chem. Soc.*, 1912, **101**, 589 (AuZn); Pushin, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 353 (AuZn, $AuZn_2$, $AuZn_6$); Vogel, *loc. cit.* (AuZn, $AuZn_8$, Au_3Zn_5).

water. The compounds $CaZn_4$, $CaZn_{10}$, Ca_2Zn_3, and Ca_4Zn appear to exist, and possibly CaZn.[1]

Cadmium.—Zinc alloys with cadmium in all proportions,[2] but no compound seems to be formed.[3] The hardness and breaking stress of zinc increase with the addition of 0·25 per cent. of cadmium, but the opposite effect occurs when more than 0·5 per cent. of the latter metal is present.[4]

Raoult's Law holds for the vapour pressures of cadmium and its alloys with zinc.[5]

Mercury.—A saturated zinc amalgam at 25° C. contains 2·2196 grm. of zinc to 100 grm. of mercury, and its density is 13·34333. At 25° C., if D is the density of the amalgam and p the grams of zinc per 100 grm. of mercury,

$$D = 13{\cdot}5340 - 0{\cdot}0859p.^6$$

Zinc amalgams can be prepared by adding zinc to mercury and warming.[7] They are also obtained by electrolysing zinc salts with mercury cathodes.[8]

No definite compounds of zinc with mercury appear to exist,[9] though some have been reported.[10]

Zinc amalgams do not alter appreciably in the air. When the solid amalgams crystallise out they tenaciously retain some of their viscous mother-liquor.[11]

Aluminium.—The hardest alloy of zinc and aluminium contains 30 per cent. of zinc.[12] There appears to be evidence for the existence of Zn_3Al_2,[13] though a larger number of compounds [14] seems to be excluded by studies of the system Zn–Al.[15]

Tin.—Molten zinc and tin mix in all proportions.[16]

Lead.—Zinc is said to be only slightly miscible with lead,[17] though alloys of the two metals have apparently been prepared.[18]

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[1] Donski, *Zeitsch. anorg. Chem.*, 1908, **57**, 185.

[2] Wright, *J. Soc. Chem. Ind.*, 1894, **13**, 1014.

[3] The system Cd–Zn has been studied by Gautier, *Bull. Soc. d'Éucour* (Paris), 1896, [5], **1**, 1293; Heycock and Neville, *Trans. Chem. Soc.*, 1892, **61**, 899; 1897, **71**, 387; *Proc. Chem. Soc.*, 1897, **13**, 60; Hindrichs, *Zeitsch. anorg. Chem.*, 1907, **55**, 415; Bruni and Sandonnini, *ibid.*, 1912, **78**, 273; Lorenz and Plumbridge, *ibid.*, 1913, **83**, 231.

[4] Novak, *ibid.*, 1905, **47**, 421.

[5] Egerton and Raleigh, *Trans. Chem. Soc.*, 1923, **123**, 3024.

[6] Crenshaw, *J. Physical Chem.*, 1910, **14**, 158. Hildebrande (*8th Inter. Cong. Appl. Chem.*, 1912, **22**, 147) has determined the vapour pressures of zinc amalgams.

[7] Willows, *Phil. Mag.*, 1899, [5], **48**, 434.

[8] Perdue and Hulett, *J. Physical Chem.*, 1911, **15**, 147.

[9] Smith, *Amer. Chem. J.*, 1906, **36**, 124. For the system Zn–Hg, see Cohen and Genneken, *Zeitsch. physikal. Chem.*, 1910–11, **75**, 437. Also see *J. Chem. Soc.*, 1910, **98**, Abs. ii, 37.

[10] Calvert and Johnson, *Jahresber.*, 1859, 120.

[11] Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, **25**, 54.

[12] Saposchnikoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 95.

[13] Smirnoff, *Compt. rend.*, 1912, **155**, 351; Rosenhain and Archbutt, *Phil. Trans.*, 1911, [A], **211**, 315.

[14] See Pécheux, *Compt. rend.*, 1904, **138**, 1042.

[15] Shepherd, *J. Physical Chem.*, 1905, **9**, 504; Heycock and Neville, *Trans. Chem. Soc.*, 1897, **71**, 389. See also Sander and Meissner, *Zeitsch. Metallk.*, 1922, **14**, 385; Bauer and Vogel, *Chem. Zentr.*, 1916, i, 551.

[16] Wright, *J. Soc. Chem. Ind.*, 1894, **13**, 1016.

[17] Matthiessen and Bose, *Proc. Roy. Soc.*, 1860, **11**, 430; Wright, *J. Soc. Chem. Ind.*, 1894, **13**, 1016.

[18] Konno, *Sci. Rep. Tôhoku, Imp. Univ.*, 1921, **10**, 57.

Antimony.—Zinc is miscible with antimony in all proportions.[1] The compounds Zn_3Sb_2 and ZnSb appear to exist.[2]

Bismuth.—Zinc and bismuth are only slightly miscible.[3]

Manganese.—Alloys of zinc and manganese are brittle, and increase in hardness with the manganese content. They cannot contain more than 50 per cent. of the latter metal.[4] The compounds Zn_7Mn and Zn_3Mn are said to exist.[5]

Iron.—Alloys of zinc and iron containing 0·7–11 per cent. of iron become harder and more brittle with an increase of the latter metal.[6] An alloy with 96 per cent. of iron is malleable when cold, though more brittle than iron, but the alloy with 80 per cent. is brittle and not malleable at the ordinary temperature.[7] The compounds Zn_3Fe and Zn_7Fe exist.[6, 7, 8]

Nickel.—Alloys of zinc with nickel, which are more brittle than zinc, have been prepared by adding nickel to zinc melted under borax.[9] The compound Zn_3Ni is brittle.[10] Zn_4Ni is said to have been isolated as a crystalline, non-magnetic powder, of density 7·71 and melting-point approximately 850° C.[11]

The alloys are not magnetic.[10]

Cobalt.—Zinc and cobalt form mixed crystals;[12] the alloys containing more than 81·6 per cent. of zinc are not magnetic, and become more brittle as the zinc decreases.[13] There is a compound Zn_4Co.[13]

COMPOUNDS OF ZINC.

ZINC AND THE HALOGENS.

Zinc Fluoride, ZnF_2.—The anhydrous salt is produced as an amorphous white powder by the direct union of fluorine and zinc, or by dehydrating the tetrahydrate $ZnF_2.4H_2O$ at 100° C.[14] Since it vaporises at 700° C. in an atmosphere of hydrogen fluoride and condenses in colourless needles, it can be prepared crystalline by the action of hydrogen fluoride at a red heat on zinc, zinc chloride, zinc oxide, or the tetrahydrate $ZnF_2.4H_2O$.[15] It crystallises in either the monoclinic or triclinic system, is insoluble in alcohol and more easily soluble in acids or ammonia.[15] It probably dissolves in aqueous hydrofluoric acid to the acid salt $ZnF_2.2HF$.[1] It dissolves sparingly in water.[2] It melts at about 734° C.,[3] and at high temperatures hydrogen sulphide converts it into the sulphide, steam or oxygen converts it into the oxide, and hydrogen reduces it to metal.[4]

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[1] Wright, *J. Soc. Chem. Ind.*, 1894, 13, 1016.

[2] Schemtschuschny, *Zeitsch. anorg. Chem.*, 1906, 49, 384; Mönkemeyer, *ibid.*, 1905, 43, 182. According to Herschkonitsch (*Zeitsch. physikal. Chem.*, 1898, 27, 123) $ZnSb_2$ also exists.

[3] Wright, *loc. cit.*

[4] Siebe, *Zeitsch. anorg. Chem.*, 1919, 108, 161.

[5] Parravano, *Gazzetta*, 1915, 45, i, 1.

[6] Vegesack, *Zeitsch. anorg. Chem.*, 1907, 52, 30.

[7] Raydt and Tammann, *ibid.*, 1913, 83, 257.

[8] Vigouroux, Ducelliez, and Bourbon (*Bull. Soc. chim.*, 1912, [4], 11, 480) also affirm $ZnFe_3$ and $ZnFe_5$.

[9] Tafel, *Métallurgie*, 1907, 4, 781.

[10] Vors, *Zeitsch. anorg. Chem.*, 1908, 57, 34.

[11] Vigouroux and Bourbon, *Bull. Soc. chim.*, 1911, [4], 9, 873.

[12] Lewkonja, *Zeitsch. anorg. Chem.*, 1908, 59, 293.

[13] Ducelliez, *Bull. Soc. chim.*, 1911, [4], 9, 1017.

[14] Marignac, *Ann. Chim. Phys.*, 1860, [3], 60, 305.

[15] Poulenc, *Compt. rend.*, 1893, 116, 581; *Ann. Chim. Phys.*, 1894, [7], 2, 33. According to Gallo (*Gazzetta*, 1913, 43, i, 361), water-vapour decomposes zinc fluoride into hydrogen fluoride and zinc oxide at temperatures below its melting-point.

Its density at 15° C. is 4·84,[5] and it combines with phenylhydrazine.[6]

The *tetrahydrate*, $ZnF_2.4H_2O$, is precipitated by potassium fluoride from solutions of zinc salts, and has been prepared by dissolving zinc oxide in hydrofluoric acid. The rhombic crystals[7] dissolve in acids but are only sparingly soluble in water,[8] and their density is 2·535 at 12° C., or 2·567 at 10° C.[9]

The following *double fluorides* have been described: $NaF.ZnF_2$,[10] $KF.ZnF_2$,[4, 10] $2KF.ZnF_2$,[11] $2NH_4F.ZnF_2$,[4] $ZnF_2.AlF_3.7H_2O$,[12] $ZnF_2.2CeF_4.7H_2O$,[13] $ZnF_2.SiF_4.6H_2O$,[14] $ZnF_2.TiF_4.6H_2O$, $ZnF_2.ZrF_4.6H_2O$, and $2ZnF_2.ZrF_4.12H_2O$.[7]

Zinc Chloride, $ZnCl_2$.—The pure anhydrous salt has been prepared by heating $3NH_4Cl.ZnCl_2$ in a current of dry hydrogen chloride.[15] The anhydrous salt has also been prepared by distilling anhydrous zinc sulphate with sodium or calcium chloride,[16] by the action of heated zinc vapour and hydrogen on barium chloride,[17] by distilling zinc with mercuric chloride, and by the action of chlorine on zinc oxide.[18] Hydrous zinc chloride partially decomposes on heating, but the anhydrous salt may be obtained from it by treatment with concentrated hydrochloric acid and evaporation in an atmosphere of hydrogen chloride. It may also be prepared by adding zinc to molten lead chloride, passing dry chlorine into fused zinc,[19] or by fusing zinc bromide in an atmosphere of chlorine.[20]

Commercially, the salt is obtained anhydrous by distilling a mixture of zinc sulphate and sodium chloride, and in solution by dissolving zinc scraps, zinc blende, or zinc oxide in hydrochloric acid.

Anhydrous zinc chloride is white or greyish white, and derives its name, "butter of zinc," from its waxlike consistency. It is very hygroscopic, and the density of the fused salt at 25° C. is 2·907 (compared with water at 4° C.).[15] It sublimes in chlorine to needle-shaped crystals that melt at 365° C.[21] and boil at 730° C.[22]

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[1] Nonotny, *Chem. Zentr.*, 1908, ii, 355.

[2] Bodlander, *Zeitsch. physikal. Chem.*, 1898, 27, 63; Kohlrausch, *ibid.*, 1903, 44, 213.

[3] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 279.

[4] See note [15], p. 109.

[5] Poulenc, *loc. cit.*; Clarke, *Jahresber.*, 1877, 269 (4·556 at 17° C. and 4·612 at 12° C.).

[6] Moitessier, *Compt. rend.*, 1898, 121, 722.

[7] Marignac, *loc. cit.*

[8] Kohlrausch, *loc. cit.*

[9] Clarke, *loc. cit.*

[10] Wagner, *Ber.*, 1886, 19, 897.

[11] Berzelius, *Pogg. Annalen*, 1824, 1, 26.

[12] Weinland and Koppen, *Zeitsch. anorg. Chem.*, 1900, 22, 272.

[13] Rimbach and Kilian, *Annalen*, 1909, 368, 106.

[14] Marignac, *Ann. Mines*, 1859, [5], 15, 221.

[15] Baxter and Lamb, *Amer. Chem. J.*, 1904, 31, 229.

[16] Persoz, *Jahresber.*, 1859, 197.

[17] Beketoff, *ibid.*, 1859, 196.

[18] Weber, *Pogg. Annalen*, 1861, 112, 619.

[19] Grünauer, *Zeitsch. anorg. Chem.*, 1904, 39, 389. According to Cowper (*J. Chem. Soc.*, 1883, 43, 154), dry chlorine does not act on zinc.

[20] Baxter and Hodges, *J. Amer. Chem. Soc.*, 1921, 43, 1243.

[21] Grünauer, *loc. cit.*, 410. About 260° C. according to Braun and Graetz, and 290°–300° C. according to Schultze. See *Zeitsch. anorg. Chem.*, 1899, 20, 338. 262° C. according to Dietz, *Zeitsch. anorg. Chem.*, 1899, 20, 252. Hachmeister (*Zeitsch. anorg. Chem.*, 1919, 109, 145) gives 283° C.

[22] Freyer and Meyer, *Ber.*, 1892, 25, 622.

The solubility of zinc chloride has been given as 78·5 parts $ZnCl_2$ in 100 parts of solution,[1] but the equilibrium curves between $ZnCl_2$ and water[2] are difficult to interpret.

It is strongly dissociated in aqueous solution, though the anion $ZnCl'$ appears to be present in considerable concentration even in solutions more dilute than 0·1 molar.[3] It is only hydrolysed slightly,[4] and, according to Vogel,[5] hydrous zinc chloride can be converted into the anhydrous by evaporation under about 20 inches of mercury, though water, especially at higher temperatures and concentrations, tends to form basic compounds.[6]

Zinc chloride is soluble in many organic solvents, including alcohol,[7] and combines with a number of organic compounds.[8] It is indefinitely soluble in glycerine.[9]

Nitrosyl chloride acts upon zinc to form pale yellow $ZnCl_2.NOCl$, which is unstable under ordinary conditions.[10]

The formula $ZnCl_2$ is indicated by the vapour density,[11] the freezing-points of solutions in urethane,[12] and the boiling-points of quinoline solutions.[13]

Molten zinc chloride conducts electricity well, and pure zinc separates at the cathode on electrolysis.[14]

The specific heat of the fused salt is 0·13618.[15]

Anhydrous zinc chloride is poisonous, and is used industrially for impregnating wood, for preserving animal stuffs, in the manufacture of parchment paper, for weighting cotton goods, in the dye industry, and as a disinfectant. It is also employed as a caustic in surgery and as a dehydrating reagent in many organic reactions. Its solution in water, since it destroys organic substances, is used for cleansing and as a flux in soldering.

$$[Zn]+(Cl_2) = [ZnCl_2]+97{\cdot}140 \text{ Cal.}$$[16]

$$[ZnCl_2]+Aq. = ZnCl_2.Aq.+15{\cdot}220 \text{ Cal. } (+9{\cdot}767 \text{ Cal. in alcohol}).$$[17]

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[1] Hasenfratz, *Ann. Chim.*, 1799, **28**, 291. For densities of solutions, see Kremers, *Pogg. Annalen*, 1858, **105**, 360; Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 283. For freezing-point determinations, see Chambers and Frazer, *Amer. Chem. J.*, 1900, **23**, 516. For vapour pressures of concentrated solutions, see Menzies and Boring, *8th Inter. Cong. Appl. Chem.*, 1912, **22**, 219.

[2] Dietz, *Ber.*, 1899, **32**, 90; Mylius and Dietz, *ibid.*, 1905, **38**, 921.

[3] Drucker, *Zeitsch. Elektrochem.*, 1912, **79**, 236.

[4] Ley, *Zeitsch. physikal. Chem.*, 1899, **30**, 225; Sordelli, *J. Chem. Soc.*, 1915, **108**, Abs. ii, 17.

[5] Vogel, *Trans. Faraday Soc.*, 1906, **2**, 58.

[6] Grünauer, *loc. cit.*, 431; Perrot, *Bull. Soc. chim.*, 1895, **13**, 975. According to Baxter and Hodges (*loc. cit.*), zinc chloride easily hydrolyses to a basic salt.

[7] Krug and Elroy, *Jahresber.*, 1892, 1554; Naumann, *Ber.*, 1899, **32**, 1000; Castoro, *Gazzetta*, 1898, **28**, ii, 317; Kahlenberg, *J. Physical Chem.*, 1899, **3**, 388; Lincoln, *ibid.*, 1899, **3**, 460.

[8] Lachowicz, *J. prakt. Chem.*, 1889, [2], **39**, 99; Stoehr, *ibid.*, 1895, [2], **51**, 457.

[9] Lloyd, *J. Physical Chem.*, 1913, **17**, 264.

[10] Sudborough, *J. Chem. Soc.*, 1891, **59**, 656.

[11] V. and C. Meyer, *Ber.*, 1879, **12**, 1197.

[12] Castoro, *Gazzetta*, 1898, **28**, ii, 317.

[13] Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 236.

[14] Braun, *Pogg. Annalen*, 1874, **154**, 190; Graetz, *Wied. Annalen*, 1890, **40**, 26; Lorenz, *Zeitsch. anorg. Chem.*, 1895, **10**, 78; Schultze, *ibid.*, 1899, **20**, 331; Grünauer, *loc. cit.*, 389.

[15] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 155.

[16] Berthelot, *ibid.*, 1875, [5], **4**, 189.

[17] Pickering, *Trans. Chem. Soc.*, 1888, **53**, 865.

According to Mylius and Dietz, zinc chloride can crystallise out with 1 or $1\frac{1}{2}$ or $2\frac{1}{2}$ or 3 or 4 molecules of water.[1]

The *trihydrate*, $ZnCl_2.3H_2O$, separates in large crystals, when a solution containing 70·5 per cent. $ZnCl_2$ is cooled for twenty-four hours at 0° C.[2] The crystals are hygroscopic rhombic tablets that begin to melt at 4° or 5° C., and form a homogeneous liquid at 9° C.[3]

The needles of a *dihydrate* said to be obtained by cooling a saturated solution to −20° C.[4] are doubtful.[1]

The hydrate, $ZnCl_2.1\frac{1}{2}H_2O$, was obtained in bulky crystals by evaporating a solution of zinc chloride over phosphorus pentoxide.[5]

A bluish-white mass of *zincoso-zincic chloride*, Zn_3Cl_5, results from the solution of metallic zinc in molten zinc chloride. It is very hygroscopic, rapidly hydrolysed by water, and is probably best formulated as $ZnCl.2ZnCl_2$.[6]

Deliquescent rhombic crystals of the *acid salt*, $2ZnCl_2.HCl.2H_2O$, separate from a solution of zinc chloride into which hydrogen chloride has been passed when the density of the liquid at 25° C. is 2. At 100° C. they lose HCl, and anhydrous $ZnCl_2$ is in contact with a concentrated solution of the salt and hydrochloric acid. If this mother-liquor is treated with hydrogen chloride more crystals separate, and finally, if the liquid is saturated with hydrogen chloride and cooled to 0° C., long needles of $ZnCl_2.HCl.2H_2O$ crystallise. These readily lose hydrogen chloride in dry air and form $2ZnCl_2.HCl.2H_2O$.[7]

Compounds of Zinc Chloride with Ammonia.—The diammoniate $ZnCl_2.2NH_3$ is formed in the active Leclanché cell.[8, 9] It can be prepared by passing ammonia gas into an alcoholic solution of zinc chloride,[10] or by passing ammonia into a hot concentrated aqueous solution of zinc chloride, and, after cooling to separate the less soluble tetrammoniate, $ZnCl_2.4NH_3.H_2O$, crystallising the mother-liquor.[9] The rhombic crystals[11] are stable in air, insoluble in water or alcohol, and soluble in acids, ammonia, caustic alkalies, and ammonium chloride. Boiling water decomposes them.[9, 10] It can also be prepared by adding ammonia to cold dilute zinc chloride solution, by dissolving freshly precipitated zinc hydroxide in ammonium chloride,[9] and by heating more highly ammoniated zinc chlorides.[12] It distils when heated into glassy, hygroscopic monammoniate, $ZnCl_2.NH_3$.[10]

The last named is very stable under heat, and is produced when ammonia acts on hot zinc chloride. Water decomposes it into $ZnCl_2.2NH_3$ and an oxychloride of zinc.[12]

The more unstable tetrammoniate, $ZnCl_2.4NH_3.H_2O$,[9, 12] and pentammoniate, $ZnCl_2.5NH_3.H_2O$,[13, 14] have been prepared: the former in pearly leaflets by saturating an aqueous solution of zinc chloride with ammonia gas and cooling, the latter in octahedra by cooling a solution of zinc chloride in ammonia after passing ammonia gas. Isambert prepared $ZnCl_2.6NH_3$ and examined the heats of formation of the ammoniated zinc chlorides.[1]

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[1] Mylius and Dietz, *Ber.*, 1905, **38**, 921.

[2] Engel, *Compt. rend.*, 1886, **102**, 1111; Dietz, *Ber.*, 1899, **32**, 90; Mylius and Dietz, *loc. cit.*

[3] Lubarski, *Zeitsch. anorg. Chem.*, 1898, **18**, 387. They melt at 7° C. according to Engel, *loc. cit.*

[4] Étard, *Ann. Chim. Phys.*, 1894, [7], **2**, 536. See Engel, *loc. cit.*

[5] Engel, *loc. cit.*

[6] Datta and Sen, *J. Amer. Chem. Soc.*, 1913, **35**, 781.

[7] Engel, *loc. cit.*, 1068.

[8] Davis, *Jahresber.*, 1876, 253; Jaeger, *Ber.*, 1902, **35**, 3405.

[9] Thoms, *ibid.*, 1887, **20**, 743.

[10] Kwasnik, *Arch. Pharm.*, 1891, **229**, 310.

[11] Marignac, *Jahresber.*, 1857, 217.

[12] Kane, *Ann. Chim. Phys.*, 1839, [2], **72**, 290.

[13] Divers, *Chem. News*, 1868, **18**, 13.

[14] André, *Ann. Chim. Phys.*, 1884, [6], **3**, 66.

Various other compounds have been reported.[2, 3, 4]

The *hexammoniate* $ZnCl_2.6NH_3$ is apparently formed when zinc chloride absorbs ammonia gas at −18° C. At ordinary temperatures less ammonia than corresponds to this formula is absorbed. It decomposes at 57·5° C.—at about 64·5° C. the *tetrammoniate* is formed, which decomposes at 92° C. and loses increasing quantities of ammonia as the temperature rises. At about 98° C. the composition of the residue approximates to $ZnCl_2.2NH_3$.[5]

The following *double chlorides of zinc* have been described: $LiCl.ZnCl_2.3H_2O$ and $2LiCl.ZnCl_2.2H_2O$;[6] $3LiCl.ZnCl_2.10H_2O$ may exist;[6] $2NaCl.ZnCl_2.3H_2O$;[7] $KCl.ZnCl_2.2H_2O$[6] and $2KCl.ZnCl_2$;[7, 8, 9, 10, 11, 12] $2NH_4Cl.ZnCl_2$;[7, 8, 9, 13, 14, 15] $3NH_4Cl.ZnCl_2$;[7, 16, 17] $2RbCl.ZnCl_2$;[6, 18] $2CsCl.ZnCl_2$[6, 18, 19] and $3CsCl.ZnCl_2Cl_2$;[6, 18] $CaCl_2.ZnCl_2.5\frac{1}{2}H_2O$[20] and $2CaCl_2.ZnCl_2.6H_2O$;[20] $SrCl_2.ZnCl_2.4H_2O$[20] and $SrCl_2.ZnCl_2$;[21] $BaCl_2.ZnCl_2.4H_2O$;[20, 21, 22] $MgCl_2.ZnCl_2.6H_2O$;[23] $ZnCl_2.PtCl_4.6H_2O$.[24]

Zinc Oxychlorides.—Various oxychlorides have been described,[25] but Driot,[26] by determinations of the solubility of zinc oxide in aqueous solutions of zinc chloride, could only identify $ZnCl_2.4ZnO.6H_2O$ and $ZnCl_2.ZnO.1\frac{1}{2}H_2O$. The former was isolated as an amorphous powder, losing 5 molecules of water at 200° C., and the latter as microscopic crystals, losing 1 molecule of water at 230° C. and decomposing at a higher temperature.

Zinc Bromide, $ZnBr_2$.—The pure salt has been prepared by dissolving pure zinc in pure hydrobromic acid or by dissolving pure zinc in pure bromine. The salt was purified by crystallisation, sublimation in an atmosphere of carbon dioxide, and heating in nitrogen or carbon dioxide containing some hydrogen bromide.[1] Distilled zinc has also been heated to just above its melting-point in hydrogen bromide. The zinc bromide which distilled over was redistilled.[2]

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[1] Isambert, *Compt. rend.*, 1868, **66**, 1261; 1878, **86**, 968.

[2] Kane, *loc. cit.*

[3] André, *loc. cit.*

[4] Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 92.

[5] Ephraim, *Ber.*, 1919, **52**, 957.

[6] Ephraim, *Zeitsch. anorg. Chem.*, 1908, **59**, 56.

[7] Marignac, *Jahresber.*, 1857, 219.

[8] Pierre, *Ann. Chim. Phys.*, 1846, [3], **16**, 248.

[9] Rammelsberg, *Pogg. Annalen*, 1855, **94**, 507.

[10] Naumann, *Ber.*, 1904, **37**, 4339.

[11] Jones and Ota, *Amer. Chem. J.*, 1899, **22**, 7.

[12] Rüdorff, *Ber.*, 1888, **21**, 3048.

[13] Déhérain, *Bull. Soc. chim.*, 1861, [1], **3**, 81.

[14] Boedeker, *Jahresber.*, 1860, 17.

[15] Romanis, *ibid.*, 1884, 79.

[16] Meerburg, *Zeitsch. anorg. Chem.*, 1903, **37**, 199.

[17] Baxter and Lamb, *Amer. Chem. J.*, 1904, **31**, 229.

[18] Goddefroy, *Ber.*, 1875, **8**, 9.

[19] Wells and Campbell, *Zeitsch. anorg. Chem.*, 1894, **5**, 273.

[20] Ephraim and Model, *ibid.*, 1910, **67**, 379.

[21] Sandonnini, *Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 524.

[22] Warner, *Chem. News*, 1873, **27**, 271.

[23] Warner, *ibid.*, 1873, **28**, 186.

[24] Topsöe, *Jahresber.*, 1868, 273; Eberhard, *Arch. Pharm.*, 1917, **255**, 65.

[25] Schindler, *Ann. Mag. Pharm.*, 1831, **36**, 45; Kane, *Ann. Chim. Phys.*, 1839 [2], **72**, 296; André, *ibid.*, 1884, [6], **3**, 93; Mailhe, *Bull. Soc. chim.*, 1901, [3], **25**, 786; Tassilly *Ann. Chim. Phys.*, 1899, [7], **17**, 72.

[26] Driot, *Compt. rend.*, 1910, **150**, 1426.

Bromine water converts zinc into the bromide with the evolution of heat, and the anhydrous salt also results from the action of bromine vapour on zinc heated to redness. $ZnBr_2$ is very deliquescent, melts to a clear liquid, sublimes in white vapours at a red heat, and its taste is both sweet and astringent.[3] The anhydrous substance crystallises in white rhombic needles,[4] with a density of 4·22 at 20° C. (compared with water at 4° C.),[1, 5] which melt at 394° C.[6] and boil at 650° C.[7] Its heat of formation at 390° C. is 80·100 Cal.[8] The fused salt is a good electrolyte.[9]

Zinc bromide is very soluble in water. When cooled to −25° C. an 80 per cent. solution deposits needle-shaped crystals of the *trihydrate.* Octahedral crystals of the *dihydrate* separate when an 86 per cent. solution is cooled to 0° C. They melt at 37° C. The following solubilities, in grm. $ZnBr_2$ per 100 grm. solution, have been determined :—

$ZnBr_2$.

Temperature, ° C.	35	40	60	80	100
Solubility	83·45	85·53	86·08	86·57	87·05

$ZnBr_2.2H_2O$.

Temperature, ° C.	−8	0	+13	+25	+30	+37
Solubility	79·06	79·55	80·76	82·46	84·08	86·20

$ZnBr_2.3H_2O$.

Temperature, ° C.	−15	−10	−5
Solubility	77·13	78·45	80·64.[10]

Its aqueous solutions are strongly ionised,[11] and their conductivities are lowered by the addition of non-electrolytes.[12]

Zinc bromide is also soluble in alcohol or ether,[3] and its molecular weight in boiling quinoline corresponds to the formula $ZnBr_2$.[13]

$$[ZnBr_2]+400Aq.=ZnBr_2.Aq.+15{\cdot}030\ \text{Cal.}$$[14]

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[1] Richards and Rogers, *Zeitsch. anorg. Chem.*, 1895, 10, 1; Baxter and Grose, *J. Amer. Chem. Soc.*, 1916, 38, 868. For rate of action of bromine on zinc, see Charpy, *Compt. rend.*, 1891, 113, 597.

[2] Baxter and Hodges, *J. Amer. Chem. Soc.*, 1921, 43, 1243.

[3] Berthemot, *Ann. Chim. Phys.*, 1830, [2], 44, 388. Baxter and Warren (*J. Amer. Chem. Soc.*, 1911, 33, 340) have investigated its efficacy as a drying agent.

[4] Ortloff, *Zeitsch. physikal. Chem.*, 1896, 19, 210.

[5] Boedeker (*Jahresber.*, 1860, 17) found 3·643.

[6] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 277; Dietz, *Zeitsch. anorg. Chem.*, 1899, 20, 252.

[7] Freyer and Meyer, *Ber.*, 1892, 25, 633. Carnelley and Williams (*Trans. Chem. Soc.*, 1878, 33, 283) found 695°–699° C.

[8] Czepinski, *Zeitsch. anorg. Chem.*, 1899, 19, 208.

[9] Graetz, *Wied. Annalen*, 1890, 40, 26.

[10] Dietz, *Zeitsch. anorg. Chem.*, 1899, 20, 247. Ljubarski (*Zeitsch. physikal. Chem.*, 1897, 23, 557) described a trihydrate. For densities of solutions, see Kremers, *Pogg. Annalen*, 1859, 108, 122; Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 256.

[11] Jaeger, *Monatsh.*, 1887, 8, 723.

[12] Arrhenius, *Zeitsch. physikal. Chem.*, 1892, 9, 487.

[13] Beckmann, *Zeitsch. anorg. Chem.*, 1906, 51, 236.

[14] Thomsen, *J. prakt. Chem.*, 1877, [2], 16, 323; *Ber.*, 1877, 10, 1017.

Andre[1] has described some *oxybromides* of zinc.

Compounds of Zinc Bromide with Ammonia.—Rammelsberg obtained octahedral crystals of the diammoniate $ZnBr_2.2NH_3$ by evaporating a solution of zinc bromide in warm ammonia.[2] According to André,[3] their formula is $ZnBr_2.2NH_3.H_2O$. André also obtained $3ZnBr_2.8NH_3.2H_2O$ in fine needles by evaporating a solution of zinc bromide in warm ammonia, fine needles of $3ZnBr_2.10NH_3.H_2O$ by passing ammonia gas into a concentrated solution of the salt till the precipitate first formed dissolved, and evaporating, and the pentammoniate $ZnBr_2.5NH_3$ in brilliant crystals by a method corresponding to the preparation of $ZnCl_2.5NH_3.2H_2O$ by Divers.[4]

All these compounds are decomposed by water.

Zinc bromide hexammoniate, $ZnBr_2.6NH_3$, results when zinc bromide absorbs ammonia gas at −18° C. It decomposes at 62° C., and about 4° higher forms the *tetrammoniate*, that begins to decompose at 143° C. The composition of the residue at 148° C. corresponds to the *diammoniate.*[5]

The following *double bromides of zinc* have been prepared: $NaBr.ZnBr_2.H_2O$;[6] $2NaBr.ZnBr_2.5H_2O$;[6] $KBr.ZnBr_2.2H_2O$;[6] $2KBr.ZnBr_2.2H_2O$;[6] $2CsBr.ZnBr_2$;[6, 7] $3CsBr.ZnBr_2$;[6, 7] $NH_4Br.ZnBr_2.xH_2O$;[6] $2NH_4Br.ZnBr_2$;[6, 8, 9] $2NH_4Br.ZnBr_2.H_2O$;[9, 10] $3NH_4Br.ZnBr_2$;[11] $3NH_4Br.ZnBr_2.H_2O$;[6] $ZnBr_2.PtBr_4.12H_2O$.[12]

Zinc Iodide.—Vigorous action occurs when water is dropped on a mixture of zinc dust and iodine,[13] and solutions of zinc iodide have usually been prepared in this way.[14] Anhydrous ZnI_2 separates at ordinary temperatures from its aqueous solutions that have been saturated at 100° C.[15]

It forms octahedral crystals, of density 4·696,[16] that melt at 446° C.[15, 17] Unlike the chloride and bromide, it is readily oxidised by nitrogen peroxide[18] and by warming in the air—if the air is moist the reaction occurs at ordinary temperatures.

Fused zinc iodide conducts electricity.[19]

The formula ZnI_2 is indicated by the boiling-points of its solutions in quinoline.[20]

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[1] André, *Compt. rend.*, 1883, **96**, 703. See Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 74.

[2] Rammelsberg, *Pogg. Annalen*, 1842, **55**, 240.

[3] André, *Ann. Chim. Phys.*, 1884, [6], **3**, 99.

[4] Divers, *Chem. News*, 1868, **18**, 13. See Tassilly, *loc. cit.*, 96.

[5] Ephraim, *Ber.*, 1919, **52**, 957.

[6] Ephraim, *Zeitsch. anorg. Chem.*, 1908, **59**, 56.

[7] Wells and Campbell, *ibid.*, 1894, **5**, 273.

[8] Boedeker, *Jahresber.*, 1860, 17.

[9] Tassilly, *loc. cit.*, 97.

[10] André, *loc. cit.*, 101.

[11] Jones and Knight, *Amer. Chem. J.*, 1899, **22**, 130.

[12] Topsöe, *Jahresber.*, 1868, 273; Eberhard, *Arch. Pharm.*, 1917, **255**, 65.

[13] Bodroux, *Bull. Soc. chim.*, 1902, [3], **27**, 349.

[14] Lubarski, *Zeitsch. anorg. Chem.*, 1898, **18**, 387.

[15] Dietz, *ibid.*, 1899, **20**, 250.

[16] Boedeker, *Jahresber.*, 1860, 17.

[17] Carnelley, *Trans. Chem. Soc.*, 1878, **33**, 278.

[18] Thomas, *Ann. Chim. Phys.*, 1898, [7], **13**, 222.

[19] Graetz, *Ann. Phys. Chem.*, 1890, [2], **40**, 18.

[20] Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 236.

Zinc iodide is very soluble in water,[1] and the *dihydrate* separates in hygroscopic prismatic crystals when an 83·5 per cent. solution of ZnI_2 is cooled to −8° C. They melt at 27° C. and form the anhydrous salt.[2] The existence of a *tetrahydrate*[3] is doubtful.[2]

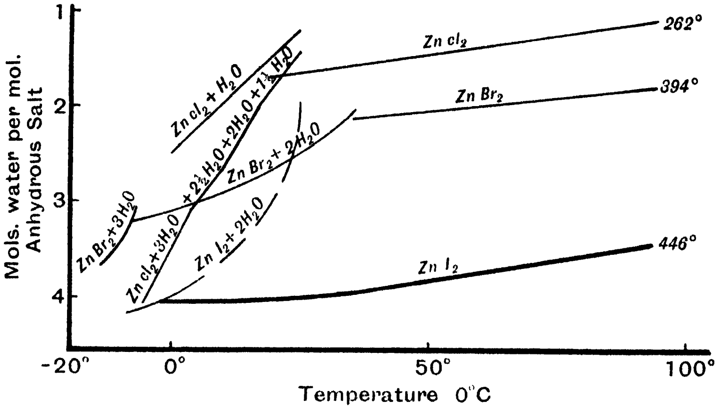

FIG. 3.—Solubility curves of the zinc halides. The temperatures appended for the anhydrous salts represent melting-points.

The following solubilities have been determined in grm. ZnI_2 per 100 grm. solution[2]:—

$ZnI_2.2H_2O$.

Temperature, ° C.	−10	−5	0	+10	+22	+27
Solubility	80·5	80·77	81·16	82·06	83·12	89·52

ZnI_2.

Temperature, ° C.	0	+18	+40	+60	+80	+100
Solubility	81·11	81·20	81·66	82·37	83·05	83·62

$$[ZnI_2]+Aq.=ZnI_2.Aq.+11{\cdot}300\text{ Cal.}^4$$

Compounds of Zinc Iodide with Ammonia.—Dry ZnI_2 absorbs ammonia gas to form the white *pentammoniate*, $ZnI_2.5NH_3$, which is decomposed by water. Rhombic prisms of the *tetrammoniate*, $ZnI_2.4NH_3$, decomposed by warmth or moisture, are obtained by dissolving the anhydrous salt in ammonia solution and evaporating. Tassilly obtained crystals of $3ZnI_2.5NH_3.3H_2O$ by heating zinc oxide with concentrated ammonium iodide solution, filtering, and crystallising.[5]

Zinc iodide hexammoniate, $ZnI_2.6NH_3$, can be obtained, even at ordinary temperatures, by allowing zinc iodide to absorb ammonia gas. It decomposes at 65° C.—the tetrammoniate being finally produced which decomposes at higher temperatures and forms the *diammoniate* at 199° C.[6]

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[1] For densities of solutions, see Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 285. For conductivity data, see Jaeger, *Monatsh.*, 1887, 8, 723.

[2] Dietz, *Zeitsch. anorg. Chem.*, 1899, 20, 250.

[3] Lubarski, *ibid.*, 1898, 18, 387.

[4] Tassilly, *Ann. Chim. Phys.*, 1899, [7], 17, 79.

[5] Rammelsberg, *Pogg. Annalen*, 1839, 48, 152; 1853, 90, 19; Tassilly, *loc. cit.*, 97.

[6] Ephraim, *Ber.*, 1919, 52, 957.

The following *double iodides of zinc* are known: $NaI.ZnI_2.1\frac{1}{2}H_2O$;[1] $NaI.ZnI_2.2H_2O$;[2] $2NaI.ZnI_2.3H_2O$;[3, 4] $KI.ZnI_2$;[3, 4] $2KI.ZnI_2$;[3] $2KI.ZnI_2.2H_2O$;[2] $2CsI.ZnI_2$;[1, 3] $3CsI.ZnI_2$;[1, 3] $NH_4I.ZnI_2.4\frac{1}{2}H_2O$;[2] $2NH_4I.ZnI_2$;[3, 4] $CaI_2.ZnI_2.8H_2O$;[2] $SrI_2.ZnI_2.9H_2O$;[2] $BaI_2.ZnI_2.4\frac{1}{2}H_2O$.[2]

Tassilly has described some *oxyiodides* of zinc.[5]

OXYHALOGEN COMPOUNDS OF ZINC.

Zinc Hypochlorite.—A solution obtained by dissolving zinc oxide or hydroxide in hypochlorous acid or chlorine water decolorises indigo and readily decomposes.[6]

Zinc Chlorate has been prepared by dissolving zinc carbonate in chloric acid, and by interaction between either zinc sulphate and barium chlorate or zinc fluosilicate and potassium chlorate in solution.[7]

Vauquelin described the crystals as octahedral, and Meusser[8] as belonging to the monoclinic system. They are very soluble in water, and crystallise as $Zn(ClO_3)_2.6H_2O$ or $Zn(ClO_3)_2.4H_2O$. The transition temperature from the *hexa-* to *tetra-hydrate* is 14·5°-15° C. The *dihydrate*, if it exists, is more difficult to isolate.[9]

Zinc Perchlorate. Deliquescent prismatic crystals are obtained by double decomposition between zinc sulphate and barium perchlorate. They dissolve in alcohol.[10] Salvadori has obtained the *hydrates* $Zn(ClO_4)_2.6H_2O$ and $Zn(ClO_4)_2.4H_2O$, and the compound $Zn(ClO_4)_2.4NH_3$. Both hydrates are strongly hygroscopic, and decompose on heating before all water is eliminated. The ammonia compound is not very stable.[11]

Zinc Bromate. Crystals of the *hexahydrate* $Zn(BrO_3)_2.6H_2O$, efflorescent *in vacuo*, are obtained by evaporating a solution of zinc oxide in bromic acid. Deliquescent, unstable crystals of $Zn(BrO_3)_2.3H_2O.2NH_3$ were obtained by adding ammonia to a solution of the salt. Zinc bromate is soluble in its own weight of water at 15° C.,[12] and its density is 2·506.[13]

The crystals, formed by slow cooling or evaporation, are mostly octahedral in habit.[14]

Zinc Iodate, $Zn(IO_3)_2.2H_2O$, is obtained as a white crystalline powder by interaction between sodium iodate and a zinc salt. It is sparingly soluble in water,[15] but a very soluble modification may exist.[16]

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[1] Wells and Campbell, *Zeitsch. anorg. Chem.*, 1894, 5, 273.

[2] Ephraim and Model, *ibid.*, 1910, 67, 382.

[3] Ephraim, *ibid.*, 1908, 59, 56.

[4] Rammelsberg, *Pogg. Annalen*, 1838, 43, 665.

[5] Tassilly, *Ann. Chim. Phys.*, 1899, [7], 17, 76.

[6] Grouvelle, *ibid.*, 1821, [2], 17, 40; Balard, *ibid.*, 1834, [2], 57, 297.

[7] Vauquelin, *ibid.*, 1815, 95, 113; Henry, *J. Pharm. Chim.*, 1839, 25, 269; Wächter, *J. prakt. Chem.*, 1843, 30, 321.

[8] Meusser, *Ber.*, 1902, 35, 1416.

[9] Meusser, *loc. cit.* See Mylius and Funk, *Ber.*, 1897, 30, 1718.

[10] Sérullas, *Ann. Chim. Phys.*, 1831, [2], 46, 305.

[11] Salvadori, *Gazzetta*, 1912, 42, i, 458.

[12] Rammelsberg, *Pogg. Annalen*, 1841, 52, 89.

[13] Ortloff, *Zeitsch. physikal. Chem.*, 1896, 19, 211.

[14] Wyckoff, *Amer. Chem. J.*, 1922, [5], 4, 193. See Rammelsberg, *loc. cit.*

[15] Rammelsberg, *Pogg. Annalen*, 1838, 44, 563.

[16] Mylius and Funk, *Ber.*, 1897, 30, 1723.

It can also be prepared by dissolving zinc or zinc carbonate in aqueous hydriodic acid, and needle-shaped crystals of the *anhydrous* salt are said to be obtained by crystallising in the presence of much nitric acid, or evaporating at 60° C. a solution of the iodate in phosphoric acid.

The dihydrate loses its moisture at 200° C., and decomposes at a red heat into iodine, oxygen, and zinc oxide.

Efflorescent rhombic prisms, decomposed by water, of $3Zn(IO_3)_2.8NH_3$, are obtained by dissolving zinc iodate in concentrated ammonia solution, and either adding alcohol or allowing the solution to evaporate spontaneously. Another compound with ammonia, insoluble in water and stable in air, has been obtained by slow evaporation of an ammoniacal solution of zinc iodate. It decomposes explosively at 150° C. Dry powdered zinc iodate absorbs ammonia gas to form $Zn(IO_3)_2.4NH_3$.[1]

Zinc Periodate.—Various compounds of the type $xZnO.yI_2O_7.zH_2O$ have been prepared by treating zinc oxide or carbonate with periodic acid, or by precipitating zinc salts with alkaline periodates.[2] The white precipitate given by potassium periodate with solutions of zinc salts is soluble in ammonium chloride and ammonia in the cold. Boiling causes precipitation.[3]

ZINC AND OXYGEN.

Zinc Oxide occurs naturally as *zincite* or *red zinc ore* crystallised in the hemimorphic group of the hexagonal system, with a hardness of 4–4·5 and a density of 5·5–5·55.[4]

Zinc oxide is prepared on the large scale by heating the metal to near its boiling-point. The vapours burn in the air and a white woolly mass of oxide condenses. It has been known under various names: *pompholix* and *nix alba*, or *philosophical wool*, in ancient times; *zinc white*, and occasionally *flowers of zinc*, in modern.

Proposals have been made to prepare it commercially by heating zinc sulphate or various zinc minerals with carbon,[5] and by electrolysing a solution of sodium sulphate between zinc electrodes. The zinc hydroxide formed in the latter process is finally calcined to the oxide.

Amorphous zinc oxide is also obtained by igniting zinc hydroxide or carbonate.[6]

A crystalline oxide results from igniting zinc nitrate,[7] and zinc oxide also sublimes in crystals when (*a*) zinc is heated to redness in a current of steam;[8] (*b*) zinc chloride is heated in a current of steam;[9] (*c*) zinc oxide is heated in a *slow* current of hydrogen;[10] (*d*) zinc oxide is heated in a current of oxygen;[1] (*e*) zinc oxide is volatilised in the electric furnace.[2]

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[1] Ditte, *Ann. Chim. Phys.*, 1890, [6], **21**, 163.

[2] Langlois, *ibid.*, 1852, [3], **34**, 269; Rammelsberg, *Ber.*, 1868, **1**, 73; *Pogg. Annalen*, 1868, **134**, 516.

[3] Benedict, *Amer. Chem. J.*, 1905, **34**, 581.

[4] Ortloff, *Zeitsch. physikal. Chem.*, 1896, **19**, 209.

[5] Darlington, *Chem. Zentr.*, 1863, 957; Hampe and Schnabel, *ibid.*, 1897, ii, 880.

[6] Regnault (*Ann. Chim. Phys.*, 1836, [2], **62**, 351) said that zinc oxalate gave ZnO when heated in a closed vessel.

[7] Brügelmann, *Zeitsch. anal. Chem.*, 1880, **19**, 283.

[8] Regnault, *loc. cit.*, 350.

[9] Daubrée, *Compt. rend.*, 1854, **39**, 153.

[10] Deville, *Ann. Chim. Phys.*, 1855, [3], **43**, 477. A *rapid* current reduces the oxide to metal.

Gorgeu, by heating zinc sulphate with an alkaline sulphate, obtained transparent, nacreous, greenish-yellow or greenish hexagonal prisms that belonged to the hexagonal system and were identical with zincite in hardness and density. He also obtained good crystals by heating equal parts of zinc fluoride and potassium fluoride in the presence of steam.[3]

The artificial crystals are usually hexagonal, though some crystals, artificially produced during the distillation of zinc, belong to the regular system.[4] Moissan obtained his crystals in long transparent needles.[2]

According to Brügelmann,[5] the density of amorphous zinc oxide, prepared by igniting the hydroxide or carbonate, is 5·47, and of the crystals obtained by igniting the nitrate, 5·78.

The specific heat of zinc oxide has been given as 0·12480.[6]

Ordinary amorphous zinc oxide is a white powder with a creamy tint, that goes yellow when hot and white again on cooling. The yellow tint in some commercial samples has been traced to cadmium sulphide.[7] Zinc oxide has been said to lose part of its oxygen on heating, and the yellow lower oxide to remain stable if no oxygen is present during cooling.[8] Crystalline samples often have a yellow tinge.[9] The yellow colour is said to appear whether the oxide is heated in an atmosphere of oxygen or carbon dioxide or nitrogen, or in a partial vacuum.[10]

At 18° C., 236,000 parts of water dissolve 1 part of zinc oxide.[11] The precipitated oxide retains small quantities of moisture at high temperatures.[12] Even after ignition it dissolves in ammonium chloride solution or in a solution of ammonia and ammonium carbonate.[13] Acids readily dissolve it.

Hydrogen begins to reduce zinc oxide at 454° C.,[14] and the reduction can be carried to completion in dry hydrogen,[15] though the reversible character of the reaction

$$H_2+ZnO \rightleftharpoons Zn+H_2O$$

renders this difficult.[16] Zinc oxide is also reduced by carbon at a red heat [17] and by heating with magnesium.[18]

The reduction of zinc oxide by carbon is metallurgically important.

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[1] Sidot, *Compt. rend.*, 1869, 69, 201.

[2] Moissan, *ibid.*, 1892, 115, 1036; *Ann. Chim. Phys.*, 1895, [7], 4, 143.

[3] Gorgeu, *Compt. rend.*, 1887, 104, 120.

[4] Weber, *Jahresber.*, 1858, 182. See Laurent and Holms, *Ann. Chim. Phys.*, 1835, [2], 60, 333.

[5] Brügelmann, *Zeitsch. anal. Chem.*, 1880, 19, 283.

[6] Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 173.

[7] Fuchs and Schiff, *J. Soc. Chem. Ind.*, 1896, 15, 363.

[8] Schüpphaus, *ibid.*, 1899, 18, 987.

[9] de Forcrand, *Ann. Chim. Phys.*, 1902, [7], 27, 37.

[10] *Annalen*, 1834, 9, 165.

[11] Dupre and Bialas, *Zeitsch. angew. Chem.*, 1903, 16, 54.

[12] de Forcrand, *Ann. Chim. Phys.*, 1902, [7], 27, 29.

[13] Tambon, *Bull. Soc. chim.*, 1907, [4], i, 823.

[14] Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 25.

[15] Gillet, *Bull. Soc. chim. Belg.*, 1912, 26, 106.

[16] Deville, *Ann. Chim. Phys.*, 1855, [3], 43, 477; Ditte, *Compt. rend.*, 1871, 73, 108.

[17] Desormes and Clermont, *Ann. Chim. Phys.*, 1801, [1], 39, 26.

[18] Winkler, *Ber.*, 1890, 23, 120.

According to Boudouard,[1] carbon monoxide is the immediate agent of reduction. The reduction of zinc oxide by carbon monoxide begins at a lower temperature than the reduction by carbon in an atmosphere of nitrogen.[2] According to Lemarchands, zinc oxide can be reduced directly by carbon, and the reduction of the oxide is normally effected simultaneously by carbon and carbon monoxide.[3] The amount of carbon entering into the reaction is intermediate between the quantities required by

$$ZnO+C=Zn+CO$$

and

$$2ZnO+C=2Zn+CO_2,$$

because the reduction of zinc oxide by carbon monoxide

$$ZnO+CO=Zn+CO_2$$

is more rapid than the reduction of carbon dioxide by carbon.[4] The reaction

$$ZnO+C \rightleftharpoons Zn+CO$$

proceeds from left to right at 600° C. The reverse reaction is only observable at much higher temperatures. Carbon monoxide can reduce zinc oxide at temperatures as low as 350°–400° C.[3]

Zinc oxide and carbon are converted into zinc vapour and carbon monoxide at 1033° C.[5]

Sulphur dioxide has no action on heated zinc oxide,[6] but chlorine converts it into the chloride.[7]

It is said to dissociate when heated with metallic zinc.[8]

The heat of formation of zinc oxide has been frequently determined,[9] and, according to de Forcrand, it varies from 80·29 to 84·7 Cal. for solid zinc and gaseous oxygen. Apparently the values are higher, as the temperatures at which the oxide is prepared are greater. This may be connected with increasing polymerisation as the temperature of the oxide is raised.[10] Dilute sulphuric acid dissolves zinc oxide much less rapidly when it has been raised to a red heat than when it has been prepared at 350° C.[11] The strongly heated oxide also dissolves relatively slowly in alkaline hydroxides.[12]

Its heat of solution in aqueous hydrofluoric acid has been given as 21·820 Cal.[13]

Zinc oxide is used as a polishing powder, especially for glass. It is employed in the manufacture of dental cements, crystalline glazes, glass, and porcelain. As a pigment it has the advantage over lead compounds of not darkening under the action of hydrogen sulphide.

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[1] Boudouard, *Bull. Soc. chim.*, 1901, [3], 25, 282.

[2] Doeltz and Graumann, *Metallurgie*, 1907, 4, 290.

[3] Lemarchands, *Rev. Mét.*, 1920, 17, 803.

[4] Lemarchands, *Compt. rend.*, 1920, 170, 805.

[5] Bodenstein and Schubart, *Zeitsch. Elektrochem.*, 1917, 23, 105.

[6] Schiff, *Annalen*, 1861, 117, 94.

[7] Weber, *Pogg. Annalen*, 1861, 112, 619.

[8] Morse and White, *Amer. Chem. J.*, 1889, 11, 258.

[9] Favre and Silbermann, *Ann. Chim. Phys.*, 1853, [3], 37, 441; Dulong, *ibid.*, 444; Andrews, *Phil. Mag.*, 1848, [3], 32, 426; Ditte, *Jahresber.*, 1871, 73.

[10] de Forcrand, *Compt. rend.*, 1902, 134, 1426; *Ann. Chim. Phys.*, 1902, [7], 27, 26.

[11] Ditte, *Compt. rend.*, 1871, 72, 858.

[12] Foerster and Günther, *Zeitsch. Elektrochem.*, 1899, 6, 301.

[13] Mulert, *Zeitsch. anorg. Chem.*, 1912, 75, 218.

Zinc ointment, which contains zinc oxide, is a familiar pharmaceutical product.

Zinc Hydroxide.—When solutions of caustic alkalies or ammonia are added to solutions of zinc salts, $Zn(OH)_2$ falls as a white amorphous precipitate which dissolves in excess of the precipitant.[1] It was obtained in rhombic prisms by allowing zinc to remain in contact with iron or copper under aqueous solutions of ammonia or caustic alkalies,[2] or by adding zinc carbonate to an excess of potassium hydroxide solution.[3] Becquerel obtained colourless octahedra by coiling copper strips round strips of zinc and leaving them in a solution of either silicic acid or clay in caustic alkali.[4]

The amorphous variety is difficult to obtain pure by precipitating zinc salts with alkali,[1, 5] but a pure product has been prepared by treating a solution of the nitrate with carbonate-free alkali.[6] Pure zinc hydroxide can be readily prepared by electrolysing a solution of a salt of an alkali metal (such as sodium sulphate) with a platinum cathode and a zinc anode. Zinc is dissolved by the anions, and precipitation is effected, more readily if the liquid is agitated, by the hydroxyl ions formed at the cathode.[7] Electrolytically prepared zinc hydroxide has occurred crystalline.[8]

The density of zinc hydroxide has been given as 3·053.[9]

Octahedral crystals of the *monohydrate* $Zn(OH)_2.H_2O$ have been obtained by allowing a saturated solution of zinc oxide in sodium hydroxide to stand for some weeks.[10] According to de Forcrand only the crystalline variety is the *anhydrous* hydroxide. This becomes anhydrous zinc oxide at 125° C. in a current of dry air, which combines with water to form the crystalline $ZnO.H_2O$ again—the heat of solution being 2·190 Cal. The amorphous hydroxide prepared by precipitation of zinc salts with alkalies corresponds, according to the conditions and temperature of desiccation, to $3ZnO.5H_2O$, or $3ZnO.4H_2O$, or $4ZnO.5H_2O$. These hydrates still retain water when heated to 250° C. (perhaps forming $5ZnO.2H_2O$), and even resist a prolonged temperature of 400° C. The anhydrous ZnO prepared at a red heat gives a number of differently hydrated compounds.[11]

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[1] *Annalen*, 1834, **9**, 165. The reaction between zinc sulphate and potassium hydroxide depends upon temperature, dilution, and the relative masses of the reacting substances. See Lineberger, *J. Amer. Chem. Soc.*, 1895, **17**, 356. According to Pickering (*Trans. Chem. Soc.*, 1907, **91**, 1986; *Proc. Chem. Soc.*, 1907, **23**, 261), 0·795 equivalents of the alkali completely precipitate the zinc from its sulphate solution, and the composition of the precipitate is $5ZnO.SO_3$. The zinc hydroxide may adsorb some zinc sulphate (Tschumanoff, *Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 230).

[2] Runge, *Pogg. Annalen*, 1829, **16**, 129; Nicklès, *Ann. Chim. Phys.*, 1848, [3], **22**, 31; Cornu, *Chem. Zentr.*, 1863, 896.

[3] Ville, *Compt. rend.*, 1885, **101**, 375.

[4] Becquerel, *Annalen*, 1855, **94**, 358.

[5] Hantzsch, *Zeitsch. anorg. Chem.*, 1902, **30**, 298.

[6] Euler, *Ber.*, 1903, **36**, 3400.

[7] Lorenz, *Zeitsch. anorg. Chem.*, 1896, **12**, 439. See Strecker, *Zeitsch. Elektrochem.*, 1898, **5**, 133.

[8] Morel, *Chem. Zentr.*, 1892, i, 375.

[9] Filhol, *Annalen*, 1847, **64**, 156.

[10] Becquerel, *loc. cit.*

[11] de Forcrand, *Compt. rend.*, 1902, **134**, 1428; **135**, 37. For heat of solution of ZnO, also see Massol, *Bull. Soc. chim.*, 1896, [3], **15**, 1104.

The zinc hydroxide precipitated by potassium hydroxide is said to become less soluble in the alkali on drying at 60°–70° C.,[1] and by the action of caustic potash on zinc sulphate three different varieties are said to be produced. One of these corresponds to the formula $2ZnO.H_2O$, and two to $ZnO.H_2O$: each one is differently soluble in potassium hydroxide from the others.[2]

Zinc hydroxide is very sparingly soluble in water,[3] but the solubility is increased by the presence of various salts.[4]

Its amphoteric character is very marked—both acids and alkalies readily dissolving it. Its acid character is less pronounced than that of aluminium hydroxide.[5]

Zincates.—Zinc hydroxide dissolves in excess of potassium hydroxide. A precipitate falls when the solution (*a*) stands; (*b*) is treated with alcohol; (*c*) is treated with carbon dioxide; (*d*) is diluted and boiled.[6]

The zinc hydroxide acts as an extremely weak acid, and it has been suggested that it exists in alkaline solution largely in colloidal form,[7] though the electrolysis of these solutions indicates zinc anions.[8] When solutions of zinc hydroxide in sodium hydroxide are dialysed, the passage of the zinc through the membrane seems to vary with the physical condition of the zinc hydroxide before solution.[9]

A maximum value has been found for the solubility of zinc hydroxide in caustic soda when the atomic ratios were $Zn : Na = 1 : 3$. This might be due partly to hydrolysis and partly to dehydration of the hydroxide by the alkali.[10] According to Moir, the solution of zinc hydroxide in caustic alkalies is essentially an equilibrium between zincic acid and the alkali. The reactions

$$K_2ZnO_2 + H_2O = KHZnO_2 + KHO = H_2ZnO_2 + 2KHO$$

are slow, but hydrolysis is finally very complete.[11] Klein found that the solubility of the zinc hydroxide was proportional to the alkali present, and referred the separation of zinc hydroxide on boiling to its conversion into a more stable and less soluble form.[12] The differences in solubility may be due to both physical and chemical causes.[13]

According to Hildebrand and Bowers, part of the zinc dissolves colloidally on the addition of the alkali and the rest reacts as a monobasic acid. Finally, the colloidal particles disappear and the solution contains the ion $HZnO'_2$.[14]

Crystalline *potassium zincate*, $K_2O.ZnO$, has been obtained by covering a solution of zinc hydroxide in caustic potash with alcohol. It dissolved in cold water, and boiling water decomposed it into $K_2O.2ZnO$.[1] The latter compound was obtained crystalline : water appears to decompose it.[2] Prescott also obtained crystalline $K_2O.ZnO$, and the corresponding sodium compound probably occurs in aqueous solutions that are not too dilute.[3] Zinc has been very generally assumed to dissolve in aqueous sodium hydroxide with the formation of $Zn(ONa)_2$,[4] and a stable *sodium zincate*, $Na_2O.ZnO.4H_2O$, has been described.[5]

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[1] Herz, *Zeitsch. anorg. Chem.*, 1901, 28, 474.
[2] Klein, *ibid.*, 1912, 74, 157.
[3] Bodländer, *Zeitsch. physikal. Chem.*, 1898, 27, 66; Herz, *Zeitsch. anorg. Chem.*, 1900, 23, 227.
[4] Snyders, *Ber.*, 1878, 11, 940.
[5] Slade, *Zeitsch. anorg. Chem.*, 1912, 77, 457.
[6] *Annalen*, 1834, 9, 177.
[7] Hantzsch, *Zeitsch. anorg. Chem.*, 1902, 30, 298.
[8] Kreman, *ibid.*, 1902, 33, 94.
[9] Herz, *ibid.*, 1902, 31, 459; 32, 357.
[10] Rubenbauer, *ibid.*, 1902, 30, 331.
[11] Moir, *Proc. Chem. Soc.*, 1905, 21, 310.
[12] Klein, *Zeitsch. anorg. Chem.*, 1912, 74, 157.
[13] Hantzsch, *ibid.*, 1912, 75, 371.
[14] Hildebrand and Bowers, *J. Amer. Chem. Soc.*, 1916, 38, 785.

The two crystalline sodium zincates, $H_2Na_4Zn_3O_6.17H_2O$ and $HNaZnO_2.3\frac{1}{2}H_2O$, were isolated by alcoholic treatment of a solution of zinc oxide in strong aqueous sodium hydroxide. The former melted at 100° C. and the latter at 300° C.[6]

Needle-shaped crystals of $Zn(OH)(ONa).3H_2O$ have separated from a solution of zinc hydroxide in caustic soda which was kept in the winter cold.[7]

Some zincoxides that may have the constitution $M''(O.ZnOH)_2+xH_2O$, where M''=Ca, Sr, or Ba, have been described.[8]

Zinc hydroxide dissolves in excess of ammonia.[9] Up to 1880 several compounds of zinc oxide with ammonia had been reported.[10] The solutions of zinc hydroxide or oxide in ammonia probably contain the complex $Zn(NH_3)_4$, or, according to Bonsdorff, the complex $Zn_m(NH_3)_{3m}$.[11]

A solution described as containing cuprammonium and zinc-ammonium hydroxide was used for producing parchment from paper.[12]

Zinc Peroxide.—Thénard obtained an incompletely peroxidised oxide of zinc by (*a*) dissolving zinc hydroxide in hydrochloric acid containing hydrogen peroxide and precipitating with an alkali hydroxide ; (*b*) acting on gelatinous zinc hydroxide with hydrogen peroxide.[13]

Haass precipitated zinc salts with ammonia in the presence of hydrogen peroxide and obtained white precipitates that, after drying at 110° C., varied in composition between Zn_5O_8 and Zn_3O_5.[14]

Kouriloff, by evaporating zinc oxide or hydroxide nearly to dryness with dilute hydrogen peroxide solution, obtained a white, finely crystalline powder, to which he assigned the formula $ZnO_2.Zn(OH)_2$.[15]

de Forcrand agitated zinc oxide with hydrogen peroxide solution and obtained $Zn_3O_5.2H_2O$, $Zn_3O_5.3H_2O$, and $Zn_4O_7.4H_2O$ as gelatinous white precipitates that became white powders on drying. They were stable in air, but on heating $Zn_4O_7.4H_2O$ to 100° C. it became $Zn_3O_5.3H_2O$. By continued treatment with hydrogen peroxide he obtained $2ZnO_2.5H_2O$, which, however, gradually changed into $Zn_3O_5.2H_2O$. He preferred to formulate these substances as –

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[1] Laux, *Annalen*, 1834, **9**, 183.

[2] Frémy, *Compt. rend.*, 1846, **15**, 1106.

[3] Prescott, *Chem. News*, 1880, **42**, 31 ; Carrara and Vespignani, *Gazzetta*, 1900, **30**, ii, 35 ; Herz, *Zeitsch. anorg. Chem.*, 1901, **28**, 474.

[4] Jordis, *Zeitsch. Elektrochem.*, 1900, **7**, 469.

[5] Goudriaan, *Annual Report Chem. Soc.*, 1920, **17**, 41.

[6] Comey and Jackson, *Ber.*, 1888, **21**, 1589 ; *Amer. Chem. J.*, 1889, **11**, 145.

[7] Foerster and Günther, *Zeitsch. Elektrochem.*, 1899, 6, 302.

[8] Bertrand, *Compt. rend.*, 1892, **115**, 939.

[9] Bonnet, *Annalen*, 1834, **9**, 176.

[10] Runge, *Pogg. Annalen*, 1829, **16**, 129 ; Weyl, *ibid.*, 1864, **123**, 353 ; Malaguti, *Compt. rend.*, 1866, **62**, 413 ; Prescott, *Chem. News*, 1880, **42**, 31.

[11] Konowaloff, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 910 ; Dawson and McCrae, *Trans. Chem. Soc.*, 1900, **77**, 1239 ; Euler, *Ber.*, 1903, **36**, 3400 ; Bonsdorff, *ibid.*, 1903, **36**, 2323 ; *Zeitsch. anorg. Chem.*, 1904, **41**, 142. Herz has determined the solubilities of zinc hydroxide in ammonia solutions (*Zeitsch. anorg. Chem.*, 1902, **30**, 280), and studied the dialysis of the solutions (*ibid.*, 1902, **32**, 357).

[12] Wright, *J. Soc. Chem. Ind.*, 1884, **3**, 121.

[13] Thénard, *Ann. Chim. Phys.*, 1818, [2], **9**, 55. See *J. Chem. Soc.*, 1885, **48**, Abs. 20.

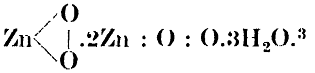
[14] Haass, *Ber.*, 1884, **17**, 2249.

[15] Kouriloff, *Ann. Chim. Phys.*, 1891, [6], **23**, 1891. Prud'homme (*Compt. rend.*, 1891, **112**, 1374) obtained a mixture roughly corresponding to $2ZnO+ZnO(OH)_2$.

$3ZnO.2H_2O_2$.
$3ZnO.H_2O + 2H_2O_2$ or $HO.Zn.O.Zn.O.Zn.OH + 2H_2O_2$.
$4ZnO.H_2O + 3H_2O_2$ or $HO.Zn.O.Zn.O.Zn.O.Zn.OH + 3H_2O_2$.
$ZnO.H_2O + H_2O_2$ or $HO.Zn.OH + H_2O_2$.[1]

Eijkmann described the preparation of $3ZnO_2.Zn(OH)_2$ by the action of 30 per cent. hydrogen peroxide on an ammoniacal solution of zinc sulphate.[2]

Kazanecky obtained a fine crystalline precipitate of $ZnO_2.H_2O$ by acting with 30 per cent. hydrogen peroxide on alkali zincates. It decomposed explosively at 178° C. He regarded it as



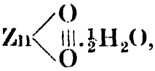
$$Zn\langle\begin{matrix}O\\ |\\ O\end{matrix}.2Zn : O : O.3H_2O.$$[3]

When pure zinc oxide reacts with an ethereal solution of hydrogen peroxide, the product, after drying at 60°–70° C., has the composition $Zn_4O_7.2H_2O$. It loses oxygen when heated with water at 100° C., and forms $Zn_3O_5.H_2O$. Both these peroxides are reddish-yellow powders that are stable under ordinary conditions and explode at 212°–216° C. Carrasco regarded them as perzincic acids—

$$HO.Zn.O.O.Zn.O.O.Zn.O.O.ZnOH$$

and

$$HO.Zn.O.O.Zn.O.O.ZnOH.$$[4]



Ebler and Krause obtained $ZnO_2.\frac{1}{2}H_2O$, which they formulated as $Zn\langle\begin{matrix}O\\ |||\\ O\end{matrix}.\frac{1}{2}H_2O$, by acting upon a cooled solution of zinc ethyl in dry ether with a dry ethereal solution of hydrogen peroxide. The white amorphous precipitate was decomposed by acids and slowly hydrolysed by water.[5] A similar product was obtained by dissolving zinc nitrate in concentrated ammonia solution, cooling to −5° C., adding a concentrated solution of hydrogen peroxide, and stirring the filtered precipitate for some time with more of the hydrogen peroxide. The product was either moist ZnO_2 or $ZnO_2.\frac{1}{2}H_2O$.[6]

Sjöström obtained a white powder by carefully drying the product of the prolonged action of the calculated amount of 30 per cent. hydrogen peroxide solution on freshly ignited zinc oxide. Its composition corresponded to the formula $Zn_2O(OH)(O.OH)$. It was stable under ordinary conditions and only slowly decomposed by $2N$ NaHO.

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[1] de Forcrand, *Compt. rend.*, 1902, **134**, 601; **135**, 103. Kouriloff obtained similar products (*J. Russ. Phys. Chem. Soc.*, 1890, **22**, 180), but contended that they were mixtures of ZnO_2 with ZnO and $Zn(OH)_2$, and that only the zinc peroxide $ZnO_2.Zn(OH)_2$ had been proved to exist (*Compt. rend.*, 1903, **137**, 618). de Forcrand replied to these criticisms (*Compt. rend.*, 1904, **138**, 129).

[2] Eijkmann, *Chem. Zentr.*, 1905, i, 1628.

[3] Kazanecky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1452.

[4] Carrasco, *Gazzetta*, 1911, **41**, i, 16.

[5] Ebler and Krause, *Zeitsch. anorg. Chem.*, 1911, **71**, 150.

[6] Riesenfeld and Nottebohm, *ibid.*, 1914–15, **90**, 150.

He concluded that zinc perhydrate is usually a mixture of substances derived from $Zn(OH)_2$ and HO.Zn.O.ZnOH, and that the hydroperoxides are of the types HO.Zn.O.OH and Zn(OH).O.Zn.O.OH.[1]

Commercially, zinc peroxide has been prepared by allowing barium peroxide suspended in water to act on the zinc salt of an acid that forms an insoluble barium salt. The electrolytic preparation, however, is most satisfactory. A solution of zinc chloride, neutralised by adding zinc oxide, is electrolysed in a vessel containing a porous diaphragm, and hydrogen peroxide is added to the cathode cell. The precipitated hydrated peroxides are carefully dried.[2]

The commercial product is a dense, yellowish-white powder of density 1·571, and appears to contain about 50 per cent. of ZnO_2 mixed with zinc hydroxide and free moisture. It is very stable—losing only water at 100° C. and not being decomposed by water. One part dissolves in 45,500 parts of water. It has strong antiseptic properties, and has the advantage of being odourless and non-irritant. It is soluble in acids but is indifferent to mineral hydrocarbons. This last property is important for its extensive use in ointments. It is much used in surgery and dermatology.[3]

Preparations of zinc peroxide are known under the trade names of *zinkonal*, *dermogen*, *eklogan*, and *zinc perhydrol*.

ZINC AND SULPHUR.

Zinc Sulphide, ZnS, occurs naturally as the valuable ores *wurtzite* and *zinc blende*.[4] Zinc blende (*sphalerite*) crystallises in the tetrahedral group of the isometric system, with a hardness of 3·5–4 and a density of 4·05. Wurtzite crystallises in the hemimorphic group of the hexagonal system, with a hardness of 3·54 and a density of 3·98.[5] Both minerals vary in colour from dark brown to black—blende being often black like coal.[6]

Crystalline zinc sulphide is prepared most directly by subliming the amorphous form in an electric furnace.[7] Since the crystals of zinc sulphide obtained by sublimation are hexagonal, wurtzite apparently represents the more stable form at high temperatures.[8] The transformation temperature of blende into wurtzite apparently varies with the associated impurities. The reverse change, when the temperature falls, is slow, and may occupy two or three days.[9] The sublimation of zinc sulphide, amorphous or crystalline, has been performed in the presence of alumina,[1] and in an atmosphere of hydrogen,[2] nitrogen, sulphur dioxide, or hydrogen sulphide.[3]

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[1] Sjöström, *Zeitsch. anorg. Chem.*, 1917, 100, 237.

[2] Hinz, *J. Chem. Soc.*, 1904, 86, Abs. ii, 562.

[3] Foregger and Philipp, *J. Soc. Chem. Ind.*, 1906, 25, 300.

[4] Friedel, *Compt. rend.*, 1861, 52, 983.

[5] See also Ortloff, *Zeitsch. physikal. Chem.*, 1896, 19, 208.

[6] For some chemical differences, see Beutell and Matzke, *Centr. Min.*, 1915, 263.

[7] Mourlot, *Ann. Chim. Phys.*, 1899, [7], 17, 532.

[8] Deville and Troost, *ibid.*, 1865, [4], 5, 118; Hautefeuille, *Compt. rend.*, 1881, 93, 824; Vermeuil, *ibid.*, 1888, 106, 1105; 107, 101; Mourlot, *ibid.*, 1896, 123, 54.

[9] Allen, Crenshaw, and Mervin, *Amer. J. Sci.*, 1912, [4], 34, 341.

Other methods of obtaining crystalline zinc sulphide (wurtzite) are—

(*a*) Heating zinc oxide or silicate in sulphur vapour at a red heat.[4]
(*b*) Interaction between zinc vapour and hydrogen sulphide.[5]
(*c*) Melting together zinc sulphate, barium sulphide, and calcium fluoride.[6]
(*d*) Action of zinc chloride vapour, diluted with carbon dioxide, on some metallic sulphides, especially tin sulphide.[7]

Crystals of blende are said to be obtained by heating zinc sulphide in a solution of hydrogen sulphide under pressure,[8] by subjecting zinc chloride vapour to the action of hydrogen sulphide,[9] and by the action of carbon disulphide on zinc oxide at a white heat.[10]

White amorphous zinc sulphide is precipitated by passing hydrogen sulphide through solutions of zinc salts. Since it is less soluble than the oxide or carbonate, suspensions of these in water are converted into sulphide by hydrogen sulphide.[11] Zinc sulphide is perceptibly soluble in sodium hydrogen sulphide,[12] freely in mineral acids, and somewhat soluble in ammonium chloride on boiling.[13]

The precipitation of zinc sulphide by passing hydrogen sulphide through solutions of its salts is not usually quantitative: this is usually explained by the reversibility of the reaction

$$ZnCl_2+H_2S \rightleftharpoons ZnS+2HCl.^{14}$$

According to Glixelli,[15] the reaction

$$ZnSO_4+H_2S=ZnS+H_2SO_4$$

is not reversible, partial precipitation arising from false equilibria, and prolonged passage of hydrogen sulphide, at ordinary temperature, through $\frac{1}{4}$ and $\frac{1}{2}$ molar solutions of zinc sulphate, precipitates the zinc completely.[16]

When zinc sulphide is precipitated in media in which it is slightly soluble, as in the presence of weak acids, it is either crystalline or becomes so on standing. According to Villiers, it is soluble in sodium hydrogen sulphide at the moment of precipitation, and passes from this *état protomorphique* into a crystalline insoluble form with a rapidity which varies with conditions.[1] According to Glixelli,[2] the β-sulphide precipitated from alkaline solutions is forty-six times as soluble as the α-sulphide precipitated from acid solutions.

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[1] Hautefeuille, *Compt. rend.*, 1881, 93, 824.
[2] Deville and Troost, *ibid.*, 1861, 52, 920.
[3] Sidot, *ibid.*, 1866, 63, 188.
[4] Sidot, *ibid.*, 1866, 62, 699; Friedel, *Bull. Soc. chim.*, 1883, 40, 526.
[5] Lorenz, *Ber.*, 1891, 24, 1507.
[6] Deville and Troost, *Ann. Chim. Phys.*, 1865, [4], 5, 118; *Compt. rend.*, 1861, 52, 920.
[7] Viard, *ibid.*, 1903, 136, 892.
[8] Sénarmont, *Ann. Chim. Phys.*, 1850, [3], 30, 129; *Compt. rend.*, 1851, 32, 409.
[9] Durocher, *ibid.*, 1851, 32, 823.
[10] Frémy, *Jahresber.*, 1888, 536.
[11] Nandin and Monthollon, *Compt. rend.*, 1876, 83, 60.
[12] Immerwahr, *Zeitsch. Elektrochem.*, 1901, 7, 482. According to McCay (*J. Amer. Chem. Soc.*, 1908, 30, i, 376), an unstable alkali thiozincate may be formed when hydrogen sulphide acts on alkaline solutions of zinc salts.
[13] de Clermont, *Bull. Soc. chim.*, 1879, 31, 483.
[14] Ostwald, *J. prakt. Chem.*, 1879, [2], 19, 468; Schümann, *Annalen*, 1888, 249, 326.
[15] Glixelli, *Zeitsch. anorg. Chem.*, 1907, 55, 297. See Baubigny, *Compt. rend.*, 1888, 107, 1148; 1882, 94, 1183.
[16] For precipitation of ZnS, see under Estimation of Zinc.

When zinc sulphide is first precipitated in media in which it is very insoluble it readily goes into colloidal solution. A *colloidal solution* has been prepared by precipitation with hydrogen sulphide in ammoniacal or neutral solution and washing with hydrogen sulphide water, and by passing hydrogen sulphide into an aqueous suspension of zinc oxide. The addition of glycerine, or other substances increasing the viscosity of the solution, facilitates the formation of these colloidal solutions,[3] which are milky by reflected and orange by transmitted light.

Seligmann[4] obtains a readily filterable zinc sulphide by heating a strongly ammoniacal solution, containing 0·5 grm. zinc in 200 c.c., to 60° or 80° C. and adding a slight excess of ammonium sulphide.

Zinc sulphide is tinged light brown or grey by exposure to light or heating to 60°–70° C. This behaviour, which may be due to polymerisation, is promoted by various substances and inhibited by others,[5] and is important for the use of zinc sulphide as a pigment, whether alone or, mixed with finely divided barium sulphate, in lithophone.[6]

The ordinary sulphide, natural or artificial, phosphoresces after exposure to light. This phosphorescence is affected by traces of other metals, but the data seem to be somewhat contradictory.[7] A similar phosphorescence is also stimulated by exposing the sulphide to the action of ozone.[8] Apparently there is no phosphorescence in ordinary precipitated zinc sulphide, but if it is heated for about one and a half hours at 650°–900° C. it will phosphoresce under light, Becquerel rays, X-rays, cathode rays, and radioactive emanations. The favouring conditions for phosphorescent behaviour seem to be semi-crystalline condition and the presence of chlorine ions. The latter may strain the particles of zinc sulphide by coating them with zinc chloride.[9] The luminescence of crystalline zinc sulphide under X-rays is increased by the presence of 1–30 per cent. of cadmium sulphide in solid solution.[10]

The reaction

$$ZnS + H_2O = H_2S + ZnO$$

begins at a dull red heat and is rapid at higher temperatures.[11]

Oxygen converts zinc sulphide into sulphate at 500° C., and the sulphate decomposes into oxide at higher temperatures. Carbon reduces zinc sulphide to metal at a high temperature—carbon disulphide being formed.

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[1] Villiers, *Compt. rend.*, 1895, **120**, 98, 149, 188, 322, 498.

[2] Glixelli, *loc. cit.*

[3] Winssinger, *Jahresber.*, 1888, 287; Donnini, *Gazzetta*, 1894, **24**, i, 219; Muller, *Ber.*, 1904, **37**, 11.

[4] Seligmann, *Zeitsch. anal. Chem.*, 1914, **53**, 594.

[5] Yâshichi Nishizana, *J. Tokio Chem. Soc.*, 1920, **41**, 1054.

[6] Riederer, *J. Soc. Chem. Ind.*, 1909, **28**, 403; O'Brien, *J. Physical Chem.*, 1915, **19**, 113; Maas and Kempf, *Zeitsch. angew. Chem.*, 1923, **36**, 293; Renversade, *J. Pharm. Chim.*, 1923, **27**, 458.

[7] Grüne, *Ber.*, 1904, **37**, 3076; Hofmann and Ducca, *ibid.*, 1904, **37**, 3407; Jorissen and Ringer, *ibid.*, 1904, **37**, 3983; Jorissen and Ringer, *J. Chem. Soc.*, 1906, **90**, Abs. ii, 448; Tomaschek, *Ann. Physik*, 1921, [4], **65**, 189; Tiede and Schleede, *Ber.*, 1923, **56**, 674; Schmidt, *ibid.*, 1922, **55**, 3988.

[8] Schenk and Mir, *ibid.*, 1904, **37**, 3464.

[9] MacDougall, Stewart, and Wright, *Trans. Chem. Soc.*, 1917, **111**, 663.

[10] Guntz, *J. Soc. Chem. Ind.*, 1923, **42**, 191A.

[11] Regnault, *Ann. Chim. Phys.*, 1836, [2], **62**, 380.

The specific heat of zinc blende is about 0·12.[1] According to Regnault,[2] the specific heat of zinc sulphide is 0·12303.

$$[Zn]+[S]=[ZnS]+43{\cdot}0\ \text{Cal.}^3$$
$$[Zn]+[S(\text{rhombic})]=[ZnS(\text{cryst.})]+41{\cdot}3\ \text{Cal.}^4$$

The reaction

$$ZnS+3CO_2=ZnO+SO_2+3CO$$

begins at 750° C. and is vigorous at 1000° C.[5]

There are probably no definite *hydrates* of zinc sulphide,[6] though some have been reported.[7]

A white *pentasulphide*, ZnS_5, is said to be precipitated from solutions of zinc salts by potassium pentasulphide, which is decomposed by acids with the evolution of hydrogen sulphide and deposition of sulphur.[8]

An unstable *zinc hydrogen sulphide*, $Zn(HS)_2$, may be produced during the action of hydrogen sulphide or sodium hydrogen sulphide on solutions of zinc salts.[9]

The *oxysulphide*, $4ZnS.ZnO$, occurs naturally as *voltzite* in globular masses with a hardness of 3–3·5 and a density of 4·9–5·0.

The *double sulphides*, $Na_2S.3ZnS$, $K_2S.3ZnS$, $Ag_2S.3ZnS$, and $CuS.3ZnS$, have been described.[10]

Zinc Hydrosulphite, ZnS_2O_4, was first obtained in solution by acting on zinc with sulphurous acid,[11] and subsequently in minute rhombic needles by passing dry sulphur dioxide through a suspension of zinc in absolute alcohol.[12] A stiff paste has been prepared commercially by the former method.[13]

It dissolves readily in water, and forms double salts like $Na_2S_2O_4.ZnS_2O_4$.[14] A crystalline paste of the double salt, $Na_2SO_3.2ZnS_2O_4$, has been commercially prepared.[15]

Zinc Thiosulphate, ZnS_2O_3.—When sulphur dioxide is passed through an aqueous suspension of zinc sulphide, insoluble crystals of zinc sulphite separate,

$$ZnS+H_2SO_3=ZnSO_3+H_2S,$$

that finally dissolve as the acid sulphite. Some thiosulphate is simultaneously produced: reactive sulphur produced by reaction between the hydrogen sulphide and sulphur dioxide[1] acts on the acid sulphite according to the equation

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[1] Ortloff, *Zeitsch. physikal. Chem.*, 1896, **19**, 208.
[2] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 175.
[3] Berthelot, *ibid.*, 1875, [5], **4**, 187.
[4] Mixter, *Amer. J. Sci.*, 1913, [4], **36**, 55.
[5] Bacho, *Monatsh.*, 1916, **37**, 119.
[6] Glixelli, *Zeitsch. anorg. Chem.*, 1907, **55**, 297.
[7] Souchay, *Zeitsch. anal. Chem.*, 1868, **7**, 78; Berthelot, *Ann. Chim. Phys.*, 1875, [5], **4**, 201; Baubigny, *Compt. rend.*, 1888, **107**, 1148.
[8] Schiff, *Annalen*, 1860, **115**, 74.
[9] Berthelot, *Ann. Chim. Phys.*, 1875, [5], **4**, 187; Thomsen, *Ber.*, 1878, **11**, 2044. *Cf.* Renversade, *J. Pharm. Chim.*, 1923, **27**, 458; Zotta, *Monatsh.*, 1889, **10**, 807.
[10] Schneider, *Pogg. Annalen*, 1873, **149**, 381.
[11] Bernsthen, *Annalen*, 1880, **208**, 177.
[12] Nabl, *Monatsh.*, 1899, **20**, 679.
[13] *J. Chem. Soc.*, 1908, **94**, Abs. ii, 185.
[14] Bazlen, *Ber.*, 1905, **38**, 1060.
[15] *J. Chem. Soc.*, 1910, **98**, Abs. ii, 411.

$$Zn(HSO_3)_2+S=ZnS_2O_3+H_2O+SO_2.$$

If the zinc sulphide suspension is added slowly to aqueous sulphurous acid, so that the latter is always in excess, the resulting solution contains principally thiosulphate and but little acid sulphite—

$$2ZnS+3SO_2=2ZnS_2O_3+S.^2$$

Zinc thiosulphate has also been obtained in solution by dissolving the metal in aqueous sulphurous acid. Solutions of the salt are colourless and transparent and decompose readily—

$$2ZnS_2O_3=ZnS+ZnS_3O_6.^3$$

The *double salts*, $3Na_2S_2O_3.2ZnS_2O_3.10H_2O$,[4] $K_2S_2O_3.ZnS_2O_3.H_2O$, and $(NH_4)_2S_2O_3.ZnS_2O_3.H_2O$,[5] have been prepared.

Zinc Sulphite is obtained in small, slightly soluble crystals by dissolving zinc,[6] zinc carbonate,[7] zinc oxide,[8] or zinc sulphide [9] in aqueous sulphurous acid. Excess of acid converts the sparingly soluble normal sulphite into the readily soluble *acid sulphite* (from which solution the normal sulphite is precipitated on warming), and if zinc sulphide is slowly added to the excess of acid, zinc thiosulphate is the principal product.[10] Zinc sulphite also separates slowly in the cold from mixed 25 per cent. solutions of sodium sulphite and zinc sulphate (acidified with acetic acid).[11]

The crystals are either $ZnSO_3.2H_2O$ [12] or $ZnSO_3.2\frac{1}{2}H_2O$,[13] and either monoclinic [14] or orthorhombic.[15]

The *basic salt*, $5ZnSO_3.8Zn(OH)_2$, is said to be produced by boiling the normal or acid sulphite with water, and $8ZnSO_3.7Zn(OH)_2.7H_2O$ by mixing boiling normal solutions of zinc sulphate and sodium sulphite.[16]

The *double salts*, $Na_2SO_3.3ZnSO_3.7\frac{1}{2}H_2O$, $K_2SO_3.3ZnSO_3.7\frac{1}{2}H_2O$, and $(NH_4)_2SO_3.ZnSO_3$, have been reported.[17]

Zinc Sulphate.—The *heptahydrate*, $ZnSO_4.7H_2O$, occurs naturally as *goslarite*, which crystallises in rhombic needles of hardness 2–2·5 and density 1·95–2·04. Shining rectangular tabular crystals, belonging to the rhombic system, of density 3·74 at 15° C., that are identical with natural *zincosite*, $ZnSO_4$, are obtained by evaporating down a solution of zinc sulphate in sulphuric acid and carefully heating off the excess of acid. They soon become cloudy on exposure to air.[1] Octahedral crystals of *anhydrous* zinc sulphate were prepared by heating hydrated zinc sulphates with ammonium sulphate. They dissolved slowly in cold water and rapidly in hot.[2]

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[1] Wackenroder, *Annalen*, 1846, **60**, 189 ; Debus, *Trans. Chem. Soc.*, 1888, **53**, 278.

[2] Henderson and Weiser, *J. Amer. Chem. Soc.*, 1913, **35**, 240.

[3] Fordos and Gélis, *Ann. Chim. Phys.*, 1843, [3], **8**, 350.

[4] Vortmann and Padberg, *Ber.*, 1889, **22**, 2640.

[5] Rosenheim and Davidsohn, *Zeitsch. anorg. Chem.*, 1904, **41**, 238.

[6] Fordos and Gélis, *loc. cit.*

[7] Muspratt, *Annalen*, 1844, **50**, 283.

[8] Vogel, *J. prakt. Chem.*, 1843, **29**, 280.

[9] Henderson and Weiser, *loc. cit.*

[10] See Zinc Thiosulphate.

[11] Denigès, *Bull. Soc. chim.*, 1892, [3], **7**, 569. According to Berthier (*Ann. Chim. Phys.*, 1843, [3], **7**, 81), zinc salts are not precipitated by ammonium sulphite.

[12] Muspratt, *loc. cit.* ; Fordos and Gélis, *loc. cit.*

[13] Röhrig, *J. prakt. Chem.*, 1888, [2], **37**, 217 ; Denigès, *loc. cit.* ; Marignac, *Jahresber.*, 1857, 119.

[14] Marignac, *loc. cit.*

[15] Denigès, *loc. cit.*

[16] Seubert, *Arch. Pharm.*, 1891, **229**, 316.

[17] Berglund, *Ber.*, 1874, **7**, 469.

White amorphous anhydrous zinc sulphate is easily obtained by heating the hydrated sulphates.[3] It may be heated to a dull red heat without decomposition, though it is converted into zinc oxide at higher temperatures.[4]

The specific heat of anhydrous zinc sulphate is 0·174,[5] and its density has been given variously from 3·400–3·681.[6]

Zinc sulphide is formed by heating zinc sulphate either with an excess of sulphur or rapidly (to a white heat) with carbon. Zinc oxide is produced when a mixture of zinc sulphate and carbon is raised more slowly to dull redness, and metallic zinc if the temperature is raised to a bright red.[7] Ammonia gas reduces the heated sulphate to a residue with the composition $ZnO.ZnS$.[8]

One hundred parts of methyl alcohol dissolve 0·65 parts of anhydrous zinc sulphate,[9] and the salt dissolves readily in water with the evolution of heat.

$$[ZnSO_4]+400Aq.=ZnSO_4.Aq.+18{\cdot}43\ \text{Cal.}$$[10]

At 20° C. 100 parts of water dissolve over 50 parts of $ZnSO_4$.[11]

Aqueous solutions of zinc sulphate are only slightly hydrolysed—0·03 per cent. in $\frac{1}{16}$ molar solution.[12]

At temperatures below 39° C. the *heptahydrate*, $ZnSO_4.7H_2O$, usually crystallises from pure solutions of zinc sulphate made by dissolving the metal, sulphide, oxide, hydroxide, or carbonate in dilute sulphuric acid.

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[1] de Schulten, *Compt. rend.*, 1888, 107, 405.

[2] Klobb, *ibid.*, 1892, 114, 837.

[3] According to Graham (*Ann. Chim. Phys.*, 1836, [2], 63, 55), the heptahydrate is only completely dehydrated at temperatures above 210° C. Thorpe and Watts (*Trans. Chem. Soc.*, 1880, 37, 108) heated to 280°–300° C. Pierre (*Ann. Chim. Phys.* 1846, [3], 16, 241) said it became anhydrous at 110° C. in a current of dry air.

[4] Euler, *Zeitsch. anorg. Chem.*, 1900, 25, 146. According to Baubigny (*Compt. rend.*, 1883, 97, 906) it is stable up to 440° C. According to Bailey (*Trans. Chem. Soc.*, 1887, 51, 681) it begins to decompose at approximately 410° C. It does not dissociate below 675° C. according to recent research. See under Estimation of Zinc.

[5] Pape, *Jahresber.*, 1863, 51.

[6] Thorpe and Watts, *loc. cit.*

[7] Gay-Lussac, *Ann. Chim. Phys.*, 1836, [2], 63, 432.

[8] Hodgkinson and Trench, *Chem. News*, 1892, 66, 223.

[9] de Bruyn, *Zeitsch. physikal. Chem.*, 1892, 10, 784.

[10] Thomsen, *J. prakt. Chem.*, 1878, [2], 17, 165; *Ber.*, 1878, 11, 1021.

[11] For some earlier solubility determinations, see Poggiale, *Ann. Chim. Phys.*, 1843, [3], 8, 467; Tobler, *Annalen*, 1855, 95, 198; von Hauer, *Jahresber.*, 1866, 59; Tilden, *Trans. Chem. Soc.*, 1884, 45, 266; Étard, *Ann. Chim. Phys.*, 1894, [7], 2, 551; Callendar and Barnes, *Proc. Roy. Soc.*, 1897, 62, 147. For densities of solutions, see Schiff, *Annalen*, 1859, 110, 72; Gerlach, *Zeitsch. anal. Chem.*, 1869, 8, 288; Favre and Valson, *Compt. rend.*, 1874, 79, 968; Barnes and Scott, *J. Physical Chem.*, 1898, 2, 536. For conductivity data, see Horsford, *Pogg. Annalen*, 1847, 70, 238; Paalzow, *Jahresber.*, 1868, 91; Tartar and Keyes, *J. Ind. Eng. Chem.*, 1921, 13, 1127. For electrolytic deposition, see M'Intosh, *Trans. Roy. Soc. Canada*, 1917–18, [3], 11, 113. For thermal expansion, see Lannoy, *Zeitsch. physikal. Chem.*, 1895, 18, 442. For thermal effects of dilution, see Pollok, *Proc. Chem. Soc.*, 1899, 15, 8. For osmotic data, see Coppet, *Zeitsch. physikal. Chem.*, 1897, 22, 239; Lescœur, *Ann. Chim. Phys.*, 1896, [7], 19, 213.

[12] Ley, *Ber.*, 1897, 30, 2194; *Zeitsch. physikal. Chem.*, 1899, 30, 193.

It is prepared industrially by carefully roasting zinc blende, extracting with water, and crystallising. Zinc sulphide ores are also treated with sulphuric acid, and the resulting sulphate, after treating with water and filtering, crystallised out.[1] It is known commercially as *white vitriol*, and has a great variety of uses. It is used in dyeing and calico printing, for preparing pigments, varnishes, and various zinc compounds, and in disinfection, preserving wood or hides, flame proofing, and pharmacy.

It crystallises in rhombic prisms, isomorphous with Epsom salts.[2]

Monoclinic crystals, isomorphous with $FeSO_4.7H_2O$, have been obtained by introducing a crystal of a monoclinic vitriol, like $CoSO_4.7H_2O$, into the supersaturated solution. They have been usually obtained as mixed crystals.[3]

The density of white vitriol has been variously given from 1·931–1·976.[4] The specific heat of the crystals is 0·328;[5] they melt at about 50° C.,[6] effloresce slowly in the air and lose water more completely, eventually becoming anhydrous, as the temperature is raised.[7]

$$[ZnSO_4.7H_2O]+400Aq.=ZnSO_4.Aq.-4{\cdot}26 \text{ Cal.}^8$$

The solubility of $ZnSO_4.7H_2O$ is—

Temperature, ° C. . . .	0·1	15	30	35	39
Grm. $ZnSO_4$ in 100 grm. water[9]	41·93	50·88	61·92	66·61	70·05

At 39° C. the heptahydrate is transformed into the *hexahydrate*. This is important for the use of the Clark standard cell, which consists of the system mercury—mercurous sulphate—zinc sulphate crystals—zinc sulphate solution—zinc sulphate crystals—zinc amalgam (the mercurous sulphate being made into a paste with some zinc sulphate).[10]

The solubility of the hexahydrate is—

Temperature, ° C. .	0·1	15	30	35	39
Grm. $ZnSO_4$ in 100 grm. water[9]	49·48	57·15	65·82	67·99	70·08

Both the hepta- and hexa-hydrate can exist for some time in a labile state outside their normal range of existence.

Monoclinic crystals of the hexahydrate, isomorphous with the corresponding magnesium salt, separate from solutions of zinc sulphate at temperatures above 39° C.[1] Tetragonal crystals have been obtained by introducing a tetragonal crystal of $NiSO_4.6H_2O$ into the supersaturated solution.[2] The density of the monoclinic crystals is 2·056.[3]

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[1] *J. Soc. Chem. Ind.*, 1923, 42, 19A. Certain bacteria can convert blende into sulphate (Helbronner and Rudolfs, *Compt. rend.*, 1922, 174, 1378).

[2] Sénarmont, *Ann. Chim. Phys.*, 1851, [3], 23, 406; Topsöe and Christiansen, *ibid.*, 1873, [4], 31, 1.

[3] Nicklès, *ibid.*, 1848, [3], 23, 104; de Boisbaudran, *ibid.*, 1869, [4], 18, 263; Hollemann, *Zeitsch. physikal. Chem.*, 1902, 40, 574.

[4] Thorpe and Watts, *Trans. Chem. Soc.*, 1880, 37, 110.

[5] Pape, *Jahresber.*, 1863, 51.

[6] Tilden, *Trans. Chem. Soc.*, 1884, 45, 266.

[7] Wiedemann, *J. prakt. Chem.*, 1874, [2], 9, 338; Muller-Erzbach, *Chem. Zentr.*, 1885, 470; Schulze, *Ann. Phys. Chem.*, 1887, [2], 31, 204; Lescœur, *Ann. Chim. Phys.*, 1890, [6], 21, 541. See also under Anhydrous Zinc Sulphate.

[8] Thomsen, *J. prakt. Chem.*, 1878, [2], 17, 165; *Ber.*, 1878, 11, 1021; *ibid.*, 1873, 6, 710 (−4·24).

[9] Cohen, *Zeitsch. physikal. Chem.*, 1900, 34, 182. According to Schröder (*Annalen*, 1859, 109, 51), a more soluble β-heptahydrate may separate.

[10] Cohen, *Zeitsch. physikal. Chem.*, 1894, 14, 75; Jaeger, *Ann. Phys. Chem.*, 1897, [2], 63, 354; Callendar and Barnes, *Proc. Roy. Soc.*, 1897, 62, 148; Cohen, *Zeitsch. physikal. Chem.*, 1898, 25, 304; 1899, 31, 164; 1900, 34, 179; Barnes, *J. Physical Chem.*, 1900, 4, 1; Barnes and Cooke, *ibid.*, 1902, 6, 172.

Pierre obtained a *pentahydrate* by evaporating a solution of zinc sulphate at 40°-50° C. till it began to crystallise, and cooling slowly to 35° C.,[4] and a salt of density 2·206 was obtained by boiling the finely powdered heptahydrate with alcohol of density 0·825.[5]

The existences of a *tetrahydrate* and a *trihydrate* were deduced from the heats of hydration of zinc sulphates.[6]

A *dihydrate* has been prepared by pouring a saturated solution of zinc sulphate into concentrated sulphuric acid and washing the precipitate with absolute alcohol. This salt had a density of 2·958.[5] The heptahydrate is said to become the dihydrate in dry air,[7] and, according to Étard, the same salt is obtained by evaporating a zinc sulphate solution at 120° C., or by heating a solution saturated at 15° C. in a closed vessel at 180° C.[8]

When a solution of zinc sulphate is evaporated on the water-bath the residue is the *monohydrate* $ZnSO_4.H_2O$.[9] It also deposits from a boiling saturated solution [10] and crystallises from a solution of the heptahydrate in methyl alcohol.[11] It has been prepared by heating heptahydrated zinc sulphate to 100° C. or 110° C.[5, 10]

The density of $ZnSO_4.H_2O$ has been given as 3·076 [12] and 3·289.[5] Its specific heat is 0·202.[13]

$$[ZnSO_4.H_2O]+400Aq.=ZnSO_4.Aq.+9{\cdot}95\ Cal.$$[14]

Rhombohedral crystals of $ZnSO_4.3\frac{1}{2}H_2O$ have been reported.[15]

Lescœur [6] suggested that the number of hydrates had been overestimated.

Basic Sulphates of Zinc.—The following basic sulphates have been reported: $8ZnO.SO_3.16H_2O$;[16] $8ZnO.SO_3.7H_2O$;[16] $8ZnO.SO_3.6H_2O$;[16] $8ZnO.SO_3.2H_2O$;[17] $8ZnO.SO_3.H_2O$;[16] $6ZnO.SO_3.10H_2O$;[17] $5ZnO.SO_3$;[18] $4ZnO.SO_3.7H_2O$;[19] $4ZnO.SO_3.6H_2O$;[20] $4ZnO.SO_3.5H_2O$;[21] $4ZnO.SO_3.3H_2O$;[22] $(ZnOH)_4SO_4$.[19]

According to Lubkowskaia [23] only $4ZnO.SO_3.3H_2O$ exists as a definite compound.

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[1] Marignac, *Jahresber.*, 1855, 389; Wyrouboff, *Bull. Soc. chim.*, 1889, [3], **2**, 500.

[2] de Boisbaudran, *Ann. Chim. Phys.*, 1869, [4], **18**, 263.

[3] Thorpe and Watts, *Trans. Chem. Soc.*, 1880, **37**, 110.

[4] Pierre, *Ann. Chim. Phys.*, 1846, **16**, 241.

[5] Thorpe and Watts, *Trans. Chem. Soc.*, 1880, **37**, 109.

[6] Lescœur, *Ann. Chim. Phys.*, 1890, [6], **21**, 154.

[7] Baubigny and Péchard, *Compt. rend.*, 1892, **115**, 173.

[8] Étard, *Ann. Chim. Phys.*, 1894, [7], **2**, 551.

[9] Callendar and Barnes, *Proc. Roy. Soc.*, 1897, **62**, 147; Cohen, *Zeitsch. physikal. Chem.*, 1900, **34**, 181.

[10] Graham, *Ann. Chim. Phys.*, 1836, [2], **63**, 55. See Anhydrous Sulphate.

[11] de Bruyn, *Zeitsch. physikal. Chem.*, 1892, **10**, 788.

[12] Schröder, *J. prakt. Chem.*, 1879, [2], **19**, 288.

[13] Pape, *Jahresber.*, 1863, 51.

[14] Thomsen, *J. prakt. Chem.*, 1878, [2], **17**, 165; *Ber.*, 1878, **11**, 1021.

[15] Kane, *Ann. Chim. Phys.*, 1839, [2], **72**, 367.

[16] Reindel, *J. prakt. Chem.*, 1869, **106**, 371.

[17] Kane, *loc. cit.*, 311.

[18] Pickering, *Proc. Chem. Soc.*, 1907, **23**, 261.

[19] Athanasesco, *Compt. rend.*, 1886, **103**, 271.

[20] Schultze, *Zeitsch. anorg. Chem.*, 1897, **13**, 5.

[21] Habermann, *Jahresber.*, 1884, i, 321.

[22] Thugutt, *Zeitsch. anorg. Chem.*, 1892, **2**, 151.

[23] Lubkowskaia, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 989.

Ammoniates.—Zinc sulphate absorbs ammonia gas in proportions depending upon the temperature. Zinc sulphate pentammoniate, $ZnSO_4.5NH_3$, decomposes at 19° C., the tetrammoniate at 98·5° C., and the triammoniate at 185° C. A hexammoniate exists at temperatures less than this range and a diammoniate at higher.[1]

From a solution obtained by passing ammonia gas into a warm concentrated solution of zinc sulphate until it just cleared, the hydrated compounds $ZnSO_4.4NH_3.4H_2O$, $ZnSO_4.4NH_3.2H_2O$, and $ZnSO_4.2NH_3.H_2O$ were obtained. They lose ammonia and water progressively when heated —anhydrous zinc sulphate being ultimately left.[2]

Deliquescent needles or tabular crystals of $ZnSO_4.4NH_3.3H_2O$ were obtained by treating a cooled solution of zinc sulphate in aqueous ammonia with ammonia gas.[3]

In ammoniacal solutions of zinc sulphate there are probably complex ions containing NH_3.[4]

Acid Sulphates of Zinc.—The acid sulphate $H_2SO_4.ZnSO_4.8H_2O$ deposits in monoclinic crystals from solutions of zinc sulphate containing sulphuric acid. It dissolves sparingly in cold water, readily in hot, and loses water and sulphuric acid when heated.[5]

Crystals of $3H_2SO_4.ZnSO_4$ have been separated by cooling the acid in the first chambers during the manufacture of sulphuric acid from zinc blende. When heated strongly they decompose into zinc sulphate and sulphuric acid.[6]

Double Sulphates of Zinc.—There is a large group of salts represented by the general formula $M_2SO_4.RSO_4.6H_2O$, where R is a divalent metal and M is NH_4, thallium, or any alkali metal except lithium or sodium. The lithium and sodium salts either do not exist or have a different proportion of water of crystallisation.[7] The salts with R=zinc can be prepared by dissolving the constituent simple salts in molecular proportions and crystallising.[8]

Zinc sulphate also forms a series of double salts with the general formula $ZnSO_4.MSO_4.14H_2O$, where M is magnesium, copper, manganese, iron (ferrous), or nickel.[9]

The following salts have also been described: $Na_2SO_4.ZnSO_4.4H_2O$;[10]

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[1] Ephraim, *Ber.*, 1919, **52**, 957. Isambert (*ibid.*, 1870, **3**, 246) recorded $2ZnSO_4.5NH_3$.

[2] Kane, *Ann. Chim. Phys.*, 1839, [2], **72**, 304. See Müller, *Annalen*, 1869, **149**, 70.

[3] André, *Compt. rend.*, 1885, **100**, 241.

[4] Dawson and McCrae, *Trans. Chem. Soc.*, 1900, **77**, 1239; *Proc. Chem. Soc.*, 1900, **16**, 172. Lubkowskaia (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 989) and Shumakoff (*ibid.*, 1908, **40**, 476) have studied the system $ZnSO_4$—NH_3—H_2O.

[5] von Kobell, *J. prakt. Chem.*, 1843, **28**, 492.

[6] Hoffmann, *Zeitsch. angew. Chem.*, 1910, ii, 1672.

[7] Locke, *Amer. Chem. J.*, 1902, **27**, 455.

[8] For data, see Perrot, *Compt. rend.*, 1890, **111**, 969; Pope, *Trans. Chem. Soc.*, 1896, **69**, 1540; Ortloff, *Zeitsch. physikal. Chem.*, 1896, **19**, 218; Tutton, *Trans. Chem. Soc.*, 1893, **63**, 356; 1896, **69**, 374, 504; 1905, **87**, ii, 1140, 1165; *Proc. Roy. Soc.*, 1910, **83A**, 211. Also for $K_2SO_4.ZnSO_4.6H_2O$, see Joule and Playfair, *Jahresber.*, 1847–48, 59; Schröder, *ibid.*, 1879, 31; Schiff, *Annalen*, 1858, **107**, 64; Tobler, *ibid.*, 1855, **95**, 198. For $(NH_4)_2SO_4.ZnSO_4.6H_2O$, see Marignac, *Jahresber.*, 1857, 217; Tröger and Eners, *Chem. Zentr.*, 1898, i, 658; Schröder, *loc. cit.*; Schiff, *loc. cit.*; Tobler, *loc. cit.*

[9] Schauffele, *J. prakt. Chem.*, 1852, **55**, 371; de Boisbaudran, *Ann. Chim. Phys.* 1869, [4], **18**, 276; Hannay, *Trans. Chem. Soc.*, 1879, **35**, 456; Retgers, *Zeitsch. physikal. Chem.*, 1894, **15**, 558; Stortenbeker, *Zeitsch. physikal. Chem.*, 1897, **22**, 62; Foote, *Amer. Chem. J.*, 1901, **26**, 418; Hollman, *Zeitsch. physikal. Chem.*, 1902, **40**, 561. For $MgSO_4.ZnSO_4.14H_2O$, also see Schiff, *loc. cit.*

[10] Bucholz, *Jahresber.*, 1866, 222; Tomlinson, *Pogg. Annalen*, 1870, **141**, 626.

$K_2SO_4.ZnSO_4$;[1] $K_2SO_4.2ZnSO_4$;[2] $CuSO_4.3ZnSO_4.28H_2O$;[3] (Zn, Fe) $SO_4.H_2O$, and (Zn, Cr) $SO_4.H_2O$.[4]

Zinc sulphate is also a constituent of numerous complex salts.[5]

Zinc Dithionate, $ZnS_2O_6.6H_2O$,[6] crystallises in the triclinic system with a density of 1·915.[7] It is prepared by interaction between barium dithionate and zinc sulphate. The crystals are stable in air and very soluble in water: the solution decomposes on boiling.[8]

The *double salts* $4(NH_4)_2S_2O_6.ZnS_2O_6$ [9] and $9(NH_4)_2S_2O_6.ZnS_2O_6.16\frac{1}{2}H_2O$ [6] have been reported.

$$[ZnS_2O_6.6H_2O]+400Aq.=ZnS_2O_6.Aq.-2{\cdot}42\ \text{Cal.}^{10}$$

Zinc Tetrathionate.—The *acid salt*, $ZnH_2(S_2O_6)_2$, is obtained by half neutralising Wackenroder's solution (aqueous sulphurous acid decomposed by passing hydrogen sulphide [11]) with zinc carbonate. It is very soluble in cold water or alcohol, and crystallises in small, slightly hygroscopic needles from its alcoholic solution. It decomposes above 100° C., and sulphur separates when its aqueous solution is treated with potassium hydroxide.[12]

Zinc Pentathionate has been prepared as a crystalline mass by adding zinc acetate to sulphurous acid through which hydrogen sulphide has been passed and allowing the liquid to evaporate. The impure product was soluble in water and unstable.[13]

ZINC AND SELENIUM.

Zinc Selenide, ZnSe, is produced by heating zinc and selenium together at a high temperature.[14, 15] The amorphous substance thus produced has a brilliant yellow colour, is infusible up to 1100° C., and has a density of 5·29 at 21° C.[15] It is more easily obtained by heating zinc in a current of hydrogen selenide.[14]

Reddish-yellow crystals, of density 5·40 and belonging to the regular system,[16] were obtained by subliming the amorphous form in a current of hydrogen.[14] Yellow crystals of density 5·42 at 15° C. were obtained by heating precipitated zinc selenide, dried in a current of hydrogen, in the electric furnace, and a partially crystalline ZnSe was prepared by similarly heating a mixture of zinc selenate and carbon.[17] Crystals belonging to the hexagonal system were obtained by heating zinc chloride vapour with a mixture of nitrogen and hydrogen selenide. Zinc selenide is thus dimorphous analogously to zinc sulphide. Needle-shaped crystals were also obtained by reducing highly heated zinc selenate with hydrogen.[1]

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[1] Schröder, *Jahresber.*, 1879, 31.

[2] Mallet, *Trans. Chem. Soc.*, 1900, 77, 220.

[3] Hannay, *ibid.*, 1879, 35, 456.

[4] Scott, *ibid.*, 1897, 71, 567.

[5] Vohl, *Annalen*, 1855, 94, 57; Étard, *Compt. rend.*, 1878, 87, 602.

[6] Klüss, *Annalen*, 1888, 246, 296.

[7] Topsöe, *Jahresber.*, 1872, 163.

[8] Heeren, *Pogg. Annalen*, 1826, 7, 183.

[9] Rammelsberg, *ibid.*, 1843, 58, 297.

[10] Thomsen, *J. prakt. Chem.*, 1877, [2], 16, 323; *Ber.*, 1877, 10, 1017.

[11] Wackenroder, *Annalen*, 1846, 60, 189; Debus, *Trans. Chem. Soc.*, 1888, 53, 278.

[12] Curtius, *J. prakt. Chem.*, 1881, [2], 24, 225; Curtius and Henkel, *ibid.*, 1888, [2], 37, 147.

[13] Debus, *Trans. Chem. Soc.*, 1883, 53, 299.

[14] Margottet, *Compt. rend.*, 1877, 84, 1293.

[15] Chikashigé and Kurosawa, *Mem. Coll. Sci. Kyoto*, 1917, 2, 245.

[16] Margottet, *Zeitsch. Kryst. Min.*, 1878, 2, 106.

[17] Fonzes-Diacon, *Compt. rend.*, 1900, 130, 832.

Crystalline zinc selenide dissolves (evolving hydrogen selenide) in aqueous hydrochloric acid, though gaseous hydrogen chloride, even at a high temperature, has no action on it. It burns in oxygen, forming a basic selenite and selenium dioxide. Chlorine displaces selenium from it.[1]

$$[Zn]+[Se]=[ZnSe]\ (\text{cryst.})+40{\cdot}4\ \text{Cal.}$$

The corresponding figures for precipitated ZnSe are 34·0 (crystalline) and 33·60 (amorphous).[2]

Zinc Selenites.—The *biselenite*, $ZnO.2SeO_2.3H_2O$, has been prepared in colourless transparent crystals by adding 5–6 grm. zinc carbonate, in successive portions, to a solution containing 20 grm. selenium dioxide in 30 grm. water. The deposit becomes crystalline after decanting off the syrupy liquid.

The *anhydrous neutral selenite*, $ZnSeO_3$, is obtained by heating the mother-liquor from the preparation of the biselenite in a sealed tube at 200° C. It separates as prismatic orthorhombic crystals that are insoluble in water, soluble in acids, and calcine in air to zinc oxide. The biselenite also becomes zinc oxide when heated in air, dissolves in cold water, and is converted by hot water into white pulverulent $ZnSeO_3$.[3]

The *dihydrate*, $ZnSeO_3.2H_2O$,[4] and the *monohydrate* [3] have also been prepared.

Orange crystals, resembling potassium chromate, of the *tetraselenite*, $ZnSeO_3.3H_2SeO_3$, were obtained by dissolving zinc in a concentrated solution of selenious acid. They are stable in air, very soluble in water, and become white and opaque at 40° C.[5]

Zinc Selenate.—The colourless *hexahydrate*, $ZnSeO_4.6H_2O$, crystallises in the tetragonal system,[6] and the *pentahydrate* occurs in triclinic crystals.[7]

Zinc selenate forms a series of double salts represented by the general formula $R_2SeO_4.ZnSeO_4.6H_2O$, where R is an alkali metal or NH_4.[8]

The double salt, $K_2SeO_4.ZnSeO_4.2H_2O$, is known,[7] and some complex salts containing zinc selenate have been prepared.[9, 10] The *acid salt*, $ZnSeO_4.H_2SeO_4.2H_2O$, has also been obtained.[10]

ZINC AND TELLURIUM.

Zinc Telluride.—Margottet prepared ZnTe by melting zinc and tellurium together, and obtained red crystals by subliming the original amorphous product in hydrogen.[11]

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[1] Fonzes-Diacon, *loc. cit.*

[2] Fabre, *Compt. rend.*, 1886, **103**, 345.

[3] Boutzoureanao, *Ann. Chim. Phys.*, 1889, [6], **18**, 304.

[4] Nilson, *Ber.*, 1875, **8**, 656.

[5] Wöhler, *Annalen*, 1847, **63**, 279.

[6] Topsöe and Christiansen, *Jahresber.*, 1873, 140; Kopp, *Ber.*, 1879, **12**, 903.

[7] Schröder, *J. prakt. Chem.*, 1879, [2], **19**, 275.

[8] Topsöe and Christiansen, *Ann. Chim. Phys.*, 1874, [5], **1**, 1; Tutton, *Zeitsch. Kryst. Min.*, 1900, **33**, 1.

[9] Wohlwill, *Annalen*, 1860, **114**, 187.

[10] Gerichten, *ibid.*, 1873, **168**, 221.

[11] Margottet, *Compt. rend.*, 1877, **84**, 1293.

Zinc and tellurium form only this single compound, which melts at 1238·5° C. and has a density of 5·54 at 13° C.[1]

A yellow-brown precipitate of the *monohydrate*, $ZnTe.H_2O$, is formed by adding a solution of sodium telluride to zinc acetate solution made acid with acetic acid. It is brown when dry, and when heated out of contact with air forms a dark dull red anhydrous telluride.

Dilute sulphuric acid has no action on zinc telluride, dilute hydrochloric acid liberates hydrogen telluride from it, and it is readily oxidised by nitric acid.[2]

$$[Zn]+[Te]\ (cryst.)=[ZnTe]\ (cryst.)+37{\cdot}22\ Cal.^{3}$$

Zinc Tellurate.—A thick white precipitate falls when zinc chloride and potassium tellurate solutions are mixed. It has not been obtained crystalline.[4]

ZINC AND CHROMIUM.

Zinc Chromite, $ZnO.Cr_2O_3$, is obtained by heating chromium trioxide and zinc oxide with boric acid,[5] or by heating potassium chromate in hydrogen or carbon dioxide containing zinc chloride vapour.[6]

Zinc chromite thus prepared consists of microscopic regular octahedra with a very dark green colour. They are harder than quartz, and their density at 15° C. is 5·29,[6] or 5·309 at 11° C.[5]

Acids do not attack it,[6] potassium bisulphate only with great difficulty,[5] but it is decomposed by fused potassium hydroxide and nitrate.[5, 6]

An insoluble violet zinc chromite, $8ZnO.3Cr_2O_3$, has been obtained by fusing zinc potassium chromate.[7]

A dark brownish-violet powder of *zinc thiochromite*, $ZnO.Cr_2S_3$, was prepared by heating zinc oxide with sulphur in a stream of hydrogen and then in sulphur vapour. It decomposes into greyish-green zinc chromite when heated in air.[8]

Zinc Chromate.—When solutions of zinc salts are precipitated with potassium or sodium chromate, basic zinc chromates or complex double salts are produced.[9]

The *anhydrous normal chromate*, $ZnCrO_4$, has been obtained as a fine light crystalline powder by heating zinc hydroxide with a dichromate solution containing a slight excess of chromic acid in a sealed tube at 220° C.[10] It was also obtained in microscopic citron-yellow prisms by heating equal weights of chromium trioxide and zinc carbonate with a little water in a sealed tube at 220° C., warming the precipitate formed with some concentrated chromic acid solution, and drying the washed residue over sulphuric acid.[1]

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[1] Kobayashi, *Mem. Coll. Sci. Eng. Kyoto*, 1911, 3, 217.

[2] Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 908.

[3] Fabre, *Compt. rend.*, 1887, 105, 277.

[4] Gutbier, *Zeitsch. anorg. Chem.*, 1902, 31, 349.

[5] Ebelmen, *Ann. Chim. Phys.*, 1851, [3], 33, 45.

[6] Viard, *Compt. rend.*, 1889, 109, 142.

[7] Gröger, *Monatsh.*, 1904, 25, 520.

[8] Gröger, *Jahresber.*, 1880, 311.

[9] Thomson, *Phil. Mag.*, 1828, [2], 3, 81; Malaguti and Sarzeau, *Ann. Chim. Phys.*, 1843, [3], 9, 431; Philippona and Prüssen, *Annalen*, 1869, 149, 92; Freese, *Ber.*, 1869, 2, 478; Gröger, *Monatsh.*, 1904, 25, 520; Briggs, *Zeitsch. anorg. Chem.*, 1908, 56, 254; Gröger, *ibid.*, 1907, 54, 189. The basic chromates $4ZnO.CrO_3.3H_2O$, $3ZnO.CrO_3.2H_2O$, $4ZnO.2CrO_3.3H_2O$, and $3ZnO.2CrO_3.H_2O$ have been identified by phase-rule methods (Gröger, *Zeitsch. anorg. Chem.*, 1911, 70, 139). For zinc chromates, basic and alkali, in the pigment industry, see Bock, *Kolloid Zeitsch.*, 1917, 20, 145.

[10] Schulze, *Zeitsch. anorg. Chem.*, 1895, 10, 154.

The *monohydrate*, $ZnCrO_4.H_2O$, was obtained in microscopic citron-yellow prisms by shaking 11 grm. zinc oxide with 50 c.c. of a 5-molar solution of chromic acid, filtering, and crystallising *in vacuo* over sulphuric acid.[2]

The anhydrous salt is insoluble in water, easily soluble in acids, and forms a greyish-yellow crystalline basic salt on boiling with water.[3] The monohydrate does not lose its water at 125° C., and cannot be converted by heat into the anhydrous salt (when the water is liberated it seems to hydrolyse the monochromate).[2]

The hydrated *tetrammoniate*, $ZnCrO_4.4NH_3.5H_2O$, has been prepared.[4]

The following *double chromates* and their *ammoniates* have been prepared: $K_2O.5ZnO.4CrO_3.6H_2O$;[5] $K_2O.4ZnO.3CrO_3.3H_2O$;[6] $K_2CrO_4.ZnCrO_4.2H_2O$;[7] $2(NH_4)_2CrO_4.4ZnCrO_4.3NH_3.3H_2O$;[8] and $(NH_4)_2CrO_4.ZnCrO_4.2NH_3$.[8, 9]

Zinc Dichromate.—The *trihydrate*, $ZnCr_2O_7.3H_2O$, is difficult to crystallise from its solutions,[10] but has been prepared by evaporating a solution of zinc carbonate in chromic acid under reduced pressure over sulphuric acid. It crystallises in hygroscopic, transparent orange crystals that dissolve easily in water. Boiling water only affects them slightly.[11, 12]

Dark red deliquescent crystals of the *trichromate*, $ZnO.3CrO_3.3H_2O$,[12] and the salt, $ZnCr_2O_7.2Hg(CN)_2.7H_2O$,[10] have been prepared.

ZINC AND MOLYBDENUM.

Zinc Molybdate, $ZnMoO_4$, is obtained in white needles, with a slight yellow tinge, by melting sodium molybdate, zinc chloride, and salt together. A reddish crystalline mass remained when it was melted in the blowpipe.[13]

The *monohydrate*, $ZnMoO_4.H_2O$, is obtained in crystalline clusters of white transparent needles by mixing solutions of zinc nitrate and ammonium molybdate and digesting the originally amorphous precipitate. It is slightly soluble in water, easily in dilute acids, and is attacked by alkalies.[14]

A dark grey powder of the composition $2ZnO.3MoO_2$ is obtained by fusing sodium trimolybdate with metallic zinc,[15] the compound ZnO.

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[1] Briggs, *loc. cit.*

[2] Gröger, *Zeitsch. anorg. Chem.*, 1911, 70, 135. The phases of the system $ZnO—CrO_3—H_2O$ vary with conditions.

[3] Schulze, *loc. cit.*

[4] Malaguti and Sarzeau, *Ann. Chim. Phys.*, 1843, [3], 9, 431.

[5] Philippona and Prüssen, *Annalen*, 1869, 149, 92.

[6] Freese, *Ber.*, 1869, 2, 476.

[7] Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185.

[8] Gröger, *ibid.*, 1908, 58, 416.

[9] Briggs, *Trans. Chem. Soc.*, 1903, 83, 394.

[10] Krüss and Unger, *Zeitsch. anorg. Chem.*, 1895, 8, 452.

[11] Schulze, *ibid.*, 1895, 10, 153.

[12] Gröger, *ibid.*, 1910, 66, 8.

[13] Schulze, *Annalen*, 1863, 126, 50.

[14] Coloriano, *Bull. Soc. chim.*, 1888, [2], 50, 451.

[15] Muthmann, *Annalen*, 1887, 238, 134.

$3MoO_3.10H_2O$ by melting zinc oxide and molybdic acid with sodium carbonate,[1] and crystalline $ZnO.H_2O.8MoO_3.14H_2O$ by mixing solutions containing equivalent quantities of zinc sulphate and ammonium tetramolybdate.[2] $(I_2O_5.2MoO_3).ZnO.16H_2O$ has been prepared.[3]

ZINC AND TUNGSTEN.

Zinc Tungstate, $ZnWO_4$, has been prepared by melting sodium tungstate with zinc chloride and common salt,[4] and by heating sodium paratungstate with zinc.[5]

The *monohydrate*, $ZnWO_4.H_2O$, falls as an amorphous precipitate when solutions of sodium tungstate and zinc acetate are mixed. One part dissolves in about 500 parts of water at 15° C. It remains white when dehydrated by heat.[6]

The *metatungstate*, $ZnO.4WO_3.10H_2O$,[7] the *paratungstate*, $5ZnO.12WO_3.37H_2O$,[8] the *tungstate*, $ZnO.2WO_3.3H_2O$,[6] and the *double tungstates*, $Na_2O.2ZnO.7WO_3.15$ (and 21) H_2O[9] and $(NH_4)_2O.2ZnO.7WO_3.13H_2O$,[10] have been prepared.

ZINC AND NITROGEN.

Zinc Nitride, Zn_3N_2, is obtained as a grey powder by heating zinc amide to a red heat—

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3.$$

Water acts so violently on it that it incandesces—

$$Zn_3N_2 + 6H_2O = 3Zn(OH)_2 + 2NH_3.^{11}$$

Small quantities of zinc nitride are formed between the poles of an electric arc maintained between zinc electrodes in an atmosphere of nitrogen,[12] and when zinc is heated strongly in nitrogen it is covered by a grey deposit that gives off a corresponding amount of ammonia with molten potassium hydroxide.[13]

Zinc dust absorbs nitrogen when heated in either nitrogen or ammonia. The most favourable temperature for absorption seems to be 600° C., but since zinc nitride begins to decompose below this temperature,[11] the zinc is only incompletely converted into nitride.[14] Distilled zinc may contain small quantities of nitride;[13] about 4 per cent.

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[1] Ullik, *Annalen*, 1867, **144**, 232.
[2] Wempe, *Zeitsch. anorg. Chem.*, 1912, **78**, 324.
[3] Chrétien, *Ann. Chim. Phys.*, 1898, [7], **15**, 358.
[4] Geuther and Forsberg, *Annalen*, 1861, **120**, 272.
[5] Hallopeau, *Compt. rend.*, 1904, **139**, 283.
[6] Lefort, *Ann. Chim. Phys.*, 1878, [5], **15**, 344.
[7] Scheibler, *J. prakt. Chem.*, 1861, [1], **83**, 273.
[8] Gonsalez, *ibid.*, 1887, [2], **36**, 44.
[9] Knorre, *Ber.*, 1886, **19**, 823.
[10] Lotz, *Annalen*, 1854, **91**, 62.
[11] Frankland, *Phil. Mag.*, 1858, [4], **15**, 149; *J. prakt. Chem.*, 1858, [1], **73**, 35. He said it was stable under heat.
[12] Arens, *Chem. Zentr.*, 1899, ii, 643.
[13] Briegleb and Geuther, *Annalen*, 1862, **123**, 237.
[14] White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1344. When zinc is heated in ammonia at temperatures below its melting-point (about 420° C.), its physical character changes and the ammonia is partly converted into nitrogen and hydrogen (Beilby and Henderson, *Trans. Chem. Soc.*, 1901, **79**, 1255).

of zinc nitride, determined by the ammonia liberated by boiling with aqueous potassium hydroxide, was found in some zinc dusts, and commercial fused zincs may contain traces of it.[1]

Zinc nitride has been said to be produced in small quantities by heating zinc and calcium carbide in the presence of air,[2] and when zinc is dissolved by electro solution—using an ammonium salt as solvent.[3]

Zinc Azide, $Zn(N_3)_2$, is a white sandy powder consisting of columnar crystals. Since it is hydrolysable it smells of azoimide in the air, and forms basic salts with water. It gives a clear solution, containing complex compounds, with azoimide or sodium azide. It detonates under a sharp blow, but is not more explosive than the alkaline earth azides.

It is prepared by acting upon metallic zinc with an ethereal solution of azoimide, but its hygroscopic character makes it difficult to obtain dry. One grm. of the azide evolves 0·360 Cal. on detonation.[4]

By dissolving zinc or freshly precipitated zinc hydroxide in azoimide, and by interaction between zinc sulphate and barium azide in dilute solution, slightly soluble, ill-defined anisotropic crystals of the basic salt, $Zn.N_3.OH$, were obtained.[5]

Zinc Amide, $Zn(NH_2)_2$, is a white amorphous powder obtained by leading dry ammonia gas through an ethereal solution of zinc ethyl. Ammonia is evolved from it by the action of water or alcohol. It is stable up to 200° C., and decomposes into zinc nitride and ammonia at a red heat.[6]

Hydrogen chloride converts it into the double chloride of ammonium and zinc, $2NH_4Cl.ZnCl_2$.[7]

Zinc Ammoniate, $Zn(NH_3)_2$, is said to be produced by the interaction of sodium, ammonia, and zinc oxide.[8]

Zinc Nitrite.—Colourless prismatic crystals of $Zn(NO_2)_2.2H_2O.C_6H_{12}N_4$ are obtained by adding sodium nitrite to the solution of a zinc salt containing hexamethylenetetramine.[9] Zinc nitrite also occurs in the hygroscopic yellow crystalline double salt, $3KNO_2.Zn(NO_2)_2.3H_2O$, obtained by acting with nitrous acid on zinc hydroxide suspended in potassium nitrite solution,[10] and in the similar salt, $2KNO_2.Zn(NO_2)_2.H_2O$, prepared by mixing solutions of potassium nitrite and zinc acetate or nitrate.[11] According to Rây, zinc nitrite can only exist pure and uncombined in dilute solutions. This solution is acid, and the nitrous acid set free by hydrolysis decomposes on concentration—

$$3HNO_2 = HNO_3 + 2NO + 2H_2O.$$

Zinc nitrate is thus continuously formed, and the residue from evaporation, even when conducted *in vacuo*, is a basic nitrate.[12]

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[1] Matignon, *Compt. rend.*, 1911, 152, 1309.

[2] Rossel, *ibid.*, 1895, 121, 942.

[3] Warren, *Chem. News*, 1887, 55, 156.

[4] Wöhler and Martin, *Ber.*, 1917, 50, 594.

[5] Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], 58, 292. For action of zinc on azoimide, also see Curtius and Darapsky, *ibid.*, 1900, [2], 61, 420.

[6] Frankland, *Phil. Mag.*, 1858, [4], 15, 149; *J. prakt. Chem.*, 1858, [1], 73, 35.

[7] Peltzer, *Annalen*, 1865, 134, 52.

[8] Wehl, *Pogg. Annalen*, 1850, 73, 350.

[9] Scagliarini, *Atti R. Accad. Lincei*, 1912, [5], 21, ii, 640.

[10] Rosenheim and Oppenheim, *Zeitsch. anorg. Chem.*, 1901, 28, 173.

[11] Lang, *J. prakt. Chem.*, 1862, [1], 86, 295; Hampe, *Annalen*, 1863, 125, 347.

[12] Rây, *Trans. Chem. Soc.*, 1917, 111, 160. Rây and Dhar (*ibid.*, 1913, 103, 13) have determined the conductivities of dilute solutions.

A dilute solution of zinc nitrite may be prepared by interaction between solutions of zinc sulphate and barium nitrite, but, though the *trihydrate*, $Zn(NO_2)_2.3H_2O$, is said to have been obtained from such a solution, only basic [1] or very impure zinc nitrites have usually been obtained.[2]

The *monohydrate*, $Zn(NO_2)_2.H_2O$, was said to be obtained in fine needles by treating a mixture of sodium nitrite and magnesium sulphate with alcohol, filtering, and evaporating *in vacuo*. The dry salt, its aqueous solution, and (more gradually) its alcoholic solution, give off nitrogen oxides and leave a mixture of zinc nitrate and hydroxide.[3] Vogel could not in this way obtain a salt with a higher ratio for $NO_2 : Zn$ than 1·76 : 1.[2]

Zinc Nitrate, $Zn(NO_3)_2$.—The anhydrous salt may be prepared by dehydrating the hydrated salt at 130°–135° C. in an atmosphere of nitrogen pentoxide. The pasty mass crystallises on cooling and dissolves in water with great evolution of heat.[4] According to Pierre,[5] the hexahydrate loses all its water at 105° C. in a current of dry air.

From solutions of zinc nitrate obtained by ordinary methods, the *hexahydrate*, $Zn(NO_3)_2.6H_2O$, crystallises at ordinary temperatures in transparent four-sided prisms.[6] It is deliquescent,[5, 7] has a density of 2·063 at 13° C. and 2·067 at 15° C.,[8] melts at 36·4° C.,[9] and is very soluble both in water [5, 7, 10] and alcohol.[5]

Its solubility varies from 44·63 parts of $Zn(NO_3)_2$ in every 100 parts of solution at $-18°$ C. to 63·63 parts at $+36°$ C.[11]

It loses half of its water at 100° C.,[7] but prolonged heating results in the formation of basic salts,[12] and if the heating is conducted *in vacuo* a mixture of zinc oxide and the trihydrate appears to remain.[13] It boils at 131° C., and remains clear till it loses 42 per cent. of its weight. The glassy mass then cools to crystalline $3Zn(NO_3)_2.ZnO.3H_2O$.[9] At higher temperatures it is completely converted into zinc oxide.[7]

On prolonged desiccation over sulphuric acid it loses half of its water and some nitric acid, a basic salt being left.[6]

Its *heat of solution* is $-5·840$ Cal.[14]

Between 34° C. and 36·4° C. it is transformed into the *trihydrate*, which crystallises in small needles when the hexahydrate is kept molten for some time at 37°–40° C., or when a solution of zinc nitrate, containing a little sulphuric acid, is concentrated on the water-bath and allowed to stand over sulphuric acid. The needles melt at 45·5° C. and quickly become the hexahydrate in the air.[1] The solubility of the trihydrate varies from 66·38 parts of anhydrous salt in every 100 parts of solution at 37° C. to 77·77 parts at 45·5° C.[2]

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[1] Lang, *J. prakt. Chem.*, 1862, [1], 86, 295; Hampe, *Annalen*, 1863, **125**, 347.

[2] Vogel, *Zeitsch. anorg. Chem.*, 1903, **35**, 400.

[3] Matuschek, *Chem. Ind.*, 1902, **25**, 705.

[4] Markétos, *Compt. rend.*, 1912, **155**, 213.

[5] Pierre, *Ann. Chim. Phys.*, 1846, [3], **16**, 247.

[6] Funk, *Zeitsch. anorg. Chem.*, 1899, **20**, 398.

[7] Graham, *Annalen*, 1839, **29**, 17.

[8] Laws, *Jahresber.*, 1877, 43.

[9] Ordway, *ibid.*, 1859, 113.

[10] For densities of solutions, see Oudemans, *Zeitsch. anal. Chem.*, 1868, **7**, 422; Franz, *J. prakt. Chem.*, 1872, [2], **5**, 292; Barnes and Scott, *J. Physical Chem.*, 1898, **2**, 536; Jones and Getman, *Zeitsch. physikal. Chem.*, 1904, **49**, 417 (also osmotic and conductivity data). For osmotic data, see Lescœur, *Ann. Chim. Phys.*, 1896, [7], **7**, 422. For optical data, see Dijken, *Zeitsch. physikal. Chem.*, 1897, **24**, 95.

[11] Funk, *Ber.*, 1899, **32**, 99.

[12] Vogel and Reischauer, *Jahresber.*, 1859, 196.

[13] Lescœur, *Ann. Chim. Phys.*, 1896, [7], **7**, 422.

[14] Thomsen, *Ber.*, 1878, **11**, 1022.

Zinc nitrate crystallises from its solutions at temperatures below about −17·5° C. as the *nonahydrate*. This is most easily obtained by cautiously melting the cryohydrate formed at −29° C.[1] Its solubility varies from 40·12 parts of anhydrous salt in 100 parts of solution at −25° C. to 43·59 parts at −18° C.[2]

Basic Zinc Nitrates.—The following have been described :—

(*a*) By evaporating zinc nitrate solutions or heating hydrated zinc nitrate (sometimes followed by treatment with water), $Zn(NO_3)_2.7ZnO.2H_2O$;[3] $3Zn(NO_3)_2.ZnO.3H_2O$;[4, 5] $4Zn(NO_3)_2.3ZnO.14H_2O$;[5] $Zn(NO_3)_2.3ZnO.3H_2O$;[6] $2Zn(NO_3)_2.7ZnO.Aq.$;[7] $Zn(NO_3)_2.2ZnO$.[8]

(*b*) By treating nitric acid with excess of zinc, $Zn(NO_3)_2.5ZnO.8H_2O$;[5, 9] $Zn(NO_3)_2.4ZnO.5H_2O$;[10] $Zn(NO_3)_2.3ZnO.4H_2O$.[11]

(*c*) By precipitating excess of zinc nitrate solution with ammonia, $Zn(NO_3)_2.7ZnO.4H_2O$.[3, 11, 12]

(*d*) By heating hydrated or basic zinc nitrates with water in sealed tubes, $Zn(NO_3)_2.5ZnO.7H_2O$;[9] $Zn(NO_3)_2.4ZnO.6H_2O$;[13] $HNO_3.2ZnO.H_2O$.[11]

(*e*) By heating zinc nitrate solution with zinc oxide, $Zn(NO_3)_2.ZnO.3H_2O$.[14]

Ammoniates.—André obtained the hydrated tetrammoniate, $3[Zn(NO_3)_2.4NH_3]+2H_2O$, from the solution prepared by passing an excess of ammonia gas into zinc nitrate solution. The deliquescent crystals are very soluble in a little water, and readily decomposed by excess with the precipitation of zinc oxide. The warm aqueous solution also dissolves zinc oxide, and $3Zn(NO_3)_2.10ZnO.4NH_3.18H_2O$, stable in air, insoluble in cold water and decomposed by hot, deposits from the filtered solution.[15]

Anhydrous $Zn(NO_3)_2.4NH_3$ is obtained by leading ammonia gas in excess through a saturated solution of zinc nitrate, adding alcohol, drying the precipitate, and finally warming it at 100° C. in a stream of ammonia.

It absorbs a quantity of ammonia gas at room temperature that closely corresponds to the formation of the *hexammoniate*, and only a little more ammonia is absorbed on cooling to −18° C. As the temperature is raised, evolution of gas commences distinctly at 30·5° C., and as the temperature rises further the *tetrammoniate* is formed, which decomposes at 206° C.[16]

The *double salt*, $3Zn(NO_3)_2.2Bi(NO_3)_3.24H_2O$, has been described.[17]

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[1] Funk, *Zeitsch. anorg. Chem.*, 1899, 20, 398.

[2] Funk, *Ber.*, 1899, 32, 99.

[3] Grouvelle, *Ann. Chim. Phys.*, 1821, [2], 19, 137.

[4] Ordway, *loc. cit.*

[5] Bertels, *Jahresber.*, 1874, 274.

[6] Gerhardt, *ibid.*, 1847–48, 436.

[7] Vogel and Reischauer, *loc. cit.*

[8] Ditte, *Ann. Chim. Phys.*, 1879, [5], 18, 335.

[9] Riban, *Compt. rend.*, 1892, 114, 1357.

[10] Terreil, *Bull. Soc. chim.*, 1892, [3], 7, 553.

[11] Athanasesco, *ibid.*, 1896, [3], 15, 1078.

[12] Stasevitch (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 354) says that probably no definite salt is formed.

[13] Rousseau and Tite, *Compt. rend.*, 1892, 114, 1185.

[14] Wells, *Amer. Chem. J.*, 1887, 9, 304.

[15] André, *Compt. rend.*, 1885, 100, 639.

[16] Ephraim, *Ber.*, 1919, 52, 961.

[17] Urbain and Lacombe, *Compt. rend.*, 1903, 137, 568.

ZINC AND PHOSPHORUS.

Zinc Phosphide.—Phosphides of zinc were obtained by heating zinc chloride in a stream of phosphine,[1] or by heating zinc with a salt containing phosphorus on charcoal in a blowpipe flame.[2]

Zn_3P_2 is obtained by heating an alloy of zinc and phosphorus in a crucible till no more phosphorus vapour is evolved. It can be freed from zinc by ignition *in vacuo* at 600° C., by treatment with mercury followed by volatilisation in a current of hydrogen at 400° C., or by fuming nitric acid, which dissolves the metal most rapidly.[3] It has also been prepared by (*a*) strongly heating a mixture of zinc oxide, phosphoric acid, and carbon ; [4] (*b*) heating vaporised zinc and phosphorus in an atmosphere of hydrogen ; [5] (*c*) strongly heating zinc sulphide with a phosphate and carbon ; [6] (*d*) passing phosphorus vapour over melted zinc ; [7] (*e*) heating zinc and phosphorus under pressure.[8]

It has been described as octahedral crystals of density 4·55 at 13° C.,[3] as prismatic crystals or needles,[5] as a steel-grey crystalline substance,[4] as compact, lead-coloured (losing its lustre in air), and of density 4·21 at 14° C.,[6] and as amorphous and pulverulent.[9]

Zn_3P_2 can be distilled in hydrogen at about 1100° C.[3] Hydrochloric and sulphuric acids act on it with the evolution of phosphine, and nitric acid dissolves it completely.[6] The reaction

$$Zn_3P_2+6HCl=3ZnCl_2+2PH_3$$

proceeds quantitatively.[3]

When the above phosphide was heated at 400° C. in phosphorus vapour, a brownish mass remained that contained ZnP_2 mixed with unaltered Zn_3P_2. The dark coloured ZnP_2 was isolated by hydrochloric acid, which acted much less readily on it than on Zn_3P_2. It was not crystalline, and its density at 15° C. was 2·97.[3]

Renault obtained fine needles of ZnP_2, varying from pale yellow to vermilion-red, by passing phosphorus vapour over zinc, zinc oxide, or zinc carbonate at a low red heat. ZnP_2 burns brightly in the air to zinc phosphate, and is rapidly attacked by nitric acid.[9] Sulphuric acid has little [9] or no [3] action upon it. It begins to dissociate at 500° C. into phosphorus and Zn_3P_2.[3]

The existence of ZnP and Zn_3P_4 is doubtful.[3]

Zinc Hydrophosphide.—White pulverulent ZnHP separates when dry phosphine is led into a cooled ethereal solution of zinc ethyl. Water decomposes it with the formation of zinc hydroxide and phosphine.[10]

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[1] Rose, *Pogg. Annalen*, 1832, **24**, 318.

[2] Wöhler, *Annalen*, 1840, **34**, 236.

[3] Jolibois, *Compt. rend.*, 1908, **147**, 801.

[4] Hooslef, *Annalen*, 1856, **100**, 101.

[5] Vigier, *Chem. News*, 1861, **3**, 273.

[6] Renault, *Ann. Chim. Phys.*, 1866, [4], **9**, 162.

[7] Hayer, *Chem. Zentr.*, 1876, 585.

[8] Emmerling, *Ber.*, 1879, **12**, 152.

[9] Renault, *Compt. rend.*, 1873, **76**, 283. According to Vigier (*loc. cit.*), the frequently noted reddish crystals are produced when crystals of zinc phosphide are oxidised to phosphate by oxygen without losing their shape. The colour is due to separated phosphorus.

[10] Drechsel and Finkelstein, *Ber.*, 1871, **4**, 352.

Zinc Hypophosphite can be prepared by dissolving distilled zinc in hypophosphorus acid.[1] When a moderately concentrated solution of the salt evaporates spontaneously, very efflorescent octahedra usually crystallise.[2] These crystals belong to the tetragonal system,[3] and have the composition $Zn(H_2PO_2)_2.6H_2O$.[3, 4]

The salt also crystallises in small rhombohedra that are stable in air.[5]

Zinc hypophosphite phenylhydrazine, $Zn(H_2PO_2)_2.2N_2H_3.C_6H_5$, has been prepared.[6]

Zinc Phosphite, $2ZnHPO_3.5H_2O$, is prepared by neutralising a solution of phosphorus trichloride in water with sodium carbonate and adding zinc sulphate at boiling heat. It is very soluble, does not alter over sulphuric acid, decomposes into $ZnHPO_3.2H_2O$ between 100° C. and 120° C., and loses all its water at 250° C. The anhydrous salt was also prepared by diluting a solution of the hydrated salt in free acid.[7]

Zinc Thiophosphite, $Zn_3(PS_3)_2$, is prepared by heating for twenty-four hours at a red heat a mixture of phosphorus, sulphur, and zinc. The clear yellow crystalline plates belong to the hexagonal system. Moist air decomposes them with evolution of hydrogen sulphide, and nitric acid acts on them readily.[8]

Zinc Orthophosphate.—The greyish-white mineral *hopeite*, $Zn_3(PO_4)_2.4H_2O$, of density 2·75–2·8 and hardness 2·5–3·9, crystallises in the orthorhombic system. It seems to occur in two modifications, and there is a parahopeite which is harder and denser than hopeite itself.[9]

Crystals resembling the naturally occurring substance are obtained by prolonged heating of zinc oxide with phosphoric acid and much water at 180° C.[10] This *tetrahydrate* has also been obtained in shining orthorhombic plates by heating a solution of zinc carbonate in phosphoric acid,[11] or making a 50 per cent. solution of phosphorus pentoxide in water, treating with zinc oxide, cooling in ice, adding ten volumes of ice-cold water, stirring, filtering, and stirring the filtrate on the water-bath.[12] Debray also obtained a crystalline product by prolonged digestion of a solution containing a zinc salt and an excess of sodium phosphate,[13] and Skey by adding a soluble phosphate to a solution of a zinc salt so that the solution remained acid.[14]

The tetrahydrate is easily soluble in acids and solutions of ammonia, ammonium carbonate, ammonium sulphate, and ammonium nitrate.[15]

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[1] Rose, *Ann. Chim. Phys.*, 1828, [2], 38, 271.
[2] Wurtz, *ibid.*, 1846, [3], 16, 195.
[3] Beckenkamp, *Zeitsch. Kryst. Min.*, 1903, 37, 620.
[4] Rammelsberg, *Ber.*, 1872, 5, 494.
[5] Wurtz, *Annalen*, 1846, 58, 53.
[6] Moitessier, *Bull. Soc. chim.*, 1899, [3], 21, 336.
[7] Rammelsberg, *Jahresber.*, 1867, 143.
[8] Ferrand, *Ann. Chim. Phys.*, 1899, [7], 17, 421.
[9] Spencer, *Min. Mag.*, 1908, 15, 1.
[10] Friedel and Sarasin, *Jahresber.*, 1892, i, 518. See Friedel, *Ber.*, 1876, 9, 734.
[11] Debray, *Annalen*, 1860, 115, 51 ; *Ann. Chim. Phys.*, 1861, [3], 61, 436.
[12] Eberley, Gross, and Cronell, *J. Amer. Chem. Soc.*, 1920, 42, 1433.
[13] Debray, *Compt. rend.*, 1864, 59, 40. Some acid phosphate may be co-precipitated (Heintz, *Annalen*, 1867, 143, 356).
[14] Skey, *Chem. News*, 1870, 22, 61.
[15] Heintz, *loc. cit.*

When it is heated to 190° C. it forms the *monohydrate*,[1] which has also been prepared by heating a solution of zinc carbonate in phosphoric acid to about 250° C.[2]

Rhombic prisms of *anhydrous* $Zn_3(PO_4)_2$, of density 3·998 at 15° C., and melting at a red heat, were obtained by dissolving the tetrahydrate in melted zinc chloride, or by heating it with a concentrated solution of zinc chloride in sealed tubes at 250° C.[3]

It absorbs hydrogen sulphide perceptibly at 100° C., rapidly at 160° C., and the absorption at any temperature is proportional to the square of the pressure.[4]

An amorphous *hexahydrate* has been obtained by the action of absolute alcohol on an acid phosphate of zinc.[5]

The *acid zinc orthophosphate*, $ZnHPO_4.H_2O$, occurs in small transparent needles which are monoclinic. $ZnHPO_4.3H_2O$ crystallises in sticky, thread-like, aggregative crystals, and $Zn(H_2PO_4)_2.2H_2O$ in transparent triclinic rhombohedra. These three salts, along with $Zn_3(PO_4)_2.4H_2O$, were identified during a study of the system zinc oxide—phosphoric oxide—water at 25° C. and 37° C.[6]

Graham described $ZnHPO_4.H_2O$ as very insoluble, losing its water on heating and becoming anhydrous when melted at a red heat.[7] According to Heintz,[8] Graham's method of precipitating zinc sulphate with ordinary sodium phosphate throws down $Zn_3(PO_4)_2.4H_2O$ mixed with a smaller proportion of $2ZnHPO_4.3H_2O$.

Zinc tetrahydrogen phosphate, $Zn(H_2PO_4)_2.2H_2O$, was prepared by dissolving zinc in an excess of aqueous phosphoric acid. It is easily soluble in hydrochloric acid, unchanged by alcohol or ether, and decomposed by excess of water into the insoluble $10ZnO.4P_2O_5.10H_2O$.[9]

The following *basic salts* occur naturally: *tarbuttite*, $Zn_3(PO_4)_2.Zn(OH)_2$;[10] *hibbenite*, $2Zn_3(PO_4)_2.Zn(OH)_2.6\frac{1}{2}H_2O$ and $Zn_3(PO_4)_2.Zn(OH)_2.3H_2O$.[11]

The basic salt $10ZnO.4P_2O_5.10H_2O$, obtained by the action of water on some of the acid phosphates, is a white crystalline powder, insoluble in water and easily soluble in dilute acids.[12]

Zinc Pyrophosphate, ZnP_2O_7.—The anhydrous salt, of density 3·7538–3·7574 at 23° C., remains when ammonium zinc orthophosphate, $NH_4.Zn.PO_4$, is ignited.[13] Under gradual heating in an open crucible this conversion is quantitative and can be used for the estimation of zinc. The pure substance is perfectly white, and any greyness indicates partial reduction. Ammonia, which is evolved during the ignition, begins to reduce it at 500° C.[14]

The *hydrated salt*, $2Zn_2P_2O_7.3H_2O$, is precipitated from a solution of zinc sulphate by sodium pyrophosphate as a white, amorphous mass. It can be obtained as a white crystalline powder from its solution in sulphurous acid. It melts in the blowpipe flame to a clear, transparent condition. If it is heated in a stream of hydrogen, metallic zinc and phosphoric acid sublime, some phosphine is evolved, and a white residue, containing zinc and phosphoric oxide, remains.

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[1] Friedel and Sarasin, *Jahresber.*, 1892, i, 518. See Friedel, *Ber.*, 1876, **9**, 734.

[2] Debray, *Annalen*, 1860, **115**, 51; *Ann. Chim. Phys.*, 1861, [3], **61**, 436.

[3] de Schulten, *Bull. Soc. chim.*, 1889, [3], **2**, 300.

[4] Colson, *Compt. rend.*, 1898, **126**, 1136.

[5] Reynoso, *Ann. Chim. Phys.*, 1855, [3], **45**, 109.

[6] Eberley, Gross, and Cronell, *J. Amer. Chem. Soc.*, 1920, **42**, 1433.

[7] Graham, *Annalen*, 1839, **29**, 23.

[8] Heintz, *ibid.*, 1867, **143**, 356.

[9] Demel, *Ber.*, 1879, **12**, 1171.

[10] Spencer, *Min. Mag.*, 1908, **15**, 1.

[11] Phillips, *Amer. J. Sci.*, 1916, [4], **42**, 275.

[12] Demel, *Ber.*, 1879, **12**, 1174.

[13] Lewis, *Jahresber.*, 1877, 45.

[14] Dakin, *Zeitsch. anal. Chem.*, 1900, **39**, 273. See also under Estimation of Zinc.

Both the crystalline and amorphous varieties dissolve in aqueous acids, alkalies, or ammonia, and give a syrupy mass with alcohol.[1]

An insoluble *pentahydrate*, $Zn_2P_2O_7.5H_2O$, has been prepared by dissolving a zinc salt in a solution of an alkaline pyrophosphate.[2]

When zinc pyrophosphate is heated with water an acid phosphate passes into solution and the tribasic phosphate is precipitated.[3]

The compound $3Zn_2P_2O_7.4NH_3.9H_2O$ has been prepared.[4]

Anhydrous crystalline **zinc metaphosphate**, $Zn(PO_3)_2$, is obtained by treating zinc oxide with excess of phosphoric acid, heating to redness, and cooling slowly. It is soluble only in hot sulphuric acid.[5]

The *tetrahydrate* is precipitated in transparent crystals from a solution of zinc chloride by ammonium metaphosphate. It is insoluble in water, but is decomposed on boiling.[6]

Bette [7] prepared a hydrated ammoniate of zinc metaphosphate.

Double Phosphates of Zinc.—The salts $NaZnPO_4$,[8] $Na_2O.ZnO.P_2O_5$,[9] $2Na_2O.ZnO.P_2O_5$,[9] $Na_2O.2ZnO.3P_2O_5$,[10] $KZnPO_4$,[8, 9, 11] $K_2O.ZnO.P_2O_5$,[8, 9] have been prepared.

$NaZnPO_4$ and $KZnPO_4$ can be precipitated from solutions of zinc salts by sodium or potassium phosphate. The original amorphous precipitates crystallise on standing. The water of crystallisation can be expelled by heating without decomposing the anhydrous salts, but since both salts are hydrolysable they are not suitable for estimating zinc.[12]

A number of other salts of the general formula $wNa_2O.uZnO.yP_2O_5.zH_2O$, and some of the general formula $wK_2O.uZnO.yP_2O_5.zH_2O$, have been reported.[13]

Ammoniates.—The following have been described: $2ZnO.P_2O_5.3NH_3.8H_2O$, $2ZnO.P_2O_5.2NH_3.4H_2O$, $6ZnO.3P_2O_5.4NH_3.4H_2O$, and $6ZnO.3P_2O_5.4NH_3.4H_2O$.[14]

Ammonium Zinc Orthophosphate.—The dihydrate, $NH_4.Zn.PO_4.2H_2O$, is precipitated from solutions of zinc salts by ammonium phosphate or by ordinary sodium phosphate in the presence of ammonium salts or ammonia. The anhydrous salt precipitates if the temperature is 80° C. or over.[1] In cold solutions the precipitate is flocculent, but it becomes crystalline on heating.[2]

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[1] Schwarzenberg, *Annalen*, 1848, 65, 151.
[2] Pahl, *Ber.*, 1873, 6, 1465; *Bull. Soc. chim.*, 1873, [2], 19, 115.
[3] Reynoso, *Ann. Chim. Phys.*, 1855, [3], 45, 108.
[4] Bette, *Annalen*, 1835, 15, 129.
[5] Fleitmann, *Pogg. Annalen*, 1849, 78, 350.
[6] Fleitmann, *ibid.*, 258; Tammann, *J. prakt. Chem.*, 1892, [2], 45, 421.
[7] Bette, *loc. cit.*
[8] Scheffer, *Annalen*, 1868, 145, 53.
[9] Ouvrard, *Compt. rend.*, 1888, 106, 1729.
[10] Fleitmann and Henneberg, *Annalen*, 1848, 65, 304.
[11] Grandeau, *Ann. Chim. Phys.*, 1886, [6], 8, 203.
[12] Finlay and Cumming, *Trans. Chem. Soc.*, 1913, 103, 1004.
[13] Pahl, *Ber.*, 1873, 6, 1465; 1874, 7, 478; Grandeau, *loc. cit.*; Ouvrard, *loc. cit.*; *Ann. Chim. Phys.*, 1889, [6], 16, 317; Tammann, *J. prakt. Chem.*, 1892, [2], 45, 417; Schwarz, *Zeitsch. anorg. Chem.*, 1895, 9, 249; Wiesler, *ibid.*, 1901, 28, 177.
[14] Rother, *Annalen*, 1867, 143; Schweikert, *ibid.*, 1868, 145, 57.

When the precipitate is dried at 100°–105° C. for several hours it has the composition $NH_4.Zn.PO_4$, and it suffers no loss by prolonged heating at this temperature. It is quantitatively converted into pyrophosphate of zinc by gradual heating in an open crucible.[3] It does not decompose at 130° C.,[4] but decomposition begins at 150° C., and ammonia is freely evolved at 200° C.[5]

One hundred c.c. of water at 17·5° C. dissolve 0·00145 grm. of $NH_4.Zn.PO_4$ ($Zn=0{\cdot}00053$ grm.) and 0·00224 grm. at boiling-point ($Zn=0{\cdot}00082$ grm.).[6]

The salt is completely hydrolysed by prolonged boiling with water into the normal phosphates of zinc and ammonium, and it is converted into zinc chloride by boiling with ammonium chloride.[7]

Zinc Thiophosphates.—Zinc *thio-orthophosphate*, $Zn_3(PS_4)_2$, is obtained by heating zinc chloride and phosphorus pentasulphide together. It is a white crystalline powder that, when heated in the absence of air, decomposes into phosphoric and zinc sulphides. It can be purified by dilute hydrochloric acid but dissolves in the concentrated acid.[8]

Pale yellow crystalline masses mixed with phosphorus pentasulphide are obtained by heating zinc, phosphorus, and sulphur together.[9] Zinc *thiohypophosphate*, $Zn_2P_2S_6$, was obtained in transparent yellow plates, apparently hexagonal, of density 2·2, by heating the above mixture in sealed tubes imbedded in iron tubes filled with sand.[10]

Though it is insoluble it slowly decomposes in water or moisture with the evolution of hydrogen sulphide. Nitric acid attacks it violently, but hydrochloric acid has no action.[11]

Zinc *thiopyrophosphate* has been prepared in small crystalline needles, rapidly decomposed by water or moist air, by a similar method.[12] The crystals are clear yellow, and are attacked violently by cold nitric acid.[11]

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[1] Bette, *Annalen*, 1835, 15, 129; Debray, *Compt. rend.*, 1864, 59, 40; Heintz, *Annalen*, 1867, 143, 361; Schweikert, *ibid.*, 1868, 145, 57. A *monohydrate* has been said to precipitate. See Finlay and Cumming, *Trans. Chem. Soc.*, 1913, 103, 1009. For best precipitation conditions, see under Estimation of Zinc.

[2] According to Garrigues (*J. Amer. Chem. Soc.*, 1897, 19, 937), when the precipitation is made by ammonium phosphate these two stages probably represent the two reactions—

$$ZnCl_2+(NH_4)_2HPO_4=ZnHPO_4+2NH_4Cl;$$
$$ZnHPO_4+(NH_4)_2HPO_4=Zn.NH_4.PO_4+2NH_4H_2PO_4.$$

According to Balareff (*Zeitsch. anal. Chem.*, 1921, 60, 442), the amorphous precipitate is also ammonium zinc phosphate, though zinc phosphate is co-precipitated if a hot acid solution containing zinc salt, ammonium chloride, and ammonium phosphate is precipitated with aqueous ammonia. See also Finlay and Cumming, *loc. cit.*, and under Estimation of Zinc.

[3] Dakin, *Zeitsch. anal. Chem.*, 1900, 39, 273.

[4] Winkler, *Zeitsch. angew. Chem.*, 1921, 34, 235.

[5] Finlay and Cumming, *loc. cit.*

[6] Artmann, *Zeitsch. anal. Chem.*, 1915, 54, 89.

[7] Artmann, *ibid.*, 1923, 62, 8.

[8] Glatzel, *Zeitsch. anorg. Chem.*, 1893, 4, 194.

[9] Friedel, *Compt. rend.*, 1894, 119, 262.

[10] Ferrand, *Bull. Soc. chim.*, 1895, [3], 13, 115.

[11] Ferrand, *Ann. Chim. Phys.*, 1899, [7], 17, 421.

[12] Ferrand, *Compt. rend.*, 1896, 122, 888.

ZINC AND ARSENIC.

Zinc Arsenide, Zn_3As_2, is prepared by melting zinc in arsenic vapour and hydrogen,[1] or by subjecting zinc and arsenic, in appropriate proportions, to a pressure of 6500 atmospheres.[2] It crystallises in octahedra or small needles,[1] and evolves arsine with dilute sulphuric acid.[2]

The *diarsenide* and *monarsenide*, $ZnAs_2$ and ZnAs, have been prepared by heating zinc and arsenic together in proper proportions. They are greyish, and dissolve in acids with the evolution of arsine. ZnAs is frequently used for preparing arsine.[3]

Heike, from a thermal study of the system Zn–As, concluded that only $ZnAs_2$ and Zn_3As_2 exist. Both are brittle, and melt at 771° C. and 1015° C. respectively.[4]

Zinc Arsenite.—A crystalline powder of normal zinc orthoarsenite, $Zn_3(AsO_3)_2$, precipitates at 100° C. when aqueous arsenious acid is added to a solution of zinc sulphate containing ammonia and ammonium chloride.[5] When precipitation occurs in the cold the precipitate rapidly crystallises into an aggregate of needles. A similar precipitate is thrown down by potassium arsenite from a solution of zinc chloride in 50 per cent. alcohol,[6] or from a solution of zinc sulphate by acid potassium arsenite, $K_2O.2As_2O_3$. Zinc arsenite dissolves readily in ammonia solution, acids, and solutions of ammonia salts.[7] It is also precipitated from zinc sulphate solutions by sodium metarsenite.[8]

A granular white powder of zinc *metarsenite*, $Zn(AsO_2)_2$, is obtained by dissolving arsenious acid in sodium hydroxide solution, making just acid to phenolphthalein with dilute sulphuric acid and adding hot zinc sulphate solution.[9]

Zinc Arsenates.—The *normal orthoarsenate* occurs naturally, as an *octahydrate*, as the pinkish mineral *köttigite*, $Zn_3(AsO_4)_2.8H_2O$. It crystallises in the monoclinic system with a density of 3·1 and a hardness of 2·5–3·0.

The *trihydrate*, $Zn_3(AsO_4)_2.3H_2O$, is precipitated from zinc sulphate solutions by trisodium arsenate.[10] The same substance is precipitated in a white voluminous form when excess of alkali is added to solutions of acid zinc phosphates in hydrochloric acid.[11]

The *anhydrous* salt has been prepared by heating zinc carbonate and a solution of arsenic acid to 200° C.,[12] and, in prismatic crystals of density 4·913 at 15° C., by fusing zinc chloride and arsenic acid.[13]

When the trihydrate remained in contact with a solution of arsenic acid for more than a year, the *metarsenate*, $Zn(AsO_3)_2$, was obtained from the filtered solution as a heavy white powder.[14]

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[1] Descamps, *Compt. rend.*, 1878, 86, 1022, 1065.
[2] Spring, *Ber.*, 1883, 16, 324.
[3] Vogel, *J. prakt. Chem.*, 1835, 6, 345.
[4] Heike, *Zeitsch. anorg. Chem.*, 1921, 118, 264.
[5] Bloxam, *J. Chem. Soc.*, 1862, 15, 281.
[6] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 21.
[7] Reichard, *Ber.*, 1894, 27, 1032.
[8] Reichard, *ibid.*, 1898, 31, 2167.
[9] Avery, *J. Amer. Chem. Soc.*, 1906, 28, 1163.
[10] Salkowski, *J. prakt. Chem.*, 1868, 104, 129.
[11] Demel, *Ber.*, 1879, 12, 1279.
[12] Friedel, *ibid.*, 1876, 9, 734.
[13] de Schulten, *Bull. Soc. chim.*, 1889, [3], 2, 300.
[14] Salkowski, *Ber.*, 1879, 12, 1446.

A precipitated jelly of the *acid orthoarsenate*, $ZnHAsO_4.H_2O$, is obtained by treating zinc with excess of arsenic acid solution, heating, and filtering at 100° C.,[1] or by mixing solutions of potassium dihydrogen arsenate and zinc sulphate in appropriate proportions.[2] The jelly gradually crystallises,[2] or forms crystals which are either rhombic or monoclinic if treated with hot water.[1] Small white tabular or needle-like crystals of this salt were prepared by dissolving zinc oxide in a solution of arsenic acid.[3] It has also been obtained by prolonged contact between zinc orthophosphate trihydrate and a solution of arsenic acid,[4] and by prolonged digestion at 100° C. of the precipitate obtained by adding ammonium arsenate to a solution of a zinc salt.[5]

The salt $5ZnO.2As_2O_5.4H_2O$, which lost one quarter of its water at 100° C., was obtained by precipitating zinc sulphate solution with sodium arsenate.[6]

The *basic salt* $4ZnO.As_2O_5.H_2O$ is produced when $ZnHAsO_4.H_2O$ is heated with water.[1] It occurs naturally as *adamine*.[7] This mineral crystallises in the orthorhombic system with a density of 4·35 and a hardness of 3·5. It is green, yellow, violet, or colourless, and is usually formulated as $Zn(Zn.OH)AsO_4$.

The following *double arsenates* have been described :—$NaZnAsO_4$, $Na_2ZnAs_2O_7$, $K_2Zn_2As_2O_8$,[8] and $NH_4.ZnAsO_4$.[9]

Yellow flocculent *zinc thioarsenate*, $Zn_3(AsS_4)_3$, has been prepared by interaction between zinc sulphate and sodium thioarsenate. The *double thioarsenate*, $NaZnAsS_4.4H_2O$, was also obtained in yellow crystals.[10]

ZINC AND ANTIMONY.

Zinc Metantimonate.—Alkaline antimonates precipitate solutions of zinc salts.[11] If an excess of a concentrated solution of a zinc salt is added to a boiling solution of sodium antimonate, zinc metantimonate, $ZnSb_2O_6.5H_2O$, precipitates.[12]

Thioantimony Salts of Zinc.—A dilute solution of potassium thioantimonite precipitates orange zinc thioantimonite, $Zn_3Sb_2S_6$, from a solution of a zinc salt. $KZnSbS_3$ results with an excess of a concentrated solution of the potassium salt.[13] Rammelsberg described zinc thioantimonate.[14]

ZINC AND CARBON.

Zinc Carbonate.—The normal carbonate, $ZnCO_3$, occurs naturally as *smithsonite*, which is also known as zinc spar or *calamine*.[15] A semi-crystalline scale of basic zinc carbonate, closely agreeing with the formula $ZnCO_3.3Zn(OH)_2$, has been found on rusted zinc.[1] Natural basic zinc carbonates, usually named *hydrozincite*, often approximate to the composition $ZnCO_3.2Zn(OH)_2$, but their constitution varies.[2] It has been suggested that smithsonite originated in interaction between calcium carbonate and zinc sulphate resulting from the oxidation of zinc blende.[3]

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[1] Coloriano, *Bull. Soc. chim.*, 1886, [2], 45, 709. According to Demel (*Ber.*, 1879, 12, 1279). $5ZnO.2As_2O_5.5H_2O$ is produced by the action of water on $ZnHAsO_4.H_2O$.

[2] Klemp and Gyulay, *Kolloid Zeitsch.*, 1918, 22, 57.

[3] Demel, *loc. cit.*

[4] Salkowski, *Ber.*, 1879, 12, 1446.

[5] Debray, *Compt. rend.*, 1864, 59, 40.

[6] Salkowski, *J. prakt. Chem.*, 1868, 104, 129.

[7] Friedel, *Compt. rend.*, 1866, 62, 692 ; Damour, *ibid.*, 1868, 67, 1124.

[8] Lefèvre, *ibid.*, 1890, 110, 405.

[9] Meade, *J. Amer. Chem. Soc.*, 1900, 22, 354.

[10] Preis, *Annalen*, 1890, 257, 201.

[11] Heffter, *Pogg. Annalen*, 1852, 86, 450.

[12] Ebell, *Ber.*, 1889, 22, 3044. According to Senderens (*Bull. Soc. chim.*, 1899, [3], 21, 47), the air-dried salt has 6 molecules of water, and loses four of them over sulphuric acid.

[13] Pouget, *Compt. rend.*, 1899, 129, 103.

[14] Rammelsberg, *Pogg. Annalen*, 1841, 52, 233.

[15] The name "calamine" has often been applied to mineral zinc silicates. Cf. *Trans. Chem. Soc.*, 1889, 55, 96. For analyses and descriptions, see Hilger, *J. Chem. Soc.*, 1880, 38, 857 ; Griffiths and Dreyfus, *Chem. News*, 1886, 54, 67 ; Eakens and Stokes, *Zeitsch. Kryst. Min.*, 1895, 24, 624 ; Miller, *Amer. Chem. J.*, 1899, 22, 218.

When solutions of zinc salts are precipitated by alkali carbonates or bicarbonates the product varies greatly in composition.[4] According to Kraut,[5] normal amorphous zinc carbonate is the first product when the carbonate solutions are poured into the solution of zinc sulphate. This is then converted into the stable crystalline *monohydrate*, $ZnCO_3.H_2O$, or into the *basic carbonate*, $5ZnO.2CO_2.4H_2O$. All other compounds described by other workers were mixtures of these two. Mikusch,[6] from a study of the system $ZnO-CO_2-H_2O$, decided that $5ZnO.2CO_2.4H_2O$ is the only chemically individual basic salt.

The basic carbonate only is formed when the zinc sulphate solution is added to the carbonate solution.[5]

The *monohydrate*, $ZnCO_3.H_2O$, was prepared in small quadratic optically active crystals, mechanically mixed with crystals of $Na_2O.3ZnO.4CO_2.3H_2O$, by allowing the precipitate from mixed solutions containing $ZnSO_4 : 4NaHCO_3$ to become crystalline under the mother-liquor.[5] The crystalline salt has also been obtained from a solution of zinc carbonate in ammonium carbonate.[7]

The *hemihydrate*, $2ZnCO_3.H_2O$, was obtained by precipitating the solution of a zinc salt with ammonium bicarbonate and digesting the gelatinous precipitate in excess of the precipitant till it became crystalline.[6]

The *basic zinc carbonate*, $5ZnO.2CO_2.4H_2O$, can be prepared by the direct hydrolysis of the normal carbonate,[6] or by boiling a solution of zinc, zinc hydroxide, or zinc carbonate in an excess of aqueous carbonic acid.[5]

Basic zinc carbonates can be converted into the normal carbonate by contact with water charged with carbon dioxide under pressure. The normal carbonate is itself somewhat soluble in water containing carbon dioxide presumably forming the bicarbonate.[8]

Crystals of the *monammoniate*, $ZnCO_3.NH_3$, are deposited from a solution of zinc carbonate in ammonium carbonate in rectangular prisms or stellate masses of needles.[1]

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[1] Moody, *Proc. Chem. Soc.*, 1903, **19**, 273.

[2] Terreil, *Compt. rend.*, 1859, **49**, 553; Cossa, *Ber.*, 1871, **4**, 412; Cesàro, *J. Chem. Soc.*, 1896, **70**, Abs. ii, 479.

[3] Piolti, *ibid.*, 1911, **100**, Abs. ii, 902.

[4] Boussingault, *Ann. Chim. Phys.*, 1825, [2], **29**, 284; Favre, *ibid.*, 1844, [3], **10**, 481; Lefort, *J. prakt. Chem.*, 1847, **41**, 126; Senármont, *Ann. Chim. Phys.*, 1850, [3], **30**, 139; 1851, [3], **32**, 154; Deville, *ibid.*, 1852, [3], **35**, 455; Rose, *ibid.*, 1854, [3], **42**, 106.

[5] Kraut, *Zeitsch. anorg. Chem.*, 1897, **13**, 1.

[6] Mikusch, *ibid.*, 1908, **56**, 365.

[7] Belar, *Zeitsch. Kryst. Min.*, 1890, **17**, 123.

[8] Smith, *J. Amer. Chem. Soc.*, 1918, **40**, 883 (study of system $ZnCO_3-CO_2-H_2O$). Amongst the various determinations of solubilities of precipitates formed from zinc salts and carbonates may be noted: Kremers, *Pogg. Annalen*, 1852, **85**, 248 (soluble in 20,895 parts of water at 15° C.); Terreil, *Compt. rend.*, 1868, **66**, 668 (soluble in aqueous ammonium salts except the sulphide); Wagner, *Zeitsch. anal. Chem.*, 1867, **6**, 169 (soluble in 188 parts of water saturated with carbon dioxide at 4–6 atmospheres); Immerwahr, *Zeitsch. Elektrochem.*, 1901, **7**, 477 (more soluble in water than the hydroxide and less than the sulphide).

Zinc Thiocarbonate.—Salmon-coloured prisms of the diammoniate of zinc thiocarbonate, $ZnCS_3.2NH_3$, were obtained by shaking an ammoniacal solution of zinc sulphate with carbon disulphide.[2]

Zinc Cyanide, $Zn(CN)_2$, is prepared by passing hydrogen cyanide into a solution of zinc acetate, or by precipitating solutions of zinc salts with solutions of alkali cyanides.[3]

It has been obtained in a reasonably pure condition by precipitation with carbonate-free alkali cyanide, washing the precipitate, dissolving in excess of the cyanide solution, filtering, and treating with a slight excess of sulphuric acid over the quantity required to decompose the alkali cyanide and liberate $Zn(CN)_2$.[4]

As ordinarily prepared it is an amorphous white powder,[5] though it can be obtained in orthorhombic prisms by arranging water, zinc acetate solution, and a solution of hydrogen cyanide in layers, ordered according to their density, in a tall jar.[5, 6]

It is insoluble in water,[5] though it is gradually hydrolysed,[4] insoluble in hydrocyanic acid, and perceptibly soluble in a solution of zinc acetate.[5, 6] It decomposes on heating [4, 7] and ammonia is evolved when it stands in the moist state.[4] Carbon dioxide slowly decomposes it in the presence of water,[8] and dilute acids dissolve it—readily when amorphous and slowly when crystalline.[5]

Its *heat of formation* from solid zinc and gaseous cyanogen is 29·3 Cal.,[5] and from its elements − 8·8 Cal.[6]

Prismatic crystals of $Zn(CN)_2.2NH_3.H_2O$, and transparent crystals of $Zn(CN)_2.2NH_3$, have been obtained by the action of ammonia upon zinc cyanide in the presence of water and alcohol respectively. Both substances are very soluble in alcohol or water, and are unstable.[9]

Precipitated zinc cyanide dissolves readily in solutions of alkali cyanides, and zinc sulphide is precipitated from these solutions by alkali sulphides.[10] When zinc cyanide dissolves in sodium cyanide, the salt $Na_2Zn(CN)_4$ is present in the solution. The same salt occurs in solutions obtained by acting with sodium cyanide solution on zinc oxide, or with aqueous caustic soda on excess of zinc cyanide.[4] From solutions of *sodium zinc cyanide* that are reasonably free from less soluble salts and free alkali, the *trihydrate*, $Na_2Zn(CN)_4.3H_2O$, can be crystallised in efflorescent orthorhombic crystals. This salt dissolves in less than half its own weight of water and is stable in air up to 105° C.[11]

Solutions of *potassium zinc cyanide* can be analogously prepared, and contain $K_2Zn(CN)_4$ in solution. The *anhydrous* salt can be crystallised from them in regular octahedra. They can be dried at 110° C. and withstand a temperature short of fusion. 100 c.c. of water at 20° C. dissolve 11 grm. of the salt, though there is a tendency to supersaturation. The solubility increases with the temperature. Carbon dioxide has almost no effect on the aqueous solution. The salt is nearly insoluble in alcohol and completely so in the other ordinary organic solvents.[1, 2]

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[1] Favre, *Ann. Chim. Phys.*, 1844, [3], **10**, 478.

[2] Hofmann, *Zeitsch. anorg. Chem.*, 1897, **14**, 277.

[3] Bette, *Annalen*, 1839, **31**, 214; Joannis, *Compt. rend.*, 1881, **92**, 1417; *Ann. Chim. Phys.*, 1882, [5], **26**, 500.

[4] Sharwood, *J. Amer. Chem. Soc.*, 1903, **25**, 570.

[5] Joannis, *Ann. Chim. Phys.*, 1882, [5], **26**, 500.

[6] Joannis, *Compt. rend.*, 1881, **92**, 1417.

[7] Cf. *Annalen*, 1847, **64**, 300.

[8] Naudin and Montholon, *Compt. rend.*, 1876, **83**, 345.

[9] Varet, *Ann. Chim. Phys.*, 1897, [7], **10**, 5.

[10] Wöhler, *Annalen*, 1854, **89**, 376.

[11] Hertz, *J. Amer. Chem. Soc.*, 1914, **36**, 912. According to Sharwood (*loc. cit.*) and Rammelsberg (*Pogg. Annalen*, 1837, **42**, 112), crystallised sodium zinc cyanide is hydrated $NaZn(CN)_3$.

Zinc Thiocyanate.—A white efflorescence of the *dihydrate* $Zn(CNS)_2.2H_2O$ has been obtained by treating zinc sulphate solution with an exact equivalent of barium thiocyanate and evaporating.[3] It is soluble in water and in alcohol.[4] The *diammoniate*, $Zn(CNS)_2.2NH_3$, is obtained by dissolving zinc oxide in ammonia and alkali thiocyanate solution.[5] The salts $K_2Zn(CNS)_4 3H_2O$,[6] $Cs_2Zn(CNS)_4 2H_2O$,[3] $Ag_2Zn(CNS)_4$,[3] $CsAgZn(CNS)_4.H_2O$,[7] $Cs_2AgZn(CNS)_5$,[7] $CsAg_3Zn_2(CNS)_8$,[7] and $CsAg_4Zn_2(CNS)_4$ [7] have been prepared.

The double thiocyanate of zinc and mercury, $ZnHg(CNS)_4$, has been used to estimate zinc.[8]

ZINC AND SILICON.

Zinc Silicide.—The solubility of silicon in zinc varies from 0·06 grm. in 100 grm. metal at 600° C. to 1·62 grm. at 850° C.,[9] but the two elements do not unite to form a silicide.[10]

When zinc sulphide and carbon are heated to 1300°–1400° C. in a quartz vessel in an atmosphere of nitrogen, volatile *ZnSiS* is formed. It can be condensed to hard brown crusts after heating zinc sulphide with silicon to 1300° C. This compound of zinc with silicon and sulphur polishes like a metal, and its sulphur is quantitatively evolved as hydrogen sulphide by the action of acids. Aqueous alkalies liberate hydrogen from it.[11]

Zinc Silicates. The *orthosilicate*, Zn_2SiO_4, occurs as *willemite* in hexagonal crystals of density 3·89–4·18 and hardness 5·5.[12] In *troostite* the zinc is partly replaced by manganese. Hydrated or basic zinc silicates also occur as minerals.[13] *Calamine* [14] or *hemimorphite* is often formulated as $(Zn.OH)_2SiO_3$; it crystallises with a density of 3·45 and a hardness of 4·5–5 in the orthorhombic system.

A solution of sodium silicate, Na_2SiO_3, precipitates an amorphous zinc silicate from a solution of zinc sulphate; it is liable to contamination by zinc hydroxide if the sodium silicate solution is excessively alkaline. Small, clear rhombic crystals of $ZnSiO_3$ were obtained by

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[1] Sharwood, *loc. cit.*

[2] Rammelsberg, *Pogg. Annalen*, 1837, 42, 112.

[3] Wells, *Amer. Chem. J.*, 1902, 28, 268.

[4] Meitzendorff, *Pogg. Annalen*, 1842, 56, 74.

[5] Fleischer, *Annalen*, 1875, 179, 233.

[6] Walden, *Zeitsch. anorg. Chem.*, 1900, 23, 374.

[7] Wells, *loc. cit.*, 278.

[8] See under Estimation of Zinc.

[9] Moissan and Siemens, *Compt. rend.*, 1904, 138, 660.

[10] Vigouroux, *Ann. Chim. Phys.*, 1897, [7], 12, 157; Winkler, *J. prakt. Chem.*, 1864, 91, 193.

[11] Fraenkel, *Metallurgie*, 1909, 6, 682.

[12] Rinne, *Zeitsch. physikal. Chem.*, 1895, 16, 536; Retgers, *ibid.*, 1895, 16, 623.

[13] Monheim, *Jahresber.*, 1847–48, 1187; Collie, *Trans. Chem. Soc.*, 1889, 55, 90.

[14] See under Zinc Carbonate.

igniting the dried precipitate with boric acid and lixiviating the residue with water. They were insoluble in acids and isomorphous with enstatite, $MgSiO_3$.[1] Ebelmen[2] obtained two mixed crystalline products by heating a mixture of silica and zinc oxide.

Artificial willemite has been prepared by the action of silicon fluoride on zinc oxide, or of zinc fluoride on silica at a white heat.[3] When zinc sulphate was heated with an alkali sulphate and hydrated silica, and the fused mass treated with water, the residue contained birefractive crystals of Zn_2SiO_4 in the form of hexagonal prisms of density 4·25 and hardness 5·5.[4]

The heats of formation of Zn_2SiO_4 and $ZnSiO_3$ have been given as −23·74 and +2·49 Cal. respectively.[5]

ZINC AND BORON.

Zinc Borates.—Anhydrous $3ZnO.B_2O_3$, or zinc *orthoborate*, $Zn_3(BO_3)_2$, has been prepared by fusing zinc oxide with molecular proportions of potassium hydrogen fluoride and boron trioxide and treating with cold water. The flattened prismatic crystals belong to the rhombic system and act markedly on polarised light. They dissolve in acids, and hot water acts upon them to leave an amorphous residue that consists largely of zinc oxide.[6]

The compound $3ZnO.2B_2O_3$ has been obtained from the fusion of zinc oxide and boron trioxide.[7] The crystals are triclinic.[8]

Precipitates of the general formula $xZnO.yB_2O_3.zH_2O$, varying in composition, have been obtained by the action of boric acid on zinc carbonate, or by precipitating solutions of zinc salts with borax.[9]

The largest yield of zinc borate is obtained by adding a concentrated solution of a zinc salt to a slight excess of saturated borax solution, or by using a supersaturated solution of borax or solid borax as precipitant.

Precipitation is more complete if a little sodium hydroxide is added, though sodium zincoxide gives no precipitate with borax.[10]

Zinc Perborate.—An amorphous, flocculent substance, containing 9·5 per cent. of active oxygen, is prepared by interaction between solutions of sodium perborate and a zinc salt. The same product is also obtained by triturating moist hydrated zinc peroxide with boric acid, or, most effectively, by treating a solution of a zinc salt and boric acid with sodium peroxide.[11]

DETECTION AND ESTIMATION OF ZINC.

Detection.—Zinc is usually detected, in the first instance, by precipitation as sulphide in ammoniacal solution. Its chloride is soluble, the sulphide does not precipitate in acid solution unless the acidity is slight, and ammonia does not precipitate the hydroxide in the presence of ammonium chloride.

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[1] Traube, *Ber.*, 1893, **26**, 2735.

[2] Ebelmen, *Ann. Chim. Phys.*, 1851, [3], **23**, 61.

[3] Daubrée, *J. prakt. Chem.*, 1854, **63**, 1; Deville, *Compt. rend.*, 1861, **52**, 1304.

[4] Gorgeu, *ibid.*, 1887, **104**, 120.

[5] Mulert, *Zeitsch. anorg. Chem.*, 1912, **75**, 219.

[6] Ouvrard, *Compt. rend.*, 1900, **130**, 335.

[7] Guertler, *Zeitsch. anorg. Chem.*, 1904, **40**, 242.

[8] Mallard, *Compt. rend.*, 1887, **105**, 1260.

[9] Rose, *Pogg. Annalen*, 1853, **88**, 289; Büscher, *Annalen*, 1869, **151**, 234; Ditte, *Ann. Chim. Phys.*, 1883, [5], **30**, 256.

[10] Borchers, *Zeitsch. anorg. Chem.*, 1910, **68**, 269.

[11] *J. Chem. Soc.*, 1906, **90**, Abs. ii, 448.

Sodium and potassium hydroxides precipitate gelatinous zinc hydroxide from solutions of zinc salts and then redissolve it. Ammonia behaves similarly, redissolving the hydroxide to a complex soluble salt. The alkali carbonates precipitate a white basic carbonate, and ammonium carbonate gives a precipitate soluble in excess.

Potassium cyanide precipitates white zinc cyanide that dissolves in excess of the reagent. Hydrogen sulphide precipitates white zinc sulphide both from this solution and from solutions of the hydroxide in alkalies or ammonia.

Potassium ferrocyanide precipitates white zinc ferrocyanide, and potassium ferricyanide precipitates brownish zinc ferricyanide which dissolves in ammonia or fairly concentrated hydrochloric acid.

Sodium phosphate and potassium oxalate both give precipitates with solutions of zinc salts.[1] No precipitate is given by sodium thiosulphate or sulphite.

Zinc oxide goes yellow when hot and becomes white again on cooling. The green colour obtained by heating a zinc salt with cobalt nitrate solution on a charcoal block is often a convenient test for zinc.

Potassium periodate gives a white precipitate with solutions of zinc salts. Ammonium chloride and ammonia prevent precipitation in the cold but not on boiling.[2]

Small quantities of zinc can be detected by the blue colour given with resorcinol by ammoniacal solutions of zinc salts;[3] this method has been applied to the colorimetric estimation of the metal.[4] The formation of crystalline $Ca(O.Zn.OH)_2.4H_2O$ by boiling a zinc salt with lime-water and excess of ammonia is said to detect 1 part of zinc in 500,000 parts of water.[5] Electrolysis in the presence of $N/10$ potassium hydroxide on to a copper wire cathode is said to be a delicate test for zinc. The deposit can be tested with $2N$ potash.[6] The salmon-coloured crystals of zinc nitroprusside, which form rectangular plates and prisms, have been used as a microchemical test for this metal.[7]

Estimation.—In estimating zinc it is frequently precipitated as *sulphide*. Zinc sulphide can be completely precipitated from dilute solutions of zinc salts slightly acidified with mineral acid.[8] Its colloidal habits make it notoriously difficult to filter or handle,[9] but it can be precipitated in a granular form, amenable to rapid filtration and washing, by confining the range of hydrogen ion concentration between 10^{-2} and 10^{-3}, and working at a temperature of 95°–100° C. on solutions containing 0·1 per cent. of zinc. A high concentration of the ammonium salt of a strong acid is a favouring condition. Ammonium citrate and a solution containing ammonium sulphate, ammonium formate, and formic acid can be used to secure an appropriate range of hydrogen ion concentration.[1] A good precipitation is also obtained at 80° C. under slight pressure in the presence of a little free formic acid.[2] Zinc sulphide is also precipitated quantitatively in a readily filterable form from boiling solutions containing benzenesulphonic acid.[3]

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[1] No precipitation occurs in the presence of ammonium chloride and excess of ammonia (Wester, *J. Chem. Soc.*, 1920, **118**, Abs. ii, 334).

[2] Benedict, *Amer. Chem. J.*, 1905, **34**, 581.

[3] Campo, *J. Chem. Soc.*, 1909, **96**, Abs. ii, 439; 1910, **98**, Abs. ii, 1111.

[4] Cerdan and Pianti, *ibid.*, 1913, **104**, Abs. ii, 246.

[5] Javillier, *Compt. rend.*, 1906, **143**, 900.

[6] Neumann, *Zeitsch. Elektrochem.*, 1907, **13**, 751. Nitrates and chlorides should be absent.

[7] Bradley, *Amer. J. Sci.*, 1906, [4], **22**, 326.

[8] Urbasch, *J. Chem. Soc.*, 1922, **122**, Abs. ii, 317.

[9] Tamm, *Chem. News*, 1871, **24**, 148.

According to Houben,[4] hydrogen sulphide completely precipitates zinc sulphide from solutions of its sulphate if the concentration of the salt is less than 0·2*N*. The corresponding concentration for the chloride is 0·067*N*. Increased pressure increases the effectiveness of precipitation by hydrogen sulphide.[5]

Zinc sulphide can be precipitated in a filterable condition by heating the strongly ammoniacal solution, containing about 0·5 grm. zinc per 100 c.c., to 60° C. or 80° C. and adding ammonium sulphide in slight excess. After boiling the mixture for a few moments the precipitate is filtered off and washed with dilute ammonium sulphide.[6]

When the zinc has been precipitated as sulphide it can be variously treated to complete the estimation. The dried sulphide can be ignited, mixed with sulphur, in a current of hydrogen and weighed as sulphide.[7] It can also be directly ignited to oxide and weighed in that form. If the sulphide has been collected on paper the dried precipitate can be ignited, without any preliminary separation from the filter, in a shallow, open porcelain crucible, or in a platinum crucible at a temperature that at first does not exceed a red heat. When the filter is completely burnt the precipitate must be heated above 935° C. to decompose zinc sulphate.[8]

Zinc can be estimated as *anhydrous zinc sulphate*. The zinc salt is evaporated with sulphuric acid, heated at 500° C. for fifteen minutes, cooled, treated with a little water, evaporated and re-ignited. Zinc sulphate does not dissociate below 675° C. It can also be converted into oxide over a blast-flame.[9] This is a convenient method of final treatment when zinc has been precipitated as sulphide.[10]

Zinc sulphide has also been shaken with excess of silver nitrate solution—

$$ZnS+2AgNO_3=Ag_2S+Zn(NO_3)_2.$$

After filtering off the silver sulphide the excess of silver is estimated.[11]

The sulphide can also be dissolved in hydrochloric acid and converted into oxide by evaporation to dryness and heating with yellow mercuric oxide.[12]

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[1] Fales and Ware, *J. Amer. Chem. Soc.*, 1919, 41, 487.

[2] Waring, *ibid.*, 1904, 26, 26.

[3] Schilling, *Chem. Zeit.*, 1912, 36, 1352.

[4] Houben, *Ber.*, 1919, 52B, 1613.

[5] Bruni and Padoa, *Atti R. Accad. Lincei*, 1905, [5], 14, ii, 525; Padoa and Cambi, *ibid.*, 1906, [5], 15, ii, 787.

[6] Seeligmann, *Zeitsch. anal. Chem.*, 1914, 53, 594.

[7] According to Thiel (*Zeitsch. anorg. Chem.*, 1902, 33, 1), it should be ignited in hydrogen sulphide.

[8] Bornemann, *ibid.*, 1913, 82, 216.

[9] Gutbier and Stair, *Zeitsch. anal. Chem.*, 1922, 61, 97. *Cf.* Euler, *Zeitsch. anorg. Chem.*, 1900, 25, 146; Sullivan and Taylor, *J. Ind. Eng. Chem.*, 1909, 1, 476.

[10] Fales and Ware, *J. Amer. Chem. Soc.*, 1919, 41, 494.

[11] Enell, *Zeitsch. anal. Chem.*, 1915, 54, 537.

[12] Treadwell, *Analytical Chemistry* (translated by Hall) (Chapman & Hall, London), 1911, ii, 142.

The cold solution of zinc chloride can also be precipitated by adding sodium carbonate solution, drop by drop, till the zinc solution becomes turbid. By then bringing the solution to the boil granular zinc carbonate precipitates. Enough sodium carbonate is next added to make phenolphthalein distinctly pink. The precipitate is filtered hot, washed with hot water and ignited to the oxide. The precipitate should be detached from the paper. Zinc should be *precipitated as carbonate* from its chloride solutions because basic zinc sulphate is co-precipitated if sulphions are present, and in the absence of ammonium salts because they prevent precipitation.[1]

Carnot [2] adds a slight excess of sodium carbonate, redissolves in just enough ammonia or ammonium carbonate, and boils.

Zinc is often estimated volumetrically in the presence of ammonium salts by precipitation with standard sodium sulphide solution. A standard solution of zinc is treated similarly to the sample and also titrated. From the relative volumes of the sodium sulphide required respectively for the standard zinc solution and the sample, the zinc in the latter can be simply calculated. In the original *Schaffner method* the end-point was indicated by the blackening of flocculent ferric hydroxide introduced into the solution. In expert hands the process gives ready results with an accuracy sufficient for many commercial purposes, but it requires practice.

Attempts have been made to substitute a better indicator than the ferric hydroxide. Ballard determined the end-point by the darkening of a silver plate, used as an external indicator; Kopenhague used a strip of filter paper impregnated with cadmium nitrate, and Hassreidter employed a lead salt similarly.[3]

It is usually considered that the success of the process depends upon identical conditions in both standard and sample.[4]

Zinc can be *titrated* in acid solution with *potassium ferrocyanide*. As in the Schaffner method, it is usual to titrate two solutions, one containing the sample and the other a known quantity of zinc that has been subjected to the same treatment and brought to the same condition as the zinc under analysis. The composition of the precipitate formed is different according to whether potassium or sodium ferrocyanide is used for titration.[5, 6]

The electrometric method of determining the end-point has been applied to this titration,[7] and is said to be trustworthy.[8] According to Treadwell and Chervet,[5] zinc salts can be readily titrated with potassium ferrocyanide in neutral or weakly acid solution if the end-point is sharpened by the presence of a little cæsium salt. Rubidium salts are less effective.

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[1] Treadwell, *loc. cit.*

[2] Carnot, *Compt. rend.*, 1918, 166, 245.

[3] Kopenhague, *Ann. Chim. anal.*, 1911, 16, 10; Ballard, *J. Soc. Chem. Ind.*, 1897, 16, 399; Hassreidter, *Zeitsch. angew. Chem.*, 1908, 21, 66.

[4] Huybrechts, *Bull. Soc. chim.*, 1907, 21, 121; Pattinson and Redpath, *J. Soc. Chem. Ind.*, 1905, 24, 228. Hassreidter (*Zeitsch. anal. Chem.*, 1917, 56, 506) has discussed the Schaffner method. See also Urbasch, *J. Chem. Soc.*, 1922, 122, Abs. ii, 317; Olivier, *Bull. Soc. chim. Belg.*, 1922, 31, 102.

[5] Treadwell and Chervet, *Helv. Chim. Acta*, 1922, 5, 633.

[6] For discussion of the method, see Springer, *Zeitsch. angew. Chem.*, 1917, 30, i, 173; Urbasch, *J. Chem. Soc.*, 1922, 122, Abs. ii, 317.

[7] Bichowsky, *ibid.*, 1917, 112, Abs. ii, 219; Treadwell and Weiss, *J. Soc. Chem. Ind.*, 1920, 39, 137A.

[8] Müller, *Zeitsch. angew. Chem.*, 1919, 32, 351.

The usual method has been to titrate in hydrochloric acid solution, using uranium acetate as (external) indicator.[1] The titration has been done in ammoniacal solution in the presence of ferric tartrate. Acetic acid can be used as an external indicator to give a blue colour.[2]

Rupp[3] precipitates with excess of potassium ferrocyanide, adds excess of iodine solution, and finally titrates with sodium thiosulphate.

Zinc can be precipitated in the presence of ammonium salts as *ammonium zinc phosphate*, and this excellent method of estimation is now much used. The final determination can be made by weighing the $NH_4.Zn.PO_4$ after washing and drying at 100° C. or a rather higher temperature, as originally suggested,[4] or igniting it to zinc pyrophosphate,[5] or by titration with standard acid—

$$NH_4.Zn.PO_4+H_2SO_4=ZnSO_4+NH_4H_2PO_4.$$

In the last method the well-washed precipitate is treated with excess of standard acid and titrated back with standard alkali—using methyl orange as indicator.[6]

The procedure of precipitation must secure a pure precipitate and avoid its marked tendency to adhere to the walls of the precipitating vessel. Since the precipitate is soluble in both acid and ammonia, the precipitation must be effected in solutions that are either neutral or only slightly acid or ammoniacal.

A pure non-adherent precipitate can be secured by heating the slightly acid solution containing the zinc salt and some ammonium chloride, and precipitating with about ten times as much ammonium phosphate as there is zinc present. The amorphous precipitate rapidly becomes crystalline, and may be filtered off after a quarter of an hour on the water-bath and a short period for settling.[7]

Balareff adds ammonia to the slightly acid solution containing ammonium chloride and ammonium phosphate until it is slightly *alkaline* to litmus. The mixture is kept at ordinary temperature for eighteen hours and heated for fifteen minutes on the water-bath before filtering.[8]

Artmann heats the *neutral* solution to 70° C. and treats with excess of diammonium phosphate. Two grm. of ammonium chloride are previously added for every 0·1 grm. of zinc present, and the precipitated solution is kept at 70° C. for fifteen minutes.[9]

If the solution is too acid, the ammonium zinc phosphate, in addition to the risk of incomplete precipitation, may be contaminated with a basic phosphate or zinc hydroxide, or, if sodium is present, with sodium zinc phosphate. When *sodium salts are present*, 10 grm. of ammonium chloride should be added to prevent any precipitation of sodium, and double precipitation. with addition of 5–10 grm. ammonium chloride before each precipitation, is necessary in the presence of *potassium salts*.[1]

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[1] Miller and Hall, *School Mines Quart.*, 1899, 21, 267; Waring, *J. Amer. Chem. Soc.*, 1904, 26, 4.

[2] Austin and Keane, *Analyst*, 1912, 37, 238.

[3] Rupp, *Arch. Pharm.*, 1903, 241, 331.

[4] Tamm, *Chem. News*, 1871, 24, 148.

[5] Löseckann and Meyer, *Chem. Zeit.*, 1886, 10, 729; Clark, *J. Soc. Chem. Ind.*, 1896, 15, 867; Garrigues, *J. Amer. Chem. Soc.*, 1897, 19, 937; Austin, *Amer. J. Sci.*, 1899, 8, 206. See also under Ammonium Zinc Phosphate.

[6] Walker, *J. Amer. Chem. Soc.*, 1901, 23, 468. Artmann and Brandis (*Zeitsch. anal. Chem.*, 1910, 49, 1) have suggested an iodometric titration.

[7] Dakin, *Zeitsch. anal. Chem.*, 1900, 39, 273.

[8] Balareff, *ibid.*, 1921, 60, 442. If ammonia is added to the hot solution some zinc phosphate is co-precipitated.

[9] Artmann, *Zeitsch. anal. Chem.*, 1915, 54, 89.

The precipitate is washed with a hot 1 per cent. solution of ammonium phosphate, then with cold water and aqueous alcohol.[2] Water saturated with ammonium zinc phosphate may be used for washing,[3] or water may be used and a correction of +0·0005 grm. zinc applied for every 100 c.c. of wash-water used.[4]

Artmann has recently recommended neutralisation of the ammoniacal solution at 60° C. or 70° C. with nitric acid. If enough ammonium phosphate is present a slight excess of the acid is not harmful, and 1 or 2 grm. of sodium acetate can be added if necessary. The concentration of ammonium ion, other than phosphate, should not exceed normality, and the concentration of ammonium phosphate after precipitation should be at least 0·2*N*. After precipitating the zinc the solution should be heated to incipient boiling and kept on a water-bath for twenty minutes.[5]

The solubility of zinc ammonium phosphate in excess of ammonia can be used to separate zinc from magnesium and manganese, which are precipitated, and its solubility in excess of acetic acid to separate zinc from iron and aluminium, which are also precipitated under these conditions.[6]

Zinc can be estimated by precipitating *zinc ammonium arsenate*, $NH_4.Zn.AsO_4$, from ammoniacal solutions of zinc salts with sodium arsenate, making acid with acetic acid, heating and stirring, filtering off, dissolving the precipitate in dilute hydrochloric acid, adding potassium iodide, and finally titrating with sodium thiosulphate.[7]

Zinc can be estimated in alloys by precipitation, in acid solution, with potassium thiocyanate and mercuric chloride. The precipitate of *zinc mercury thiocyanate* is dried at 100°–108° C. and weighed. The precipitate can also be dissolved in dilute nitric acid containing iron alum and the thiocyanate determined volumetrically.[8]

A trustworthy volumetric method is based on the reaction

$$ZnHg(CNS)_4+6KIO_3+12HCl=ZnSO_4+HgSO_4+2H_2SO_4+4HCN \\ +6ICl+6KCl+2H_2O.$$ [9]

The composition of the dried precipitate is probably $ZnHg(CNS)_4$,[9] and not $ZnHg(CNS)_4.H_2O$.[8]

The method was first used by Clève.[10]

Zinc can be separated from magnesium and the alkaline earth metals by precipitation as white $Zn(Py)_2(CNS)_4$ with ammonium thiocyanate and pyridine.[11]

The metallic content of zinc dust can be evaluated by allowing it to reduce iron-alum solution and titrating the ferrous iron with potassium permanganate.[1]

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[1] Finlay and Cumming, *Trans. Chem. Soc.*, 1913, **103**, 1004. They say that precipitation in alkaline solution gives inaccurate results.

[2] Dakin, *loc. cit.*

[3] Winkler, *Zeitsch. angew. Chem.*, 1921, **34**, 235.

[4] Artmann, *Zeitsch. anal. Chem.*, 1915, **54**, 89.

[5] Artmann, *ibid.*, 1923, **62**, 8.

[6] Luff, *Chem. Zeit.*, 1922, **46**, 365.

[7] Meade, *J. Amer. Chem. Soc.*, 1900, **22**, 354.

[8] Lundell and Bee, *Amer. Inst. Met.*, 1914, 146.

[9] Jamieson, *J. Amer. Chem. Soc.*, 1918, **40**, 1036.

[10] Clève, *Jahresber.*, 1864, 305. See also Cohn, *Ber.*, 1901, **34**, 3502; Koninck and Grandry, *Chem. Zentr.*, 1902, ii, 822.

[11] Spacu, *ibid.*, 1923, **94**, ii, 508.

The gasometric method of estimating the zinc by the hydrogen evolved by the action of acid is used commercially.[2]

A turbidimetric method has been devised for estimating small quantities of zinc. The metal is obtained as the oxide, converted into the chloride, and treated with silver nitrate solution. The estimation is completed by comparing the opalescence with that obtained from a standard.[3]

Zinc is a very difficult metal to estimate electrolytically. Many methods have been devised to secure complete precipitation of the metal in a pure and sufficiently adherent form, but the precipitation of zinc as zinc ammonium phosphate is as accurate as any electrolytic process, and much more reliable.[4]

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[1] Edwards, *Chem. Met. Eng.*, 1919, 21, 192.

[2] Berl and Jurrisseu, *Zeitsch. angew. Chem.*, 1910, 23, 248; Beyne, *Ann. Chim. anal.*, 1921, 3, 360.

[3] Winkler, *Zeitsch. angew. Chem.*, 1913, 36, 38.

[4] See under Electrodeposition.

CHAPTER V.

CADMIUM AND ITS COMPOUNDS.

CADMIUM.

Symbol, Cd. Atomic Weight, 112·41 (O=16).

Occurrence.—Cadmium has not been found in a free state and seldom as a mineral. The rare mineral *greenockite* is cadmium sulphide, CdS, but the chief source of the metal is from zinc ores containing cadmium as an impurity.

Otavite is a basic cadmium carbonate ;[1] cadmium oxide, CdO, also occurs naturally.[2]

History.—The zinc ores used for preparing this metal usually contain cadmium as an impurity, and when zinc is smelted the more volatile cadmium vapour comes off with the first portions of the zinc. The mixed vapours then burn in the air to a mixture of the two oxides. This contamination of zinc oxide led to the discovery of cadmium.

Certain samples of zinc oxide were observed to have a yellow colour and give a yellow precipitate with hydrogen sulphide when dissolved in acid. Stromeyer, in 1817, isolated a metal from this yellow sulphide and called it cadmium. Many pharmacists had supposed the yellow precipitate to be arsenic sulphide, and Hermann, who prepared large quantities of zinc oxide for pharmaceutical use, had also examined the suspicious precipitate and obtained from it a metal that was identical with Stromeyer's product.[3]

The zinc ore (calamine) used by the ancients to obtain brass by melting it with copper was called "cadmia." Names derived from this were applied to the deposits of zinc oxide obtained during the working of zinc, and the name "cadmium" was derived from these.

Preparation of Cadmium.—Cadmium oxide is produced simultaneously with zinc oxide when cadmiferous zinc ores are roasted, though much cadmium may be lost by volatilisation of the oxide or reduced metal during the process.[4] Cadmium metal is obtained by fractionally distilling the first portions of zinc that distil over from the smelting of that metal from cadmiferous ores. Charcoal is added to the metal under distillation, and by utilising the greater volatility of the cadmium a metal of 99·5 per cent. purity is obtained.

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[1] Schneider, *Centr. Min.*, 1906, 388.

[2] Neumann and Wittich, *Chem. Zeit.*, 1901, 25, 561 ; *Centr. Min.*, 1901, 549.

[3] Stromeyer, *Ann. Chim. Phys.*, 1819, [2], 11, 76 ; *Gilbert's Annalen*, 1818, 60, 193; *Schweigger's J.*, 1818, 22, 362 ; Gay-Lussac, *Ann. Chim. Phys.*, 1818, [2], 8, 100 ; Hermann, *Gilbert's Annalen*, 1818, 59, 95, 113 ; 1820, 66, 276.

[4] Stadler, *J. prakt. Chem.*, 1864, [1], 91, 359.

Purification of Cadmium.—Cadmium can be refined electrolytically by depositing the metal from a concentrated solution of cadmium sulphate, slightly acidified, on a platinum or cadmium cathode.[1] The metal is readily obtained in octahedral and other crystalline forms of the regular system by distillation in a current of hydrogen.[2] It distils *in vacuo* at a lower temperature than zinc.[3] Partridge purified his cadmium for atomic-weight determinations by a double distillation *in vacuo*,[4] but Morse and Jones,[5] after subliming purified cadmium in a current of hydrogen, distilled the sublimed metal six times *in vacuo* before they obtained a spectroscopically pure product. Bucher distilled nine times *in vacuo*.[6] Hardin prepared spectroscopically pure cadmium by three distillations in hydrogen.[7]

The crystallisation of cadmium bromide is an effective and rapid method of purifying cadmium material.[8]

Uses of Cadmium.—Cadmium is a constituent of some alloys melting at a low temperature that are used for fuses, etc. Some other alloys also contain it—usually in small quantity.

It has a limited use in electroplating, and attempts have been made to employ it for "galvanising."[9]

Physical Properties of Cadmium.—Stromeyer noted the resemblance of his new metal to tin in its colour, brightness, softness, ductility, and in its "cry" when twisted.[10] Cadmium is silver-white tinged with blue, and its bright lustre soon dulls in air.

Cadmium is said to occur in three allotropic modifications.[11]

Silver-white crystals of cadmium, in octahedra and other forms, sublimed when the metal was distilled in hydrogen,[12] and in flat needles or six-sided tablets when it was distilled *in vacuo*.[13] The metal apparently crystallises isomorphically with zinc in the hexagonal system, and holohedrally.[14]

The cast metal is crystalline,[15] and when cadmium is bent it "cries" like tin.

The density of distilled cadmium is 8·64819 at 20°/4° C., which becomes 8·64766 after compression,[16] but it varies with the history of the metal and usually diminishes on "working."[17]

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[1] Mylius and Funk, *Zeitsch. anorg. Chem.*, 1896, **13**, 157. According to Denso (*Zeitsch. Elektrochem.*, 1903, **9**, 463), cadmium can be quantitatively separated from large proportions of zinc by electrolysis. Fused cadmium chloride is not easily electrolysed (Lorenz, *Zeitsch. anorg. Chem.*, 1895, **10**, 78).

[2] Kaemmerer, *Ber.*, 1874, **7**, 1724.

[3] Demarçay, *Compt. rend.*, 1882, **95**, 183 (Cd at 160° C., Zn at 184° C.); Schuller, *Ann. Physik*, 1883, [2], **18**, 317; Kraft and Bergfield, *Ber.*, 1905, **38**, 254 (Cd at 156·5° C.).

[4] Partridge, *Amer. J. Sci.*, 1890, [3], **40**, 377.

[5] Morse and Jones, *Amer. Chem. J.*, 1892, **14**, 262.

[6] Bucher, *Thesis, Johns Hopkins University*, 1894. See Hardin, *J. Amer. Chem. Soc.*, 1896, **18**, 1016.

[7] Hardin, *loc. cit.*

[8] Baxter and Hartmann, *J. Amer. Chem. Soc.*, 1915, **37**, 130.

[9] Smith, *The Zinc Industry* (Longmans, Green & Co., London), 1918, p. 119; *J. Soc. Chem. Ind.*, 1923, **42**, 1027A.

[10] Gay-Lussac, *Ann. Chim. Phys.*, 1818, [2], **8**, 100.

[11] Cohen and Heldermann, *J. Chem. Soc.*, 1914, **106**, Abs. ii, 52, 652; 1915, **108**, Abs. ii, 40; Cohen, *ibid.*, 1918, **114**, Abs. ii, 290.

[12] Kaemmerer, *loc. cit.*

[13] Mylius and Funk, *loc. cit.*

[14] Williams, *Amer. Chem. J.*, 1892, **14**, 273.

[15] For recrystallisation of cold-worked cadmium, see Cook, *J. Soc. Chem. Ind.*, 1923, **42**, 360A.

[16] Kahlbaum, Roth, and Sielder, *Zeitsch. anorg. Chem.*, 1902, **29**, 287.

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

When cadmium is drawn into wire its density alters from 8·6434–8·6397.[1]

According to Topler,[2] 1 grm. of cadmium expands to 0·0064 c.c. on fusion, and the density of molten cadmium has been represented by the expression

$$8{\cdot}02-0{\cdot}00110\ (t-320),$$

where t is the temperature.[3]

The vapour density of cadmium corresponds to a monatomic molecule.[4] The metal also depresses the vapour pressure of mercury, in which it is dissolved, as if it were monatomic.[5]

The melting-point of cadmium is 320·9° C.[6] It rises 0·006288° C. for every pressure rise of 1 atmosphere.[7] The latent heat of fusion per gram-atom is 1·570 Cal.[8]

Berthelot found that cadmium boiled at 778° C.[9] Previous determinations had varied from 746°–860° C.[10] Egerton[11] accepted Berthelot's figure, though Heycock and Lamplough[12] had found 765·9° C.

In vacuo cadmium slowly volatilises at 160° C.[13] and boils at 450° C.[14] The boiling-point alters by 0·12° C. per each mm. change from normal pressure.[15]

According to Fogler and Rodebush,[16] the latent heat of vaporisation of cadmium at 321·1° C. is 25·350 ± 0·100 Cal., and its vapour pressure varies from 0·10 mm. at 321·1° C. to 760 mm. at 766° C.

The specific heat of cadmium varies from 0·04907 at −164·7° C. to 0·05714 at 97·8° C.[17] The specific heat of distilled cadmium is 0·0559, which becomes 0·0560 after compression.[18]

Pure cast cadmium, according to Jäger and Diesselhorst, has a thermal conductivity of 0·222 at 18° C. and 0·216 at 100° C.[19] According to Lees, pure redistilled cast cadmium varies from 0·240 at −170° C. to 0·217 at 18° C.[20]

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

[2] Topler, *Ann. Phys. Chem.*, 1894, [2], **53**, 343. See also Johnston and Adams, *Zeitsch. anorg. Chem.*, 1911, **72**, 11.

[3] Hogness, *J. Amer. Chem. Soc.*, 1921, **43**, 1624.

[4] Deville and Troost, *Ann. Chim. Phys.*, 1860, [3], **58**, 296; Cooke, *Proc. Roy. Soc.*, 1906, **77A**, 148; Biltz, *Chem. Zentr.*, 1895, i, 770.

[5] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 533; Beckmann and Liesche, *Zeitsch. anorg. Chem.*, 1914, **89**, 190.

[6] Dana and Foote, *Trans. Faraday Soc.*, 1920, **15**, 186; Scheel, *Zeitsch. angew. Chem.*, 1919, **32**, 348; Guertler and Pirani, *Chem. Zentr.*, 1919, ii, 910. *Cf.* Egerton, *Phil. Mag.*, 1917, [6], **33**, 47 (321° C.); Donski, *Zeitsch. anorg. Chem.*, 1908, **57**, 195 (326° C.); Hindrichs, *ibid.*, 1907, **55**, 416 (322° C.).

[7] Johnston and Adams, *Amer. J. Sci.*, 1911, [4], **31**, 501.

[8] Egerton, *Phil. Mag.*, 1917, [6], **33**, 33.

[9] Berthelot, *Compt. rend.*, 1900, **131**, 382.

[10] Becquerel, *Ann. Chim. Phys.*, 1863, [3], **68**, 73 (746·3° C.); Deville and Troost, *Compt. rend.*, 1859, **49**, 240 (860° C.); Carnelley, *Trans. Chem. Soc.*, 1878, **33**, 284 (763°–772° C.).

[11] Egerton, *loc. cit.*, 47.

[12] Heycock and Lamplough, *Proc. Chem. Soc.*, 1912, **28**, 3.

[13] Demarçay, *Compt. rend.*, 1882, **95**, 183.

[14] Kraft, *Ber.*, 1905, **38**, 262.

[15] Heycock and Lamplough, *loc. cit.*, 4. For vapour pressures of cadmium, see Egerton, *loc. cit.*, 33; Barus, *Phil. Mag.*, 1890, [5], **29**, 141.

[16] Fogler and Rodebush, *J. Amer. Chem. Soc.*, 1923, **45**, 2080. For vapour pressure, also see Egerton and Raleigh, *Trans. Chem. Soc.*, 1923, **123**, 3024.

[17] Griffiths and Griffiths, *Phil. Trans.*, 1914, **214A**, 335.

[18] Kahlbaum, Roth, and Siedler, *Zeitsch. anorg. Chem.*, 1902, **29**, 288.

[19] Jäger and Diesselhorst. See Lees, *Phil. Trans.*, 1908, **208A**, 426.

[20] Lees, *loc. cit.*

The electrical conductivity of cadmium in reciprocal ohms per centimetre cube varies from $15·5 \times 10^4$ at $-170°$ C. to $13·9 \times 10^4$ at 18° C.[1]

The coefficient of linear expansion was given by Schaefer as 0·00003060.[2] Unit volume at 0° C., according to Matthiessen, becomes $1 + 0·00008078t + 0·00000014t^2$ vols. at any temperature t between 0° C. and 100° C.[3]

The arc spectrum of cadmium contains the following more important lines, expressed in 10^{-8} cm. units: 3261, 3404, 3406, 3466, 3611, 3982, 4413, 4678, 4799, 908, 5085, 822, 5155, 5338, 5379, 6438, 470.

Colloidal Cadmium.—Cadmium is dispersed as a deep brown colloidal solution when an arc is obtained between cadmium electrodes immersed in pure, air-free water. The colour changes to blue-green and electrolytes coagulate the solution. Exclusion of air and thickening with gelatine preserve the solution for some time.[4]

Svedberg, by an electrical method, obtained a stable dispersion of cadmium in isobutyl alcohol that was brown by transmitted light and greyish black by reflected.[5]

Chemical Properties of Cadmium.—Cadmium burns, when heated in air, to a brown oxide. It was said to retain its brilliancy at ordinary temperatures,[6] but it tarnishes in ordinary air.[7]

Cadmium volatilises before it acts on water, but it can be converted into oxide by heating a mixture of cadmium vapour and steam.[8] The reaction

$$Cd + H_2O \rightleftharpoons CdO + H_2$$

is, however, reversible.[9] If the metal is immersed in water a layer of hydrated oxide forms upon it.[10]

Cadmium behaves towards acids very similarly to zinc. The heat of solution in aqueous hydrochloric acid has been determined thus—

$$Cd + 2HCl.200H_2O = CdCl_2.400H_2O + H_2 + 17·230 \text{ Cal.}$$

at 20° C. if the hydrogen is dry. The corresponding figure for moist hydrogen is 16·980 Cal.[11]

Heated cadmium reacts more readily than zinc with sulphur dioxide, and is converted into a mixture of cadmium sulphate and sulphide.[12]

Cadmium sulphide is produced when sulphurous acid acts on the metal. Sulphur is precipitated in the presence of hydrochloric or sulphuric acid,[13] and the complete action may be complex.[14] According to Fordos and Gélis,[15] cadmium sulphite and hydrogen are first produced. The nascent hydrogen reduces the excess of sulphurous acid to hydrogen sulphide. The latter then precipitates some of the cadmium sulphite as sulphide. They obtained cadmium sulphite and sulphide by treating cadmium with sulphurous acid. Schutzenberger[1] obtained the same products. Cadmium sulphide is also produced when cadmium is heated with sulphurous acid at 200° C. in closed vessels.[2]

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[1] Lees, *Phil. Trans.*, 1908, 208A, 437. [2] Schaefer, *Ann. Physik*, 1902, [4], 9, 671.

[3] Matthiessen, *Phil. Mag.*, 1866, [4], 32, 472.

[4] Bredig, *Zeitsch. physikal. Chem.*, 1900, 32, 127.

[5] Svedberg, *Ber.*, 1906, 39, 1712.

[6] Gay-Lussac, *Ann. Chim. Phys.*, 1818, [2], 8, 100.

[7] Stromeyer, *Schweigger's J.*, 1818, 22, 262.

[8] Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 351.

[9] Ditte, *Compt. rend.*, 1871, 73, 108; Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 16.

[10] Bonsdorff, *Pogg. Annalen*, 1837, 41, 293; 42, 325.

[11] Richards and Tamaru, *J. Amer. Chem. Soc.*, 1922, 44, 1065.

[12] Uhl, *Ber.*, 1890, 23, 2153. [13] Berthelot, *Ann. Chim. Phys.*, 1898, [7], 14, 194.

[14] According to Schweitzer (*Chem. News*, 1871, 23, 293), the final products are sulphate, sulphite, thiosulphate, trithionate, and sulphide of cadmium. Free sulphur is also present.

[15] Fordos and Gélis, *Ann. Chim. Phys.*, 1843, [3], 8, 352.

Atomic Weight of Cadmium.—The atomic weight of cadmium has been determined by—

(A) *The Conversion of the Metal into the Oxide.*—Stromeyer,[3] from the ratio Cd : CdO, obtained an atomic weight for cadmium of 111·483, if O=16.[4]

Morse and Jones[5] dissolved the purified metal in nitric acid and obtained the ratio Cd : CdO=100 : 114·27672 from ten ignitions of the nitrate into the oxide. The oxide was always tested for oxides of nitrogen. Cd=112·0706.

Morse and Arbuckle,[6] in a repetition of this work, obtained from nine determinations 112·377 for the atomic weight of cadmium. Their calculations included corrections for gases occluded by the oxide.

Between these two last determinations Bucher[7] made five determinations by the same method. He carefully considered sources of error in his method, and, after applying various corrections, his results indicate an atomic weight for cadmium of 112·39.

Lorimer and Smith[8] had obtained a value of 112·055 that agreed more with the lower values of the earlier determinations. Their ratio of Cd : CdO=100 : 114·27872 was obtained by depositing cadmium electrolytically from solutions of the oxide in potassium cyanide. They made nine determinations.[9]

(B) *The Ignition of the Oxalate into the Oxide.*—Lenssen[10] obtained the ratio $CdC_2O_4 : CdO = 100 : 64·0059$, giving cadmium as 112·043; Partridge[11] the ratio 100 : 63·9649, making cadmium 111·816; Morse and Jones[5] the ratio 100 : 64·00387, giving Cd=112·032; Bucher[7] the ratio 100 : 63·978, making cadmium 111·89.

(C) *The Conversion of the Oxalate into the Sulphide.*—Partridge[12] obtained the ratio $CdC_2O_4 : CdS = 100 : 71·973 \pm 0·0007$, and Bucher[7] the ratio 100 : 72·052 from the sum of four determinations. Partridge's result was obtained from ten determinations. The former ratio makes cadmium 111·591 and the latter makes it 112·16.

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[1] Schutzenberger, *Compt. rend.*, 1869, **69**, 196.

[2] Geitner, *Annalen*, 1864, **129**, 350.

[3] Stromeyer, *Schweigger's J.*, 1818, **22**, 366.

[4] In calculating the atomic weights in this section, which have been recalculated, when necessary, from the original experimental data, the following atomic weight values have been used:—

O=16·000 Br= 79·916 S=32·065
Cl=35·457 Ag=107·880 C=12·003
H=1·00762.

[5] Morse and Jones, *Amer. Chem. J.*, 1892, **14**, 261.

[6] Morse and Arbuckle, *ibid.*, 1898, **20**, 536. Their uncorrected value, 112·084, was very close to that of Morse and Jones.

[7] Bucher, *Thesis, Johns Hopkins University*, 1894. See Clarke, *J. Amer. Chem. Soc.*, 1896, **18**, 205; Hardin, *ibid.*, 1896, **18**, 1020.

[8] Lorimer and Smith, *Zeitsch. anorg. Chem.*, 1892, **1**, 364.

[9] Bhur made some determinations by converting the oxide into the sulphide. See *J. Amer. Chem. Soc.*, 1909, **31**, 2.

[10] Lenssen, *J. prakt. Chem.*, 1860, **79**, 281. See Morse and Jones, *loc. cit.*

[11] Partridge, *Amer. J. Sci.*, 1890, [3], **40**, 377. See Clarke, *Amer. Chem. J.*, 1891, **13**, 34; Morse and Jones, *loc. cit.*

[12] Partridge, *loc. cit.* See Clarke, *Amer. Chem. J.*, 1891, **13**, 35; Morse and Jones, *loc. cit.*, 271.

(D) *The Reduction of Cadmium Carbonate to Metal in a Current of Hydrogen.*—The sum of five determinations gave the ratio Cd : $CdCO_3$ $=100$: 153·417, from which the atomic weight of cadmium is 112·33.[1]

(E) *The Analysis of Cadmium Sulphate.*—Bucher[2] obtained the ratio Cd : SO_4 by a conversion of the metal into the sulphate, and Baxter and Wilson[3] by an electrolytic determination of cadmium in the sulphate. They made seven determinations. Bucher's ratio was 116·956 : 100 and the latter 117·019 : 100. The respective atomic weights for cadmium are 112·354 and 112·414.

These determinations were made with the anhydrous sulphate. Perdue and Hulett[4] found 43·799 per cent. of cadmium in the hydrated sulphate by estimating the metal electrolytically. Their figure was derived from seven determinations. If the salt is $3CdSO_4.8H_2O$, the atomic weight of cadmium is 112·305.

Some earlier methods converted the sulphate into the sulphide. Von Hauer, as the sum of nine determinations, obtained the ratio $CdSO_4$: $CdS=100$: 69·23,[5] and Partridge,[6] as the mean of ten experiments, the ratio 100 : 69·199 $\pm$ 0·0012. The atomic weights for cadmium are respectively 111·93 and 111·719.

(F) *The Analysis of the Chloride.*—Stromeyer obtained the ratio Cd : $Cl_2=100$: 62·89.[7] Hardin[8] obtained the ratio Cd : $Cl_2=100$: 63·2808 directly by electrolysing the chloride and weighing the cadmium. This ratio, from the sum of ten determinations, gives 112·06 as the atomic weight of cadmium.

Quinn and Hulett[9] converted the chloride into the sulphate and estimated the cadmium by electrolysis. The ratio Cd : $Cl_2=100$: 63·1375, obtained from seven determinations, makes the atomic weight of cadmium 112·32.

Baxter and Hartmann[10] obtained the ratio Cd : $Cl_2=100$: 63·0795 from eighteen electrolytic determinations of cadmium in the chloride, but they preferred the ratio 100 : 63·0811 from five selected determinations. The former ratio gave Cd=112·420 and the latter Cd=112·417.

Baxter, Grose, and Hartmann,[11] from three electrolytic determinations of cadmium in the chloride, obtained the ratio Cd : $Cl_2=100$: 63·0835, and this gave 112·413 for the atomic weight of cadmium.

Dumas[12] determined the ratio $CdCl_2$: $2Ag=100$: 117·813. He himself was uncertain about the accuracy of this ratio, which represents the sum of six experiments.

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[1] Coninck and Gérard, *Compt. rend.*, 1915, 161, 676.

[2] Bucher, *Thesis, Johns Hopkins University*, 1894. See Clarke, *J. Amer. Chem. Soc.*, 1896, 18, 205; Hardin, *ibid.*, 1896, 18, 1020.

[3] Baxter and Wilson, *ibid.*, 1921, 43, 1230.

[4] Perdue and Hulett, *J. Physical Chem.*, 1911, 15, 155. See Clarke, *J. Amer. Chem. Soc.*, 1912, 34, 228.

[5] von Hauer, *J. prakt. Chem.*, 1857, 72, 338. See Morse and Jones, *Amer. Chem. J.*, 1892, 14, 268.

[6] Partridge, *Amer. J. Sci.*, 1890, [3], 40, 377. See Clarke, *Amer. Chem. J.*, 1891, 13, 35; Morse and Jones, *loc. cit.*, 271.

[7] See Dumas, *Ann. Chim. Phys.*, 1859, [3], 55, 158.

[8] Hardin, *J. Amer. Chem. Soc.*, 1896, 18, 1016.

[9] Quinn and Hulett, *J. Physical Chem.*, 1913, 17, 780. See Baxter, *J. Amer. Chem. Soc.*, 1914, 36, 461.

[10] Baxter and Hartmann, *ibid.*, 1915, 37, 113.

[11] Baxter, Grose, and Hartmann, *ibid.*, 1916, 38, 857.

[12] Dumas, *loc. cit.* See Morse and Jones, *loc. cit.*, 261.

Baxter and Hines [1] obtained the ratio $CdCl_2 : 2Ag = 100 : 117{\cdot}6939$. This ratio, obtained from six experiments, makes Cd = 112·409.

Bucher obtained the ratio $CdCl_2 : 2AgCl = 100 : 156{\cdot}124$.[2] Cd = 112·71.

Baxter and Hines, from three experiments, obtained the ratio $CdCl_2 : 2AgCl = 100 : 156{\cdot}3694$.[3] Cd = 112·417.

(G) *The Analysis of the Bromide.*—Hardin [4] obtained the ratio $CdBr_2 : Cd = 100 : 41{\cdot}2031$ from ten electrolytic determinations of cadmium in the bromide. Cd = 112·005.

Quinn and Hulett [5] converted the bromide into the sulphate and determined the cadmium by electrolysis. The ratio $CdBr_2 : Cd = 100 : 41{\cdot}2569$ was obtained from eight determinations. Cadmium is 112·25 from this ratio.

Baxter, Grose, and Hartmann,[6] by electrolysing the bromide, found that cadmium bromide contained 41·290 per cent. of cadmium as the mean of twelve determinations. From this figure $CdBr_2 : Cd = 100 : 41{\cdot}290$ and Cd = 112·407.

Huntingdon and Cooke [7] obtained the ratio $CdBr_2 : 2Ag = 100 : 79{\cdot}3179$ from the sum of eight determinations, and Baxter, Hines, and Frevert [8] the ratio $CdBr_2 : 2Ag = 100 : 79{\cdot}24958$ from seven determinations. The former ratio gives Cd = 112·187 and the latter Cd = 112·325.

Bucher,[2] from the mean of five determinations, obtained the ratio $CdBr_2 : 2AgBr = 100 : 138{\cdot}005$, and Baxter, Hines, and Frevert,[8] from seven determinations, the ratio 100 : 137·9978. Cd is respectively 112·33 and 112·335. The sum of eight determinations by Huntingdon and Cooke [7] had given the ratio 100 : 138·077.

(H) *Determination of the Ratio Cd : Ag by the simultaneous Electrolytic Deposition of the two Metals.*—Hardin [4] did not obtain satisfactory results, but Laird and Hulett,[9] making sixteen determinations, obtained 112·31 for the atomic weight of cadmium.

The International atomic weight of cadmium is taken as

Cd = 112·41.

The atomic number is 48.

Cadmium appears to have six isotopes, their atomic weights being 110, 111, 112, 113, 114, and 116. Their relative proportions also seem to correspond closely to the atomic weight, 112·41, assigned to cadmium.[10]

Alloys of Cadmium: *Lithium.*—Cadmium forms with lithium the two compounds LiCd and $LiCd_2$.[11]

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[1] Baxter and Hines, *J. Amer. Chem. Soc.*, 1905, 27, 222.

[2] Bucher, *Thesis, Johns Hopkins University*, 1894. See Clarke, *J. Amer. Chem. Soc.*, 1896, 18, 205; Hardin, *ibid.*, 1896, 18, 1020.

[3] Baxter and Hines, *loc. cit.*

[4] Hardin, *loc. cit.*, 1016.

[5] Quinn and Hulett, *J. Physical Chem.*, 1913, 17, 780. See Baxter, *J. Amer. Chem. Soc.*, 1914, 36, 461; Quinn and Hulett, *ibid.*, 1915, 37, 1997.

[6] Baxter, Grose, and Hartmann, *ibid.*, 1916, 38, 857.

[7] Huntingdon and Cooke, *Proc. Amer. Acad.*, 1882, 17, 28. See Hardin, *loc. cit.*, 1018.

[8] Baxter, Hines, and Frevert, *J. Amer. Chem. Soc.*, 1906, 28, 770.

[9] Laird and Hulett, *Trans. Amer. Electrochem. Soc.*, 1913, 22, 385. See Baxter, *J. Amer. Chem. Soc.*, 1914, 36, 460.

[10] Aston, see *J. Soc. Chem. Ind.*, 1924, 43, 1195.

[11] Masing and Tammann, *Zeitsch. anorg. Chem.*, 1910, 67, 194.

Sodium dissolves cadmium slowly.[1] $NaCd_2$ occurs in octahedral crystals of D^{20}_{4} 5·669[2] that are slowly acted upon by water[3] and melt at 395° C.[4] It is brittle, harder than cadmium, unaffected by absolute alcohol, and coloured like its components.[5]

The cubical crystals of $NaCd_6$ melt at 363·5° C.[3] There may be compounds with a higher percentage of cadmium,[3] and $NaCd_5$ is said to exist.[5]

Potassium, according to the freezing-point curve, forms the two compounds KCd_7 and KCd_{11}.[6]

Copper.—Copper and cadmium alloy in all proportions.[7] The alloys remain silvery white up to 60 atoms per cent. of copper, and pass from yellow to red as the atomic proportions increase from 68 to 90.[8] Much cadmium makes them soft; with increasing proportions of copper they become harder and more brittle.[9] Copper-cadmium alloys have been obtained by treating solutions of copper salts with metallic cadmium.[10]

The compounds Cu_2Cd[11] and Cu_2Cd_3[12] have been obtained, and $CuCd_3$ is said to exist.[13] The heat of formation of Cu_2Cd_3 has been determined as 48 Cal., and its heat of fusion as 26·05 Cal. per grm.[14]

Silver.—Silver and cadmium alloy in all proportions.[15] Any addition of silver to cadmium raises the freezing-point.[16] High proportions of cadmium make the alloys brittle.[17] An alloy has been obtained by the action of cadmium on a solution of silver sulphate.[18]

The compounds $AgCd$,[19, 20, 21] $AgCd_3$,[19, 21, 22] $AgCd_4$,[19, 20] Ag_2Cd,[21] Ag_2Cd_3,[19, 21, 23] Ag_3Cd_2,[21] and Ag_4Cd[21] have been said to exist.

Gold.—A black spongy alloy containing equal quantities of gold and cadmium is precipitated by metallic cadmium from a solution of a gold salt.[24] The hardness of gold-cadmium alloys attains a maximum when either 18–30 or 51–63 per cent. of cadmium is present. There is also a maximum brittleness at the latter percentage.[25]

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[1] Heycock and Neville, *Trans. Chem. Soc.*, 1889, **55**, 673.

[2] Sustschinsky, *Zeitsch. Kryst. Min.*, 1904, **38**, 265.

[3] Kurnakoff and Kusnetzow, *Zeitsch. anorg. Chem.*, 1907, **52**, 173.

[4] Kurnakoff, *ibid.*, 1899, **20**, 388.

[5] Mathewson, *ibid.*, 1906, **50**, 171.

[6] Smith, *ibid.*, 1908, **56**, 119.

[7] Wright, *J. Soc. Chem. Ind.*, 1894, **13**, 1014. For freezing-point curve, see Heycock and Neville, *J. Chem. Soc.*, 1892, **61**, 898.

[8] Puschin, *Zeitsch. anorg. Chem.*, 1908, **56**, 41.

[9] Sahmen, *ibid.*, 1906, **49**, 301.

[10] Mylius and Fromm, *Ber.*, 1894, **27**, 636; Sanderers, *Bull. Soc. chim.*, 1896, [3], **15**, 1245.

[11] Mylius and Fromm, *loc. cit.*; Sahmen, *loc. cit.*; Guillet, *Compt. rend.*, 1907, **144**, 845; Puschin, *loc. cit.*

[12] Sahmen, *loc. cit.*; Schleicher, *Int. Zeitsch. Metallographie*, 1913, **3**, 102.

[13] Denso, *Zeitsch. Elektrochem.*, 1903, **9**, 135.

[14] Roos, *Zeitsch. anorg. Chem.*, 1916, **94**, 329.

[15] Wright, *J. Soc. Chem. Ind.*, 1894, **13**, 1014.

[16] Heycock and Neville, *Trans. Chem. Soc.*, 1897, **71**, 414. Rose (*Proc. Roy. Soc.*, 1905, **74**, 218) has studied silver-cadmium alloys, and Kremann and Ruderer (*Chem. Zentr.*, 1920, iii, 684) their electromotive behaviour.

[17] Wood, *Chem. News*, 1862, **6**, 135.

[18] Mylius and Fromm, *Ber.*, 1894, **27**, 630.

[19] Petrenko and Federoff, *Zeitsch. anorg. Chem.*, 1911, **70**, 157.

[20] Bruni and Quercigh, *ibid.*, 1910, **68**, 198.

[21] Rose, *loc. cit.*

[22] Maey, *Zeitsch. physikal. Chem.*, 1904, **50**, 200.

[23] Carpenter, *Int. Zeitsch. Metallographie*, 1912, **3**, 170.

[24] Mylius and Fromm, *Ber.*, 1894, **27**, 630.

[25] Vogel, *Zeitsch. anorg. Chem.*, 1906, **48**, 333.

According to Saldeau,[1] gold and cadmium form the two compounds AuCd and $AuCd_3$. Vogel[2] detected these two compounds and also Au_4Cd_3. Heycock and Neville[3] said they obtained AuCd.

Calcium.—Alloys of cadmium with up to 10 per cent. of calcium are stable in air and are little acted on by water. The action of water is more vigorous with greater proportions of calcium. The compounds CaCd and $CaCd_3$ appear to exist, and possibly Ca_2Cd_3.[4]

Mercury.—If D is the density of the amalgam at 25° C., and p the gram of cadmium per 100 grm. of mercury,

$$D = 13{\cdot}5340 - 0{\cdot}0606p.$$

The temperature coefficient is $-(0{\cdot}0024 + 0{\cdot}0003p)$. An amalgam saturated with cadmium at 25° C. contains 5·574 parts of that metal in every 100 parts of mercury.[5]

Cadmium dissolves in mercury to a considerable extent and diffuses readily through it.[6] The amalgams can be prepared by adding cadmium to mercury and warming;[7] they are also readily obtained by electrolysing cadmium salts with a mercury cathode.[8]

According to Smith,[9] cadmium does not form definite compounds with mercury, though some cadmium mercurides have been reported.[10]

Cadmium amalgams with over 18 per cent. of cadmium are solid.[11]

Aluminium.—Cadmium and aluminium are not miscible in the fused state.[12] When the two metals are melted together and allowed to remain molten, the cadmium, containing a few tenths per cent. of aluminium, sinks, and the aluminium, containing 2–3 per cent. of cadmium, floats.[13]

Thallium.—Cadmium is slightly soluble in thallium in the solid state.[14]

Tin and cadmium are reciprocally soluble to the extent of about 3 per cent. in the solid state;[15] the molten metals mix in all proportions.[16] $CdSn_4$ is said to exist,[17] though Mazzotto[18] thought that the metals probably formed no compounds.

Lead and cadmium are miscible in all proportions.[16]

Antimony.—Cadmium and antimony mix in all proportions.[16] The compound Cd_3Sb_2, crystallising in the rhombic system, separates under appropriate conditions from the molten mixture of the two metals. It is less stable than CdSb, and tends to decompose into the latter.[1] Cadmium-antimony alloys of approximately atomic composition have high thermo-electric power.[2]

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[1] Saldeau, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 994.

[2] Vogel, *loc. cit.*

[3] Heycock and Neville, *Trans. Chem. Soc.*, 1892, 61, 888. Vogel (*loc. cit.*) criticised their procedure.

[4] Donski, *Zeitsch. anorg. Chem.*, 1908, 57, 185.

[5] Hulett and de Lury, *J. Amer. Chem. Soc.*, 1908, 30, 1805.

[6] Humphreys, *Trans. Chem. Soc.*, 1896, 69, 1680.

[7] Willows, *Phil. Mag.*, 1899, [5], 48, 434.

[8] Perdue and Hulett, *J. Physical Chem.*, 1911, 15, 147.

[9] Smith, *Amer. Chem. J.*, 1906, 36, 124. For freezing-point curve, see Byjl, *Zeitsch. physikal. Chem.*, 1902, 41, 641.

[10] Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, 25, 59 (Cd_2Hg_7, m.-pt. 70°–75° C.); Stromeyer, *Schweigger's J.*, 1818, 22, 362 ($CdHg_2$).

[11] Frilley, *Rev. Mét.*, 1911, 8, 541.

[12] Guyer, *Zeitsch. anorg. Chem.*, 1908, 57, 149.

[13] Wright, *J. Soc. Chem. Ind.*, 1892, 11, 492; 1894, 13, 1017.

[14] di Capua, *Atti R. Accad. Lincei*, 1923, 32, ii, 343.

[15] Bucher, *Zeitsch. anorg. Chem.*, 1916, 98, 97.

[16] Wright, *J. Soc. Chem. Ind.*, 1894, 13, 1016.

[17] Padoa and Bovini, *Gazzetta*, 1914, 44, ii, 528.

[18] Mazzotto, *Int. Zeitsch. Metallographie*, 1913, 4, 13. For freezing-point curve, also see Schleicher, *ibid.*, 1912, 2, 76; Guertler, *ibid.*, 1912, 2, 90, 172.

Bismuth and cadmium, when molten, are miscible in all proportions,[3] but they apparently do not mix in the crystalline condition.[4]

Alloys of cadmium and *nickel* cannot be prepared with more than 15 per cent. of nickel because of the volatility of the cadmium ; they are not magnetic. Cd_4Ni exists.[5]

CADMIUM AND THE HALOGENS.

Cadmium Fluoride, CdF_2, has been prepared by evaporating a solution of the metal in hydrofluoric acid,[6] or by treating cadmium, cadmium oxide, or cadmium chloride (which decomposes incompletely) with hydrogen fluoride at a high temperature. It is a white crystalline powder, insoluble in alcohol, that is converted into oxide by oxygen and steam at a red heat, and into sulphide by hydrogen sulphide at a moderate heat. Acids dissolve it, hydrofluoric acid probably forming an acid salt,[7] and 1000 c.c. of water at 25° C. dissolve about 45 grm.[8]

It melts at 520° C.,[9] is not volatile at 1200° C., and its density is 6·64 [7]—according to Clarke and Kebler 5·994 at 22° C.[10]

The *double fluorides* $2KCl.CdF_2$,[11] $NH_4F.CdF_2$,[12] and $2CdF_2.ZrF_4.6H_2O$ [13] have been described.

Cadmium Chloride, $CdCl_2$.—Anhydrous cadmium chloride is a very stable salt, and can be prepared by dehydrating one of its hydrates or by heating the oxide in a current of chlorine.[14] Baxter and Hines [15] obtained a pure salt by igniting the double chloride $NH_4Cl.CdCl_2$. It has also been prepared pure by dissolving redistilled cadmium in hydrochloric acid, evaporating to dryness with excess of the acid, and distilling in a current of hydrogen chloride,[16] and by fusing cadmium bromide in a current of chlorine. The pure chloride can always be rendered anhydrous by heating in dry hydrogen chloride.[17] The transparent pearly mass melts at about 568° C., boils at about 964° C., and condenses, when sublimed, in transparent micaceous laminæ.[18]

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[1] Kurnakoff and Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 227 ; *Zeitsch. anorg. Chem.*, 1908, **58**, 1. See Kremann and Gmachl-Pammer, *Chem. Zentr.*, 1921, i, 123.

[2] Fischer and Pfleiderer, *ibid.*, 1921, i, 349.

[3] Wright, *J. Soc. Chem. Ind.*, 1894, **13**, 1016.

[4] Petrenko and Federov, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 785.

[5] Vors, *Zeitsch. anorg. Chem.*, 1908, **57**, 34.

[6] Berzelius, *Pogg. Annalen*, 1824, **1**, 26, 199.

[7] Poulenc, *Compt. rend.*, 1893, **116**, 581 ; *Ann. Chim. Phys.*, 1894, [7], **2**, 33.

[8] Jaeger, *Zeitsch. anorg. Chem.*, 1901, **27**, 34.

[9] Carnelley, *Trans. Chem. Soc.*, 1878, **33**, 278. Above 1000° C. according to Ruff and Plato, *Ber.*, 1903, **36**, 2357.

[10] Clarke and Kebler, *Jahresber.*, 1883, 51.

[11] Poulenc, *Ann. Chim. Phys.*, 1894, [7], **2**, 39.

[12] Marignac, *ibid.*, 1860, [3], **60**, 286.

[13] Helmholt, *Zeitsch. anorg. Chem.*, 1893, **3**, 115.

[14] Weber, *Pogg. Annalen*, 1861, **112**, 619.

[15] Baxter and Hines, *Amer. Chem. J.*, 1904, **31**, 220.

[16] Morse and Jones, *ibid.*, 1890, **12**, 488.

[17] Baxter and Hartmann, *J. Amer. Chem. Soc.*, 1915, **37**, 113.

[18] Weber, *Zeitsch. anorg. Chem.*, 1899, **21**, 305; m.-pt. 546° C. according to Carnelley, *loc. cit.*; 590° C. according to Ruff and Plato, *loc. cit.*; 568° C. according to Hachmeister, *Zeitsch. anorg. Chem.*, 1919, **109**, 145.

The fused salt has a density of 4·049 at 25° C. (referred to water at 4° C.),[1] and when strongly heated reacts with oxygen or hydrogen;[2] it does not react with nitrogen peroxide.[3]

$[\mathrm{Cd}]+(\mathrm{Cl}_2)=[\mathrm{CdCl}_2]+93{\cdot}2$ Cal.[4] (+93·0 Cal.).[5]

Molten cadmium chloride conducts electricity.[6]

It dissolves somewhat in methyl and ethyl alcohols,[7] slightly in acetone,[8] and the depression of the freezing-points of its solutions in urethane indicates the formula CdCl_2.[9]

The boiling-points of its solutions in quinoline also indicate a normal formula.[10]

Hydrates of cadmium chloride with 5, 4, $2\frac{1}{2}$, 2, and 1 molecules of water have been described, but those with 5 and 2 are doubtful.

Sulphuric acid added to a solution of cadmium chloride precipitates, according to Viard,[11] the *monohydrate* or the *dihydrate* according to the amount of acid added. Needle-shaped crystals of the monohydrate separate from a 58 per cent. solution evaporated at 40° C.,[12] or by crystallising either a neutral solution of the carbonate in hydrochloric acid or a saturated solution of cadmium chloride saturated with hydrogen chloride.[13] It is dehydrated completely at 120°–130° C.[12] According to Viard,[11] the anhydrous salt becomes the monohydrate in ordinary air, and in dry air the change is reversed.

Hauer[14] described a *dihydrate*. It has been said to separate when cold solutions of cadmium chloride are evaporated, the monohydrate separating at higher temperatures,[15] and the temperature of transition from the dihydrate to the monohydrate has been given as 34·1° C.[16] Viard says that the dihydrate becomes the monohydrate when exposed to air.[11] According to Dietz, monoclinic crystals of $\mathrm{CdCl}_2.2\frac{1}{2}\mathrm{H}_2\mathrm{O}$ separate from concentrated solutions at ordinary temperatures. This hydrate seems to exist in two modifications, and its transition temperature into the monohydrate appears to be about 34° C.[12] The crystals may be thick tables or short pyramids.[17] Sudhaus claims to have confirmed the existence of both $\mathrm{CdCl}_2.2\frac{1}{2}\mathrm{H}_2\mathrm{O}$ and $\mathrm{CdCl}_2.2\mathrm{H}_2\mathrm{O}$.[18]

The *tetrahydrate* separates in prismatic crystals from a 56–58 per cent. solution of CdCl_2 at −10° C. Above −5° C., though it may exist in a labile form, it passes into $\mathrm{CdCl}_2.2\frac{1}{2}\mathrm{H}_2\mathrm{O}$.[19]

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[1] Baxter and Hines, *loc. cit.*; Bodeker, *Jahresber.*, 1860, **17** (3·625); Knight, *Ber.*, 1878, **11**, 1505 (3·938 at 23° C.); Clarke, *Amer. Chem. J.*, 1883, **5**, 240 (3·655 at 17° C.).

[2] Potilitzen, *Ber.*, 1879, **12**, 695, 2170.

[3] Thomas, *Ann. Chim. Phys.*, 1898, [7], **13**, 222.

[4] Berthelot, *ibid.*, 1878, [5], **15**, 186.

[5] Taylor and Perrott, *J. Amer. Chem. Soc.*, 1921, **43**, 484.

[6] Graetz, *Wied. Annalen*, 1890, **40**, 463.

[7] Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1892, **10**, 783.

[8] Krug and Elroy, *Jahresber.*, 1892, 1554.

[9] Castoro, *Gazzetta*, 1898, **28**, ii, 317.

[10] Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 236.

[11] Viard, *Compt. rend.*, 1902, **135**, 244.

[12] Dietz, *Zeitsch. anorg. Chem.*, 1899, **20**, 253.

[13] Lescœur, *Ann. Chim. Phys.*, 1894, [7], **2**, 86.

[14] Hauer, *J. prakt. Chem.*, 1854, **63**, 432.

[15] Pickering, *Trans. Chem. Soc.*, 1887, **51**, 76.

[16] Cohen, *Zeitsch. physikal. Chem.*, 1894, **14**, 71.

[17] Mügge, Bömer, and Sommerfeldt, *Chem. Zentr.*, 1899, ii, 246.

[18] Sudhaus, *J. Chem. Soc.*, 1914, **106**, Abs. ii, 205.

[19] Dietz, *loc. cit.* *Cf.* Lescœur, *loc. cit.*

The *pentahydrate*, said to be obtained by crystallisation below −14° C.,[1] has not been confirmed.[2]

$[CdCl_2]+400Aq.=CdCl_2.Aq.+3{\cdot}382$ Cal. (prepared at 200° C. The fused salt gave $+3{\cdot}211$ Cal.).
$[CdCl_2.H_2O]+400Aq.=CdCl_2.Aq.+0{\cdot}625$ Cal.
$[CdCl_2.2H_2O]+400Aq.=CdCl_2.Aq.-2{\cdot}284$ Cal.[3]

The solubility of cadmium chloride in gram $CdCl_2$ per 100 grm. solution has been determined as follows[4]:—

$CdCl_2.4H_2O$.

Temperature, ° C.	−9	0	+10	+15
Solubility . .	43·58	49·39	55·58	59·12

$CdCl_2.2\frac{1}{2}H_2O$.

Temperature, ° C.	−10	0	+18	+30	+36
Solubility . .	44·35	47·37	52·53	56·27	57·91

$CdCl_2.H_2O$.

Temperature, ° C.	10	20	40	60	80	100
Solubility . .	57·47	57·35	57·51	57·77	58·41	59·32

Cadmium chloride is strongly ionised in aqueous solution.[5] Hydrolysis is slight, though it becomes noticeable at higher temperatures.[6]

By heating anhydrous cadmium chloride and metallic cadmium *in vacuo* or in an atmosphere of nitrogen to the fusing-point of the metal, a garnet-red-coloured liquid is produced that solidifies to a greyish-white mass. Its composition corresponds to the formula Cd_4Cl_7, and it may be a loose compound of CdCl and $CdCl_2$ ($CdCl.3CdCl_2$), or a solution of the former in the latter. It is a powerful reducing agent, and water decomposes it into cadmium chloride and cadmous hydroxide, CdOH. It decomposes into cadmium metal and cadmium chloride when strongly heated.[7]

Compounds of Cadmium Chloride with Ammonia.—Anhydrous cadmium chloride absorbs ammonia gas with increasing rapidity.[8] The hexammoniate, $CdCl_2.6NH_3$, is produced if the temperature is kept well below 0° C.[9] Ammoniacal compounds are obtained by dissolving cadmium chloride in ammonia solution and passing in ammonia gas.[8, 10] If the temperature is kept at 0° C. small transparent crystals of $CdCl_2.6NH_3$ separate out. This substance, which is only slightly soluble in water, cannot exist above 62° C., and decomposes at 100° C. into $CdCl_2.2NH_3$, which is quite stable under ordinary conditions and only begins to decompose at 210° C.[1] $CdCl_2.2NH_3$ crystallises out under ordinary conditions from solutions of cadmium chloride in ammonia,[2, 3] and is also obtained as a white crystalline powder by passing ammonia gas into an alcoholic solution of cadmium chloride.[4] When heated in a glass retort a transparent, yellowish, glassy mass of $CdCl_2.NH_3$ distils over.[1, 4]

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[1] Worobieff, *Zeitsch. anorg. Chem.*, 1898, **18**, 386.

[2] Dietz, *Zeitsch. anorg. Chem.*, 1899, **20**, 253. *Cf.* Lescœur, *Ann. Chim. Phys.*, 1894, [7], **2**, 86.

[3] Pickering, *Trans. Chem. Soc.*, 1887, **51**, 76. See under Dihydrate.

[4] Dietz, *loc. cit.*; Étard, *Ann. Chim. Phys.*, 1894, [7], **2**, 536.

[5] Grotrian, *Wied. Annalen*, 1883, **18**, 190; Wershoven, *Zeitsch. physikal. Chem.*, 1890, **5**, 481; Jones and Knight, *Amer. Chem. J.*, 1899, **22**, 110; Jahn, *Zeitsch. physikal. Chem.*, 1901, **37**, 673. For osmotic pressure data, see Jones and Chambers, *Amer. Chem. J.*, 1900, **23**, 89; Jones, *Zeitsch. physikal. Chem.*, 1893, **11**, 542. Varet (*Compt. rend.*, 1896, **123**, 421) has determined the heat evolved when various solutions are added to solutions of cadmium chloride.

[6] Kahlenberg, *J. Amer. Chem. Soc.*, 1899, **21**, 1; Bein, *Zeitsch. physikal. Chem.*, 1898, **27**, 51.

[7] Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 488.

[8] Croft, *Phil. Mag.*, 1842, [3], **21**, 355.

[9] Lang and Rigaut, *J. Chem. Soc.*, 1899, **71**, 883.

[10] André, *Compt. rend.*, 1887, **104**, 908.

The unstable *acid salt*, $2HCl.CdCl_2.7H_2O$, is precipitated by saturating a cold saturated solution of cadmium chloride with hydrogen chloride.[5]

Some *oxychlorides* of cadmium have been described.[6] Hexagonal crystals of $Cd(OH)Cl$, of density 4·56 at 15° C., were obtained by heating cadmium chloride with powdered marble at 200° C. in sealed tubes. Cadmium hydroxide can be substituted for the marble.[7]

The following *double chlorides of cadmium*[8] are known: $LiCl.CdCl_2.3\frac{1}{2}H_2O$;[9] $2NaCl.CdCl_2.3H_2O$[10, 11, 12, 13] and $2NaCl.CdCl_2$;[14] $KCl.CdCl_2$,[11,15,16,17] $KCl.CdCl_2.H_2O$,[13,18,19] $2KCl.CdCl_2$,[10,11,15] $4KCl.CdCl_2$;[13,14,18] $RbCl.CdCl_2$,[20] $4RbCl.CdCl_2$;[20, 21] $CsCl.CdCl_2$,[22] $2CsCl.CdCl_2$;[22, 23] $NH_4Cl.CdCl_2$,[18,19,24,25,26] $4NH_4Cl.CdCl_2$,[11,18,21,27,28] $NH_4Cl.2CdCl_2$;[26] $CuCl_2.CdCl_2.4H_2O$,[29] $4CuCl_2.CdCl_2$,[30] $2Cu_2Cl_2.CdCl_2$;[30] $BaCl_2.CdCl_2.4H_2O$.[11,12,18] $BaCl_2.CdCl_2.5H_2O$;[18] $SrCl_2.2CdCl_2.7H_2O$,[31] $CaCl_2.2CdCl_2.7H_2O$;[29] $MgCl_2.2CdCl_2.12H_2O$;[18] $2CdCl_2.MnCl_2.12H_2O$,[29] $2CdCl_2.FeCl_2.12H_2O$,[29] $2CdCl_2.CoCl_2.12H_2O$,[29] $CdCl_2.2NiCl_2.12H_2O$,[32] $2CdCl_2.NiCl_2.12H_2O$.[32]

Cadmium Bromide, $CdBr_2$.—Cadmium and bromine do not react in the cold, but if bromine vapour is passed over the metal heated almost to redness, white anhydrous $CdBr_2$ sublimes.[1] The anhydrous salt is also obtained by heating the tetrahydrate, $CdBr_2.4H_4O$.[2] It has been prepared pure by dissolving the pure carbonate in pure hydrobromic acid, drying at 200° C., and subliming in a current of pure dry carbon dioxide. The lustrous crystals thus obtained were not hydroscopic.[3] In connection with atomic-weight determinations electrolytic cadmium has been dissolved in dilute aqueous hydrobromic acid and bromine. After treatment with excess of cadmium the filtered solution of cadmium bromide was crystallised. Fractional crystallisation has been found to be very effective in preparing the pure salt. To obtain it in a final anhydrous state it was heated in nitrogen containing hydrogen bromide.[4]

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[1] Lang and Rigaut, *loc. cit.*

[2] Croft, *loc. cit.*

[3] Tassilly, *Compt. rend.*, 1897, **124**, 1022; *Ann. Chim. Phys.*, 1899, [7], **17**, 102.

[4] Kwasnik, *Arch. Pharm.*, 1891, **229**, 569.

[5] Berthelot, *Ann. Chim. Phys.*, 1881, [5], **23**, 86.

[6] Tassilly, *ibid.*, 1899, [7], **17**, 81.

[7] de Schulten, *Compt. rend.*, 1888, **106**, 1674.

[8] Cornec and Urbain have studied, by cryoscopic methods, the salts $MCl.CdCl_2$ (M = Na, K, NH_4 or H) (*Bull. Soc. chim.*, 1919, [4], **25**, 218).

[9] Chassevant, *Ann. Chim. Phys.*, 1893, [6], **30**, 39.

[10] Croft, *Phil. Mag.*, 1842, [3], **21**, 355.

[11] Hauer, *Jahresber.*, 1855, 392.

[12] Rüdorff, *Ber.*, 1888, **31**, 3048.

[13] Sudhaus, *J. Chem. Soc.*, 1914, **106**, Abs. ii, 205.

[14] Brand, *Jahrb. Min. Beil. Bd.*, 1911, **32**, 627.

[15] Varet, *Compt. rend.*, 1896, **123**, 422.

[16] Jones and Ota, *Amer. Chem. J.*, 1899, **22**, 11.

[17] Lindsay, *ibid.*, 1901, **25**, 66.

[18] Rimbach, *Ber.*, 1897, **30**, 3073.

[19] Traube, *Zeitsch. Kryst. Min.*, 1898, **29**, 602.

[20] Rimbach, *Ber.*, 1902, **35**, 1303.

[21] Rimbach, *ibid.*, 1905, **38**, 1569.

[22] Wells and Walden, *Zeitsch. anorg. Chem.*, 1894, **5**, 269.

[23] Godeffroy, *Ber.*, 1875, **8**, 9.

[24] Grossmann, *Zeitsch. anorg. Chem.*, 1903, **33**, 149.

[25] Baxter and Hines, *Amer. Chem. J.*, 1904, **31**, 220.

[26] Hachmeister, *Zeitsch. anorg. Chem.*, 1919, **109**, 145.

[27] André, *Compt. rend.*, 1887, **104**, 908.

[28] Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 109.

[29] Hauer, *J. prakt. Chem.*, 1855, [1], **66**, 176.

[30] Hermann, *Zeitsch. anorg. Chem.*, 1911, **71**, 257.

[31] Jones and Knight, *Amer. Chem. J.*, 1899, **22**, 120.

[32] Hauer, *J. prakt. Chem.*, 1856, [1], **69**, 121.

Cadmium bromide melts at 567° C.[5] and boils at 863° C.[6] It volatilises without decomposition,[1] and its vapour density corresponds to the formula $CdBr_2$.[7] The same formula is also indicated by the boiling-points of quinoline solutions.[8] Its density, referred to water at 4° C., is 5·196 at 25° C.[9]

At a red heat it is easily reduced by hydrogen or oxidised by oxygen.[10] Nitrogen peroxide liberates small quantities of bromine from it.[11] Its heat of formation is 84·2 Cal.[12]

The fused salt conducts electricity,[13] and the salt is very soluble in water.[14] Its aqueous solutions are strongly ionised.[15]

The solubilities of the *tetrahydrate* and *monohydrate* are—

$CdBr_2.4H_2O$.

Temperature, ° C.	0	18	30	38
$CdBr_2$ in grm. per 100 grm. solution	37·92	48·90	56·9	61·84

$CdBr_2.H_2O$.

Temperature, ° C.	35	40	45	60	80	100
$CdBr_2$ in grm. per 100 grm. solution	60·29	60·65	60·75	61·10	61·29	61·63

Since the transition-point between these two hydrates is about 36° C., the monohydrate is converted into the tetrahydrate under water at ordinary temperatures, and from solutions of cadmium bromide the tetrahydrate or the monohydrate crystallises according as the temperature is below or above 36° C. There is apparently no $CdBr_2.2\frac{1}{2}H_2O$, though $CdClBr.2\frac{1}{2}H_2O$ has been obtained.[1]

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[1] Berthemot, *Ann. Chim. Phys.*, 1830, [2], **44**, 387; Ragland, *Amer. Chem. J.*, 1899, **22**, 418.

[2] Croft, *Phil. Mag.*, 1842, [3], **21**, 355.

[3] Huntingdon, *Chem. News*, 1881, **44**, 268. Morse and Jones (*Amer. Chem. J.*, 1890, **12**, 490) evaporated the $CdBr_2$ to dryness with excess of the acid and heated in a current of HBr.

[4] Baxter and Hartmann, *J. Amer. Chem. Soc.*, 1915, **37**, 113; Baxter, Grose, and Hartmann, *ibid.*, 1916, **38**, 858; Baxter and Wilson, *ibid.*, 1921, **43**, 1231.

[5] Nacken, *Centr. Min.*, 1907, 301; Brand, *Jahrb. Miner.*, 1913, i, 9.

[6] Weber, *Zeitsch. anorg. Chem.*, 1899, **21**, 351. Carnelley and Williams (*Trans. Chem. Soc.*, 1880, **37**, 126) found 806°–812° C.

[7] C. and V. Meyer, *Ber.*, 1879, **12**, 1284.

[8] Beckmann, *Zeitsch. anorg. Chem.*, 1906, **51**, 236.

[9] Baxter and Hines, *Amer. Chem. J.*, 1904, **31**, 228. Boedeker (*Jahresber.*, 1860, **17**) found 4·712–4·91.

[10] Potilitzen, *Ber.*, 1879, **12**, 695, 2170.

[11] Thomas, *Ann. Chim. Phys.*, 1898, [7], **13**, 222.

[12] Berthelot, *ibid.*, 1878, [5], **15**, 186.

[13] Graetz, *Ann. Phys. Chem.*, 1890, [2], **40**, 18; Garrard, *Zeitsch. anorg. Chem.*, 1900, **25**, 297.

[14] Kremers, *Pogg. Annalen*, 1858, **103**, 57; Gerlach, *Zeitsch. anal. Chem.*, 1869, **8**, 285; Étard, *Ann. Chim. Phys.*, 1894, [7], **2**, 541.

[15] For conductivity data, see Grotrian, *Compt. rend.*, 1883, **96**, 996; Wershoven, *Zeitsch. physikal. Chem.*, 1890, **5**, 493; Jones and Knight, *Amer. Chem. J.*, 1899, **22**, 131; Fox, *Zeitsch. physikal. Chem.*, 1902, **41**, 464. For osmotic data, see Jones, *ibid.*, 1893, **11**, 543; Jones and Chambers, *Amer. Chem. J.*, 1900, **23**, 97.

The tetrahydrate crystallises in long efflorescent prisms that are dehydrated by heating to 200° C.[2] The monohydrate crystallises in shining needles that lose their water slowly at 100° C. and rapidly at 145° C.[1]

The electrical conductivity of cadmium bromide has been determined in its solutions in methyl alcohol, ethyl alcohol, ether, acetone,[3] some other ketones, and propionitrile.[4]

$$[CdBr_2]+400Aq. \quad = CdBr_2.Aq. + 0{\cdot}44 \text{ Cal.}$$
$$[CdBr_2.4H_2O]+610Aq. = CdBr_2.Aq. - 7{\cdot}29 \text{ Cal.}^5$$

Cd_4Br_7 is strictly analogous to Cd_4Cl_7, and is prepared in a similar manner.[6]

Compounds of Cadmium Bromide with Ammonia.—The anhydrous salt absorbs ammonia gas freely. The *tetrammoniate*, $CdBr_2.4NH_3$, is obtained as a white powder by complete saturation. Colourless octahedral crystals of *diammoniate*, $CdBr_2.2NH_3$, are deposited by cooling or evaporating a solution of cadmium bromide in hot ammonia solution. Both substances are decomposed by water and lose ammonia when heated.[7] The latter salt has also been obtained by warming cadmium hydroxide with a solution of ammonium bromide.[8] Tassilly obtained brilliant unstable crystals of a triammoniate, $CdBr_2.3NH_3$, by passing ammonia gas through the anhydrous salt dissolved in aqueous ammonia.

Some *oxybromides* of cadmium have been described.[9] Colourless transparent plates of Cd(OH)Br, of density 4·87 at 15° C., were obtained by heating cadmium bromide and marble to 200° C. in sealed tubes.[10]

The following *double bromides of cadmium* [11] are known: $NaBr.CdBr_2.2\frac{1}{2}H_2O$,[12,13,14] $2NaBr.3CdBr_2.6H_2O$,[15] $4NaBr.CdBr_2$;[13] $KBr.CdBr_2.\frac{1}{2}HO$,[14,15,16] $KBr.CdBr_2.H_2O$,[13,16,17] $2KBr.CdBr_2$,[18] $4KBr.CdBr_2$;[13,17] $RbBr.CdBr_2$,[16] $4RbBr.CdBr_2$;[16] $CsBr.CdBr_2$,[14] $2CsBr.CdBr_2$,[14] $3CsBr.CdBr_2$;[14] $NH_4Br.CdBr_2$,[16] $NH_4Br.CdBr_2.\frac{1}{2}H_2O$,[13,14,19,20] $4NH_4Br.CdBr_2$;[13,16,19,20] $CuBr.CdBr_2$;[21] $BaBr_2.CdBr_2.4H_2O$.[15,22,23]

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[1] Dietz, *Zeitsch. anorg. Chem.*, 1899, **20**, 260.

[2] Croft, *Phil. Mag.*, 1842, [3], **21**, 356; Rammelsberg, *Pogg. Annalen*, 1842, **55**, 241; Lescœur, *Ann. Chim. Phys.*, 1894, [7], **2**, 102.

[3] Arrhenius, *Zeitsch. physikal. Chem.*, 1892, **9**, 493.

[4] Dutoit and Aston, *Compt. rend.*, 1897, **125**, 241.

[5] Thomsen, *J. prakt. Chem.*, 1877, [2], **16**, 323; *Ber.*, 1877, [1], **10**, 1017.

[6] Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 490.

[7] Croft, *loc. cit.*; Rammelsberg, *loc. cit.*; Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 101.

[8] Grossmann, *Zeitsch. anorg. Chem.*, 1903, **33**, 151.

[9] Tassilly, *loc. cit.*, 84.

[10] de Schulten, *Compt. rend.*, 1888, **106**, 1674.

[11] Cornec and Urbain (*Compt. rend.*, 1914, **158**, 1118) have studied the cryoscopy of $CdBr_2$ and alkali bromides.

[12] Croft, *J. prakt. Chem.*, 1856, [1], **68**, 399.

[13] Eder, *Phot. Korresp. Wien*, 1876, **13**, 83; *Dingl. poly. J.*, 1876, **221**, 189; *Zeitsch. anorg. Chem.*, 1903, **36**, 412.

[14] Wells and Walden, *ibid.*, 1894, **5**, 266.

[15] Jones and Knight, *Amer. Chem. J.*, 1899, **22**, 130.

[16] Rimbach, *Ber.*, 1905, **38**, 1553.

[17] Hauer, *J. prakt. Chem.*, 1855, **64**, 477.

[18] Croft, *Phil. Mag.*, 1842, [3], **21**, 356.

[19] Tassilly, *loc. cit.*, 97.

[20] Grossmann, *Zeitsch. anorg. Chem.*, 1903, **33**, 151.

[21] Hermann, *ibid.*, 1911, **71**, 257.

[22] Hauer, *J. prakt. Chem.*, 1856, **69**, 121.

[23] Clarke, *Ber.*, 1879, **12**, 1398.

Cadmium Iodide, CdI_2.—The anhydrous salt has been prepared by heating equivalent quantities of cadmium and iodine in an evacuated tube. It also crystallises, in transparent hexagonal crystals, from solutions obtained by (*a*) the action of iodine upon cadmium under water; (*b*) the action of aqueous hydriodic acid upon cadmium carbonate or metallic cadmium, or a mixture of these two, or cadmium oxide; (*c*) interaction between potassium iodide and cadmium sulphate.[1, 2, 3]

It has been prepared pure by dissolving cadmium carbonate in hydriodic acid, evaporating to dryness with excess of the acid, and heating in a current of hydrogen iodide.[4]

Determinations of its density have varied greatly[3, 5] and Clarke and Kebler[1] inferred that the salt existed in both an α-form and a β-form of lower density that was brownish and gradually transformed into the α-variety at 50° C. According to Snell,[2] the so-called β-cadmium iodide, of low density, obtained by crystallising the salt from its solution in hydriodic acid, contained hydrogen iodide and water, and he concluded that there is no valid evidence for a cadmium iodide of lower density than 5·6. Cohen and Moesveld[6] affirm that between ordinary temperatures and its melting-point (about 400° C.) cadmium iodide exists in a stable α-form of density 5·670 at 30°/4° C., and an unstable β-form of considerably less density. If this is so, the properties of cadmium iodide, as usually described, refer to a mixture of the two forms in unknown proportions.

Cadmium iodide is said to melt at 385° C.[7] and boil at 708°–719° C.[8] It is readily oxidised by nitrogen peroxide at ordinary temperatures[9] and by oxygen when heated.[10] It dissociates slightly when heated in nitrogen, and is incompletely reduced by heating in a current of hydrogen.[11] Its heat of formation is 48·5 Cal.[12]

The salt is very soluble in water—a solution saturated at 18° C. contains 46·02 per cent. of cadmium iodide—and no hydrates have been crystallised from its solutions.[13] Its heat of solution is —9·60 Cal.[14]

Aqueous solutions of cadmium iodide are somewhat strongly ionised.[15]

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[1] Clarke and Kebler, *Amer. Chem. J.*, 1883, 5, 235.

[2] Snell, *J. Amer. Chem. Soc.*, 1907, 29, 1288.

[3] Fullerton, *Jahresber.*, 1877, 43 (density 5·9857 at 12° C. and 5·9738 at 13·5° C.).

[4] Morse and Jones, *Amer. Chem. J.*, 1890, 12, 491.

[5] Boedeker, *Jahresber.*, 1860, 17 (density 4·576 at 10° C.).

[6] Cohen and Moesveld, *Zeitsch. physikal. Chem.*, 1920, 94, 471.

[7] Nacken, *Centr. Min.*, 1907, 301; Brand, *ibid.*, 1912, 26. Ruff and Plato (*Ber.*, 1903, 36, 2357) gave 350° C., and Sandonnini (*Atti R. Accad. Lincei*, 1912, [5], 21, i, 208) gave 380° C.

[8] Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 47, 126.

[9] Thomas, *Ann. Chim. Phys.*, 1898, [7], 13, 222.

[10] Berthelot, *Mécanique Chimique* (Dunod, Paris), 1879, ii, 487.

[11] Berthelot, *Ann. Chim. Phys.*, 1881, [5], 23, 92.

[12] Taylor and Perrott, *J. Amer. Chem. Soc.*, 1921, 43, 484. Berthelot (*Ann. Chim. Phys.*, 1878, [5], 15, 186) gave 45·8 Cal.

[13] Dietz, *Zeitsch. anorg. Chem.*, 1899, 20, 262. See Étard, *Ann. Chim. Phys.*, 1894, [7], 2, 545, for solubilities at temperatures over 100° C.

[14] Thomsen, *Jahresber.*, 1879, 120.

[15] Grotrian, *Compt. rend.*, 1883, 96, 996; Wershoven, *Zeitsch. physikal. Chem.*, 1890, 5, 493; Zelinski and Krapiwin, *ibid.*, 1896, 21, 39; Jahn, *ibid.*, 1901, 37, 673; Heym, *Ann. Physique*, 1919, [9], 12, 443. For osmotic data, see Moser, *Sitzungsber. K. Akad. Wiss. Berlin*, 1878, 868; Tammann, *Zeitsch. physikal. Chem.*, 1888, 2, 45; Arrhenius, *ibid.*, 1888, 2, 496; Beckmann, *ibid.*, 1890, 6, 460; Jones, *ibid.*, 1893, 11, 544; Chambers and Frazer, *Amer. Chem. J.*, 1900, 23, 516.

The experimental data indicate the presence of complex ions,[1] and, according to McBain,[2] dilute solutions contain the ions $Cd^{\cdot\cdot}$ and I', and concentrated solutions the ions $Cd^{\cdot\cdot}$ and CdI'_3.

Cadmium iodide dissolves in alcohol, ether,[3] and amyl alcohol.[4] Its heats of solution in methyl, ethyl, and propyl alcohols are respectively 6·65, 4·31, and 2·66 Cal.[5] Neither methylene iodide[6] nor arsenic tribromide[7] has a solvent action on it. Conductivity and osmotic data indicate that complex ions exist in its solutions in the alcohols.[8]

The boiling-points of its solutions in quinoline indicate the formula CdI_2.[9]

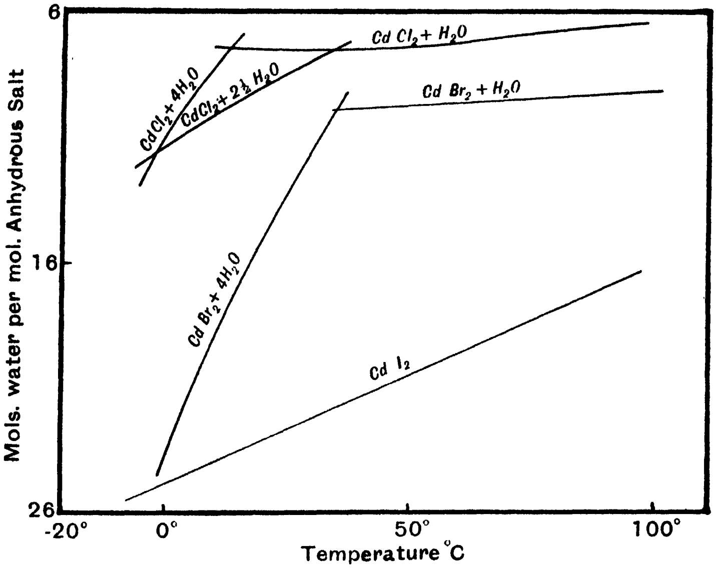

FIG. 4.—Solubility curves of the cadmium halides.

$Cd_{12}I_{23}$ is analogous to Cd_4Cl_7, and is prepared in a similar manner.[10]

Compounds of Cadmium Iodide with Ammonia.—Cadmium iodide absorbs ammonia gas, at a gentle heat, to form the *hexammoniate* $CdI_2.6NH_3$. It is a white powder, decomposed by water, that loses its ammonia when heated.[11] When a solution of the anhydrous salt in warm ammonia solution is cooled, colourless crystals of the *diammoniate* $CdI_2.2NH_3$ separate. They melt, on heating, with the loss of their ammonia, and are decomposed by water.[11] When ammonia solution is added to a solution of cadmium iodide, the product is usually a mixture of this ammoniacal and a basic salt. By using dilute solutions the basic salt only is precipitated. The diammoniate can then be crystallised from the mother-liquor. By severely limiting the quantity of ammonia any formation of the ammoniacal salt is prevented.[1]

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[1] Noyes and Falk, *J. Amer. Chem. Soc.*, 1911, 33, 1460; Name and Brown, *Amer. J. Sci.*, 1917, [4], 44, 453.

[2] McBain, *Zeitsch. Elektrochem.*, 1905, 11, 215.

[3] Eder, *Dingl. poly. J.*, 1876, 221, 189.

[4] Hittorf, *Pogg. Annalen*, 1859, 106, 551, 554, 558.

[5] Timofeiew, *Compt. rend.*, 1891, 112, 1224.

[6] Retgers, *Zeitsch. anorg. Chem.*, 1893, 3, 346.

[7] Walden, *ibid.*, 1902, 29, 374.

[8] Getman and Gibbons, *J. Amer. Chem. Soc.*, 1915, 37, 1990. See Zelinski and Krapiwin, *Zeitsch. physikal. Chem.*, 1896, 21, 39; Jones and Carroll, *Bull. Carnegie Inst.*, 1907, 80, 41.

[9] Beckmann, *Zeitsch. anorg. Chem.*, 1906, 51, 236.

[10] Morse and Jones, *Amer. Chem. J.*, 1890, 12, 491.

[11] Rammelsberg, *Pogg. Annalen*, 1839, 48, 153.

Some *oxyiodides* of cadmium have been described.[2]

Cadmium Hydrogen Iodides.—Dry cadmium iodide absorbs hydrogen iodide. It is also readily soluble in concentrated hydriodic acid solution. This solution, on cooling to −25° C., deposits a crystalline precipitate which is probably an unstable acid cadmium iodide.[3] Cryoscopic data indicate the presence of $CdI_2.2HI$ in the solution.[4] Colourless needles of $CdI_2.HI.3H_2O$ have been obtained by saturating a pasty mass of cadmium iodide and its saturated solution with hydrogen iodide and cooling to −4·7° C. They are only stable in contact with the mother-liquor or in an atmosphere of hydrogen iodide.[5]

Double Iodides of Cadmium.[6]—The following salts have been prepared: $2NaI.CdI_2.6H_2O$,[7, 8, 9] $2NaI.2CdI_2.5H_2O$;[8] $2KI.CdI_2$,[10, 11, 12, 13] $KI.CdI_2.H_2O$,[8, 14, 15] $2KI.CdI_2.2H_2O$;[7, 8, 9, 14, 16] $CsI.CdI_2.H_2O$,[9] $2CsI.CdI_2$,[9] $3CsI.CdI_2$;[9] $NH_4I.CdI_2.\frac{1}{2}H_2O$,[8, 14, 17] $NH_4I.CdI_2.H_2O$,[18] $2NH_4I.CdI_2.2H_2O$;[7, 8, 9, 14] $SrI_2.CdI_2.8H_2O$;[7, 11] $BaI_2.CdI_2.5H_2O$;[7] $CdI_2.3HgI_2$.[19]

Cadmium iodide forms double salts with many iodides of substituted ammonium bases.[20]

OXYHALOGEN COMPOUNDS OF CADMIUM.

Cadmium Chlorate has been prepared by acting on a solution of barium chlorate with a solution of cadmium sulphate.[21] The dihydrate $Cd(ClO_3)_2.2H_2O$, which is the only stable hydrate, occurs in deliquescent prismatic crystals that are very soluble in water or alcohol and melt, with decomposition, at 80° C.[22]

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[1] Tassilly, *Compt. rend.*, 1897, **124**, 1023; *Ann. Chim. Phys.*, 1899, [7], **17**, 102.

[2] Tassilly, *ibid.*, 1899, [7], **17**, 87.

[3] Berthelot, *ibid.*, 1881, [5], **23**, 88.

[4] Cornec and Urbain, *Bull. Soc. chim.*, 1919, [4], **25**, 137.

[5] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 297.

[6] Cornec and Urbain (*Compt. rend.*, 1914, **158**, 1118) have studied the cryoscopy of CdI_2 and alkali iodides.

[7] Croft, *J. prakt. Chem.*, 1856, **68**, 399.

[8] Eder, *Phot. Korresp. Wien*, 1876, **13**, 83; *Dingl. poly. J.*, 1876, **221**, 189; *Zeitsch. anorg. Chem.*, 1903, **36**, 412.

[9] Wells and Walden, *Zeitsch. anorg. Chem.*, 1894, **5**, 266.

[10] Croft, *Phil. Mag.*, 1842, [3], **21**, 357.

[11] Jones and Caldwell, *Amer. Chem. J.*, 1901, **25**, 355, 384.

[12] Brand, *Centr. Min.*, 1912, 26.

[13] Grotrian, *Wied. Annalen*, 1883, **18**, 191; Wershoven, *Zeitsch. physikal. Chem.*, 1890, **5**, 493; McBain, *Zeitsch. Elektrochem.*, 1905, **11**, 222.

[14] Rimbach, *Ber.*, 1905, **38**, 1562.

[15] Baskerville and Crozier, *J. Amer. Chem. Soc.*, 1912, **34**, 1332.

[16] Clarke, *Ber.*, 1879, **12**, 1398.

[17] Tassilly, *Ann. Chim. Phys.*, 1899, [7], **17**, 97.

[18] Grossmann, *Zeitsch. anorg. Chem.*, 1903, **33**, 151.

[19] Clarke and Kebler, *Amer. Chem. J.*, 1883, **5**, 235; Berthemot, *J. Pharm. Chim.*, 1828, **14**, 613.

[20] Datta, *J. Amer. Chem. Soc.*, 1913, **35**, 949.

[21] Wächter, *J. prakt. Chem.*, 1843, [1], **30**, 321.

[22] Meusser, *Ber.*, 1902, **35**, 1420.

Cadmium Perchlorate.—A transparent crystalline mass, deliquescent and soluble in alcohol, is obtained by evaporating a solution of cadmium oxide in perchloric acid.[1] The *hepta-* and *tetra-hydrates* are very hygroscopic and, when heated, decompose before they lose all their water. The unstable *hex-* and *tetr-ammoniates*, $Cd(ClO_4)_2.6NH_3$ and $Cd(ClO_4)_2.4NH_3$, have been obtained.[2]

Cadmium Bromate.—Rhombic prisms of cadmium bromate are obtained by double decomposition between barium bromate and cadmium sulphate. They are probably the *dihydrate* $Cd(BrO_3)_2.2H_2O$, and are very soluble in water. Unstable small white crystals of the *triammoniate*, $Cd(BrO_3)_2.3NH_3$, were obtained by the action of ammonia on a solution of the salt.[3]

Cadmium Iodate.—A white precipitate is obtained by mixing concentrated solutions of sodium iodate and cadmium acetate. The dried substance is only slightly soluble in water.[4]

Transparent prisms of the *monohydrate*, $Cd(IO_3)_2.H_2O$, separate when mixed dilute solutions of sodium iodate and cadmium nitrate are gently evaporated at the ordinary temperature. The crystals lose their water when heated, and finally evolve iodine and oxygen—cadmium oxide being left.

Cadmium iodate absorbs ammonia and forms the *tetrammoniate*, $Cd(IO_3)_2.4NH_3$. Gentle evaporation of cadmium iodate dissolved in concentrated ammonia solution yields an ammoniated salt that is insoluble in water and decomposes violently at 170° C.[5]

Cadmium Periodate.—Compounds of the general type $x\mathrm{CdO}.y\mathrm{I_2O_7}.z\mathrm{H_2O}$ have been prepared by treating cadmium carbonate with periodic acid or by treating cadmium salts with alkaline periodates.[6] A light brown powder of $CdHIO_5$ is precipitated by adding cadmium sulphate to a solution of $Na_2H_3IO_6$.[7]

CADMIUM AND OXYGEN.

Cadmium Suboxide.—There is good evidence for the existence of Cd_4O as an amorphous green powder, and of Cd_2O both as an amorphous green powder and as small yellow crystals.

Marchand obtained a green product, which he regarded as Cd_2O, by heating cadmium oxalate to the melting-point of lead.[8] Since dilute acetic acid dissolved part of it and left a residue of metallic cadmium, subsequent workers regarded his product as a mixture of cadmium and its normal oxide, CdO.[9]

According to Tanatar, amorphous green Cd_4O is formed when cadmium oxalate is carefully heated in an atmosphere of dry carbon dioxide, which is converted into a yellowish-brown mixture of cadmium and cadmic oxide by heating to the melting-point of the metal.[1] Denham says that if the metallic cadmium, which is always formed during the reaction, is distilled off *in vacuo*, green amorphous Cd_4O is obtained, but it never amounts to more than 4 per cent. by weight of the original oxalate.[2]

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[1] Sérullas, *Ann. Chim. Phys.*, 1831, [2], 46, 305.

[2] Salvadori, *Gazzetta*, 1912, 42, i, 458.

[3] Rammelsberg, *Pogg. Annalen*, 1842, 55, 74; Topsöe, *Jahresber.*, 1872, 164.

[4] Rammelsberg, *loc. cit.*, 1838, 44, 566.

[5] Ditte, *Ann. Chim. Phys.*, 1890, [6], 21, 166.

[6] Rammelsberg, *loc. cit.*, 1868, 134, 516.

[7] Kimmins, *Trans. Chem. Soc.*, 1889, 55, 151.

[8] Marchand, *Pogg. Annalen*, 1836, 38, 145.

[9] Vogel, *J. Pharm. Chim.*, 1855, [3], 28, 356; Souchay and Lenssen, *Annalen*, 1857, 103, 316.

Tanatar and Levin obtained dark green Cd_3O_2 and Cd_2O by heating cadmium oxalate and cadmic oxide in appropriate proportions. Either oxide, when heated in the absence of air, was converted into a mixture of metal and normal oxide.[3] Denham, using this method and finally distilling off metallic cadmium under reduced pressure, obtained some homogeneous green Cd_2O.[2]

Hydrogen reduces heated cadmium oxide either to metal[4] or to metal containing unchanged oxide.[2]

When cadmium oxide is reduced by carbon monoxide in the heat, there is a distinct lessening of the velocity of reduction at a point corresponding to the formation of Cd_2O,[5] but the lower oxide could not be isolated from this reaction.[2]

When the compounds Cd_4Cl_7, Cd_4Br_7, or $Cd_{12}I_{23}$ are treated with water, the normal halogen compounds and cadmous hydroxide, CdOH, are produced. Minute yellow translucent crystals of Cd_2O are obtained by heating this cadmous hydroxide in a current of dry nitrogen. When strongly heated it gives a green mixture of cadmium and cadmic oxide, and it acts as a strong reducing agent towards acids.[6] Denham could not convert more than 5 per cent. of the original chloride into suboxide.[2]

Cadmium Oxide, CdO, occurs occasionally in nature as black, shining, regular octahedra of density 6·15 and hardness 5.[7]

When cadmium is heated in the air it forms the characteristic cinnamon-brown amorphous oxide,[8] which can also be obtained by calcining the hydroxide or carbonate,[9] or by heating cadmium fluoride in air or steam.[10] Regnault obtained cadmium oxide (apparently the amorphous form) by heating the metal in steam.[11]

The crystalline oxide may form when cadmium is sublimed in a tube containing air.[12] It has been obtained in black crystalline cubes by burning cadmium in oxygen,[13] in deep red cubes by heating the oxide similarly,[14] and in microscopic octahedra by igniting cadmium nitrate.[15]

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[1] Tanatar, *Zeitsch. anorg. Chem.*, 1901, **27**, 432. Calorimetric measurements showed that it was not a mixture of Cd and CdO. Its density was 8·177–8·207 at 19° C. Acids and ammonia decomposed it into CdO and Cd. It was stable in dry air but slowly decomposed by water.

[2] Denham, *Trans. Chem. Soc.*, 1919, **115**, 556.

[3] Tanatar and Levin, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495. Both oxides were attacked by dilute hydrochloric acid or water with the formation of cadmium and cadmium chloride or oxide.

[4] Glaser, *Zeitsch. anorg. Chem.*, 1903, **36**, 16.

[5] Brislee, *Trans. Chem. Soc.*, 1908, **93**, 162.

[6] Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 488.

[7] Neumann and Wittich, *Chem. Zeit.*, 1901, **25**, 561; *Centr. Min.*, 1901, 549.

[8] Gay-Lussac, *Ann. Chim. Phys.*, 1818, [2], **8**, 100.

[9] Ditte, *Compt. rend.*, 1871, **73**, 272; Glaser, *Zeitsch. anorg. Chem.*, 1903, **36**, 15.

[10] Poulenc, *Ann. Chim. Phys.*, 1894, [7], **2**, 38.

[11] Regnault, *ibid.*, 1836, [2], **62**, 351.

[12] Werther, *J. prakt. Chem.*, 1852, **55**, 118.

[13] Wittich and Neumann, *Centr. Min.*, 1901, 549.

[14] Sidot, *Compt. rend.*, 1869, **69**, 201.

[15] Schüler, *Annalen*, 1853, **87**, 43. For behaviour of oxide and occlusion of gases during ignition of the nitrate, see Morse and Jones, *Amer. Chem. J.*, 1892, **14**, 264; Morse and Arbuckle, *ibid.*, 1898, **20**, 536.

The density of the artificial crystals has been variously given from 6·25 to 8·18.[1]

Cadmium oxide is reduced by hydrogen at 400° C.,[2] and, though the action is reversible,[3] the reduction takes place more easily than with zinc oxide.[4]

Cadmium oxide is also more easily reduced by carbon than zinc oxide, and magnesium reduces it at a red heat.[5] Chlorine, in the heat, readily converts it into the chloride,[6] and when heated with sulphur or phosphorus vapour, cadmium sulphide or phosphides result.[7]

It volatilises slowly or dissociates at 900°–1000° C., and the rate of loss becomes less as the oxide becomes denser or more crystalline.[8]

It is very insoluble in water, though acids dissolve it readily.

$$[\mathrm{Cd}]+(\mathrm{O})=[\mathrm{CdO}]\ (\text{amorphous})+57{\cdot}0\ \text{Cal.}$$
$$[\mathrm{Cd}]+(\mathrm{O})=[\mathrm{CdO}]\ (\text{mainly crystalline})+63{\cdot}0\ \text{Cal.}^{9}$$

The heat of solution in aqueous hydrofluoric acid is 23·450 Cal.[10]

Cadmous Hydroxide, CdOH, is produced as a greyish-white amorphous precipitate during the action of water on the compounds Cd_4Cl_7, Cd_4Br_7, or $Cd_{12}I_{23}$. It is a powerful reducing agent, dissolving in nitric acid with the formation of oxides of nitrogen and in other acids with the evolution of hydrogen. It ignites to yellow crystalline cadmium suboxide, Cd_2O.[11]

Cadmic Hydroxide.—Cadmium oxide, amorphous or crystalline, is converted into white cadmium hydroxide, $Cd(OH)_2$, by prolonged treatment with water or solutions of either alkalies or salts.[12] This amorphous hydroxide is often prepared by precipitating solutions of cadmium nitrate with a carbonate-free alkali hydroxide and washing the precipitate free from alkali.[13] If the cadmium nitrate solution is concentrated a basic salt may contaminate the precipitated hydroxide.[14] A pure product is obtained by electrolysing a solution of an alkali salt (such as sodium nitrate) between a platinum cathode and a cadmium anode. Cadmium is dissolved by the anions, and precipitation finally occurs, more readily if the solution is agitated, through the formation of hydroxyl ions at the cathode.[15]

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[1] Neumann and Wittich, *Chem. Zeit.*, 1901, 25, 561.

[2] Ditte, *Compt. rend.*, 1871, 73, 108.

[3] Regnault, *loc. cit.*

[4] Glaser (*Zeitsch. anorg. Chem.*, 1903, 36, 16) says the reduction begins at 282° C.

[5] Winkler, *Ber.*, 1890, 23, 120. According to Doeltz and Graumann (*Metallurgie*, 1907, 4, 419), the reduction by carbon begins at 580° C. in an atmosphere of nitrogen.

[6] Weber, *Pogg. Annalen*, 1861, 112, 619.

[7] Rénault, *Compt. rend.*, 1873, 76, 283.

[8] Mixter, *Amer. J. Sci.*, 1913, [4], 36, 55. According to Damm and Kraft (*Ber.*, 1907, 40, 4775), it dissociates *in vacuo* at 1000° C. Colson (*Compt. rend.*, 1899, 129, 827) says it dissociates under 600° C., and Morse and White said it dissociated when heated with metallic cadmium (*Amer. Chem. J.*, 1889, 11, 258). According to Doeltz and Graumann (*Metallurgie*, 1906, 3, 372), it volatilises appreciably at 800° C. and rapidly at 1000° C.

[9] Mixter, *loc. cit.* See Ditte, *Compt. rend.*, 1871, 73, 272.

[10] Mulert, *Zeitsch. anorg. Chem.*, 1912, 75, 198.

[11] Morse and Jones, *Amer. Chem. J.*, 1890, 12, 488.

[12] Follenius, *Zeitsch. anal. Chem.*, 1874, 13, 280.

[13] Euler, *Ber.*, 1903, 36, 3400; Bersch, *Zeitsch. physikal. Chem.*, 1891, 8, 392. See Gay-Lussac, *Ann. Chim. Phys.*, 1818, [1], 8, 100.

[14] Schaffner, *Annalen*, 1844, 51, 173.

[15] Lorenz, *Zeitsch. anorg. Chem.*, 1896, 12, 43. See Strecker, *Zeitsch. Elektrochem.*, 1898, 5, 133.

According to Buchner,[1] a form of cadmium hydroxide that gives yellow cadmium sulphide with sodium sulphide is precipitated by adding sodium hydroxide to solutions of cadmium salts, and a form giving red cadmium sulphide with sodium sulphide by either performing this precipitation in the heat or adding the cadmium salt solution to the sodium hydroxide.

A solution of ammonia precipitates cadmium hydroxide from solutions of cadmium salts, but the precipitate is soluble in excess of the reagent. This solution probably contains the complex group $Cd(NH_3)_4$, which is less stable than the corresponding group containing zinc.[2] Cadmium hydroxide can be precipitated in the amorphous form from its solution in ammonia by potassium hydroxide.[3]

Flattened hexagonal crystals of cadmium hydroxide, of density 4·79 at 15° C., have been obtained by heating a solution of cadmium iodide with excess of potassium hydroxide till the precipitated hydroxide dissolved, and cooling.[4] It has also been obtained crystalline by leaving cadmium and iron in contact under a solution of ammonia.[5]

Cadmium hydroxide is very slightly soluble in water[6] but more soluble in solutions of some salts[7]—including ammonium chloride.[8] It is less basic than zinc hydroxide.[9]

$$[Cd(OH)_2]+2HCl.Aq.=CdCl_2.Aq.+20{\cdot}29\ Cal.$$
$$[Cd(OH)_2]+2HBr.Aq.=CdBr_2.Aq.+21{\cdot}56\ Cal.$$
$$[Cd(OH)_2]+2HI.Aq.=CdI_2.Aq.+24{\cdot}21\ Cal.^{10}$$

The corresponding figure for HF is 25·6 Cal.[11]

An unstable *potassium cadmate* may be formed when cadmium oxide is dissolved in molten caustic potash and the melt treated with aqueous potash.[12]

An amorphous basic chloride, Cd(OH)Cl, has been obtained by adding dilute ammonia to a boiling concentrated solution of cadmium chloride.[13]

Cadmium Peroxide.—Haass[14] obtained compounds varying in composition between Cd_5O_8 and Cd_3O_5 by the action of hydrogen peroxide upon cadmium hydroxide in experiments similar to those he performed upon zinc. Kouriloff obtained a yellow, finely crystalline powder of $CdO_2.Cd(OH)_2$ by evaporating cadmium hydroxide nearly to dryness with dilute hydrogen peroxide solution. It was soluble in ammonia, and hydrogen peroxide was produced when it was acted upon by acids.[15]

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[1] Buchner, *Chem. Zeit.*, 1887, 11, 1089.

[2] Bonsdorff, *Ber.*, 1903, 36, 2323; Euler, *ibid.*, 1903, 36, 3404.

[3] Wackenroder, *Annalen*, 1842, 41, 319.

[4] de Schulten, *Compt. rend.*, 1885, 101, 72.

[5] Nicklès, *Ann. Chim. Phys.*, 1848, [3], 22, 36.

[6] Bodländer, *Zeitsch. physikal. Chem.*, 1898, 27, 66; Hertz, *Zeitsch. anorg. Chem.*, 1900, 24, 126.

[7] Bersch, *Zeitsch. physikal. Chem.*, 1891, 8, 392.

[8] Tassilly, *Ann. Chim. Phys.*, 1899, [7], 17, 107; Grossmann, *Zeitsch. anorg. Chem.*, 1903, 33, 149.

[9] Carrara and Vespignini, *Gazzetta*, 1900, 30, ii, 35.

[10] Thomsen, *Ber.*, 1883, 16, 2616.

[11] Mulert, *Zeitsch. anorg. Chem.*, 1912, 75, 198.

[12] Meunier, *Compt. rend.*, 1865, 60, 537; 1866, 63, 330.

[13] de Schulten, *ibid.*, 1888, 106, 1674.

[14] Haass, *Ber.*, 1884, 17, 2252.

[15] Kouriloff, *Ann. Chim. Phys.*, 1891, [6], 23, 429. Prud'homme (*Compt. rend.*, 1891, 112, 1374) noted that cadmium formed a peroxide.

Eijkman[1] described a yellow transparent product obtained by treating an ammoniacal solution of cadmium sulphate with 30 per cent. hydrogen peroxide solution. It became superficially coated with CdO, was insoluble in sodium hydroxide, and decomposed violently at 190° C. It corresponded to the formula $4CdO_2.Cd(OH)_2$.

Teletoff[2] prepared $5CdO_2.CdO.3H_2O$ and $5CdO_2.3CdO.5H_2O$ by adding a large excess of 30 per cent. hydrogen peroxide solution to a concentrated solution of cadmium sulphate which had been treated with ammonia till the precipitate first formed dissolved.

Small quantities of cadmium peroxide occur in the smoke when the metal is burnt at the lowest possible temperature.[3]

CADMIUM AND SULPHUR.

Cadmium Sulphide.—The precipitation of yellow cadmium sulphide from solutions of cadmium salts by hydrogen sulphide was the first known fact about cadmium.[4] CdS occurs naturally as *greenockite*, which is a brownish-yellow mineral crystallising in the hemimorphic group of the hexagonal system with a density of 4·9–5·0 and a hardness of 3–3·5.[5]

Yellow amorphous cadmium sulphide has been prepared by electrolysing a solution of an alkali salt between a cathode of copper sulphide and an anode of cadmium.[6] Its complete precipitation by hydrogen sulphide can be effected in neutral or alkaline solutions of cadmium salts, though it may be slightly soluble in ammonium sulphide when freshly precipitated.[7] Since it is distinctly soluble in mineral acids, hydrogen sulphide will not precipitate it completely, or at all, from solutions that contain much acid, especially hydrochloric acid.[8] According to Bruni and Padoa,[9] hydrogen sulphide does not precipitate cadmium sulphide from acid solutions of cadmium sulphate if the surrounding space is under low pressure. Increase of pressure increases the effectiveness of precipitation.[10] It dissolves readily in hot dilute sulphuric acid[11] and in acidified concentrated solutions of alkaline chlorides.[12]

The yellow variety of cadmium sulphide, especially in the nascent state, is (apparently) liable to be polymerised into a vermilion modification by dilute acids, alkalies, etc. This polymerisation frequently occurs during the precipitation of cadmium sulphide, and the red variety passes through the yellow stage when it is dissolved in acids.[13] The yellow variety passes into the red under friction or pressure as well as under the influence of chemical reagents. The crystalline forms of the red variety differ from the hexagonal form of the yellow, and their densities are different: from 3·906 to 4·147 for the yellow, and between 4·476 and 4·513 for the red.[1] The β- or red sulphide precipitates when relatively strongly acid solutions are precipitated by hydrogen sulphide. Precipitated cadmium sulphide is frequently a mixture of the β- and α- or yellow varieties. Prolonged heating converts the β- into the α-form, which becomes darker in colour on heating, and returns to its original yellow on cooling if it has not been oxidised.

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[1] Eijkman, *Chem. Zentr.*, 1905, i, 1628.

[2] Teletoff, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 131.

[3] Manchot, *Ber.*, 1906, 39, 1170.

[4] Gay-Lussac, *Ann. Chim. Phys.*, 1818, [2], 8, 100.

[5] Follenius, *Zeitsch. anal. Chem.*, 1874, 13, 412.

[6] Lorenz, *Zeitsch. anorg. Chem.*, 1896, 12, 442.

[7] Ditte (*Compt. rend.*, 1877, 85, 402) said that ·2 grm. would dissolve in 1000 c.c., and that cadmium sulphide could be crystallised from the solution. But the solubility under ordinary conditions appears to be very slight (Fresenius, *Zeitsch. anal. Chem.*, 1881, 20, 236), or nil (Donath and Mayrhofer, *ibid.*, 384).

[8] Follenius, *loc. cit.*, 416. See Meldrum, *Chem. News*, 1899, 79, 170.

[9] Bruni and Padoa, *Atti R. Accad. Lincei*, 1905, [5], 14, ii, 525.

[10] Padoa and Cambi, *ibid.*, 1906, [5], 15, ii, 787.

[11] *Annalen*, 1860, 115, 286.

[12] Cushman, *Amer. Chem. J.*, 1895, 17, 379.

[13] Buchner, *Chem. Zeit.*, 1887, 11, 1087, 1107. See Meldrum, *loc. cit.*

A bulky yellow δ-sulphide is precipitated from an ammoniacal solution of cadmium hydroxide by hydrogen sulphide. The same modification is produced by fusing the α-sulphide with sulphur.[2]

According to Egerton and Raleigh,[3] the yellow form is obtained from cold or alkaline solutions and the red from hot or acid solutions. Crushing, they add, converts the yellow permanently into the red form, while heating only effects the change temporarily.

These varieties of cadmium sulphide are important for its *use as a pigment.* Both the α- and β-varieties make good covering paints. The former is slowly oxidised in light and air, but the colour is very permanent when made into paint.[2] A brilliant yellow pigment can be prepared by electrolysing a sodium chloride solution between a platinum cathode and a cadmium anode and passing in hydrogen sulphide.[4] *Cadmium yellow* is an expensive pigment that is much prized by artists. The paler shades of commerce are said not to be permanent, though modern manufacturers now claim to supply them reasonably pure and stable.[5]

Great pressure converts a mixture of cadmium and sulphur powders into cadmium sulphide, which is less brightly yellow than the precipitated product.[6]

Amorphous cadmium sulphide gradually becomes a crystalline mass when it is heated for a long time at 265° C. in an exhausted glass tube,[7] and is easily converted into greenockite by heating in an electric furnace.[8] When hydrogen sulphide acted on cadmium vapour a monoclinic variety of cadmium sulphide was produced simultaneously with the hexagonal.[9]

The crystalline sulphide has been prepared by (*a*) interaction at a red heat between hydrogen sulphide and vaporised cadmium chloride,[10] (*b*) fusing cadmium sulphide with potassium carbonate and sulphur,[11]

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[1] Klobkow, *J. prakt. Chem.*, 1889, [2], 39, 412. According to Allen, Crenshaw, and Merwin (*Amer. J. Sci.*, 1912, [4], 34, 341), the colour of cadmium sulphide depends upon whether it is crystalline or amorphous, and upon the size and surface character of the grains.

[2] Buchner, *Chem. Zeit.*, 1891, 15, 329.

[3] Egerton and Raleigh, *Trans. Chem. Soc.*, 1923, 123, 3019.

[4] Hopkins, *Experimental Electro-Chemistry* (Constable & Co., London), 1905, 126.

[5] Gay, *J. Soc. Chem. Ind.*, 1924, 43, 83.

[6] Spring, *Ber.*, 1883, 16, 1001.

[7] Spring, *Zeitsch. physikal. Chem.*, 1895, 18, 556.

[8] Mourlot, *Compt. rend.*, 1896, 123, 56.

[9] Lorenz, *Ber.*, 1891, 24, 1508. See Allen, Crenshaw, and Merwin, *Amer. J. Sci.*, 1912, [4], 34, 341.

[10] Durocher, *Compt. rend.*, 1851, 32, 823.

[11] Schüler, *Annalen*, 1853, 87, 34. Schneider said he obtained $Na_2S.3CdS$, decomposable by water, when he substituted sodium for potassium carbonate (*Jahresber.*, 1873, 198).

(*c*) subliming the amorphous sulphide in a current of hydrogen,[1] (*d*) heating cadmium oxide with barium sulphate and calcium fluoride,[1] (*e*) heating cadmium oxide in sulphur vapour,[2] (*f*) heating cadmium sulphide with aluminium powder.[3]

Geitner[4] converted metallic cadmium into a mixture of the amorphous and crystalline sulphides by heating at 200° C. with a solution of sulphurous acid in a closed tube.

The artificial crystals of cadmium sulphide are usually yellow and closely resemble greenockite.[5]

The freshly precipitated δ-sulphide goes slowly into *colloidal solution* when suspended in water and treated with hydrogen sulphide. Boiling the solution produces no precipitation. A similar solution is obtained by treating a solution of cadmium iodide with hydrogen sulphide. Acids and ammonium chloride immediately precipitate it.[6] Prost[7] obtained a colloidal solution by the former method; it is golden-yellow by transmitted light and fluorescent by reflected. When very dilute solutions of cadmium salts are treated with hydrogen sulphide, colloidal solutions of cadmium sulphide are apt to be produced.[8] A colloidal solution has also been prepared by triturating cadmium sulphide with oil and adding light petroleum.[9]

Boiling water has no action on cadmium sulphide,[10] but, at a red heat, steam converts it into the oxide.[11] When heated it is reduced to metal in hydrogen,[12] and converted into chloride in hydrogen chloride.[13]

It dissociates readily when heated under reduced pressure.[14]

$$[\mathrm{Cd}]+[\mathrm{S}]\ (\text{rhombic})=[\mathrm{CdS}]\ (\text{crystalline})+34{\cdot}0\ \text{Cal.}$$[15]

Yellow *cadmium pentasulphide* was said to be precipitated from solutions of cadmium salts by potassium pentasulphide.[16]

The luminescence of crystalline zinc sulphide under X-rays is increased by the presence of 1–30 per cent. of cadmium sulphide in solid solution.[17]

The *double sulphides*, $Na_2S.3CdS$[18] and $K_2S.3CdS$,[19] have been described.

Cadmium Sulphite.—When cadmium dissolves in aqueous sulphurous acid, cadmium sulphite and a yellow precipitate of cadmium sulphide are formed.[20]

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[1] Deville and Troost, *Compt. rend.*, 1861, **52**, 920.

[2] Sidot, *ibid.*, 1866, **62**, 999.

[3] Hautefeuille, *ibid.*, 1881, **93**, 826.

[4] Geitner, *Annalen*, 1864, **129**, 350.

[5] Mourlot, *Ann. Chim. Phys.*, 1899, [7], **17**, 535.

[6] Buchner, *Chem. Zeit.*, 1891, **15**, 329. He called this the γ- or soluble cadmium sulphide.

[7] Prost, *Chem. Zentr.*, 1888, 32.

[8] Meldrum, *Chem. News*, 1899, **79**, 170.

[9] Dorp and Rodenburg, *Chem. Weekblad.*, 1909, 6, 1038.

[10] de Clermont and Frommel, *Ann. Chim. Phys.*; 1879, [5], **18**, 189.

[11] Regnault, *ibid.*, 1836, [2], **62**, 380.

[12] Rose, *Pogg. Annalen*, 1860, **110**, 120.

[13] Moyer, *J. Amer. Chem. Soc.*, 1899, **21**, 644.

[14] Colson, *Compt. rend.*, 1899, **129**, 825.

[15] Mixter, *Amer. J. Sci.*, 1913, [4], **36**, 55.

[16] Schiff, *Annalen*, 1860, **115**, 74.

[17] Guntz, *J. Soc. Chem. Ind.*, 1923, **42**, 191A.

[18] Schneider, *Pogg. Annalen*, 1873, **149**, 381.

[19] Milbauer, *Zeitsch. anorg. Chem.*, 1904, **42**, 439.

[20] Fordos and Gélis, *Ann. Chim. Phys.*, 1843, [3], 8, 352.

Crystals of *anhydrous sulphite*, $CdSO_3$, are obtained by dissolving cadmium carbonate in aqueous sulphurous acid and evaporating on the water-bath,[1, 2] or from hot mixed solutions of a cadmium salt and sodium sulphite.[3, 4]

A gelatinous *dihydrate*, $CdSO_3.2H_2O$, precipitates when alcohol is added to a solution of cadmium carbonate in aqueous sulphurous acid. It becomes crystalline on standing.[2, 5] The same hydrate is precipitated from mixed solutions of a cadmium salt and sodium sulphite at ordinary temperatures.[4] Denigès [3] said that he thus obtained crystals of a trihydrate.

Cadmium sulphite, anhydrous or hydrated, is difficultly soluble in water and readily in dilute acids.

Muspratt [5] could not confirm the $CdSO_3.NH_3$ mentioned by Rammelsberg.[1]

Cadmium Sulphate.—A mixture of cadmium sulphide and sulphate is formed by the action of sulphur dioxide on heated cadmium.[6] Rhombic prisms of *anhydrous sulphate*, $CdSO_4$, were obtained by evaporating a solution of cadmium sulphate in sulphuric acid and carefully heating off the excess of acid. Their density at 15° C. was 4·72.[7] Anhydrous cadmium sulphate is obtained as a white powder by heating hydrated salts to expel their water. The density of the unmelted salt has been given as 4·447.[8] To obtain pure $CdSO_4$, since it is difficult to free the anhydrous salt completely from moisture and it decomposes at high temperatures, the hydrated sulphate (usually $3CdSO_4.8H_2O$) should be heated to 200° C. *in vacuo*, then to 700° C. in a current of air containing sulphur trioxide, and finally in pure dry air at 200° C.[9]

It is reduced to the sulphide, with the simultaneous production of a little metal, by heating in a current of hydrogen.[10] One part of water dissolves about 0·59 part of $CdSO_4$ at 23° C., and the solubility does not increase very much with the temperature.[11]

Solutions of cadmium sulphate are readily obtained by dissolving metallic cadmium, cadmium sulphide, or cadmium oxide in sulphuric acid. Salts of cadmium with volatile acids can also be heated with sulphuric acid.[12] The *hydrate*, $CdSO_4.8/3H_2O$, or $3CdSO_4.8H_2O$, crystallises from such solutions under ordinary conditions : this is the cadmium sulphate of commerce, the most common and important salt of the metal.[11, 13] This hydrate is also precipitated when alcohol is added to a solution of cadmium sulphate.[11]

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[1] Rammelsberg, *Pogg. Annalen*, 1846, 67, 255.

[2] Röhrig, *J. prakt. Chem.*, 1888, [2], 37, 237.

[3] Denigès, *Bull. Soc. chim.*, 1892, [3], 7, 571.

[4] Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 62.

[5] Muspratt, *Annalen*, 1847, 64, 242.

[6] Uhl, *Ber.*, 1890, 23, 2153.

[7] de Schulten, *Compt. rend.*, 1888, 107, 405.

[8] Schröder, *J. prakt. Chem.*, 1879, [2], 19, 290.

[9] Baxter and Wilson, *J. Amer. Chem. Soc.*, 1921, 43, 1238; Perdue and Hulett, *J. Physical Chem.*, 1911, 15, 1579. *Cf.* Follenius, *Zeitsch. anal. Chem.*, 1874, 13, 176. According to Ruff and Plato (*Ber.*, 1903, 36, 2357), $CdSO_4$ melts at 1000° C.

[10] Schüler, *Annalen*, 1853, 87, 42.

[11] von Hauer, *J. prakt. Chem.*, 1855, [1], 64, 477.

[12] Follenius, *Zeitsch. anal. Chem.*, 1874, 13, 274.

[13] There was originally some doubt about the formula of this salt. Rammelsberg suggested $CdSO_4.3H_2O$ (*Jahresber.*, 1855, 390), but he subsequently accepted $3CdSO_4.8H_2O$ (*ibid.*, 1857, 219), and though Retgers (*Zeitsch. physikal. Chem.*, 1895, 16, 590) still preferred the former formula, the latter is now generally admitted (Kopp, *Ber.*, 1879, 12, 909; Worobjew, *Zeitsch. physikal. Chem.*, 1897, 23, 557; Mylius and Funk, *Ber.*, 1897, 30, 824; Kohnstamm and Cohen, *Ann. Phys. Chem.*, 1898, [2], 66, 344).

Cadmium can be obtained in a pure form by crystallisation as this salt. The crystals are monoclinic[1] and are stable in ordinary dry air,[2] though they effloresce rapidly if they are powdered.[3]

A very pure sample has been prepared by converting purified cadmium bromide into the nitrate by nitric acid, the nitrate into the sulphate by sulphuric acid, and recrystallising.[4]

The density of the crystals is about 3·0,[5] and their specific heat between 17° C. and 21° C. is 0·200.[6]

They have been said to lose 4 molecules of water at 150° C.,[7] but they require heating at 700° C. in air containing sulphur trioxide to make them anhydrous.[4] The deliquescent compounds $3CdSO_4.8HCl$, $3CdSO_4.4H_2O.4HCl$, and, ultimately, cadmium chloride, have been obtained by the action of hydrogen chloride on $3CdSO_4.8H_2O$ at different temperatures.[7, 8]

A saturated solution of $3CdSO_4.8H_2O$ contains 43·35 parts of $CdSO_4$ in every 100 parts of solution at −18° C., 44·99 parts at 60° C., 46·6 parts at 73·5° C., 37·8 parts at 100° C.,[9] and 2·3 parts at 200° C.[10] The diminution in solubility above 74° C. corresponds to the formation of the *monohydrate*, $CdSO_4.H_2O$, which separates when solutions of the ordinary hydrate are evaporated at temperatures above 80° C.[9] The monohydrate has been obtained by evaporating a solution of cadmium sulphate containing an excess of sulphuric acid.[11, 12] The crystals are monoclinic, and their density at 15° C. is 3·786.[13] They retain their water at 100° C.,[9, 12] and slowly combine with water at ordinary temperatures to form the ordinary hydrate.[9]

The Weston standard cell consists of the system mercury—mercurous sulphate (made into a paste with some cadmium sulphate)—cadmium sulphate crystals—cadmium sulphate solution—cadmium sulphate crystals—cadmium amalgam.[14] It has been suggested that certain irregularities noted in the behaviour of some Weston cells are due to a change undergone by $3CdSO_4.8H_2O$ at 15° C.,[15] two different modifications of the salt being possible below that temperature.[16] Careful determinations of the solubility between 13·7° C. and 25° C. did not indicate a transition-point at 15° C.[17]

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[1] Retgers, *Zeitsch. physikal. Chem.*, 1895, 16, 590; Worobieff, *Zeitsch. anorg. Chem.*, 1898, 18, 387.

[2] Perdue and Hulett, *J. Physical Chem.*, 1911, 15, 1579; Hulett and Quinn, *J. Amer. Chem. Soc.*, 1915, 37, 1997.

[3] Baxter and Wilson, *ibid.*, 1921, 43, 1237.

[4] Baxter and Wilson, *loc. cit.*, 1231.

[5] Boedeker, *Jahresber.*, 1860, 17 (3·05); Buignet, *J. Pharm. Chim.*, 1861, [3], 40, 161, 337 (2·939).

[6] Cohen and Moesveld, *Zeitsch. physikal. Chem.*, 1922, 100, 151; Cohen, Krinsheer, and Moesveld, *ibid.*, 1920, 96, 437 (0·2008); Holsboer (*ibid.*, 1902, 39, 701) found 0·2225. Seibert, Hulett, and Taylor (*J. Amer. Chem. Soc.*, 1917, 39, 46) determined the molecular heats over a considerable range of temperature.

[7] Baskerville and Harris, *J. Amer. Chem. Soc.*, 1901, 23, 896.

[8] *Cf.* Matignon, *Compt. rend.*, 1912, 154, 772.

[9] Mylius and Funk, *Ber.*, 1897, 30, 824.

[10] Étard, *Ann. Chim. Phys.*, 1894, [7], 2, 552.

[11] Kühn, *Arch. Pharm.*, 1847, [2], 50, 286.

[12] von Hauer, *J. prakt. Chem.*, 1855, [1], 64, 477.

[13] Wyrouboff, *Jahresber.*, 1889, 508; *Chem. Zentr.*, 1889, i, 341.

[14] Hagenbach, *Ann. Phys. Chem.*, 1896, [2], 58, 21; Jaeger and Wachsmuth, *ibid.*, 1896, [2], 59, 575.

[15] Kohnstamm and Cohen, *ibid.*, 1898, [2], 65, 344.

[16] Cohen, *Zeitsch. physikal. Chem.*, 1900, 34, 621.

[17] Steinwehr, *Ann. Physik*, 1902, [4], 9, 1046.

The *heptahydrate*, $CdSO_4.7H_2O$, is left as a granular powder when the cryohydrate of cadmium sulphate is melted. Above 4° C. it is slowly converted into the ordinary hydrate. Its solubility slowly rises from 44·45 per cent. $CdSO_4$ at $-17°$ C. to 48·7 at $-4·5°$ C.[1]

Various other hydrates that have been reported do not seem to exist.[1]

$$[CdSO_4]+400Aq. = CdSO_4.Aq.+10·74 \text{ Cal.}$$
$$[CdSO_4.H_2O]+400Aq. = CdSO_4.Aq.+6·05 \text{ Cal.}$$
$$[3CdSO_4.8H_2O]+400Aq. = CdSO_4.Aq.+2·66 \text{ Cal.}^2$$

Cadmium sulphate is moderately ionised in aqueous solution.[3] Ionisation has been said to proceed according to the equation

$$3CdSO_4 \rightleftharpoons [Cd_2SO_4]^{\cdot\cdot}+[Cd(SO_4)_2]''.^4$$

The *basic sulphates*, $4CdO.SO_3$ [5] and $2CdO.SO_3.H_2O$,[6] have been reported.

Compounds of Cadmium Sulphate with Ammonia.—Cadmium sulphate triammoniate, $CdSO_4.3NH_3$, is formed when cadmium sulphate absorbs ammonia gas. It decomposes into $CdSO_4.NH_3$ at 100° C.[7]

The hydrated compounds $2CdSO_4.4NH_3.5H_2O$ [8] and $CdSO_4.4NH_3.2H_2O$ [9] have been prepared.

Double Sulphates of Cadmium.—Cadmium sulphate, similarly to zinc sulphate, forms a series of double salts corresponding to the general formula $M_2SO_4.RSO_4.6H_2O$ ($M = NH_4$, Th, or any alkali metal except Li or Na, and $R =$ a divalent metal).[10]

The following double sulphates have also been described: $Na_2SO_4.CdSO_4$, $Na_2SO_4.3CdSO_4$, $3Na_2SO_4.CdSO_4$;[11] $Na_2SO_4.CdSO_4.2H_2O$;[11, 12] $K_2SO_4.2CdSO_4$, $K_2SO_4.3CdSO_4$;[13] $K_2SO_4.CdSO_4.1\frac{1}{2}H_2O$, $K_2SO_4.CdSO_4.2H_2O$;[14] $(NH_4)_2SO_4.2CdSO_4$;[15] $3(NH_4)_2SO_4.CdSO_4.10H_2O$;[16] $MgSO_4.CdSO_4.14H_2O$;[17] $3CdSO_4.Ce_2(SO_4)_3.6H_2O$;[18] $(Cd,Fe)SO_4.7H_2O$, $(Cd,Fe)SO_4.2\frac{2}{3}H_2O$.[19]

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[1] Mylius and Funk, *Ber.*, 1897, 30, 824.

[2] Thomsen, *Ber.*, 1878, 11, 1022. See Holsboer, *J. Chem. Soc.*, 1901, 80, Abs. ii, 226; Steinwehr, *Zeitsch. physikal. Chem.*, 1914, 88, 229.

[3] Lewis and Linhart, *J. Amer. Chem. Soc.*, 1919, 41, 1951. For conductivity data, see Jones and Caldwell, *Amer. Chem. J.*, 1901, 25, 376; Kahlenberg, *J. Physical Chem.*, 1901, 5, 348; Jones and Getman, *Zeitsch. physikal. Chem.*, 1904, 49, 420. For osmotic data, see Raoult, *ibid.*, 1888, 2, 489; Arrhenius, *ibid.*, 1888, 2, 497; Lescœur, *Ann. Chim. Phys.*, 1895, [7], 4, 222; Jones and Getman, *loc. cit.* For specific heats of solutions, see Cohen and Moesveld, *Zeitsch. physikal. Chem.*, 1920, 95, 305. For densities of solutions, see Barnes and Scott, *J. Physical Chem.*, 1898, 2, 536.

[4] Blomberg, *Zeitsch. anorg. Chem.*, 1915, 91, 248.

[5] Pickering, *Proc. Chem. Soc.*, 1907, 23, 261.

[6] Kühn, *Arch. Pharm.*, 1847, [2], 50, 286; Habermann, *Jahresber.*, 1884, ii, 321.

[7] Isambert, *Ber.*, 1870, 3, 246.

[8] Müller, *Annalen*, 1869, 149, 70.

[9] André, *Compt. rend.*, 1887, 104, 987.

[10] Locke, *Amer. Chem. J.*, 1902, 27, 455. For data, see Tutton, *Trans. Chem. Soc.*, 1893, 63, 356; 1896, 69, 444, 505; Pope, *ibid.*, 1896, 69, 540; Ortloff, *Zeitsch. physikal. Chem.*, 1896, 19, 218. For $K_2SO_4.CdSO_4.6H_2O$, also see Schiff, *Annalen*, 1858, 107, 64; and for the corresponding ammonium salt, see Tröger and Eners, *Chem. Zentr.*, 1898, i, 658; von Hauer, *J. prakt. Chem.*, 1855, [1], 64, 477; Schiff, *loc. cit.*

[11] Calcagni and Marotta, *Atti R. Accad. Lincei*, 1913, [5], 22, ii, 373.

[12] von Hauer, *J. prakt. Chem.*, 1855, [1], 64, 477.

[13] Calcagni and Marotta, *Atti R. Accad. Lincei*, 1913, [5], 22, ii, 442.

[14] von Hauer, *Pogg. Annalen*, 1868, 133, 176.

[15] Veres, *Compt. rend.*, 1914, 158, 39.

[16] André, *loc. cit.*

[17] Schiff, *loc. cit.*

[18] Wyrouboff, *Chem. Zentr.*, 1891, ii, 145.

[19] Stortenbeker, *Zeitsch. physikal. Chem.*, 1900, 34, 108.

Cadmium Thiosulphate, $CdS_2O_3.2H_2O$, is obtained by double decomposition between cadmium sulphate and barium or strontium thiosulphate. A colourless or yellowish oil separates when the solution, filtered free from insoluble sulphate, is treated with alcohol or alcohol and ether. After some time this oil solidifies into crystals.[1, 2]

The yellow-tinged crystals are monosymmetrical, retain their water in dry air, and decompose, gradually at low temperatures and quickly at high, according to the equation

$$4CdS_2O_3 = 3CdS + CdSO_4 + 4SO_2.^2$$

The *double salts*, as follows, have been prepared: $Na_2S_2O_3.3CdS_2O_3.9H_2O$, $Na_2S_2O_3.2CdS_2O_3.7H_2O$, and $3Na_2S_2O_3.CdS_2O_3.9H_2O$;[1] $3Na_2S_2O_3.CdS_2O_3.16H_2O$, $3Na_2S_2O_3.CdS_2O_3.3H_2O$; $5K_2S_2O_3.3CdS_2O_3$, $3K_2S_2O_3.CdS_2O_3.2H_2O$; $3(NH_4)_2S_2O_3.CdS_2O_3.3H_2O$, $3(NH_4)_2S_2O_3.CdS_2O_3$; $2BaS_2O_3.CdS_2O_3.8H_2O$, $3BaS_2O_3.CdS_2O_3.8H_2O$; $3SrS_2O_3.CdS_2O_3.10H_2O$.[3]

Cadmium Dithionate.—Soluble deliquescent crystals of the *dihydrate*, $CdS_2O_6.2H_2O$, were obtained by dissolving cadmium carbonate in the acid.[4]

Cadmium Tetrathionate has been prepared as unstable, deliquescent crystals.[5]

CADMIUM AND SELENIUM.

Cadmium Selenide.—When cadmium and selenium are heated together they form cadmium selenide, CdSe.[6] The reaction begins at 360° C. and becomes more vigorous with rising temperature. The selenide is infusible up to 1350° C., and its density is 5·81 at 16° C.[7] It also results when cadmium is heated in hydrogen selenide.[6]

Dark brown CdSe is precipitated from solutions of cadmium salts by hydrogen selenide or alkaline selenides. Acids liberate hydrogen selenide from it.[8]

When cadmium and selenium vapours were heated at a high temperature the resulting selenide was a crystalline mass, golden yellow and lustrous.[9] Margottet obtained lamellated crystals belonging to the regular system[10] by subliming the selenide in hydrogen. They were yellow to blood-red, and their density was 5·80.[6] Brown rhombic crystals, isomorphous with the corresponding zinc selenide, of density 5·81 at 15° C., were obtained by heating cadmium chloride in a current of hydrogen containing hydrogen selenide.[11]

Cadmium selenide is easily decomposed by acids, and chlorine displaces selenium from it on warming. Cadmium oxide and selenium dioxide are formed when it is heated in a current of oxygen.[1]

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[1] Vortmann and Padberg, *Ber.*, 1889, **22**, 2638.

[2] Fock and Klüss, *ibid.*, 1890, **23**, 534.

[3] Fock and Klüss, *loc. cit.*, 1753.

[4] Heeren, *Pogg. Annalen*, 1826, **7**, 183.

[5] Kessler, *ibid.*, 1848, **74**, 249.

[6] Margottet, *Compt. rend.*, 1877, **84**, 1293.

[7] Chikashige and Hikosaka, *Mem. Coll. Sci. Kyoto*, 1917, **2**, 239.

[8] Uelsmann, *Annalen*, 1860, **116**, 126. The *yellow* precipitate obtained by passing a little hydrogen selenide through a concentrated solution of cadmium iodide is $3CdSe.CdI_2$ (Fonzes-Diacon, *Compt. rend.*, 1900, **131**, 896).

[9] Little, *Annalen*, 1859, **112**, 213.

[10] Margottet, *Zeitsch. Kryst. Min.*, 1878, **2**, 106.

[11] Fonzes-Diacon, *Compt. rend.*, 1900, **131**, 896.

$$[\mathrm{Cd}]+[\mathrm{Se}]=[\mathrm{CdSe}]\ (\text{cryst.})+26{\cdot}0\ \text{Cal.}$$

The corresponding figure for precipitated CdSe is 22·9 Cal.[2]

Cadmium Selenites.—A yellow crystalline powder of the acid selenite, $2CdO.3SeO_2.H_2O$, deposits when cadmium carbonate is heated in a solution of selenious acid. It is insoluble in water, soluble in acids, and leaves a residue of cadmium oxide on calcination. If it is heated in a sealed tube to 230° C. with three times its weight of selenium dioxide it forms yellow orthorhombic crystals of the biselenite, which has similar properties ($CdO.2SeO_2$). If heated with water in a sealed tube to 200° C. it forms the *neutral anhydrous* selenite, $CdSeO_3$. This is a pale yellow powder consisting of small orthorhombic crystals. It behaves like the acid salts towards water, acids, and heat.

This salt has also been obtained by dissolving cadmium hydroxide in selenious acid.

The *hydrate*, $2CdSeO_3.3H_2O$, precipitates as a white amorphous powder by adding a solution of sodium selenite to a solution of zinc chloride.

The salts, $3CdO.4SeO_2.H_2O$ and $3CdO.4SeO_2.2H_2O$, have been prepared.[3]

Cadmium Selenate.—The *dihydrate*, $CdSeO_4.2H_2O$, can be crystallised in transparent tabular crystals from a solution of cadmium oxide in selenic acid. It dissolves readily in water, loses half its water at 100° C., and becomes anhydrous at higher temperatures.[4] It crystallises in the monoclinic system.[5]

The *double salts*, $Rb_2SeO_4.CdSeO_4.6H_2O$,[6] $Cs_2SeO_4.CdSeO_4.6H_2O$,[6] $(NH_4)_2SeO_4.CdSeO_4.6H_2O$,[6,7] and $(NH_4)_2SeO_4.CdSeO_4.2H_2O$,[7] have been prepared.

CADMIUM AND TELLURIUM.

Cadmium Telluride, CdTe, was obtained as a dark powder by heating cadmium tellurite or tellurate in a stream of hydrogen. When it is strongly heated some tellurium is liberated and a porous grey metallic mass results.[8] Dark crystals belonging to the cubic system, of density 6·20, were prepared by melting cadmium and tellurium together and subliming the product in a current of hydrogen.[9]

CdTe falls as a heavy maroon precipitate when sodium telluride solution is added to a solution of cadmium acetate acidified with acetic acid. It oxidises readily when moist and is almost black when dry. Only nitric acid of the ordinary dilute acids attacks it in the cold.[10]

$$[\mathrm{Cd}]+[\mathrm{Te}]\ (\text{cryst.})=[\mathrm{CdTe}]\ (\text{cryst.})+19{\cdot}96\ \text{Cal.}^{11}$$

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[1] Fonzes-Diacon, *Compt. rend.*, 1900, 131, 896.
[2] Fabre, *ibid.*, 1886, 103, 345.
[3] Boutzoureano, *Ann. Chim. Phys.*, 1889, [6], 18, 291, 307.
[4] von Hauer, *J. prakt. Chem.*, 1860, [1], 80, 214.
[5] Topsöe and Christiansen, *Jahresber.*, 1873, 141.
[6] Tutton, *Proc. Roy. Soc.*, 1922, [A], 101, 245.
[7] Gerichten, *Annalen*, 1873, 168, 221.
[8] Oppenheim, *J. prakt. Chem.*, 1857, [1], 71, 266.
[9] Margottet, *Compt. rend.*, 1877, 84, 1293.
[10] Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 908.
[11] Fabre, *Compt. rend.*, 1887, 105, 277.

Cadmium Tellurite.—White amorphous cadmium tellurite is precipitated by interaction in solution between a cadmium salt and an alkaline tellurite.[1, 2] The composition of the precipitate, when pure, appears to be $3CdTeO_3.2H_2O$.[2]

Cadmium Tellurate.—A white precipitate was obtained by precipitating cadmium nitrate solution with potassium tellurate.[3]

CADMIUM AND CHROMIUM.

Cadmium Chromite.—A small yield of $CdO.Cr_2O_3$ is obtained by heating potassium chromate in hydrogen or carbon dioxide containing cadmium chloride vapour. The black aggregations of octahedra are harder than glass but less hard than quartz. Their density is 5·79 at 17° C.[4]

Cadmium Chromate.—Alkali chromates precipitate basic or double chromates from solutions of cadmium salts.[5]

The *normal anhydrous chromate*, $CdCrO_4$, was obtained as a yellow powder, consisting of transparent prisms, by heating cadmium oxide, chromium trioxide, and water to 200° C. in a sealed tube.[6]

The *dihydrate*, $CdCrO_4.2H_2O$, was obtained by heating the dichromate with cadmium hydroxide in a sealed tube at 200° C. It is an orange crystalline powder, insoluble in water, soluble in acids, and goes brown on heating.[7]

The *ammoniates*, $CdCrO_4.NH_3.H_2O$[8] and $CdCrO_4.4NH_3.3H_2O$,[9] have been prepared.

The following *double chromates of cadmium and their ammoniates* have been prepared: $K_2O.CdO.4CrO_3.2H_2O$;[10] $K_2CrO_4.CdCrO_4.2H_2O$;[11] $(NH_4)_2CrO_4.CdCrO_4.2NH_3$;[12] $2(NH_4)_2CrO_4.2CdCrO_4.2NH_3.3H_2O$.[13]

Cadmium Dichromate, $CdCr_2O_7.H_2O$, is difficult to crystallise from its solutions,[10] but has been obtained by evaporating a solution of cadmium carbonate in chromic acid under reduced pressure.[14]

The crystals are orange and their aqueous solution easily decomposes. Dark red deliquescent crystalline crusts of a *trichromate*, $CdO.3CrO_3.H_2O$, have been obtained from such decomposed solutions.[15]

The salt, $CdCr_2O_7.2Hg(CN)_2.7H_2O$, has been obtained,[10] and the double salt, $K_2Cr_2O_7.CdCr_2O_7.2H_2O$.[10]

CADMIUM AND MOLYBDENUM.

Cadmium Molybdate.—Yellow shining leaf-like crystals of $CdMoO_4$ were obtained by melting sodium molybdate, cadmium chloride,

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[1] Oppenheim, *J. prakt. Chem.*, 1857, [1], 71, 266.

[2] Lenher and Wolesensky, *J. Amer. Chem. Soc.*, 1913, 35, 725.

[3] Oppenheim, *loc. cit.*

[4] Viard, *Compt. rend.*, 1889, 109, 142.

[5] Gröger, *Monatsh.*, 1904, 25, 520; Freese, *Ber.*, 1869, 2, 478; Malaguti and Sarzeau, *Ann. Chim. Phys.*, 1843, [3], 9, 431.

[6] Briggs, *Zeitsch. anorg. Chem.*, 1908, 56, 253.

[7] Schulze, *ibid.*, 1895, 10, 152.

[8] Gröger, *ibid.*, 1908, 58, 418.

[9] Malaguti and Sarzeau, *loc. cit.*

[10] Krüss and Unger, *Zeitsch. anorg. Chem.*, 1895, 8, 452.

[11] Gröger, *ibid.*, 1907, 54, 189.

[12] Briggs, *Trans. Chem. Soc.*, 1903, 83, 395.

[13] Gröger, *Zeitsch. anorg. Chem.*, 1908, 58, 418.

[14] Schulze, *ibid.*, 1895, 10, 153.

[15] Gröger, *ibid.*, 1910, 66, 10.

and salt together.[1] As precipitated by adding an alkaline molybdate to a solution of cadmium nitrate it is a heavy granular salt, insoluble in water and, when moist, soluble in ammonia, acids, and potassium cyanide. Ignition does not make it insoluble in acids.[2] $CdO.H_2O.8MoO_3.6H_2O$ [3] and $(I_2O_5.2MoO_3).3CdO.15H_2O$ [4] have been prepared.

CADMIUM AND TUNGSTEN.

Cadmium Tungstate.—$CdWO_4$ has been prepared as colourless imperfect crystals by melting sodium tungstate, cadmium chloride, and salt.[5]

A white amorphous *monohydrate*, $CdWO_4.H_2O$, is precipitated from solutions of cadmium acetate by sodium tungstate. One part dissolves in about 2000 parts of water at 15° C.[6]

The *dihydrate*, $CdWO_4.2H_2O$, is precipitated from mixed solutions of a cadmium salt and sodium tungstate. It is very insoluble in water and, after ignition, in acids.[7]

The *metatungstate*, $CdO.4WO_3.10H_2O$,[8] and the *paratungstate*, $3CdO.7WO_3.16H_2O$,[9] have been prepared.

The *double salts*, $Na_2O.2CdO.7WO_3.18H_2O$ [10] and $3(NH_4)_2O.12CdO.35WO_3.35H_2O$,[11] have been reported.

CADMIUM AND NITROGEN.

Cadmium Nitride, Cd_3N_2, is a black amorphous powder obtained by heating cadmium amide *in vacuo* at 180° C. On exposure to moist air it becomes orange and then white. In contact with water it explodes, and metallic cadmium is deposited.[12]

Cadmium Azide, $Cd(N_3)_2$, was obtained by Curtius and Rissom by dissolving cadmium carbonate in azoimide and evaporating in a desiccator. It crystallises in yellow tabular biaxial crystals. It does not explode under the hammer, but decomposes with a brilliant light when heated, though without any noteworthy detonation.[13]

The decomposition of 1 grm. is accompanied by the evolution of 0·558 Cal.[14]

Cadmium Amide.—When solutions of cadmium iodide or potassium cadmium cyanide are treated with potassamide dissolved in liquid ammonia, cadmium amide, $Cd(NH_2)_2$, is formed if the latter reagent is in excess. It is a white powder that becomes orange in moist air and finally changes to white cadmium hydroxide. It reacts violently with water, and explodes on heating with the liberation of metallic cadmium.

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[1] Schulze, *Annalen*, 1863, **126**, 51.

[2] Smith and Bradbury, *Ber.*, 1891, **24**, 2935.

[3] Wempe, *Zeitsch. anorg. Chem.*, 1912, **78**, 323.

[4] Chrétien, *Ann. Chim. Phys.*, 1898, [7], **15**, 358.

[5] Geuther and Forsberg, *Annalen*, 1861, **120**, 272.

[6] Lefort, *Ann. Chim. Phys.*, 1878, [5], **15**, 345.

[7] Anthon, *J. prakt. Chem.*, 1836, [1], **9**, 341; Smith and Bradbury, *loc. cit.*; *Bull. Soc. chim.*, 1891, [3], 8, 279.

[8] Scheibler, *J. prakt. Chem.*, 1861, [1], **83**, 273.

[9] Gonzalez, *ibid.*, 1887, [2], **36**, 44.

[10] Knorre, *Ber.*, 1886, **19**, 823.

[11] Lotz, *Annalen*, 1854, **91**, 63.

[12] Bohart, *J. Physical Chem.*, 1915, **19**, 537.

[13] Curtius and Rissom, *J. prakt. Chem.*, 1898, [2], **58**, 294.

[14] Wöhler and Martin, *Ber.*, 1917, **50**, 594.

Potassium Cadmium Amide, $Cd(NHK)_2.2NH_3$, is produced as a white flocculent powder when the cadmium salt in the above reaction is in excess. Light turns it grey and it reacts violently with water, producing ammonia and the hydroxides of potassium and cadmium.[1]

Cadmium Nitrite.—Pale yellow crystals of *anhydrous nitrite*, $Cd(NO_2)_2$, are obtained by triturating cadmium chloride and silver nitrite together, adding water, filtering, and evaporating *in vacuo* over sulphuric acid. Its decomposition by heat seems to be represented by the two equations

$$3Cd(NO_2)_2 = 2CdO + Cd(NO_3)_2 + 4NO;$$
$$Cd(NO_2)_2 = CdO + NO + NO_2.$$

Cadmium nitrate is ionised very distinctly in aqueous solution and tends to form basic salts.[2]

A solution of cadmium nitrite is obtained by interaction between equivalent quantities of barium nitrite and cadmium sulphate in solution. A hygroscopic crystalline mass of the *monohydrate*, $Cd(NO_2)_2.H_2O$, has been obtained from such a solution,[3] but, even by careful evaporation, a basic salt is often obtained,[4] and it is difficult to obtain a salt in which the ratio $NO_2 : Cd$ is as high as 2 : 1.[5]

The colourless double salt, $KNO_2.Cd(NO_2)_2$,[4] and the yellow salts, $2KNO_2.Cd(NO_2)_2$ and $4KNO_2.Cd(NO_2)_2$,[3] have been prepared crystalline by treating a solution of cadmium acetate with potassium nitrite. The salt $2NH_4.NO_2.Cd(NO_2)_2.H_2O.CdO.2NH_3$ has been obtained in transparent rhomboidal prisms by treating a saturated solution of ammonium nitrate with granulated cadmium,[6] and the complex nitrites, $4KNO_2.2Cd(NO_2)_2.Ni(NO_2)_2$, $4TlNO_2.2Cd(NO_2)_2.Ni(NO_2)_2$, and $2NH_4NO_2.Cd(NO_2)_2.Ni(NO_2)_2$, have also been prepared.[7]

Cadmium nitrite also forms the compound $Cd(NO_2)_2.2H_2O.C_6H_{12}N_4$ with hexamethylenetetramine.[8]

Cadmium Nitrate.—The *tetrahydrate*, $Cd(NO_3)_2.4H_2O$, crystallises in mixed prisms and needles from solutions of cadmium nitrate at ordinary temperatures.[9, 10] It is deliquescent,[9, 10] has a density of 2·450 at 14° C. or 2·460 at 20° C.,[11] melts at 59·5° C.,[12] and boils at about 132° C. The latter solution remains clear till about three-quarters of the water is lost.[9, 12] According to Ditte,[13] some nitric acid is also lost and a basic salt remains. A red heat finally decomposes the salt into crystalline cadmium oxide.[14]

The solubility of the tetrahydrate varies from 52·31 parts of $Cd(NO_3)_2$

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[1] Bohart, *loc. cit.*

[2] Rây, *Trans. Chem. Soc.*, 1917, **111**, 160.

[3] Lang, *J. prakt. Chem.*, 1862, [1], **86**, 295.

[4] Hampe, *Annalen*, 1863, **125**, 347.

[5] Vogel, *Zeitsch. anorg. Chem.*, 1903, **35**, 400.

[6] Morin, *Compt. rend.*, 1885, **100**, 1497.

[7] Cuttica, *Gazzetta*, 1922, **52**, i, 210.

[8] Scagliarini, *Atti R. Accad. Lincei*, 1912, [5], **21**, ii, 640.

[9] Funk, *Zeitsch. anorg. Chem.*, 1899, **20**, 414.

[10] Hauer, *J. prakt. Chem.*, 1855, **64**, 477.

[11] Laws, *Jahresber.*, 1877, 43.

[12] Ordway, *ibid.*, 1859, 113. Funk (*loc. cit.*) confirms 59·5° C. against the 100° C. of Hauer, *loc. cit.* Hasselblatt (*Zeitsch. anorg. Chem.*, 1921–22, **119**, 319) gives 59·3° C. for the melting-point.

[13] Ditte, *Ann. Chim. Phys.*, 1879, [5], **18**, 341.

[14] Schüler, *Annalen*, 1853, **87**, 43.

in 100 parts of solution at 0° C. to 76·54 parts at 59·5° C. At lower temperatures a *heptahydrate* separates from the solution—its solubility varies from 37·37 at −13° C. to 52·73 at +1° C.[1]

$$[Cd(NO_3)_2.4H_2O]+400Aq.=Cd(NO_3)_2.Aq.-5{\cdot}04\ Cal.^2$$

Vasilieff obtained *anhydrous* cadmium nitrate, melting at about 350° C. and dissolving in water with much evolution of heat, by evaporating the hydrated salt, and an *octahydrate* by crystallisation at low temperatures. He could not obtain a di- or hexa-hydrate.[3]

The *basic nitrates*, $Cd(OH)(NO_3).H_2O$,[4] $12CdO.N_2O_5.11H_2O$,[5] $2CdO.N_2O_5.3H_2O$,[6] and $5CdO.2N_2O_5.8H_2O$,[7] have been described.

Ammoniates.—Bulky anhydrous crystals of the *hexammoniate*, $Cd(NO_3)_2.6NH_3$, were prepared by passing ammonia gas into a solution of cadmium nitrate in ammonia solution. Its *dihydrate* was obtained by cooling a solution of cadmium nitrate in 20 per cent. ammonia solution. It melts when heated, evolving a little water, and then blackens with a slight explosion.[8]

CADMIUM AND PHOSPHORUS.

Cadmium Phosphide.—A fused crystalline grey phosphide of cadmium is obtained by heating cadmium and phosphorus vapours in an atmosphere of hydrogen.[9]

A brown powder is precipitated when a solution of cadmium oxide in potassium hydroxide is heated with phosphorus and some benzene. It evolves phosphine with hydrochloric acid and explodes with nitric acid. A grey crystalline mass of Cd_3P_2, with a metallic lustre, is produced by heating it in a current of hydrogen.[10]

Rénault obtained Cd_3P_2, which closely resembled the corresponding zinc phosphide in properties and was prepared similarly. He prepared the *diphosphide*, CdP_2, most easily by heating a mixture of ammonium phosphate (or phosphate of mercury or tin) with cadmium carbonate and carbon. After condensing the volatile products the cadmium phosphide was washed with dilute hydrochloric acid.

The diphosphide usually occurs in bright red crystals, though it is sometimes obtained in indigo-blue scales or plates. Its chief chemical difference from ZnP_2 is its ready decomposition by boiling hydrochloric acid.[11]

Emmerling prepared the *subphosphide*, Cd_2P, by heating cadmium and phosphorus together. It is a greyish or silver-white mass consisting of fine needles. Hydrochloric acid evolves phosphine from it.[12]

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[1] Funk, *Ber.*, 1899, 32, 105. Franz (*J. prakt. Chem.*, 1872, [2], 5, 274) has determined the densities of cadmium nitrate solutions.

[2] Thomsen, *Ber.*, 1878, 11, 1022. He also gave +4·180 Cal. for a monohydrate.

[3] Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 562.

[4] Klinger, *Ber.*, 1883, 16, 997.

[5] Habermann, *Jahresber.*, 1884, i, 320.

[6] Wells, *Amer. Chem. J.*, 1887, 9, 304.

[7] Rousseau and Tite, *Compt. rend.*, 1892, 114, 1186.

[8] André, *ibid.*, 1887, 104, 987.

[9] Vigier, *Chem. News*, 1861, 3, 274.

[10] Oppenheim, *Ber.*, 1872, 5, 980.

[11] Rénault, *Compt. rend.*, 1873, 76, 283.

[12] Emmerling, *Ber.*, 1879, 12, 154.

Cadmium Hypophosphite separates in very small crystals when a solution of cadmium carbonate in hypophosphorous acid is evaporated.[1] The salt is anhydrous, $Cd(H_2PO_2)_2$.[2]

Cadmium Orthophosphate.—When cadmium pyrophosphate is heated in sealed tubes to about 300° C. with water, a solution of acid phosphate and an insoluble tribasic phosphate result.[3] Amorphous $Cd_3(PO_4)_2$ is also precipitated from solutions of cadmium salts by normal sodium phosphate. When its solution in fused cadmium chloride is slowly cooled, long hexagonal prisms of *cadmium chlorapatite*, $3Cd_3(PO_4)_2.CdCl_2$, of density 5·46 at 15° C., separate. The analogous *cadmium bromapatite* occurs in flattened oblique lamellæ of density 4·965 at 15° C.[4]

The *acid phosphate*, $Cd_5H_2(PO_4)_4.4H_2O$, is precipitated by hydrogen disodium phosphate from hot solutions of cadmium chloride or sulphate. The amorphous precipitate quickly becomes crystalline and, after purification, forms small prismatic hexagons of density 3·98 at 15° C. The density of the crystals becomes 4·12 at 15° C. when they are precipitated from their solution in phosphoric acid.

When a saturated solution of the above salt in cold dilute phosphoric acid is slowly evaporated at normal temperature, orthorhombic prisms of monocadmium phosphate, $H_4Cd(PO_4)_2.2H_2O$, crystallise.

Cadmium Pyrophosphate.—The *dihydrate*, $Cd_2P_2O_7.2H_2O$, is precipitated as a heavy white powder by adding a solution of sodium pyrophosphate to a solution of cadmium sulphate. It can be obtained crystalline from its solution in sulphurous acid. It behaves similarly to $2Zn_2P_2O_7.3H_2O$ when heated in air, dissolves in aqueous ammonia, acids, or sodium pyrophosphate, but not in caustic alkalies, and becomes anhydrous on heating.[5]

The *anhydrous* salt was obtained in flattened oblique lamellæ of density 4·965 at 15° C., along with cadmium bromapatite, $3Cd_3(PO_4)_2.CdBr_2$, by cooling a melt of cadmium orthophosphate and cadmium bromide. Cold dilute nitric acid dissolved the latter and left the pyrophosphate.[6]

Heating with water decomposes cadmium pyrophosphate into a solution of acid cadmium phosphate and tribasic cadmium orthophosphate.[3]

Some *double salts* of the general formula $w(Na_2 \text{ or } K_2)O.74CdO.7P_2O_5.LH_2O$ have been reported.[7] The double orthophosphate of ammonium and cadmium is used for estimating cadmium.[8]

Cadmium Thiophosphates.—*Cadmium Thio-orthophosphate*, $Cd_3(PS_4)_2$, is obtained as a white crystalline powder by heating phosphorus pentasulphide with cadmium chloride or sulphate. It behaves similarly to the corresponding zinc salt.[9]

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[1] Rose, *Ann. Chim. Phys.*, 1828, [2], 38, 270.

[2] Rammelsberg, *Ber.*, 1872, 5, 494.

[3] Reynoso, *Ann. Chim. Phys.*, 1855, [3], 45, 108.

[4] de Schulten, *Bull. Soc. chim.*, 1889, [3], 1, 473.

[5] Schwarzenberg, *Annalen*, 1848, 65, 153.

[6] de Schulten, *Bull. Soc. chim.*, 1889, [3], 1, 473.

[7] Pahl, *Ber.*, 1873, 6, 1465; Wallroth, *Bull. Soc. chim.*, 1883, [2], 39, 316; Grandeau, *Ann. Chim. Phys.*, 1886, [6], 8, 203; Ouvrard, *Compt. rend.*, 1888, 106, 1730; *Ann. Chim. Phys.*, 1889, [6], 16, 320.

[8] See under Estimation of Cadmium.

[9] Glatzel, *Zeitsch. anorg. Chem.*, 1893, 4, 202.

Cadmium Thio-hypophosphate, $Cd_2P_2S_6$, is prepared, similarly to the corresponding zinc salt, in orange-yellow biaxial crystals.[1] It decomposes partially in moist air. Aqueous alkalies liberate some hydrogen sulphide from it, and nitric acid acts on it very rapidly.[2]

Cadmium Thio-pyrophosphate, $Cd_2P_2S_7$, was obtained similarly. The white crystalline powder decomposes rapidly in air but is resistant to acids, and even hot concentrated nitric acid has only a slight action.[3]

CADMIUM AND ARSENIC.

Cadmium Arsenide.—The freezing-point, density, and atomic volume curves, supplemented by an examination of the microstructure, confirm the existence of Cd_3As_2 and $CdAs_2$. Cd_3As_2 is reddish grey, of density 6·25, and it melts at 721° C. Its hardness is less than 3·5. $CdAs_2$ is bluish grey, of density 5·86, and it melts at 621° C. Its hardness is 3·5–4·0.[4]

Cd_3As_2 has been prepared by subjecting cadmium and arsenic, in appropriate proportions, to a pressure of 6500 atmospheres. Some Cd_6As was formed when cadmium and arsenic were melted together;[5] but Cd_3As_2 is readily formed by heating cadmium in arsenic vapour mixed with hydrogen or an inert gas. It was thus obtained in reddish octahedra of density 6·211 at 15° C. It reacts with acids and the halogens like the arsenides in general.[6]

Descamps obtained Cd_3As by reducing cadmium arsenate with potassium cyanide. It was white, with a slight reddish colour and a metallic lustre.[7]

Cadmium Arsenite, $Cd_3(AsO_3)_2$, is precipitated from a solution of cadmium chloride in 50 per cent. alcohol by a solution of potassium arsenite neutralised with acetic acid,[8] or from a solution of cadmium sulphate by sodium metarsenite.[9] The impure arsenite, precipitated by mixing solutions of cadmium sulphate and potassium arsenite,[8] can be purified by solution in dilute acid and re-precipitation.[10]

The white precipitate is slightly soluble in water, easily in ammonia solution or dilute acids, and can be converted into anhydrous $Cd_3(AsO_3)_2$ by heating at 100° C. in a stream of hydrogen.[8] Alkalies do not attack it, and ignition leaves a residue of cadmium oxide contaminated with arsenic.[10]

Cadmium Arsenates.—The hydrated *normal cadmium orthoarsenate*, $2Cd_3(AsO_4)_2.3H_2O$, falls as a white voluminous precipitate on adding alkali to a solution of an acid cadmium arsenate.[11]

Cadmium Chlorarsenioapatite, $3Cd_3(AsO_4)_2.CdCl_2$, is produced by fusing normal ammonium arsenate or the salt $H_2Cd_5(AsO_4)_4.4H_2O$

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[1] Ferrand, *Bull. Soc. chim.*, 1895, [3], 13, 115.

[2] Ferrand, *Ann. Chim. Phys.*, 1899, [7], 17, 423.

[3] Ferrand, *Compt. rend.*, 1896, 122, 888.

[4] Schemtschuschny, *Int. Zeitsch. Metallographie*, 1913, 4, 228; *J. Russ. Phys. Chem. Soc.*, 1913, 45, 1137.

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

[6] Granger, *Compt. rend.*, 1904, 138, 574.

[7] Descamps, *ibid.*, 1878, 86, 1022, 1065.

[8] Stavenhagen, *J. prakt. Chem.*, 1895, [2], 51, 22.

[9] Reichard, *Ber.*, 1898, 31, 2168.

[10] Reichard, *ibid.*, 1894, 27, 1033.

[11] Demel, *ibid.*, 1879, 12, 1281.

with excess of cadmium chloride. Its density at 15° C. is 5·865, and it resembles the corresponding phosphatic compound. The analogous bromo compound is analogously prepared in long yellow prisms of density 6·017.[1]

The precipitate from mixed solutions of cadmium sulphate and hydrogen disodium arsenate is $5CdO.2As_2O_5.5H_2O$[2] (or $H_2Cd_5(AsO_4)_4.4H_2O$). If the saturated solution of this salt in arsenic acid is heated, crystals of the *acid salt*, $HCdAsO_4.H_2O$, of density 4·164 at 15° C., separate.[1] It has also been prepared by dissolving cadmium carbonate in a solution of arsenic acid. The white crystalline substance dissolves easily in dilute hydrochloric acid, and is said to be decomposed by water into $5CdO.2As_2O_5.5H_2O$.[3]

If the arsenic acid solution of $H_2Cd_5(AsO_4)_4.4H_2O$ evaporates at ordinary temperatures, rhombic prisms of $H_4Cd(AsO_4)_2.2H_2O$, of density 3·241 at 15° C., separate. They are isomorphous with the corresponding phosphate, lose their water with partial decomposition at 70°–80° C., and excess of water converts them into flocculent $H_2Cd_5(AsO_4)_4.4H_2O$.[1]

Firm transparent jellies are produced when solutions of dihydrogen potassium arsenate and cadmium sulphate, of suitable concentrations, are mixed. They are unstable, and crystallise into $2Cd_3(AsO_4)_2.4CdHAsO_4.9H_2O$.[4]

The following *double arsenates* have been described: $Na_4CdAs_2O_8$, $Na_8Cd_2As_2O_{11}$, $K_2Cd_2As_2O_8$.[5]

CADMIUM AND ANTIMONY.

Cadmium Metantimonate, $CdSb_2O_6.6H_2O$, is precipitated by adding excess of a concentrated solution of a cadmium salt to boiling aqueous sodium antimonate.[6]

CADMIUM AND CARBON.

Cadmium Carbonate.—Solutions of cadmium salts are less liable than those of zinc to give basic carbonates when precipitated with alkali carbonate solutions.

The *normal anhydrous carbonate*, $CdCO_3$, mixed with some of the basic sulphate, $2CdO.SO_3$, is precipitated by adding cadmium sulphate solution to dissolved sodium carbonate,[7] and it has been prepared by adding a large excess of concentrated ammonium carbonate solution to dissolved cadmium chloride. A pure product was secured by dissolving the precipitated carbonate in hydrochloric acid and re-precipitating—repeating three times.[1]

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[1] de Schulten, *Bull. Soc. chim.*, 1889, [3], 1, 473.

[2] Salkowski, *J. prakt. Chem.*, 1868, [1], 104, 129.

[3] Demel, *loc. cit.*

[4] Klemp and Gyulay, *Kolloid Zeitsch.*, 1921, 28, 262.

[5] Lefèvre, *Compt. rend.*, 1890, 110, 405.

[6] Ebell, *Ber.*, 1889, 22, 3044. The air-dried salt, according to Sanderens (*Bull. Soc. chim.*, 1899, [3], 21, 47), has 5 molecules of water, and loses 3 over sulphuric acid.

[7] Kraut, *Zeitsch. anorg. Chem.*, 1897, 13, 14. Lefort obtained $2CdCO_3.H_2O$ by precipitating a solution of a cadmium salt with an alkaline carbonate solution. It lost its water between 80° C. and 120° C. (*Compt. rend.*, 1847, 27, 268). Rose (*Ann. Chim. Phys.*, 1854, [3], 42, 107) obtained the basic salt, $10CdCO_3.Cd(OH)_2.2H_2O$, from cold concentrated solutions of cadmium sulphate and potassium carbonate. A salt with an extra molecule of water was obtained from more dilute solutions. Almost pure $CdCO_3$ resulted with an excess of sodium carbonate.

Rhombohedra of $CdCO_3$, similar to those of calcite, were obtained by heating the white amorphous carbonate with water and ammonium chloride in a tube at 150°–180° C.[2] Similar crystals, of density 4·960, were formed by adding excess of ammonium carbonate to a solution of cadmium chloride, dissolving the precipitate in just enough ammonia solution and heating on the water-bath.[3]

Cadmium carbonate is only slightly soluble in water[4] and is not very soluble in carbonated water, even when the carbon dioxide is forced in under pressure.[5] It is more or less soluble in solutions of ammonium salts, and slightly in dissolved alkaline carbonates. The precipitation of cadmium carbonate and its ignition to oxide provides a method for estimating cadmium.[6]

The mineral *otavite*, crystallised in minute curved octahedra, is a basic cadmium carbonate containing 61·5 per cent. of cadmium.[7]

Cadmium Thiocarbonate is too unstable to examine, though it may be temporarily produced analogously to zinc thiocarbonate.[8]

Cadmium Cyanide.—White crystalline $Cd(CN)_2$ has been precipitated from a saturated solution of cadmium sulphate with concentrated potassium cyanide solution,[9] and in a similar way, as a voluminous, more amorphous mass, the salt has been precipitated from a fairly concentrated solution of cadmium chloride.[10] Rammelsberg evaporated a solution of freshly precipitated cadmium hydroxide in hydrocyanic acid,[11] but, according to Joannis,[9] some insoluble *basic* cadmium cyanide, $2Cd(CN)_2.CdO.5H_2O$, is simultaneously produced.

One hundred c.c. of water at 15° C. dissolve 1·7 grm. $Cd(CN)_2$. It dissolves in acids[9] and is insoluble in ammonium chloride solution.[12] It is stable in air, but on ignition leaves cadmium oxide, or, if access of air is restricted, metallic cadmium.[10]

The heat of formation of cadmium cyanide is 40·0 Cal. from solid cadmium and gaseous cyanogen, and of $2Cd(CN)_2.CdO.5H_2O$, 22·0 Cal.[9]

The *diammoniate* of *cadmium thiocyanate*, $Cd(CNS)_2.2NH_3$, is analogous to the corresponding zinc compound and is similarly prepared.[13]

CADMIUM AND SILICON.

Cadmium Silicate.—When cadmium nitrate is heated in a glass tube at about 300° C., the hydrated cadmium *silicate*, $2(CdSiO_3).3H_2O$, forms on the inner surface in long scales which break between the fingers into microscopic needles. The compound is soluble in hydrochloric acid with the separation of silica. Under strong ignition it finally leaves a residue of silica, but there is very little loss, even of water, until it melts and intumesces at an orange-red heat.[1]

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[1] Coninck and Gérard, *Compt. rend.*, 1915, 161, 676. According to Follenius (*Zeitsch. anal. Chem.*, 1874, 13, 296), precipitated cadmium carbonate is always somewhat basic unless ammonium carbonate is the precipitant.

[2] Bourgeois, *Compt. rend.*, 1886, 103, 1088.

[3] de Schulten, *Bull. Soc. franç. Min.*, 1897, 20, 195.

[4] Immerwahr, *Zeitsch. Elektrochem.*, 1901, 7, 477.

[5] Kraut, *loc. cit.*

[6] Follenius, *Zeitsch. anal. Chem.*, 1874, 13, 292.

[7] Schneider, *Centr. Min.*, 1906, 388.

[8] Hofmann, *Zeitsch. anorg. Chem.*, 1897, 14, 277.

[9] Joannis, *Ann. Chim. Phys.*, 1882, [5], 26, 506.

[10] Schüler, *Annalen*, 1853, 87, 46.

[11] Rammelsberg, *Pogg. Annalen*, 1836, 38, 364.

[12] Bret, *Annalen*, 1837, 23, 136.

[13] Fleischer, *ibid.*, 1875, 179, 233.

CADMIUM AND BORON.

Cadmium Borates.—The anhydrous *orthoborate*, $Cd_3(BO_3)_2$, has been prepared by fusing potassium hydrogen fluoride, boron trioxide, and cadmium oxide in molecular proportions. On treating the cooled melt with water prismatic crystals of $3CdO.B_2O_3$ are obtained. They have a marked effect on polarised light, dissolve readily in acids, and are not acted upon by water.[2]

A *metaborate*, $CdO.B_2O_3$, has been obtained by melting cadmium oxide and boron trioxide together.[3]

Various compounds of the general formula $xCdO.yB_2O_3.zH_2O$ have been prepared by precipitating a solution of a cadmium salt with borax or treating cadmium carbonate with boric acid.[4]

DETECTION AND ESTIMATION OF CADMIUM.

Detection.—Cadmium chloride is soluble in water, and yellow cadmium sulphide precipitates, in the ordinary course of analysis, when hydrogen sulphide is passed through solutions of its salts acidified with hydrochloric acid. The precipitate does not dissolve in ammonium sulphide or caustic alkalies.

Sodium and potassium hydroxides precipitate cadmium hydroxide from solutions of cadmium salts. Excess of these reagents does not redissolve the precipitate, but ammonia, after first precipitating the hydroxide, redissolves it to a complex salt.

Alkali carbonates and ammonium carbonate give a white precipitate with solutions of cadmium salts. Potassium cyanide precipitates cadmium cyanide, soluble in excess. Hydrogen sulphide precipitates yellow cadmium sulphide from the solution.

Sodium thiosulphate or sulphite does not precipitate cadmium salts.

Hydrogen sulphide precipitates cadmium sulphide from ammoniacal solutions of cadmium.

White octahedra of $Cd(NH_3)_2I_2$ are precipitated by concentrated potassium iodide solution from ammoniacal solutions of cadmium salts.[5] Cadmium and uranium are the only metals that give a yellow precipitate when their salt solutions, alkaline with caustic soda, are treated with 5 per cent. thiosinamine.[6]

Cadmium can be detected microchemically as cadmium oxalate or cadmium tetrarubidium chloride.[7]

Small quantities of cadmium can be detected by the green colour

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[1] Rousseau and Tite, *Compt. rend.*, 1892, 114, 1262.
[2] Ouvrard, *ibid.*, 1900, 130, 174.
[3] Guertler, *Zeitsch. anorg. Chem.*, 1904, 40, 242.
[4] Rose, *Pogg. Annalen*, 1853, 88, 299; Ditte, *Ann. Chim. Phys.*, 1883, [5], 30, 255.
[5] Agrestini, *Gazzetta*, 1918, 48, ii, 30.
[6] Lemaire, *Ann. Chim. anal.*, 1909, 14, 6.
[7] Schoorl, *Zeitsch. anal. Chem.*, 1908, 47, 729.

given by ammoniacal solutions of its salts with resorcin.[1] This reaction has been applied to the colorimetric estimation of cadmium.[2]

Estimation.—Cadmium can be *electrolytically estimated* by deposition from cyanide solutions, and, according to Treadwell, this is the most convenient and accurate method of estimating cadmium. The solution, containing not more than 0·5 grm. cadmium, is made alkaline to phenolphthalein with caustic soda and the precipitate just redissolved in potassium cyanide solution. After dilution to 100–150 c.c. the solution is electrolysed on a gauze cathode. The electrolysis is effected in the cold with a current of 0·5-0·7 amp. and an E.M.F. of about 5 volts. After five or six hours the current is increased to 1–1·2 amp. and the electrolysis continued for another hour. If a stronger starting current is used the electrode should be rotated. The electrolyte should always be tested at the end for cadmium with hydrogen sulphide, and if there is only enough cadmium to give a colloidal yellow solution of cadmium sulphide it can be estimated colorimetrically.[3]

Benner and Ross used a more alkaline cyanide solution,[4] and it is possible to estimate cadmium electrolytically in acid or ammoniacal solutions,[5] in solutions of its salts [6] (though the nitrate is not suitable unless cyanide is present [7]), and in various electrolytes containing organic material.[8]

Cadmium can be electrolysed on to a mercury cathode for weighing,[9] and a special cell has been used for estimating cadmium in determining its atomic weight.[10] Cadmium has been thus electrolytically estimated in its sulphate,[11] bromide,[12] and chloride.[13]

To estimate cadmium electrolytically in the presence of zinc, 1 grm. of the mixed chlorides or sulphates is dissolved with 8 grm. potassium oxalate and 2 grm. ammonium oxalate. With a current of 0·05 amp., a P.D. of 1·4–1·6 volts, a temperature of 70°–80° C., and gauze electrodes, 0·1 grm. of cadmium is deposited in four or five hours if the solution is made acid with 0·3–0·5 grm. oxalic acid.

From 0·04–0·2 grm. cadmium can be deposited from a solution containing fifty times its amount of zinc by electrolysing cold with quickly rotating electrodes in the presence of sodium bisulphate.[14]

Copper can be estimated in the presence of cadmium by electrolysis in nitric acid solution.[15]

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[1] Campo, *J. Chem. Soc.*, 1909, **96**, Abs. ii, 439; 1910, **98**, Abs. ii, 1111.

[2] Cerdan and Piente, *ibid.*, 1913, **104**, Abs. ii, 246.

[3] Treadwell, *Analytical Chemistry* (translated by Hall) (Wiley & Sons, New York; Chapman & Hall, London), 1919, ii, 189.

[4] Benner and Ross, *J. Amer. Chem. Soc.*, 1911, **33**, 1106.

[5] Luckow, *Zeitsch. anal. Chem.*, 1880, **19**, 1.

[6] Flora, *Amer. J. Sci.*, 1905, [4], **20**, 268, 392. See also Davison, *J. Amer. Chem. Soc.*, 1905, **27**, 1275; Sand, *Trans. Chem. Soc.*, 1907, **91**, 8, 403.

[7] Flora, *loc. cit.*, 392.

[8] Dover, *J. Amer. Chem. Soc.*, 1911, **33**, 1577.

[9] Benner, *ibid.*, 1910, **32**, 1231.

[10] Baxter and Hartmann, *ibid.*, 1915, **37**, 123; Baxter, Grose, and Hartmann, *ibid.*, 1916, **38**, 857; Baxter and Wilson, *ibid.*, 1921, **43**, 1230.

[11] Perdue and Hulett, *J. Physical Chem.*, 1911, **15**, 155; Quinn and Hulett, *ibid.*, 1913, **17**, 780.

[12] Baxter, Grose, and Hartmann, *loc. cit.*

[13] Baxter and Hartmann, *ibid.*, 1915, **37**, 113; Baxter, Grose, and Hartmann, *loc. cit.*

[14] Treadwell and Guitermann, *Zeitsch. anal. Chem.*, 1913, **52**, 459.

[15] Treadwell, *Analytical Chemistry* (translated by Hall) (Wiley & Sons, New York; Chapman & Hall, London), 1919, ii, 203.

Cadmium can be precipitated as sulphide from solutions containing 2 c.c. concentrated sulphuric acid per 100 c.c. solution. Treadwell advises dissolving the precipitate in hydrochloric acid (concentrated acid diluted with its own volume of water), evaporating the solution down with some dilute sulphuric acid on the water-bath, and driving off the excess of sulphuric acid by careful heating in an air-bath.[1] This method of weighing as sulphate is in common commercial use.[2]

In the presence of zinc the solution should contain free 4–5 N sulphuric acid; the solution should be hot, and hydrogen sulphide passed in until the solution is cold. If much zinc is present the precipitate should be dissolved in hydrochloric acid, evaporated with a slight excess of sulphuric acid, and reprecipitated.[3]

If hydrochloric acid is present during precipitation with hydrogen sulphide, the precipitate will contain basic salt and there will be loss in the final operation.[4] Winkler passes hydrogen sulphide through a strongly acid solution of cadmium sulphate to which a little hydrochloric acid has been added. The solution should be hot, and a red crystalline precipitate of cadmium sulphide precipitates which contains 1·01 per cent. SO_4. By collecting this precipitate and finally drying it at 130° C. the cadmium can be estimated. Zinc, as before, is liable to co-precipitation.[5]

According to Egerton and Raleigh,[6] cadmium can be precipitated as sulphide from its alloys by dissolving 0·2 grm. in as little concentrated hydrochloric acid as possible, neutralising with ammonia, diluting to 100 c.c., adding 4 c.c. of concentrated hydrochloric acid, heating to 80° C., and saturating with hydrogen sulphide. The filtered and washed precipitate is dried at 110°–120° C.

Waring [7] precipitates cadmium and zinc by hydrogen sulphide in slightly acid solution, and dissolves out the zinc sulphide, leaving the sulphide of cadmium, with 5·5 per cent. hydrochloric acid or 8 per cent. sulphuric acid.

Cadmium may be precipitated as sulphide in the presence of copper from cyanide solutions.[8]

According to Flora, the precipitation of cadmium as carbonate and ignition to oxide is a good method if the precipitate is collected on asbestos in a Gooch crucible.[9] Treadwell advises precipitation of boiling solutions with a slight excess of potassium carbonate. After standing, the precipitate is filtered, washed with hot water, and dried. If filter paper is used the precipitate should be detached and the residue dissolved out with dilute nitric acid. The nitric acid solution is evaporated to dryness and the main precipitate added to the residue. The whole is then ignited to the oxide.[10]

The electrometric method of estimation with potassium ferrocyanide, as applied to zinc, has been recently used to estimate cadmium.[11]

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[1] Treadwell, *loc. cit.*, 190.

[2] *Ann. Report Chem. Soc.*, 1915, 12, 177.

[3] Treadwell and Guitermann, *Zeitsch. anal. Chem.*, 1913, 52, 459.

[4] Treadwell, *loc. cit.*, 191.

[5] Winkler, *Chem. Zeit.*, 1921, 34, 383.

[6] Egerton and Raleigh, *Trans. Chem. Soc.*, 1923, 123, 3019.

[7] Waring, *J. Amer. Chem. Soc.*, 1904, 26, 12.

[8] Treadwell, *loc. cit.*, 202.

[9] Flora, *Amer. J. Sci.*, 1905, [4], 20, 456.

[10] Treadwell, *loc. cit.*, 192.

[11] Treadwell and Chervet, *Helv. Chim. Acta*, 1922, 5, 633.

Cadmium can be estimated by precipitation as *ammonium cadmium phosphate* and ignition of the precipitate to cadmium pyrophosphate. Twenty-five c.c. of solution, containing about 0·5 grm. cadmium, are treated with 25 c.c. of a saturated solution of ammonium chloride, heated to boiling, and precipitated with 50 c.c. of a saturated solution of microcosmic salt previously heated to 60° C. After boiling, cooling, and filtering, the precipitate is washed with cold water, dried at 100° C., and ignited to bright redness. The precipitate, which melts at a bright red heat, should be detached from the filter if paper is used. Precipitation is incomplete in the absence of ammonium chloride, or in the presence of alkaline acetates or free acetic acid.[1] The solution should be practically neutral—10 per cent. of ammonium chloride should be present, and the precipitated solution should stand for several hours before filtering.[2]

Winkler adds a considerable excess of 20 per cent. diammonium hydrogen phosphate to the faintly acid solution. The solution should be dilute, hot, and contain about 2 per cent. of ammonium chloride. Moderate amounts of other ammonium salts or of the chlorides of sodium and potassium have no appreciable effect upon the estimation. The amorphous precipitate becomes crystalline, and it should be allowed to stand for two hours before filtering. The precipitate is the monohydrate, and it can be washed with 50 c.c. of a cold saturated solution of ammonium cadmium phosphate, then with methyl alcohol, and finally dried at 100° C. without alteration.[3]

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[1] Carnot and Proromont, *Compt. rend.*, 1885, 101, 59.

[2] Austin, *Amer. J. Sci.*, 1899, [4], 8, 206.

[3] Winkler, *Zeitsch. angew. Chem.*, 1921, 34, 466. Corrections are given to apply to the weight of precipitate found.

CHAPTER VI

MERCURY AND ITS COMPOUNDS.

MERCURY.

Symbol, Hg. Atomic Weight, 200·61 (O=16).

Occurrence.—The principal ore of mercury is the red sulphide, *cinnabar*, HgS. It is far more abundant than any other, and is found in rocks of very different ages, generally occurring in a massive or granular condition. Several varieties are known, such as *steel ore* (which is the richest), *hepatic cinnabar*, *coralline ore*, and *brick ore*. The hardness is 2–2·5 on Mohs' scale, and the density is 8–8·2. The chief European cinnabar mines are at Almaden in Spain, but the ore also occurs in Idria, where it was mined as early as 1497,[1] and, to a less extent, in the Balkan Peninsula, Russia, Siberia, Caucasia, Australia, New Zealand, China, Japan, and certain parts of Central and South America. Important mines are to be found in California and Peru.[2] *Metacinnabarite* is a black sulphide abundant in some of the Californian mines.[3]

Mercury occurs in the metallic state to a certain extent, generally as a decomposition product of cinnabar. Mercury minerals of less importance are the chloride *calomel*, Hg_2Cl_2,[4,5,6] the oxide *montroydite*, HgO,[5,6] and two oxychlorides, one a mercurous-mercuric compound, *terlinguaite*, $2HgO.Hg_2Cl_2$,[5,6] and the other *eglestonite*, $Hg_2O.Hg_2Cl_2$,[5] to which the empirical formula $Hg_6Cl_3O_2$ has also been ascribed.[6,7] An interesting mineral is *kleinite*, which was regarded as an oxychloride by Moses,[6,8] but which is apparently a mercury-ammonium derivative, NHg_2Cl, mixed with a small quantity of a mercury oxychloride and sulphate, or oxysulphate.[9]

Amalgams of silver of different concentrations have been found. For example, a crystalline amalgam of the approximate composition

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[1] Payssé, *Ann. Chim.*, 1814, **91**, 161.

[2] Silliman, *Amer. J. Sci.*, 1864, [2], **38**, 190; Blake and Rolland, *J. Chem. Soc.*, 1881, **40**, Abs., 689.

[3] Clarke, *Data of Geochemistry*, 1916, *U.S. Geol. Survey*, Bull. 616, p. 664.

[4] Goldschmidt and Mauritz, *Zeitsch. Kryst. Min.*, 1908, **44**, 393.

[5] Hillebrand and Schaller, *J. Amer. Chem. Soc.*, 1907, **29**, 1180; *Amer. J. Sci.*, 1907, [4], **24**, 259; *U.S. Geol. Survey*, 1909, Bull. 405.

[6] Moses, *Amer. J. Sci.*, 1903, [4], **16**, 253; *Zeitsch. Kryst. Min.*, 1904, **39**, 3.

[7] Hill, *Amer. J. Sci.*, 1903, [4], **16**, 251.

[8] See also Sachs, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 1091.

[9] Hillebrand, *J. Amer. Chem. Soc.*, 1906, **28**, 122; *Amer. J. Sci.*, 1906, [4], **21**, 85; Hillebrand and Schaller, *J. Amer. Chem. Soc.*, 1907, **29**, 1180; *Amer. J. Sci.*, 1907, [4], **24**, 259; *U.S. Geol. Survey*, 1909, Bull. 405. See also Sachs, *Centr. Min. Geol. Pal.*, 1906, 200.

Ag_5Hg_3 occurs in Chili.[1] A crystallised gold amalgam from California, $AuHg_3$, has also been described.[2] There are rare compounds of mercury with antimony sulphide, titanium, and iodine,[3] and the selenide, *tiemannite*, was formerly commercially worked in Utah.[4]

Mercury and mercury sulphide have been found in hot-spring deposits in New Zealand and Nevada,[4] and it is, in fact, generally considered that cinnabar and other ores of mercury have been deposited originally from aqueous solution by cooling and reduction of pressure. Mercury ores are much more frequently found as narrow veins, or disseminated through siliceous or limestone rocks, than in the massive state.[3]

History.—Mercury was known to the Greeks and Romans, but probably not so early as gold, tin, lead, and iron.[5] It is mentioned by Aristotle, 320 B.C., as liquid silver. A distinction was made by Pliny between native mercury, which was known as *argentum vivum*, or quicksilver, on account of its mobility, and mercury prepared from cinnabar, called *hydrargyrum*, or silver water. Apart from the mercury as known to us, the early alchemists spoke of a mercury which they regarded as the spirit or essence of metals, the constituent to which these owed their metallic properties; the other constituent, or earthy principle, being sulphur.

The alchemists experimented with amalgams, and, as early as the middle of the sixteenth century, mercury was used medicinally, both in the metallic state and also in the combined state as the precipitated oxide, basic sulphate, or chloride.

Preparation of Mercury.—Mercury is extracted from cinnabar by calcination at a high temperature, either alone in contact with air, when sulphur dioxide and mercury are formed, or along with iron or lime with the exclusion of air. With iron, ferrous sulphide and mercury are obtained, and with lime, calcium sulphide, calcium sulphate, and mercury. The first method is most frequently used, the two latter being only employed for rich ores. Since the temperature employed is higher than the boiling-point of mercury, the metal is collected by condensation.

The old type of furnace, long used in Peru and Spain, was discontinuous. The ore in lumps was placed in a shaft on a perforated arch, and heated by the hot gases from the fire below. This has been superseded almost everywhere by a continuous furnace, of which the Exeli, Novak, and Czermak-Spirek shaft furnaces are examples. In these, the heating gases enter at the side, or the furnace is charged with a mixture of ore and charcoal.

In California, the Hüttner and Scott shelf furnaces are extensively used, and are especially suitable for finely divided ores. The ore, in small pieces of about one inch diameter, is placed upon inclined shelves, sloping at an angle of 45° alternately in opposite directions, so that the ore slides down to fill up some of the space between the shelves. The furnace gases pass horizontally between the surface of the ore and the shelf above. The ore, after roasting, is discharged at the bottom of the furnace.

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[1] Domeyko, *Compt. rend.*, 1864, 58, 556.

[2] Sonnenschein, *Zeitsch. deutsch. geol. Gesell.*, 1854, 6, 243; *Jahresber.*, 1854, 807.

[3] Halse, *Mercury Ores*, Monographs on Mineral Resources, with Special Reference to the British Empire (John Murray), 1923.

[4] Clarke, *Data of Geochemistry*, 1916, *U.S. Geol. Survey*, Bull. 616, pp. 664–669.

[5] Kopp, *Geschichte der Chemie*, 1847, 4, 172.

Multiple-hearth, mechanically stirred furnaces have also been used, and even, in very recent times, rotary furnaces, such as are used for cement-burning. For certain types of ore, reverberatory furnaces are more satisfactory than shelf furnaces.

When the ore is treated with lime or iron, retort furnaces are necessary. The mixture is heated in cast-iron or clay retorts of cylindrical or pear-shaped form, and may contain 1 5 cwt. of ore. The method is more costly than the air-roasting process, and produces vapours which are more injurious to the workmen. It has therefore practically fallen into disuse.

In all the processes employed, a mercurial soot known as "stupp" is obtained. It consists of finely divided mercury, together with mercury sulphate and chloride, and the sooty products and ash of the fuel. It accumulates in the condensers, and is collected and treated for the recovery of mercury. Some of the mercury may be removed mechanically by pressure or friction. The residue may be mixed with ore and returned to the furnace.

In the earlier types of condensing apparatus, part of the condensation was effected in a series of "aludels," or pear-shaped fireclay condensers, glazed on the outside and with a narrow neck fitting into the wide end of the succeeding one. Forty to forty-five of these were arranged in parallel rows, and communicated ultimately with condensing chambers. The aludel furnace used at Almaden in Spain was introduced into Idria about 1750, but was soon altered to the form known as the Idrian furnace, in which the aludels were replaced by large brick chambers. In the present-day furnaces the condensers consist of cast-iron pipes of elliptical section. Where acid vapours are likely to condense, the pipe is lined with cement to avoid corrosion of the iron, or glazed stoneware may be used. These condensers are water-cooled. From the condensers the vapours pass into flat wooden flues or dust chambers, in which the soot poor in mercury is collected.[1]

Purification of Mercury.—Since mercury is used in the construction of many instruments of precision, and for other scientific purposes, much attention has been given to the question of the purification of mercury. The methods employed generally resolve themselves into one of three types. Purification from mechanical impurities is effected by filtration through leather, muslin, or filter paper pierced by small holes. Purification from dissolved impurities—that is, foreign metals—may be brought about by distillation *in vacuo*,[2] or by some chemical method, such as the oxidation of the metallic impurities by heating in a current of air, and subsequent removal of the oxides by filtration,[3] or the solution of the impurities by some modification of Lothar Meyer's method,[1] in which mercury is allowed to fall in a finely divided stream through dilute nitric acid, acidified mercurous nitrate, or ferric chloride.[2] The test for pure mercury is the ability to form spherical globules on a clean glass plate, without showing any tendency to adhere to the plate.

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[1] For fuller details see Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1922, vol. iv. p. 265.

[2] Wetzel, *Chem. Zeit.*, 1908, 32, 1228; Dunoyer, *Compt. rend.*, 1912, 154, 1344; *Ann. Chim. Phys.*, 1912, [8], 26, 419; Duschak and Spencer, *J. Physical Chem.*, 1917, 21, 311; Dunnicliffe, *Chem. News*, 1917, 116, 41; Hostetter and Sosman, *J. Wash. Acad. Sci.*, 1918, 8, 11.

[3] Forbes, *Chem. News*, 1912, 106, 74; Margot, *Arch. Sci. phys. nat. Genève*, 1914, [4], 38, 46; Harries, *Zeitsch. angew. Chem.*, 1921, 34, 359; Harries and Evers, *ibid.*, 541. See also Bettel, *Chem. News*, 1908, 97, 158. Lead might also be turned to sulphide. See Banerjee, *Zeitsch. anorg. Chem.*, 1913, 83, 113.

Physical Properties.—Mercury is a silvery-white metal of density 13·59535 at 0° C.[3] It is liquid at the ordinary temperature and freezes at −38·88° C. to −38·89° C.,[4] forming regular octahedra with a silvery lustre. The effect of pressure on the melting-point has been examined.[5] Reduction in volume takes place on freezing,[6] the density of the liquid at freezing-point being 13·6902 [7] and of the solid 14·193.[8] The density at the temperature of liquid air is 14·382,[9] and the density at absolute zero has been calculated to be 16·39.[10] X-Ray determinations of the crystal structure at −115° C., however, indicate a density of 13·97, assuming one atom per cell.[11] The hardness of solid mercury is 1·5 on Mohs' scale.[12] The atomic latent heat of fusion is approximately 0·56 Cal.[13] The specific heat of mercury is 0·03325 at 0°–19° C.,[14] or atomic heat 6·67. Between −71·0° C. and −183·3° C. the specific heat is 0·0316.[15] Simon finds 1·107 for the atomic heat at 9·78° abs., and 1·570 at 13·35° abs.[16] Pollitzer has obtained values varying from 3·89 at 31·1° abs. to 6·70 at 232° abs.[17]

The following values for the vapour pressure at different temperatures have been compiled from the experimental data of several investigators[1, 2] :—

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[1] Meyer, *Ber.*, 1879, 12, 437.

[2] Desha, *Amer. Chem. J.*, 1909, 41, 152; Moore, *Chem. Zeit.*, 1910, 34, 735; Hildebrand, *J. Amer. Chem. Soc.*, 1909, 31, 933; Friedrichs, *Zeitsch. angew. Chem.*, 1914, 27, 24; Pulten and Mains, *J. Ind. Eng. Chem.*, 1917, 9, 600.

[3] Volkmann, *Wied. Annalen*, 1881, [2], 13, 209. See also Thiesen, Scheel, and Sell, *Wissenschaftl. Abhandl. phys.-tech. Reichsanst.*, 1895, 2, 73; Thiesen and Scheel, *Zeitsch. Instrumentenkunde*, 1898, 18, 138.

[4] Vincentini and Omodei, *Atti Acc. Torinò*, 1887, 23, 38; Grunmach, *Physikal. Zeitsch.*, 1902, 3, 136; Henning, *Ann. Physik*, 1914, [4], 43, 290; Wilhelm, *J. Franklin Inst.*, 1916, 182, 525; Scheel, *Zeitsch. angew. Chem.*, 1919, 32, 347; Keyes, Townshend, and Young, *J. Chem. Soc.*, 1923, 124, Abs. ii, 376. Guertler and Pirani (*Zeitsch. Metallkunde*, 1919, 11, 1) give −39·7° C.

[5] Tammann, *Wied. Annalen*, 1889, [2], 68, 636.

[6] Grunmach, *loc. cit.*

[7] Vincentini and Omodei, *loc. cit.*

[8] Mallet, *Proc. Roy. Soc.*, 1877, 26, 71. According to Grunmach (*Physikal Zeitsch.*, 1902, 3, 134), the increase in density on freezing is greater than this, namely, about 5 per cent.

[9] Dewar, *Chem. News*, 1902, 85, 289.

[10] Herz, *Zeitsch. anorg. Chem.*, 1919, 105, 171.

[11] McKeehan and Cioffi, *Phys. Review*, 1922, [2], 19, 444.

[12] Rydberg, *Zeitsch. physikal. Chem.*, 1900, 33, 358.

[13] Egerton, *Phil. Mag.*, 1917, [6], 33, 47. See also Person, *Ann. Chim. Phys.*, 1848, [3], 24, 257; Langlois, *Jahresber.*, 1886, 468; Pollitzer, *Zeitsch. Elektrochem.*, 1911, 17, 10; Koref, *Ann. Physik*, 1911, [4], 36, 56.

[14] Brönsted, *Zeitsch. Elektrochem.*, 1912, 18, 714. Kurbatoff (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 811) found 0·0325 to 0·0331 at 0°–306° C. See also Dulong and Petit, *Ann. Chim. Phys.*, 1817, [2], 7, 147; de la Rive and Marcet, *ibid.*, 1840, [2], 75, 139; Regnault, *ibid.*, 1840, [2], 73, 54; 1849, [3], 26, 268; Langlois, *Jahresber.*, 1886, 468; Winkelmann, *Pogg. Annalen*, 1876, 159, 152; *Zeitsch. physikal. Chem.*, 1891, 8, 142; Heilborn, *ibid.*, 1891, 7, 85; Pettersson, *Ber.*, 1879, 12, 1718; *J. prakt. Chem.*, 1881, [2], 24, 144; Milthaler, *Wied. Annalen*, 1889, [2], 36, 897; Naccari, *Atti Acc. Torinò*, 1888, 23, 1; Bartoli and Stracciati, *Gazzetta*, 1895, 25, i, 380; *Nuovo Cim.*, 1895, [4], 1, 291.

[15] Barschall, *Zeitsch. Elektrochem.*, 1911, 17, 341.

[16] Simon, *Zeitsch. physikal. Chem.*, 1923, 107, 279. See also Egerton, *Phil. Mag.*, 1920, [6], 39, 1.

[17] Pollitzer, *Zeitsch. Elektrochem.*, 1913, 19, 513.

Temperature, ° C.	16	50	121·8	150	191·5	264·16	356·95	433·96
Vapour pressure, mm. mercury	0·0010	0·0113	0·829	2·802	13·02	106·52	760	2598·67

The vapour pressures at higher temperatures have also been determined[3] :—

Temperature, ° C.	450	500	600	700	800	880
Vapour pressure, atmospheres	4·25	8	22·3	50	102	162

The vapour pressures between the temperatures 120° C. and 435° C. may be represented by the following equation[1] :—

$$\log p = 9{\cdot}9073436 - \frac{3276{\cdot}628}{\theta} - 0{\cdot}6519904 \log \theta.$$

The boiling-point is practically 357° C.,[4, 5] and the rise of boiling-point per mm. of pressure is 0·0746° C.[5] The atomic latent heat of vaporisation is $14{\cdot}67 \pm 0{\cdot}05$ Cal. at 298·1° abs.,[6] and at the freezing-point of mercury it is calculated to be $15{\cdot}536 \pm 0{\cdot}033$ Cal.[7]

Vapour density determinations,[8] and the ratio of the specific heats at constant pressure and constant volume respectively,[9] indicate that the vapour is monatomic.

The approximate critical constants of mercury are: $T_c = 1700°$ abs., $p_c = 1040$ atmospheres, $d_c = 5$.[10]

The thermal conductivity is 0·0248 Cal. per cm. per sec. per degree at 0° C., and increases with rise of temperature.[1, 2] The ratio of the thermal conductivity of solid to that of liquid mercury is 3.[1, 3]

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[1] Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, 32, 1434; *Ann. Physik*, 1910, [4], 33, 979; Menzies, *J. Amer. Chem. Soc.*, 1919, 41, 1783.

[2] Morley, *Phil. Mag.*, 1904, [6], 7, 662; *Zeitsch. physikal. Chem.*, 1904, 49, 95. See also Ruff and Bergdahl, *Zeitsch. anorg. Chem.*, 1919, 106, 76; Knudsen, *Ann. Physik*, [4], 29, 179; Laby, *Phil. Mag.*, 1908, [6], 16, 789; Gebhardt, *Verh. Deut. physikal. Ges.*, 1905, 8, 184; Pfaundler, *Wied. Annalen*, 1897, [2], 63, 36; Hertz, *ibid.*, 1882, [2], 17, 193; Ramsay and Young, *Trans. Chem. Soc.*, 1886, 49, 37.

[3] Cailletet, Colardeau, and Rivière, *Compt. rend.*, 1900, 130, 1585.

[4] Smith and Menzies, *loc. cit.*; Ruff and Bergdahl, *loc. cit.*

[5] Heycock and Lamplough, *Proc. Chem. Soc.*, 1912, 28, 3.

[6] Fogler and Rodebush, *J. Amer. Chem. Soc.*, 1923, 45, 2080. See also Kurbatoff, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 659; *Zeitsch. physikal. Chem.*, 1903, 43, 104; Konowaloff, *ibid.*, 1887, 1, 39; Langlois, *Jahresber.*, 1886, 468.

[7] Simon, *loc. cit.*

[8] von Wartenberg, *Zeitsch. anorg. Chem.*, 1908, 56, 320; Jewett, *Phil. Mag.*, 1902, [6], 4, 546; Kurbatoff, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 659; Baker, *Trans. Chem. Soc.*, 1900, 77, 648; Biltz and Meyer, *Ber.*, 1889, 22, 725; Meyer, *ibid.*, 1879, 12, 1426.

[9] Kundt and Warburg, *ibid.*, 1875, 8, 948. Leduc (*Compt. rend.*, 1898, 127, 662) suggested that this does not necessarily prove the monatomicity of mercury.

[10] Weber, *Chem. Zentr.*, 1922, iii, 27; Onnes, *ibid.*, 1921, iii, 769; Meyer, *Physikal. Zeitsch.*, 1921, 22, 76; Bender, *ibid.*, 1915, 16, 246; 1918, 19, 410; van Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 267, 282; Ariès, *Compt. rend.*, 1918, 166, 334; Königsberger, *Chem. Zeit.*, 1912, 36, 1321. Much lower values for the critical temperature have been given by Happel, *Ann. Physik*, 1904, [4], 13, 340; van Laar, *Beibl. Wied. Annalen*, 1918, 42, 42; Rassow, *Zeitsch. anorg. Chem.*, 1918, 104, 81; 1920, 114, 149; Walden, *ibid.*, 1920, 112, 225. Menzies (*J. Amer. Chem. Soc.*, 1913, 35, 1065) stated that calculation from Davies' and Thorpe and Rücker's formulæ indicates a value above 2600° abs.

The electrical conductivity, which diminishes with rise of temperature,[1] has been studied by numerous investigators.[4] The unit of electrical resistance, the international ohm, is expressed in terms of mercury. The ohm is defined as the resistance offered to an unvarying electric current by a column of mercury of length 106·300 cm., of mass 14·4521 grm., and of constant cross-sectional area, at the temperature of melting ice. The ratio of the resistances of liquid and solid mercury at the melting-point is about 5.[1, 5]

The thermo-electric power of mercury against different metals undergoes a sudden change at the melting-point, and therefore there is a contact difference of potential between liquid and solid mercury.[1, 6]

The coefficient of cubical expansion by heat is given by Callendar and Moss as 0·0001820536 between 0° and 100° C.,[7] but this is criticised by Scheel and Heuse,[8] who support Chappuis' determinations,[9] according to which the value at 100° C. is 0·000182541. Hoffman and Meissner adopt the value 0·00018252 at 100° C.[10] Between —190° and —39° C. the coefficient is 0·0000887,[11] and between —78° and —38° C. it is 0·000123.[12]

The compressibility of mercury is $3{\cdot}96\times10^{-6}$ megabars at 20° C.[13] It increases with temperature and decreases with pressure.[14]

The surface tension of mercury in air is 464·9 dynes/cm., and in water 374·8.[15] The surface tension *in vacuo* is practically the same as in dry air, and its dependence on temperature is expressed by the following equation [16]:—

$$\sigma=467-0{\cdot}043(t+39)-0{\cdot}000386(t+39)^2.$$

The surface tension of mercury in contact with solutions of electrolytes depends on the difference of potential established between the liquid and the mercury, a phenomenon which led to the construction of Lippmann's capillary electrometer.[1] The most sensitive liquid is ordinary sulphuric acid solution.[2] The effect has been studied for a number of solutions,[3] and also for organic liquids[4] and for air ionised by X-rays.[5]

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[1] Gehlhoff and Neumeiers, *Verh. Deut. physikal. Ges.*, 1919, 21, 201.

[2] See also Beetz, *Wied. Annalen*, 1879, [2], 7, 441 ; Herwig, *ibid.*, 1880, [2], 10, 662 ; Weber, *ibid.*, 1880, [2], 11, 345 ; *Ann. Physik*, 1903, [4], 11, 1047 ; Berget, *Compt. rend.*, 1887, 105, 224 ; 1888, 107, 171 ; 1890, 110, 76 ; Nettleton, *Phil. Mag.*, 1910, [6], 19, 587.

[3] Porter and Simeon (*Proc. Phys. Soc.*, 1915, 27, 307) found 3·91.

[4] Matthiessen, *Pogg. Annalen*, 1858, 103, 428 ; Siemens and Halske, *Beibl. Wied. Annalen*, 1883, 7, 129 ; Lenz and Restzoff, *ibid.*, 1884, 8, 593 ; Weber, *ibid.*, 1884, 8, 1838 ; *Wied. Annalen*, 1885, [2], 25, 245 ; Strecker, *ibid.*, 1885, [2], 25, 252, 456 ; Kohlrausch, *ibid.*, 1888, [2], 35, 700 ; Grunmach, *ibid.*, 1888, [2], 35, 764 ; Rayleigh and Sidgewick, *Proc. Roy. Soc.*, 1883, 34, 27 ; Berget, *Compt. rend.*, 1890, 110, 76 ; Glazebrook, *Phil. Mag.*, 1891, [5], 32, 70.

[5] Onnes and Holst, *J. Chem. Soc.*, 1914, 106, Abs. ii, 832 ; Dewar and Fleming, *Proc. Roy. Soc.*, 1896, 60, 76.

[6] See also Burnie, *Phil. Mag.*, 1897, [5], 43, 397.

[7] Callendar and Moss, *Phil. Trans.*, 1911, 211A, 1 ; Callendar, *Phil. Mag.*, 1912, [6], 23, 679.

[8] Scheel and Heuse, *ibid.*, 1912, [6], 23, 412 ; *Ber. Deut. physikal. Ges.*, 1912, 14, 139.

[9] Chappuis, *Trav. et Mém. du Bureau intern. des Poids et Mes.*, 1907, 13, c3–c31. See also Thiesen, Scheel, and Sell, *Wissenschaftl. Abhandl. phys.-tech. Reichsanst.*, 1895, 2, 73.

[10] Hoffman and Meissner, *Zeitsch. Instrumentenkunde*, 1919, 39, 212.

[11] Dewar, *Proc. Roy. Soc.*, 1902, 70, 237.

[12] Grunmach, *Physikal. Zeitsch.*, 1902, 3, 134.

[13] Richards and Bartlett, *J. Amer. Chem. Soc.*, 1915, 37, 470. See also Lewis, *Zeitsch. physikal. Chem.*, 1912, 79, 185 ; Hulett, *ibid.*, 1900, 33, 237.

[14] Carnazzi, *Nuovo Cim.*, 1903, [5], 5, 180, see *J. Chem. Soc.*, 1903, 84, Abs. ii, 714.

[15] Harkins and Grafton, *J. Amer. Chem. Soc.*, 1920, 42, 2534.

[16] Hogness, *ibid.*, 1921, 43, 1626. See also Harkins and Ewing, *ibid.*, 1920, 42, 2539 ; Palacios, *J. Chem. Soc.*, 1921, 120, Abs. ii, 304.

The physical properties of mercury at the temperature of liquid helium have been examined by Onnes. The electrical resistance at 4·3° abs. is 0·0021 of the value for solid mercury at 273° abs., and at 3° abs. it is only 0·0000001. Further lowering of the temperature to 1·5° abs. produces no measurable alteration in resistance. When a definite current strength, known as the "threshold value," is reached, the resistance practically disappears at a temperature of 4·19° abs. There is apparently a slight increase at 3·65° abs., and the specific resistance at 2·45° abs. is about 2×10^{-10} ohm. In the presence of impurities the resistance completely disappears at 4·19° abs.[6] The mean specific heat between 4·26° and 6·48° abs. is 0·00142, and between 2·93° and 3·97° abs. 0·000534. Measurements of thermal conductivity give $K=0·27$ between 4·5° and 5·1° abs., and 0·40 between 3·7° and 3·9° abs. The specific heat and thermal conductivity of mercury give no evidence of the discontinuity shown by the electrical conductivity at 4·19° abs.[7]

The chief lines in the spectrum of mercury, measured in Ångström units, are[8] :—

Arc: Infra-red: 11288·2, 10140·6; Visible: 7729·46, 7092·46, 7082·92, 6908, 6234·6, 6123·8, 6073·0, 5790·5, 5769·6, 5461·0, 4358·6, 4078·1, 3654·9, 3650·3, 3125·8, 3021·6; Ultra-violet: 2967·4, 2847·8, 2752·9, 2652·2, 2536·7.

Spark: Visible: 6152·3, 5804·3, 5790·5, 5769·5, 5679·1, 5461·0, 5426·5, 4959·7, 4358·6, 4078·1, 4046·8, 3984·1, 3654·9, 3650·3, 3131·9, 3125·8; Ultra-violet: 2967·4, 2847·9, 2752·9, 2536·7.

The extreme ultra-violet between $\lambda = 2054$ Å. and 1435 Å. has been studied by McLennan and Lang,[9] and, by the methods recently developed for examining the ultra-violet spectrum in the regions beyond that reached by Schumann and Lyman, it has been shown that the limiting wave-lengths of the mercury spectrum probably lie between 1000 Å. and 1200 Å.[10] The mercury arc is rich in ultra-violet rays, and the quartz-mercury lamp is used as a source of ultra-violet radiation in photochemical investigations, and also for purposes of sterilisation.[11]

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[1] Lippmann, *Ann. Chim. Phys.*, 1875, [5], 5, 494; 1877, 12, 265; Gouy, *Compt. rend.*, 1892, 114, 22, 343, 657; Pellat, *ibid.*, 164; Berget, *ibid.*, 531, 742.

[2] Roshdestwensky and Lewis, *Trans. Faraday Soc.*, 1912, 8, 220.

[3] Meyer, *Zeitsch. physikal. Chem.*, 1910, 70, 315; Polara, *Atti R. Accad. Lincei*, 1918, [5], 27, ii, 322.

[4] Polara and Maresca, *Chem. Zentr.*, 1918, i, 608, 815; Polara, *ibid.*, 1919, i, 896.

[5] Polara, *Atti R. Accad. Lincei*, 1918, [5], 27, i, 324.

[6] Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1274; 1912, 14, 113; 1913, 15, 1406; 16, 113, see *J. Chem. Soc.*, 1913, 104, Abs. ii, 748, 822; Onnes and Holst, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 508.

[7] Onnes and Holst, *ibid.*, 1914, 17, 760.

[8] Watts, *Index of Spectra*, Appendix "U" (1911) (Wesley & Son, London; Abel Heywood & Son, Manchester); McLennan and Shaver, *Proc. Roy. Soc.*, 1921, [A], 100, 200.

[9] McLennan and Lang, *Proc. Roy. Soc.*, 1919, [A], 95, 258. See also Bloch and Bloch, *Compt. rend.*, 1920, 171, 909.

[10] Richardson and Bazzoni, *Phil. Mag.*, 1917, [6], 34, 285.

[11] Lowry, *Trans. Faraday Soc.*, 1912, 7, 267; Weigert, *Zeitsch. physikal. Chem.*, 1912, 80, 67; Henri, Helbronner, and de Recklinghausen, *Compt. rend.*, 1912, 155, 852.

Emission and absorption in the infra-red spectrum has been examined by Dearle.[1]

The fluorescence of mercury vapour under various conditions has been studied—for example, under excitation by X-rays,[2] ultra-violet rays,[3] or an electrical discharge.[4] The fluorescent spectrum cannot, apparently, be excited in mercury vapour which is quiescent, but only in vapour which is being distilled from the metal at a temperature of not less than 150° C. Hence it has been concluded that the active molecules are not the neutral monatomic molecules, but probably diatomic.[5] The luminescence continues after the removal of the exciting influence, and is probably due to the recombination of positive and negative ions.[6]

Two resonance potentials have been found for mercury vapour, one at 4·9 volts stimulating the line 2536·72 Å.,[7, 8] and a second at 6·7 volts giving the line 1849 Å.[9] The ionisation potential is 10·38±0·05 volts,[8, 9, 10] but, according to Hebb,[11] it is a function of the temperature of the cathode, values as low as 5 volts being obtained at high temperatures. The striking voltage is $V=10{\cdot}5-0{\cdot}002T$, where T is the absolute temperature.

Doubly charged mercury ions have been found at 19±2 volts.[9, 12]

The refractive indices of gaseous mercury, for different wave-lengths, have been determined,[13, 14] and also the dispersion and magnetic rotation.[14]

Chemical Properties.—Mercury reacts readily with the halogens, whether moist or dry,[15] especially with fluorine.[16] In the presence of halogens or ozone it acquires the property of adhering firmly to glass.[15, 17] Pure, dry hydrochloric acid has no action, even at 200° C., nor hydrogen sulphide at 100° C.[18] By the action of gaseous hydrochloric acid mixed with air, calomel is formed after some months,[1] and hydrogen sulphide gas in the presence of air also attacks mercury.[1] Gaseous hydrogen bromide only reacts slowly at ordinary temperatures, but rapidly at 100° C.[2] Hydrogen iodide is readily decomposed in the cold, mercurous and mercuric iodides being formed.[3] Mercury is unattacked by nitrogen, nitrous oxide, nitric oxide, and carbon dioxide, and is only superficially oxidised to a practically inappreciable extent in contact with air.[2] In presence of ammonia,[4] however, or if heated up to boiling-point,[5] it is readily oxidised by oxygen. It is at once oxidised by ozone in the cold,[6] but if heated to 250° C. it is not attacked, owing to the decomposition of the ozone. Mercury readily combines with sulphur. Hot concentrated sulphuric acid is decomposed by mercury with the production of sulphur dioxide and mercurous or mercuric sulphate,[7] but with dilute acid there is no action. With nitric acid, even somewhat dilute, mercurous and mercuric nitrites and nitrates are formed with the evolution of oxides of nitrogen.[8] Under certain conditions hydrogen is displaced from hydrochloric and sulphuric acids by the action of mercury. The mercury should impinge on the solution of acid, so that the concentration of mercury salt at the surface of the metal does not become large enough to inhibit the action. In the case of sulphuric acid, secondary effects, resulting in the production of hydrogen sulphide and free sulphur, have also been observed.[9]

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[1] Dearle, *Proc. Roy. Soc.*, 1916, [A], **92**, 608 ; 1919, [A], **95**, 280. See also McLennan and Shaver, *ibid.*, 1921, [A], **100**, 200 ; McLennan and Dearle, *Phil. Mag.*, 1915, [6], **30**, 683 ; Paschen, *Ann. Physik*, 1910, [4], **33**, 717 ; Rubens and von Baeyer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 339, 666 ; *Phil. Mag.*, 1911, [6], **21**, 689.

[2] van der Lingen, *Zeitsch. Physik*, 1922, **10**, 38 ; Landau and Piwnikiewicz, *Physikal. Zeitsch.*, 1913, **14**, 381.

[3] Phillips, *Proc. Roy. Soc.*, 1913, [A], **89**, 39 ; Hartley, *ibid.*, 1905, [A], **76**, 428 ; Wood, *Phil. Mag.*, 1909, [6], **18**, 240 ; Franck and Wood, *ibid.*, 1911, [6], **21**, 314.

[4] Metcalfe and Venkatesachar, *Proc. Roy. Soc.*, 1921, [A], **100**, 149 ; Horton, *ibid.*, 1911, [A], **85**, 288 ; Child, *Astrophysical J.*, 1922, **55**, 329 ; Stark, Wendt, and Kirschbaum, *Ann. Physik*, 1913, [4], **42**, 278.

[5] van der Lingen and Wood, *Astrophysical J.*, 1921, **54**, 149.

[6] Ricker, *Phys. Review*, 1921, **17**, 195 ; Child, *Phil. Mag.*, 1913, [6], **26**, 906.

[7] Franck and Hertz, *Ber. Deut. physikal. Ges.*, 1914, **16**, 457 ; Newman, *Phil. Mag.*, 1914, [6], **28**, 753 ; McLennan and Henderson, *Proc. Roy. Soc.*, 1915, [A], **91**, 485. Goucher (*Phys. Review*, 1916, 8, 561) supposed it to be the ionisation potential.

[8] Tate, *ibid.*, 1916, **7**, 686.

[9] Einsporn, *Zeitsch. Physik*, 1921, **5**, 208.

[10] McLennan and Young, *Proc. Roy. Soc.*, 1919, [A], **95**, 279 ; Gibson and Noyes, *J. Amer. Chem. Soc.*, 1922, **44**, 2091 ; Found, *Phys. Review*, 1920, **16**, 41 ; Davis and Goucher, *ibid.*, 1917, **10**, 101.

[11] Hebb, *ibid.*, 1920, **16**, 375.

[12] Smyth, *Proc. Roy. Soc.*, 1922, [A], **102**, 283.

[13] Cuthbertson and Metcalfe, *Phil. Trans.*, 1907, [A], **207**, 135 ; *Proc. Roy. Soc.*, 1908, [A], **80**, 411.

[14] Wood, *Phil. Mag.*, 1909, [6], **18**, 240.

[15] Shenstone, *Trans. Chem. Soc.*, 1897, **71**, 479 ; Cowper, *ibid.*, 1883, **43**, 153.

[16] Moissan, *Le Fluor et ses Composés* (Paris), 1900, p. 211 ; *Ann. Chim. Phys.*, 1891, [6], **24**, 248.

[17] Shenstone, *Trans. Chem. Soc.*, 1892, **61**, 452 ; Shenstone and Beck, *Chem. News*, 1895, **67**, 116 ; Manchot and Kampschulte, *Ber.*, 1907, **40**, 2891.

[18] Berthelot, *Ann. Chim. Phys.*, 1856, [3], **46**, 492.

Mercury may act as a reducing agent towards such substances as potassium permanganate, dichromate, and persulphate, ferric salts, copper sulphate, nitrobenzene, and vanadic acid.[10] Mercury also reacts with thionyl and sulphuryl chlorides,[11] with phosphorus halides,[12] and with halogen substitution products of the paraffins.[13] The metal can apparently dissolve in and diffuse through water which contains air, nitrogen, carbon dioxide, sulphuric acid, or potassium hydroxide, and also through benzene, nitrobenzene, and alcohol.[14] Mercury may act as a contact poison to catalysts—for example, to palladium [15] or platinum.[16]

Colloidal Mercury.—Attempts to prepare pure colloidal mercury by the reduction of a mercury salt with hydrazine hydrate [17] or formaldehyde,[18] by the electrical dispersion of a mercury cathode under potassium hydroxide solution,[1] by the mechanical dispersion method, in which the mercury is ground with grape sugar and then treated with water,[2] or by the electrolysis of very dilute solutions of mercurous nitrate between large platinum, zinc, iron, lead, or nickel electrodes with a current of 0·2–0·3 amp. at 220 volts,[3] result in very unstable and dilute products. To form stable hydrosols some protective colloid is necessary. In the last method the presence of gelatine greatly increases the stability.[3] By the method of electrolytic pulverisation of an amalgam another colloidal metal is introduced into the solution,[3, 4] or an arc may be struck between a clean mercury surface and a thin platinum wire cathode in the presence of gum arabic.[5] A mercurous salt may be reduced in the presence of an alkaline solution of protalbinic or lysalbinic acid, by hydrazine hydrate, hydroxylamine, or, preferably, by sodium hyposulphite, because, in the latter case, colloidal mercuric sulphide is probably formed and acts as a second protective colloid.[6] By the addition of acetic acid a solid adsorption compound of the colloidal mercury with the protective acid is precipitated in brown flakes. These may be dried with or without previous treatment with the minimum quantity of sodium hydroxide necessary for the formation of the salt of the acid. The dried product may be redissolved to form a colloidal solution again. Solid hydrosols containing up to as much as 92·6 per cent. of mercury are obtained with lysalbinic acid, whilst those with protalbinic acid do not reach so high a concentration. The colloidal solution is red-brown by transmitted and blue-grey and opaque by reflected light. Gutbier and Wagner[7] used quince seed extract as the protective colloid. A solution of mercuric chloride may also be added to mixtures of gluten or dextrin with pyrogallol, catechol, or certain aminophenols, with subsequent addition of alkali.[8]

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[1] Berthelot, *Ann. Chim. Phys.*, 1881, [5], **23**, 110.

[2] Berthelot, *ibid.*, 1856, [3], **46**, 492.

[3] Norris and Cottrell, *Amer. Chem. J.*, 1896, **18**, 99.

[4] Matignon and Desplantes, *Compt. rend.*, 1905, **140**, 853.

[5] Lavoisier, *Œuvres*, I, p. 35 ; *Traité de Chimie*, 1789.

[6] Volta, *Gazzetta*, 1879, **9**, 521 ; Manchot and Kampschulte, *Ber.*, 1907, **40**, 2891.

[7] Baskerville and Miller, *J. Amer. Chem. Soc.*, 1897, **19**, 873.

[8] See Mercurous Nitrite, Mercuric Nitrite, Mercurous Nitrate, and Mercuric Nitrate.

[9] Smith, *Phil. Mag.*, 1909, [6], **17**, 833.

[10] Schaffhäutl, *Annalen*, 1842, **44**, 25 ; Kirchmann, *Arch. Pharm.*, 1872, [2], **150**, 203 ; Carnegie, *Trans. Chem. Soc.*, 1888, **53**, 471 ; Borar, *ibid.*, 1911, **99**, 1414 ; *Proc. Chem. Soc.*, 1911, **27**, 128 ; McCay and Anderson, *J. Amer. Chem. Soc.*, 1921, **43**, 2372 ; 1922, **44**, 1018 ; Giles, *Chem. News*, 1867, **15**, 204.

[11] North, *J. Amer. Chem. Soc.*, 1910, **32**, 184.

[12] Wolf, *Ber.*, 1915, **48**, 1272.

[13] Tammann, *Zeitsch. anorg. Chem.*, 1921, **115**, 145.

[14] Christoff, *Zeitsch. physikal. Chem.*, 1908, **63**, 346.

[15] Paal and Hartmann, *Ber.*, 1918, **51**, 711.

[16] Bredig and von Berweck, *Zeitsch. physikal. Chem.*, 1899, **31**, 327 ; Bredig, *Ber.*, 1918, **51**, 1477.

[17] Gutbier, *Zeitsch. anorg. Chem.*, 1902, **32**, 347.

[18] von Weimarn, *Kolloid-Zeitsch.*, 1923, **33**, 81.

Davis obtained a rhythmic precipitation of colloidal mercury by the interaction of an aqueous solution of mercurous nitrate with an agar-agar gel containing sodium formate.[9] He suggested that the formation of a banded deposit is due to the production of a supersaturated solution of colloidal mercury.

By reduction of a mercury salt by stannous salts and addition of ammonium citrate a black precipitate of mercury containing colloidal stannic acid, and comparable with the Purple of Cassius, is obtained. It forms a deep brown solution with water.[10] By reduction of mercurous nitrate with a nitric acid solution of stannous oxide, and coagulation by ammonium citrate, a product with a silvery lustre, and soluble in water with the formation of a deep brown colloidal solution, is obtained.[10]

The different dispersion methods for the production of mercury hydrosols, including the thermic dispersion method by which superheated mercury vapour is passed into water, have been discussed by Nordlund.[11]

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[1] Bredig and Haber, *Ber.*, 1898, 31, 2745.
[2] Utzino, *Kolloid-Zeitsch.*, 1923, 32, 149.
[3] Billitzer, *Ber.*, 1902, 35, 1929.
[4] Gutbier, *loc. cit.*
[5] Gutbier and Weise, *Kolloid-Zeitsch.*, 1919, 25, 97.
[6] Amberger, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 88.
[7] Gutbier and Wagner, *Kolloid-Zeitsch.*, 1916, 19, 291.
[8] Amberger, *ibid.*, 1916, 18, 97.
[9] Davis, *J. Amer. Chem. Soc.*, 1917, 39, 1312.
[10] Lottermoser, *J. prakt. Chem.*, 1898, [2], 57, 484.
[11] Nordlund, *Kolloid-Zeitsch.*, 1920, 26, 121.

Colloidal mercury acts as a catalytic agent—for example, in the decomposition of hydrogen peroxide.[1] In this case the action is rhythmic.[2]

On shaking up mercury with various liquids, such as water, ether, acetic acid, and certain salt solutions, it takes up such a finely divided state as to appear to be a grey powder, and it retains this form so long as it remains under the liquid.[3] By grinding up with some fatty medium for pharmaceutical preparations the same effect is produced, and is known as the *extinction of mercury*.[4]

Physiological Action.—Mercury and mercurial compounds, applied in the form of an ointment, have an irritating local action on the skin. Taken internally they have a strong toxic action, producing nausea, colic, and salivation. They bring about a sudden fall in blood-pressure, paralysis of respiration, and sometimes serious cardiac disturbances.[5] The most rapid effect is produced by inhalation of mercury vapour. In cases of mercurial poisoning the metal accumulates to the highest concentration in the liver.[6] Mercury vapours and compounds are also toxic to plants.[7] Owing to their toxic effect on bacteria, mercury compounds, especially mercuric chloride,[8] are used as antiseptics. They are also used medicinally.

The physiological effect is considered to be due to the mercury ion.[9] The toxic action of corrosive sublimate has been ascribed to the ion $HgCl_4''$.[8] The ionisable mercury compounds are more poisonous than the non-ionising organic mercury compounds,[10] and the addition of sodium chloride, for example, which represses the ionisation, reduces the toxic action.[11] It has also been found that the antiseptic power of mercury is greatest in solutions of hydrion concentration 10^{-5}–$10^{-6 \cdot 6}$, whilst solutions of concentration $10^{-7 \cdot 8}$–$10^{-10 \cdot 1}$ are unfavourable to the action.[12] That is, the antiseptic solution should be feebly acid rather than feebly alkaline.

Uses.—Mercury is used industrially in the extraction of gold and silver,[13] and also as a catalyst in the form of both metal and salts.[14] It is employed in thermometers, barometers, and other scientific instruments where a heavy, non-volatile, and non-adherent liquid is required, and also for mirrors, although in the latter case a deposit of silver is now generally used. Mercury forms the cathode in the production of amalgams and the manufacture of caustic alkalies by electrolytic methods. Its employment in medicine and the mercury arc lamp have already been mentioned. Mercury is also used in the manufacture of various of its compounds of commercial importance—for example, vermilion and fulminates. The mercury cathode may be used in quantitative analysis for electrolytic estimations,[1] and it is also used in the construction of standard cells and electrodes.

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[1] McIntosh, *J. Physical Chem.*, 1902, 6, 15.

[2] Bredig and Weinmayr, *Zeitsch. physikal. Chem.*, 1903, 42, 601.

[3] Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 340.

[4] Voit, *Annalen*, 1857, 104, 358.

[5] Salant and Kleitman, *J. Pharm. Expt. Ther.*, 1922, 19, 315, see *J. Chem. Soc.*, 1922, 122, Abs. i, 794.

[6] Rosenbloom, *J. Biol. Chem.*, 1915, 20, 123; Abelin, *Chem. Zentr.*, 1912, ii, 1575; Slowtzoff, *Beitr. Chem. Physiol. Path.*, 1901, 1, 281, see *J. Chem. Soc.*, 1902, 82, Abs. ii, 34.

[7] Dafert, *Chem. Zentr.*, 1901, i, 331; Coupin, *Compt. rend.*, 1901, 132, 645.

[8] Clark, *J. Physical Chem.*, 1901, 5, 289.

[9] Paul and Krönig, *Zeitsch. physikal. Chem.*, 1896, 21, 414; Sabbatini, *Biochem. Zeitsch.*, 1908, 11, 294; Fleckseder, *Arch. exp. Pathol. Pharmak.*, 1912, 67, 409, see *J. Chem. Soc.*, 1912, 102, Abs. ii, 582; but see Borkowski, *Bull. Acad. Sci. Cracow*, 1908, 494, from *J. Chem. Soc.*, 1908, 94, 1049.

[10] Abelin, *Chem. Zentr.*, 1912, ii, 1575.

[11] Joachimogen, *Biochem. Zeitsch.*, 1921, 121, 259.

[12] Joachimogen, *ibid.*, 1923, 134, 489.

[13] Thorpe, *Dictionary of Applied Chemistry* (Longmans, Green & Co.), 1922, vol. iii, p. 452.

[14] Henderson, *Catalysis in Industrial Chemistry* (Longmans, Green & Co.), 1919; Cain and Thorpe, *Synthetic Dyestuffs and Intermediate Products* (Griffin), 1923.

Atomic Weight.—*Approximate Atomic Weight.*—Vapour density determinations indicate a molecular weight of 200. The ratio of the specific heats leads to the conclusion that the vapour is monatomic. Mercury, in its compounds, has two equivalents, 100 and 200. These facts point to an atomic weight of approximately 200. This is confirmed by the value for the specific heat which, on the assumption that the atomic weight is 200, leads to an atomic heat of 6·6.

Exact Atomic Weight.[2]—The following is a summary of the earlier investigations on the atomic weight of mercury :—

Date.	Investigator.	Ratio Measured.	Atomic Weight.[2]
	Sefström [3] .	$Hg : O$ by calcination of oxide.	200·75–202·79
1833	Turner [4] .	$HgO : Hg$ by calcination of oxide.	200·93
		$HgCl_2 : 2AgCl$ by precipitation.	202·3
		$HgCl_2 : 2AgCl$ by calcination with lime and precipitation with silver chloride.	201·65
		$Hg_2Cl_2 : 2AgCl$ by calcination with lime and precipitation with silver chloride.	201·26
		$HgCl_2 : Hg$ by reduction with stannous chloride.	199·66
1844	Erdmann and Marchand.[5]	$HgO : Hg$ by calcination.	200·204
1846	Millon [6] .	$HgCl_2 : Hg$ by distillation with calcium oxide.	200·215
1848	Svanberg [7] .	$HgCl_2 : Hg$ by reduction by hydrogen.	199·7
1896	Hardin [8] .	$HgO : Hg$ by electrolysis in potassium cyanide solution.	200·03
		$HgCl_2 : Hg$	200·04
		$HgBr_2 : Hg$	199·75
		$Hg(CN)_2 : Hg$	199·77
		$Hg : 2Ag$ by electrolysis.	199·89

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[1] Böttger, *Ber.*, 1909, **42**, 1824.

[2] All atomic weights in this section have been recalculated from the experimental data given in the original memoirs, using the following atomic weight values :—

O = 16·000 Br = 79·916 N = 14·008
Cl = 35·457 Ag = 107·880 C = 12·003

[3] See Berzelius, *Schweigger's J.*, 1818, **22**, 328 ; *Pogg. Annalen*, 1826, **8**, 181.

[4] Turner, *Phil. Trans.*, 1833, 540 ; *Annalen*, 1835, **13**, 25.

[5] Erdmann and Marchand, *J. prakt. Chem.*, 1844, [1], **31**, 395.

[6] Millon, *Ann. Chim. Phys.*, 1846, [3], **18**, 344.

[7] Svanberg, *J. prakt. Chem.*, 1848, [1], **45**, 468.

[8] Hardin, *J. Amer. Chem. Soc.*, 1896, **18**, 1003.

The earliest of the series of investigations that led to the adoption of the accepted value for the atomic weight of mercury were carried out by Easley. In his first experiments,[1] the mercury in carefully purified mercuric chloride was determined by precipitation of the oxide by sodium hydroxide, and reduction to mercury by hydrogen peroxide. The finely divided metal was made to coalesce to a globule which could be washed with water and dried with acetone. A small amount of finely divided mercury which did not coalesce had to be estimated separately. It was filtered, treated first with nitric acid and finally with bromine to ensure the presence of mercuric salts only, and the resulting solution was diluted, boiled to eliminate excess of bromine, added to the original filtrate, and precipitated with hydrogen sulphide. The sulphide mixed with sulphur was filtered, placed in a platinum crucible, covered with water acidulated with a few drops of hydrochloric acid, and electrolysed, using a gold foil cathode. To prevent solution of the platinum a very small current was used, so that two days were often required for completion. A mean of 200·46 was found in four experiments in which the value for the atomic weight varied between 200·42 and 200·50.

In a second series of experiments, the chlorine left in the liquid when the mercury was removed was estimated gravimetrically by silver chloride, after acidifying with nitric acid. The filtrate from the silver chloride was examined for any of the latter kept in solution by the action of any mercury salts that might still be present. The correction required proved to be very small. The mean of six experiments, giving values for the atomic weight varying from 200·59 to 200·65, was 200·615.

In 1910, Easley estimated the mercury in mercuric chloride by electro-deposition.[2] He used a mercury cathode and found its gain in weight. A correction had also to be made for the transference of a certain amount of platinum from the anode to the cathode. This was found to be exceedingly small, since, during the electrolysis of over 125 grm. of mercuric chloride, the anode only lost 0·00015 grm. The mercury was washed and dried without being removed from the vessel in which it had been deposited. After some preliminary experiments, a series of six gave values for the atomic weight varying between 200·58 and 200·64, with a mean of 200·61.

Easley and Brann [3] confirmed this value by the analysis of mercuric bromide. The latter was precipitated by sodium hydroxide and reduced by hydrazine hydrate or hydrogen peroxide. The bromine left in solution was then estimated as silver bromide. Eleven experiments gave values varying between 200·59 and 200·68, and the mean was 200·63.

In 1913, Taylor and Hulett [4] determined the atomic weight of mercury by reducing pure mercuric oxide. It was heated with finely divided iron at 275°–300° C. for two or three hours, and then at about 600° C. for twenty-four to thirty-six hours. During the last half-hour the protruding end of the tube containing the oxide was cooled in ice, and the globule of condensed mercury transferred to a porcelain crucible and weighed. The mean percentage value of mercury in mercuric oxide, derived from nine experiments, was 92·6053±0·0008, corresponding with an atomic weight of 200·37±0·025, somewhat lower than that found by Easley.

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[1] Easley, *J. Amer. Chem. Soc.*, 1909, 31, 1207.
[2] Easley, *ibid.*, 1910, 32, 1117.
[3] Easley and Brann, *ibid.*, 1912, 34, 137.
[4] Taylor and Hulett, *J. Physical Chem.*, 1913, 17, 755.

Baker and Watson [1] determined the amount of mercuric bromide formed by the direct action of liquid bromine on mercury, and obtained as the mean of nine experiments an atomic weight of 200·55±0·008.

In 1923, Hönigschmid, Birckenbach, and Steinheil,[2] in the course of an investigation of the isotopes of mercury, revised the estimation of the atomic weights. Carefully purified mercury was converted into the chloride or bromide by heating in a quartz vessel in a current of dry halogen. Weighed quantities of the halides were reduced with halogen-free hydrazine and the resulting ammonium halide titrated nephelometrically with silver nitrate. Twelve determinations of the ratio $HgCl_2$: 2Ag gave values varying between 1·258403 and 1·258583, or atomic weights 200·60–200·64, with a mean value of 200·61±0·006, and eight determinations of the ratio $HgBr_2$: 2Ag, 1·670522–1·670591, or atomic weights 200·60–200·61, mean value 200·61±0·00.

The International Committee on Atomic Weights for 1925 have adopted the value

Hg=200·61.

Isotopes of Mercury.—Aston has demonstrated the existence of several different isotopes of mercury.[3] The mass spectrum indicates a strong component of atomic weight 202, a weak one of 204, and a strong band of atomic weights from 197 to 200 containing three or four more which are unresolvable at present.

The actual separation of the isotopes has been attempted with at least partial success. By evaporation, and also by effusion, a separation into two fractions, with a density difference between them of 0·49 per cent., equivalent to a difference of atomic weight of 0·1 unit, has been effected.[4] Mulliken found that a film of dirt on the surface of the mercury aided separation,[5] and devised a combined process of distillation and molecular diffusion at low pressures through filter paper, which effected a preliminary separation equivalent to a difference of 0·102 unit of atomic weight between extreme fractions of 22 c.c. of mercury. With a year of steady work a separation of 0·3 unit should be obtained by such a process.[6] On distillation at a low temperature *in vacuo* the extreme fractions gave atomic weights of 200·564±0·006 and 200·632±0·007 respectively.[7]

The possibility of separation by centrifuging has been discussed.[8]

Determinations of the density of mercury from minerals of different origin have not revealed any variations in excess of the experimental error.[9]

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[1] Baker and Watson, *Proc. Chem. Soc.*, 1914, 30, 243; *Trans. Chem. Soc.*, 1914, 105, 2530.

[2] Hönigschmid, Birckenbach, and Steinheil, *Ber.*, 1923, 56, [B], 1212.

[3] Aston, *Phil. Mag.*, 1920, [6], 39, 611; *Trans. Chem. Soc.*, 1921, 119, 677.

[4] Brönsted and von Hevesy, *Zeitsch. physikal. Chem.*, 1921, 99, 189; *Phil. Mag.*, 1922, [6], 43, 31; *Nature*, 1920, 106, 144. See also Mulliken and Harkins, *J. Amer. Chem. Soc.*, 1922, 44, 37; Harkins and Madorsky, *ibid.*, 1923, 45, 591; *Nature*, 1923, 111, 148.

[5] Mulliken, *J. Amer. Chem. Soc.*, 1922, 44, 2387.

[6] Mulliken, *ibid.*, 1923, 45, 1592.

[7] Hönigschmid and Birckenbach, *Ber.*, 1923, 56, [B], 1219.

[8] Poole, *Phil. Mag.*, 1921, [6], 41, 818.

[9] Brönsted and von Hevesy, *Nature*, 1922, 109, 780.

ALLOYS.[1]

Most metals are soluble in mercury to some extent, and they form liquid or solid alloys, or amalgams, according to the proportions of the two constituents and to the nature of the reaction between them. The principal methods of formation are[2]: (1) Direct solution of the metal in mercury; (2) treatment of a salt of a metal with another amalgam which acts as a reducing agent; (3) electrolysis of a salt solution using a mercury cathode; (4) electrolysis of a double salt of mercury and another metal using platinum electrodes.

The molecular state of metals dissolved in mercury has been investigated by many different methods [3, 4, 5, 6]:—

1. Measurement of the electromotive force of amalgams of different concentrations.[4, 6, 7, 8, 9, 10]
2. Measurement of electrical resistance or conductivity.[9, 11]
3. Study of the electrolytic transport of metals through amalgams.[10, 12]
4. Study of chemical equilibria between amalgam and corresponding aqueous salt solution.[5, 13]
5. Measurement of the mercury vapour pressure of amalgams.[6, 8, 14]
6. Examination of the effect of dissolved metals on the freezing-point of mercury.[15, 16, 17, 18]
7. Measurement of rise of boiling-point of mercury due to dissolved metal.[19]

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[1] Sack (*Zeitsch. anorg. Chem.*, 1903, **35**, 249) gives a bibliography of metal alloys, including amalgams.

[2] Smith and Bennett, *J. Amer. Chem. Soc.*, 1909, **31**, 799. See also Giesy and Withrow, *J. Ind. Eng. Chem.*, 1923, **15**, 57.

[3] See Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, **25**, 1; Skaupy, *Zeitsch. Elektrochem.*, 1922, **28**, 23.

[4] Richards and Forbes, *Zeitsch. physikal. Chem.*, 1907, **58**, 683.

[5] Smith, *Zeitsch. anorg. Chem.*, 1908, **58**, 381.

[6] Beck, *Rec. Trav. chim.*, 1922, **41**, 353.

[7] Lindeck, *Wied. Annalen*, 1888, **35**, 311; Meyer, *Zeitsch. physikal. Chem.*, 1891, **7**, 477; Richards and Lewis, *ibid.*, 1899, **28**, 1; Haber, *ibid.*, 1902, **41**, 399; Richards and Wilson, *ibid.*, 1910, **72**, 129; Richards and Garrod-Thomas, *ibid.*, 165; Cady, *J. Physical Chem.*, 1898, **2**, 551; Puschin, *Zeitsch. anorg. Chem.*, 1903, **36**, 225: Schoeller, *Zeitsch. Elektrochem.*, 1898–99, **5**, 259; Reuter, *ibid.*, 1902, 8, 801; Spencer, *ibid.*, 1905, **11**, 681; Sucheni, *ibid.*, 1906, **12**, 726; Richards and Daniels, *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 343; *J. Amer. Chem. Soc.*, 1919, **41**, 1732; Hildebrand and Eastman, *ibid.*, 1914, **36**, 2020; 1915, **37**, 2452.

[8] Hildebrand, *ibid.*, 1913, **35**, 501; *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 335.

[9] Skaupy, *Physikal. Zeitsch.*, 1920, **21**, 597.

[10] Skaupy, *Zeitsch. Physik*, 1920, **3**, 178.

[11] Weber, *Wied. Annalen*, 1887, **31**, 243; Willows, *Phil. Mag.*, 1899, [5], **48**, 433; Larsen, *Ann. Physik*, 1900, [4], **1**, 123; Skaupy, *Zeitsch. physikal. Chem.*, 1907, **58**, 560; Vanstone, *Trans. Faraday Soc.*, 1914, **9**, 291; *Trans. Chem. Soc.*, 1914, **105**, 2617; *Proc. Chem. Soc.*, 1914, **30**, 241; Hine, *J. Amer. Chem. Soc.*, 1917, **39**, 882.

[12] Lewis, Adams, and Lanman, *ibid.*, 1915, **37**, 2656; Mayr, *Nuovo Cim.*, 1920, [6], **19**, i, 116.

[13] Smith, *Amer. Chem. J.*, 1907, **37**, 506; **38**, 67; *J. Amer. Chem. Soc.*, 1910, **32**, 502; 1915, **37**, 76; Byers, *ibid.*, 1908, **30**, 1584.

[14] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 521; Ogg, *Zeitsch. physikal. Chem.*, 1898, **27**, 301; Hildebrand, Foster, and Beebe, *J. Amer. Chem. Soc.*, 1920, **42**, 545; Sieverts and Oehme, *Ber.*, 1913, **46**, 1238.

[15] Puschin, *Zeitsch. anorg. Chem.*, 1903, **36**, 201.

[16] Richards and Daniels, *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 343; *J. Amer. Chem. Soc.*, 1919, **41**, 1732.

[17] Beck, *Rec. Trav. chim.*, 1922, **41**, 367.

[18] Tammann, *Zeitsch. physikal. Chem.*, 1889, **3**, 441; Heycock and Neville, *Trans. Chem. Soc.*, 1890, **57**, 376.

[19] Beckmann and Liesche, *Zeitsch. anorg. Chem.*, 1914, **89**, 171.

8. Determination of density or specific volume.[1, 2, 3, 4, 5]

9. Measurement of rate of diffusion of metals into mercury.[6, 7]

10. Measurement of the heat of formation of amalgams[8] and heat of dilution.[2, 4, 9]

11. Microscopical study of solid amalgams.[10]

12. Measurement of the specific heat of amalgams.[11]

Battelli[12] has shown that the thermoelectric behaviour of mercury and of liquid amalgams is the same as for other metals, whereas that of solid amalgams is irregular.

The results of the above investigations seem to indicate that, in the more dilute liquid amalgams, the metals are monatomic and obey the laws of ideal gases. Deviations are probably due to association, as, for example, in the case of lead, bismuth, cadmium, zinc, and tin, or to hydrargyrate formation, as with alkali and alkaline earth metals.[6, 13] Solid amalgams may consist of either solid solutions or of definite chemical compounds.[3, 11, 14, 15, 16]

Amalgams with the following metals have been described: –

Lithium,[17, 18, 19, 20] $\mathrm{Li_3Hg}$, LiHg, $\mathrm{LiHg_3}$, $\mathrm{LiHg_4}$, $\mathrm{LiHg_5}$.

Sodium.[17, 18, 21, 22, 23, 24]—A large number of different compounds of

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[1] Richards and Daniels, *loc. cit.*

[2] Richards and Forbes, *Zeitsch. physikal. Chem.*, 1907, 58, 683.

[3] Schumann, *Wied. Annalen*, 1891, 43, 101.

[4] Macy, *Zeitsch. physikal. Chem.*, 1899, 29, 119.

[5] Richards and Wilson, *ibid.*, 1910, 72, 129; Richards and Garrod-Thomas, *ibid.*, 165; Bachmetjeff, *J. Russ. Phys. Chem. Soc.*, 1893, 25, i, 219.

[6] Smith, *Ann. Physik*, 1908, [4], 25, 252.

[7] Smith, *Zeitsch. anorg. Chem.*, 1914, 88, 161; *J. Amer. Chem. Soc.*, 1914, 36, 859; von Wogau, *Ann. Physik*, 1907, [4], 23, 345; Humphreys, *Trans. Chem. Soc.*, 1896, 69, 243, 1679; Meyer, *Wied. Annalen*, 1897, 61, 225.

[8] Richards and Lewis, *Zeitsch. physikal. Chem.*, 1899, 28, 1; Littleton, *Chem. News*, 1896, 74, 289.

[9] Berthelot, *Ann. Chim. Phys.*, 1879, [5], 18, 433, 442; Richards and Daniels, *J. Amer. Chem. Soc.*, 1919, 41, 1732.

[10] Puschin, *Zeitsch. anorg. Chem.*, 1903, 36, 241.

[11] Schüz, *Wied. Annalen*, 1892, 46, 177.

[12] Battelli, *Jahresber.*, 1887, 293.

[13] Schoeller, *Zeitsch. Elektrochem.*, 1898-99, 5, 259; Haber and Sack, *ibid.*, 1902, 8, 245; Skaupy, *ibid.*, 1922, 28, 23; Smith, *Amer. Chem. J.*, 1906, 36, 124; 1907, 37, 506; 38, 671; Hildebrand, *J. Amer. Chem. Soc.*, 1913, 35, 501.

[14] Puschin, *loc. cit.*, 201.

[15] Beck, *Rec. Trav. chim.*, 1922, 41, 367.

[16] Kraut and Popp, *Annalen*, 1871, 159, 188; Kurnakoff, *Zeitsch. anorg. Chem.*, 1900, 23, 439; Kerp, *ibid.*, 1898, 17, 284; Kerp and Böttger, *ibid.*, 1900, 25, 1; Weber, *Phil. Mag.*, 1899, [5], 48, 433.

[17] Maey, *Zeitsch. physikal. Chem.*, 1899, 29, 119.

[18] Smith and Bennett, *J. Amer. Chem. Soc.*, 1910, 32, 622.

[19] Smith, *Amer. Chem. J.*, 1907, 37, 506.

[20] Ramsay, *Trans. Chem. Soc.*, 1889, 55, 530; Guntz and Férée, *Bull. Soc. chim.*, 1896, [3], 15, 834; Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, 25, 16; Smith, *ibid.*, 1912, 74, 172; Schukowsky, *ibid.*, 1911, 71, 403; *J. Russ. Phys. Chem. Soc.*, 1911, 43, 708; Richards and Garrod-Thomas, *Zeitsch. physikal. Chem.*, 1910, 72, 165.

[21] Kraut and Popp, *Annalen*, 1871, 159, 188; de Souza, *Ber.*, 1876, 9, 1050; Berthelot, *Ann. Chim. Phys.*, 1879, [5], 18, 433, 442; Maey, *Zeitsch. physikal. Chem.*, 1901, 38, 292; Kurnakoff, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 927; Kerp, *Zeitsch. anorg. Chem.*, 1898, 17, 284; Tammann, *ibid.*, 1903, 37, 303; Beckmann and Liesche, *ibid.*, 1914, 89, 171; Guntz and Férée, *Compt. rend.*, 1900, 131, 182; Reuter, *Zeitsch. Elektrochem.*, 1902, 8, 801; Bain and Withrow, *J. Physical Chem.*, 1921, 25, 535; Giesy and Withrow, *J. Ind. Eng. Chem.*, 1923, 15, 57.

[22] Smith and Bennett, *J. Amer. Chem. Soc.*, 1909, 31, 799.

[23] Smith, *Amer. Chem. J.*, 1907, 38, 671.

[24] Draper, *Chem. News*, 1876, 33, 94; Schumann, *Wied. Annalen*, 1891, 43, 110; Kurnakoff, *Zeitsch. anorg. Chem.*, 1900, 23, 439; Kerp and Böttger, *ibid.*, 1900, 25, 7; Sack, *ibid.*, 1903, 34, 337; Kettembeil, *ibid.*, 1904, 38, 226; Schöller, *ibid.*, 1904, 40, 385; Haber and Sack, *Zeitsch. Elektrochem.*, 1902, 8, 250; Shepherd, *J. Physical Chem.*, 1903, 7, 29; Richards and Conant, *J. Amer. Chem. Soc.*, 1922, 44, 601; Vanstone, *Trans. Faraday Soc.*, 1911, 7, 42; Würschmidt, *Ber. Deut. physikal. Ges.*, 1912, 14, 1065.

sodium and mercury, for the most part of definite crystalline form, have been mentioned, namely, Na_3Hg, Na_5Hg_2, Na_3Hg_2, $NaHg$, Na_7Hg_8, $NaHg_2$, $NaHg_4$, $NaHg_5$, $NaHg_6$, and there are also liquid amalgams consisting of solutions of these compounds in mercury. Sodium amalgam may also be obtained in a flocculent, pulverisable form by pouring the hot liquid amalgam into xylene or petroleum which is mechanically agitated.[1] The alkali metal amalgams are more stable in air and less readily attacked by water than the alkali metals themselves.

A ternary sodium-lead amalgam has been studied.[2] The presence of sodium apparently increases the facility with which mercury amalgamates with other metals.[3]

Potassium,[4, 5, 6, 7, 8, 9, 10] KHg_{18}, KHg_{14}, KHg_{12}, KHg_{11}, KHg_{10}, KHg_9, KHg_6, KHg_5, K_2Hg_9, KHg_4, KHg_3, KHg_2, KHg, K_2Hg.

Rubidium,[5, 8, 9, 11, 12] $RbHg_6$, $RbHg_{12}$, and possibly $RbHg_n$, where n lies between 6 and 14.

Cæsium,[5, 8, 9, 11] $CsHg_2$, $CsHg_1$, $CsHg_6$, $CsHg_{12}$, $CsHg_{13}$, and possibly $CsHg_n$, comparable with $RbHg_n$.

Calcium,[13, 14, 15, 16, 17, 18, 19] Ca_3Hg_4, $CaHg_5$, $CaHg_8$.

Strontium,[13, 14, 16, 17, 20, 21, 22] Sr_2Hg_5, $SrHg_{11}$, $SrHg_{12}$, $SrHg_{13}$, $SrHg_{14}$.

Barium,[13, 14, 15, 18, 20, 21, 23] $BaHg_{12}$, $BaHg_{13}$, $BaHg_{16}$.

Beryllium.[16]—Amalgam formed but rapidly oxidised.

Magnesium,[14, 15, 16, 24] $MgHg_6$, $MgHg_4$, $MgHg_2$, $MgHg$, Mg_3Hg_2, Mg_2Hg,

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[1] Hirschfelder and Hart, *J. Ind. Eng. Chem.*, 1920, **12**, 499.

[2] Grebel, *Zeitsch. anorg. Chem.*, 1919, **106**, 209.

[3] Cailletet, *Compt. rend.*, 1867, **64**, 857; Silliman, *Chem. News*, 1866, **14**, 170; *Bull. Soc. chim.*, 1867, [2], **7**, 91; Nicklès, *J. Pharm. Chim.*, 1866, [4], **4**, 330; Smith and Bennett, *J. Amer. Chem. Soc.*, 1910, **32**, 626.

[4] Macy, *Zeitsch. physikal. Chem.*, 1899, **29**, 119.

[5] Smith and Bennett, *J. Amer. Chem. Soc.*, 1910, **32**, 622.

[6] Smith, *Amer. Chem. J.*, 1907, **37**, 506.

[7] *Loc. cit.*, note 21, p. 216.

[8] Smith and Bennett, *J. Amer. Chem. Soc.*, 1909, **31**, 799.

[9] Smith, *Amer. Chem. J.*, 1907, **38**, 671.

[10] Davy, *Phil. Trans.*, 1808, 17; Croockewit, *Annalen*, 1848, **68**, 291; Merz and Weith, *Ber.*, 1881, **14**, 1438; Schumann, *Wied. Annalen*, 1891, [2], **43**, 107; Jänecke, *Zeitsch. physikal. Chem.*, 1907, **58**, 245; Frank and Withrow, *J. Amer. Chem. Soc.*, 1920, **42**, 671; Smith and Withrow, *ibid.*, 1907, **29**, 321.

[11] Kurnakoff and Schukowsky, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1216; *Zeitsch. anorg. Chem.*, 1906, **52**, 416.

[12] Kerp and Böttger, *ibid.*, 1900, **25**, 29.

[13] Davy, *Phil. Trans.*, 1808, 333.

[14] Smith, *Amer. Chem. J.*, 1907, **37**, 506.

[15] Klauer, *Annalen*, 1834, **10**, 89.

[16] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 530.

[17] Frank and Withrow, *J. Amer. Chem. Soc.*, 1920, **42**, 671.

[18] Smith and Bennett, *ibid.*, 1909, **31**, 799.

[19] Maquenne, *Bull. Soc. chim.*, 1892, [3], **7**, 373; Férée, *Compt. rend.*, 1898, **127**, 618; Moissan and Chavanne, *ibid.*, 1905, **140**, 125; Moissan, *Ann. Chim. Phys.*, 1899, [7], **18**, 306; Schürger, *Zeitsch. anorg. Chem.*, 1900, **25**, 425; Bain and Withrow, *J. Physical Chem.*, 1921, **25**, 535; Neuhausen, *J. Amer. Chem. Soc.*, 1922, **44**, 1445.

[20] Böttger, *J. prakt. Chem.*, 1834, [1], **1**, 302.

[21] Smith and Bennett, *J. Amer. Chem. Soc.*, 1910, **32**, 622.

[22] Maquenne, *Bull. Soc. chim.*, 1892, [3], **7**, 371; Guntz and Férée, *ibid.*, 1897, [3], **17**, 390; Kerp, *Zeitsch. anorg. Chem.*, 1898, **17**, 284; Kerp and Böttger, *ibid.*, 1900, **25**, 35; Guntz, *Compt. rend.*, 1902, **134**, 838.

[23] Crookes, *Chem. News*, 1862, **6**, 194; Schumann, *Wied. Annalen*, 1891, **43**, 103; Maquenne, *Bull. Soc. chim.*, 1892, [3], **7**, 366; Guntz and Férée, *ibid.*, 1896, [3], **15**, 834; Kerp, *Zeitsch. anorg. Chem.*, 1898, **17**, 303; Kerp and Böttger, *ibid.*, 1900, **25**, 44; Guntz, *Compt. rend.*, 1901, **133**, 872; *Ann. Chim. Phys.*, 1905, [8], **4**, 5; Fernekes, *J. Physical Chem.*, 1904, **8**, 566; Smith, *ibid.*, 1905, **9**, 13.

[24] Wanklyn and Chapman, *J. Chem. Soc.*, 1866, **19**, 141; Schumann, *Wied. Annalen*, 1891, **43**, 109; Bachmetjeff and Wsharoff, *J. Russ. Phys. Chem. Soc.*, 1893, **25**, i, 115; Willows, *Phil. Mag.*, 1899, [5], **48**, 433; Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, **25**, 33; le Bon, *Compt. rend.*, 1900, **131**, 706; Beck, *Rec. Trav. chim.*, 1922, **41**, 353; Loomis, *J. Amer. Chem. Soc.*, 1922, **44**, 8.

$Mg_{10}Hg$. Magnesium amalgam is more effective than the zinc-copper couple as a reducing agent for organic substances.[1]

Zinc,[2, 3, 4, 5, 6, 7] $HgZn$, Hg_2Zn_3, $HgZn_4$, $HgZn_6$.

Cadmium,[2, 3, 4, 5, 8] $CdHg$, $CdHg_2$, Cd_2Hg_5, Cd_2Hg_7, and two series of mixed crystals. For the concentrations between 1 part of cadmium to 100 of mercury, and 1 part of cadmium to 1,000,000 of mercury, the potentials of any two amalgams obey Nernst's equation for concentration electrodes.[9] Cadmium amalgam is employed as one of the electrodes in the Weston standard cell, but it is necessary to observe certain limits as to the concentrations employed. All difficulties may be avoided by the use of a 12–13 per cent. amalgam.[10]

There is a double amalgam of cadmium and tin which can be used in dentistry.[11]

Aluminium,[12] Al_2Hg_3.—Amalgamation results in rapid oxidation of aluminium.[4, 13] The aluminium-mercury couple is much used in organic reactions as a reducing [14] or condensing agent,[15] or as a halogen carrier.[16] Müller and Hölzl have compared the electromotive behaviour of pure and amalgamated aluminium.[17]

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[1] Meunier, *Compt. rend.*, 1902, **134**, 472. See also Fleck and Bassett, *J. Amer. Chem. Soc.*, 1895, **17**, 789; Evans and Fetsch, *ibid.*, 1904, **26**, 1158; Evans and Fry, *ibid.*, 1161.

[2] Böttger, *J. prakt. Chem.*, 1834, [1], **3**, 278; Croockewit, *Annalen*, 1848, **68**, 291; Gaugain, *Compt. rend.*, 1856, **42**, 430; Meyer, *Wied. Annalen*, 1897, **61**, 225; Willows, *Phil. Mag.*, 1899, [5], **48**, 433; Richards and Lewis, *Zeitsch. physikal. Chem.*, 1899, **28**, 1; Coehn, *ibid.*, 1901, **38**, 612; Maey, *ibid.*, 1905, **50**, 211; Richards and Garrod-Thomas, *ibid.*, 1910, **72**, 165; Puschin, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 856; *Zeitsch. anorg. Chem.*, 1903, **36**, 201; Merz and Weith, *Ber.*, 1881, **14**, 1438; Würschmidt, *Ber. Deut. physikal. Ges.*, 1912, **14**, 1065.

[3] Rothmund, *Zeitsch. physikal. Chem.*, 1894, **15**, 20; Puschin, *Chem. Zeit.*, 1900, **24**, 950.

[4] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 531.

[5] Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 501.

[6] Puschin, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, i, 635.

[7] Damour, *Ann. Mines*, 1839, [3], **15**, 46; Regnauld, *Compt. rend.*, 1860, **51**, 779; 1861, **52**, 533; Matthiessen and Vogt, *Pogg. Annalen*, 1862, **116**, 369; Calvert and Johnson, *Phil. Mag.*, 1859, [4], **18**, 354; *Jahresber.*, 1864, 170; Joule, *J. Chem. Soc.*, 1863, **16**, 378; Lippmann, *J. Physique*, 1884, [2], **3**, 388; Haga, *Wied. Annalen*, 1882, **17**, 897; Robb, *ibid.*, 1883, **20**, 798; Schumann, *ibid.*, 1891, **43**, 112; Schüz, *ibid.*, 1892, **46**, 177; Richards and Forbes, *Zeitsch. physikal. Chem.*, 1907, **58**, 683; Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, **25**, 54; Hildebrand, *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 319.

[8] Kopp, *Annalen*, 1841, **40**, 186; Regnauld, *Compt. rend.*, 1860, **51**, 778; Wood, *Chem. News*, 1862, **6**, 135; Mazzotto, *Beibl. Wied. Annalen*, 1885, **9**, 664; *Zeitsch. physikal. Chem.*, 1894, **13**, 571; Robb, *Wied. Annalen*, 1883, **20**, 798: Schumann, *ibid.*, 1891, **43**, 105, 115; Weber, *ibid.*, 1887, **31**, 243; Jaeger, *ibid.*, 1898, **65**, 106; Bijl and Roozeboom, *Beibl. Wied. Annalen*, 1901, **25**, 777; Kerp and Böttger, *Zeitsch. anorg. Chem.*, 1900, **25**, 59; Bachmetjeff, *J. Russ. Phys. Chem. Soc.*, 1894, **26**, i, 265; Hildebrand, Foster, and Beebe, *J. Amer. Chem. Soc.*, 1920, **42**, 545.

[9] Hulett and De Lury, *ibid.*, 1908, **30**, 1805.

[10] Jaeger, *Zeitsch. physikal. Chem.*, 1903, **42**, 632; Bijl, *ibid.*, 1902, **41**, 641; but see Cohen, *ibid.*, 1900, **34**, 621.

[11] Warrentrapp, *Annalen*, 1850, **73**, 256.

[12] Klauer, *Annalen*, 1834, **10**, 89; Cailletet, *Compt. rend.*, 1857, **44**, 1250; Tissier, *ibid.*, 1859, **49**, 54; 1860, **51**, 833; Schönbein, *Pogg. Annalen*, 1861, **112**, 448; Baille and Féry, *Ann. Chim. Phys.*, 1889, [6], **17**, 246; Schumann, *Wied. Annalen*, 1891, **43**, 102.

[13] Jehn and Hinze, *Ber.*, 1874, **7**, 1498; Henze, *ibid.*, 1878, **11**, 677; Krouchkoll, *J. Physique*, 1884, [2], **3**, 139; Biernacki, *Wied. Annalen*, 1896, **59**, 664; le Bon, *Compt. rend.*, 1900, **131**, 706; Ronceray, *Chem. Zentr.*, 1918, ii, 699; Casamajor, *Chem. News*, 1876, **34**, 36.

[14] Wislicenus and Kaufmann, *Ber.*, 1895, **28**, 1323; Kaufmann, *ibid.*, 1983; Cohen and Ormandy, *ibid.*, 1505; Wislicenus, *ibid.*, 1896, **29**, 494; *J. prakt. Chem.*, 1896, [2], **54**, 40; Konowaloff, *J. Chem. Soc.*, 1897, **72**, Abs. ii, 374.

[15] Hirst and Cohen, *Trans. Chem. Soc.*, 1895, **67**, 826; Cohen and Skirrow, *ibid.*, 1899, **75**, 887.

[16] Cohen and Dakin, *ibid.*, 1899, **75**, 893; 1901, **79**, 1111; 1902, **81**, 1324.

[17] Müller and Hölzl, *Zeitsch. anorg. Chem.*, 1922, **121**, 103.

Indium,[1,2] Hg_4In.—Simpler compounds are found in the more concentrated amalgams.

Gallium[3] readily dissolves in mercury, forming an amalgam which does not tarnish.

Thallium,[1,2,3,4,5,6] $HgTl_2$, $HgTl$, Hg_5Tl_2, $Hg_{10}Tl_2$, Hg_6Tl.

Copper,[7,8,9,10,11,12] $HgCu$, $HgCu_{14}$, $HgCu_{16}$.—Colloidal copper amalgam, which forms a colloidal solution with water, has been obtained.[13]

Silver.—Silver amalgam occurs naturally as the minerals *arguerite*, $AgHg_2$, and *amalgam*, Ag_3Hg_4, both crystallising in the regular system but of variable composition.[14] Sjögren examined two samples of amalgam from Sala and assigned the formulæ Ag_5Hg_6 and Ag_2Hg_3. According to Jones,[15] two series of silver amalgams may be obtained, $AgHg$, $AgHg_3$, $AgHg_7$, $AgHg_{15}$, $AgHg_{31}$, $AgHg_{63}$, and so on, and also Ag_2Hg, $AgHg_2$, $AgHg_5$, $AgHg_{11}$, $AgHg_{23}$, etc. Others that have been described are: $Ag_{13}Hg$, $Ag_{11}Hg$, Ag_4Hg, Ag_3Hg, Ag_3Hg_2, Ag_3Hg_4, Ag_2Hg_3, Ag_2Hg_4, Ag_2Hg_8.[7,8,9,11,16,17,18,19]

Gold,[7,9,10,11,16,17,18,20,21] Au_9Hg, Au_8Hg, Au_3Hg, Au_2Hg, Au_2Hg_3, $AuHg_2$.—Gold amalgam is of importance in the gold industry. Solutions of gold in mercury have been used for a long time for gilding purposes, probably by the Phœnicians, and were described by Vitruvius in 85 B.C. Colloidal gold amalgam has been prepared.[22]

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[1] Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 501.

[2] Richards and Wilson, *Zeitsch. physikal. Chem.*, 1910, **72**, 129.

[3] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 531.

[4] Rothmund, *Zeitsch. physikal. Chem.*, 1894, **15**, 20; Puschin, *Chem. Zeit.*, 1900, **24**, 950.

[5] Puschin, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, i, 635.

[6] Nicklès, *J. Pharm. Chim.*, 1866, [4], **4**, 127; Carstanjen, *J. prakt. Chem.*, 1867 [1], **102**, 65; Regnauld, *Compt. rend.*, 1867, **64**, 611; Tammann, *Zeitsch. physikal. Chem.*, 1889, **3**, 443; Kurnakoff and Puschin, *Zeitsch. anorg. Chem.*, 1902, **30**, 86; Hildebrand and Eastman, *J. Amer. Chem. Soc.*, 1915, **37**, 245; Richards and Daniels, *ibid.*, 1919, **41**, 1732; Richards and Smyth, *ibid.*, 1922, **44**, 524.

[7] Böttger, *J. prakt. Chem.*, 1834, [1], **3**, 278.

[8] Joule, *J. Chem. Soc.*, 1863, **16**, 378.

[9] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 532.

[10] Horsford, *Amer. J. Sci.*, 1852, [2], **13**, 305.

[11] de Souza, *Ber.*, 1876, **9**, 1050; Merz and Weith, *ibid.*, 1881, **14**, 1438.

[12] König, *J. prakt. Chem.*, 1857, [1], **70**, 64; Klauer, *Annalen*, 1834, **10**, 89; Pettenkofer, *Dingl. poly. J.*, 1848, **109**, 444; *Jahresber.*, 1847–48, 1036; Gersheim, *ibid.*, 1857, 620; Nicklès, *Compt. rend.*, 1853, **36**, 154; Becquerel, *ibid.*, 1863, **56**, 237; Schumann, *Wied. Annalen*, 1891, **43**, 108, 119; Rothmund, *Zeitsch. physikal. Chem.*, 1894, **15**, 19; Coehn, *ibid.*, 1901, **38**, 609; Richards and Garrod-Thomas, *ibid.*, 1910, **72**, 165; Puschin, *Zeitsch. anorg. Chem.*, 1903, **36**, 225.

[13] Paal and Steyer, *Kolloid-Zeitsch.*, 1922, **30**, 215.

[14] Domeyko, *Compt. rend.*, 1842, **14**, 566; Sjögren, *Zeitsch. Kryst. Min.*, 1900, **32**, 611; 1902, **36**, 192.

[15] Jones, *Trans. Chem. Soc.*, 1910, **97**, 336.

[16] Croockewit, *Annalen*, 1848, **68**, 289.

[17] Gouy, *J. Physique*, 1895, [3], **4**, 320.

[18] Hildebrand and Eastman, *J. Amer. Chem. Soc.*, 1914, **36**, 2020.

[19] Matthiessen and Vogt, *Pogg. Annalen*, 1862, **116**, 369; Dumas, *Compt. rend.*, 1869, **69**, 759; Berthelot, *ibid.*, 1901, **132**, 241, 290; *Ann. Chim. Phys.*, 1901, [7], **22**, 317, 320; de Souza, *Ber.*, 1875, **8**, 1616; Littleton, *Trans. Chem. Soc.*, 1895, **67**, 239; *Proc. Chem. Soc.*, 1896, **12**, 220; *Chem. News*, 1895, **71**, 98; 1896, **74**, 289; Schumann, *Wied. Annalen*, 1891, **43**, 112; Ogg, *Zeitsch. physikal. Chem.*, 1898, **27**, 30; Coehn, *ibid.*, 1901, **38**, 615; Maey, *ibid.*, 1905, **50**, 209; Reinders, *ibid.*, 1906, **54**, 609; Parravano and Jovanovich, *Gazzetta*, 1919, **49**, i, 6; *Atti R. Accad. Lincei*, 1918, [5], **27**, ii, 411; Müller and Hönig, *Zeitsch. anorg. Chem.*, 1922, **121**, 344.

[20] Skey, *Chem. News*, 1870, **22**, 282.

[21] Henry, *Phil. Mag.*, 1855, [4], **9**, 458; Sonnenschein, *Zeitsch. geol. Ges.*, 1854, **6**, 243; Chester, *Amer. J. Sci.*, 1878, [3], **16**, 29; Knaffl, *Jahresber.*, 1863, 288; de Souza, *Ber.*, 1875, **8**, 1616; Wilm, *Zeitsch. anorg. Chem.*, 1893, **4**, 325; Tammann, *Zeitsch. physikal. Chem.*, 1889, **3**, 445; Parravano, *Gazzetta*, 1918, **48**, ii, 123; *Atti R. Accad. Lincei*, 1918, [5], **27**, ii, 168; Parravano and Jovanovich, *ibid.*, 1918, [5], **27**, ii, 364; *Gazzetta*, 1919, **49**, i, 1.

[22] Paal and Steyer, *Kolloid-Zeitsch.*, 1918, **23**, 145; 1919, **25**, 21.

Platinum.[1, 2, 3, 4, 5, 6]—Platinum black dissolves in gently heated mercury, but compact platinum is very difficult to amalgamate.[2] The presence of sodium appears to be necessary.[7] It may also be produced electrolytically.[8]

Osmium.[9]—This amalgam wets glass.

Iridium.[10]

Palladium.[3, 5]—Palladium is not very soluble in mercury.[2]

Tin,[11, 12, 13, 14, 15] Hg_8Sn, Hg_2Sn, $HgSn$, Hg_3Sn_5, $HgSn_2$, $HgSn_3$, $HgSn_4$, $HgSn_5$, $HgSn_7$.—The amalgam for mirrors has approximately the composition Hg_2Sn_{17}.[16]

Lead,[11, 12, 14, 17, 18] Hg_7Pb_2, Hg_6Pb_2, Hg_2Pb, Hg_3Pb_2, $HgPb$, $HgPb_2$, $HgPb_8$.—Hydrogen peroxide is formed by the action of lead amalgam on acidulated water in the presence of oxygen.[19] The electrical resistance of lead amalgam has been studied at low temperatures.[20] Ternary lead amalgams with antimony,[21] bismuth,[22] and tin[14] have been prepared, and also a quaternary amalgam of low melting-point, about 77° C., with bismuth and tin.[23]

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[1] Böttger, *loc. cit.*

[2] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 532.

[3] Horsford, *loc. cit.*

[4] Skey, *loc. cit.*

[5] Casamajor, *Chem. News*, 1876, **34**, 36.

[6] Cailletet, *Compt. rend.*, 1857, **44**, 1250; Krouchkoll, *J. Physique*, 1884, [3], **3**, 139; Schumann, *Wied. Annalen*, 1891, **43**, 121; Tarugi, *Gazzetta*, 1896, **26**, i, 425.

[7] Vickers, *Metals and their Alloys* (Crosby, Lockwood & Son), 1923, p. 56. See also Schumann, *Wied. Annalen*, 1891, **43**, 111.

[8] Joule, *loc. cit.*

[9] Tennant, *Phil. Trans.*, 1804, 418; Berzelius, *Ann. Chim. Phys.*, 1829, [2], **40**, 258; Deville and Debray, *ibid.*, 1859, [3], **56**, 405.

[10] Böttger, *J. prakt. Chem.*, 1837, **12**, 350.

[11] Horsford, *Amer. J. Sci.*, 1852, [2], **13**, 305; Matthiessen, *Pogg. Annalen*, 1860, **110**, 21; Joule, *J. Chem. Soc.*, 1863, **16**, 378; Schüz, *Wied. Annalen*, 1892, **46**, 177; Mazzotto, *Beibl. Wied. Annalen*, 1885, **9**, 664; *Zeitsch. physikal. Chem.*, 1894, **13**, 571, 572; Würschmidt, *Ber. Deut. physikal. Ges.*, 1912, **14**, 1065; Hildebrand, Foster, and Beebe, *J. Amer. Chem. Soc.*, 1920, **42**, 545.

[12] Croockewit, *Annalen*, 1848, **68**, 290; Böttger, *J. prakt. Chem.*, 1834, [1], **3**, 278; Matthiessen and Vogt, *Pogg. Annalen*, 1862, **116**, 369; Merz and Weith, *Ber.*, 1881, **14**, 1438; Weber, *Wied. Annalen*, 1887, **31**, 243; Puschin, *Chem. Zeit.*, 1900, **24**, 950; *J. Russ. Phys. Chem. Soc.*, 1900, **32**, i, 635; 1902, **34**, 856; *Zeitsch. anorg. Chem.*, 1903, **36**, 201; Tammann, *Zeitsch. physikal. Chem.*, 1889, **3**, 444.

[13] Calvert and Johnson, *Phil. Mag.*, 1859, [4], **18**, 354, 541; *Jahresber.*, 1864, 170; Matthiessen, *Pogg. Annalen*, 1860, **110**, 190; Schönbein, *ibid.*, 1861, **112**, 446; Michaëlis, *Beibl. Wied. Annalen*, 1885, **9**, 267.

[14] Daniell, *Pogg. Annalen*, 1830, **20**, 260.

[15] Kuppfer, *Ann. Chim. Phys.*, 1829, [2], **40**, 293; Regnault, *ibid.*, 1841, [3], **1**, 137; Lampadius, *J. prakt. Chem.*, 1839, [1], **17**, 34; Regnauld, *Compt. rend.*, 1861, **52**, 533; Matthiessen, *Pogg. Annalen*, 1862, **116**, 369; Weber, *Wied. Annalen*, 1884, **23**, 447; Schumann, *ibid.*, 1891, **43**, 113; Heycock and Neville, *Trans. Chem. Soc.*, 1890, **57**, 376; Ramsay, *ibid.*, 1889, **55**, 531; Rothmund, *Zeitsch. physikal. Chem.*, 1894, **15**, 18; Richards and Wilson, *ibid.*, 1910, **72**, 129; van Heteren, *Zeitsch. anorg. Chem.*, 1904, **42**, 129.

[16] Harrison, *Amer. Chem. J.*, 1886, **8**, 430.

[17] de Souza, *Ber.*, 1876, **9**, 1050.

[18] Kuppfer, *Ann. Chim. Phys.*, 1829, [2], **40**, 300; Regnault, *ibid.*, 1841, [3], **1**, 138; Henry, *Pogg. Annalen*, 1841, **52**, 187; Nickèls, *Compt. rend.*, 1853, **36**, 154; Regnauld, *ibid.*, 1861, **52**, 533; Becquerel, *ibid.*, 1863, **56**, 237; Bauer, *Bull. Soc. chim.*, 1871, [2], **16**, 78; *Ber.*, 1871, **4**, 449; Schumann, *Wied. Annalen*, 1891, **43**, 104, 122; Meyer, *ibid.*, 1897, **61**, 225; Fay and North, *Amer. Chem. J.*, 1901, **25**, 216; Rothmund, *Zeitsch. physikal. Chem.*, 1894, **15**, 16; Maey, *ibid.*, 1901, **38**, 292; Richards and Garrod-Thomas, *ibid.*, 1910, **72**, 165.

[19] Schönbein, *J. prakt. Chem.*, 1864, [1], **93**, 35.

[20] Gressmann, *Sci. Abstracts*, 1899, **2**, 360, No. 824; *Physikal. Zeitsch.*, 1900, **1**, 345.

[21] Jordan, *J. prakt. Chem.*, 1837, [1], **10**, 439.

[22] Döbereiner, *Schweigger's J.*, 1824, **42**, 182; Englisch, *Wied. Annalen*, 1892, **45**, 591.

[23] Döbereiner, *loc. cit.*; Göbel, *Schweigger's J.*, 1830, **58**, 486; Brame, *Jahresber.*, 1853, 260; Phipson *Bull. Soc. chim.*, 1866, [2], **5**, 243.

Bismuth,[1, 2, 3, 4, 5] $HgBi$, $HgBi_2$, $HgBi_3$, $HgBi_4$, $HgBi_5$.

Antimony dissolves freely in boiling mercury.[4] A solid amalgam has been obtained.[6]

Iron.[7, 8, 9, 10, 11]—There are both liquid and solid amalgams, two of the latter being of composition corresponding with the formulæ Hg_2Fe and Hg_3Fe_2, and all of them are magnetic. Amalgamation does not take place directly, but is generally brought about by the reduction of a salt of one metal in the presence of the other. An amalgam may also be prepared electrolytically,[12] but it is very dilute.[13]

Cobalt,[7, 8, 14, 15, 16, 17] $Hg_{10}Co_3$.—The amalgam is magnetic.

Nickel.[7, 8, 10, 14, 15, 16, 18]—Magnetic amalgams of indefinite composition are formed.

Manganese.[7, 13, 14, 15, 19]—A pasty product and also a crystalline one have been obtained. Mn_2Hg_5, prepared electrolytically, is a good reducing agent.[20]

Chromium,[7, 9, 14, 21] Hg_3Cr, $HgCr$.

Molybdenum,[22] $MoHg_9$, $MoHg_3$, $MoHg_3$.

Cerium.[23]—Liquid and solid amalgams, which react readily with water, are formed.

Uranium[24] forms a readily oxidisable amalgam which, on distillation, leaves pyrophoric uranium.

A good account of the amalgams and their uses is given by Vickers.[25]

Ammonium Amalgam.—The nature of the product obtained by electrolysing a solution of ammonia or an ammonium salt, using a

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[1] *Loc. cit.*, note 12, p. 220.

[2] *Loc. cit*, note 13, p. 220.

[3] de Souza, *loc. cit.*

[4] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 532.

[5] Sérullas, *Ann. Chim. Phys.*, 1827, [2], **34**, 195 ; Schumann, *Wied. Annalen*, 1891, **43**, 112 ; Bachmetjeff and Wsharoff, *J. Russ. Phys. Chem. Soc.*, 1893, **25**, i, 115 ; Rothmund, *Zeitsch. physikal. Chem.*, 1894, **15**, 17 ; Hildebrand and Eastman, *J. Amer. Chem. Soc.*, 1914, **36**, 2020.

[6] Schumann, *Wied. Annalen*, 1891, **43**, 102.

[7] Schönbein, *Pogg. Annalen*, 1861, **112**, 445.

[8] Regnauld, *Compt. rend.*, 1861, **52**, 533.

[9] Bunge, *Jahresber.*, 1865, 165.

[10] Nicklès, *J. Pharm. Chim.*, 1853, [3], **23**, 50.

[11] Vogel, *Ann. Chim.*, 1790, 6, 39 ; Aiken, *Gilbert's Annalen*, 1803, **14**, 242 ; Klauer, *Annalen*, 1834, **10**, 89 ; Böttger, *J. prakt. Chem.*, 1834, [1], **1**, 302 ; 1857, [1], **70**, 436 ; *Pogg. Annalen*, 1857, **101**, 10 ; Horsford, *Amer. J. Sci.*, 1852, [2], **13**, 305 ; Cailletet, *Compt. rend.*, 1857, **44**, 1250 ; Regnauld, *ibid.*, 1860, **51**, 778 ; Casamajor, *Chem. News*, 1876, **34**, 34 ; Ramann, *Ber.*, 1881, **14**, 1438 ; Krouchkoll, *J. Physique*, 1884, [2], **3**, 139 ; Schumann, *Wied. Annalen*, 1891, **43**, 106 ; Zamboni, *Nuovo Cim.*, 1895, [4], **2**, 26 ; *Jahresber.*, 1896, 557 ; Coehn, *Zeitsch. physikal. Chem.*, 1901, **38**, 613 ; Smith and Bennett, *J. Amer. Chem. Soc.*, 1909, **31**, 799.

[12] Joule, *J. Chem. Soc.*, 1863, **16**, 378.

[13] Ramsay, *loc. cit.*

[14] Moissan, *Compt. rend.*, 1879, 88, 180.

[15] Böttger, *J. prakt. Chem.*, 1837, [1], **12**, 350.

[16] Damour, *Ann. Mines*, 1839, [3], **15**, 46 ; Casamajor, *Chem. News*, 1876, **34**, 36.

[17] Schumann, *Wied. Annalen*, 1891, **43**, 107.

[18] Schumann, *ibid.*, 111 ; Wünsche, *Ann. Physik*, 1902, **7**, 116.

[19] Schumann, *loc. cit.*, 110.

[20] Prelinger, *Monatsh.*, 1893, **14**, 353.

[21] Vincent, *Phil. Mag.*, 1862, [4], **24**, 328 ; Férée, *Compt. rend.*, 1895, **121**, 822.

[22] Férée, *ibid.*, 1896, **122**, 733.

[23] Winkler, *Ber.*, 1891, **24**, 883 ; Muthmann and Beck, *Annalen*, 1904, **331**, 56.

[24] Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 622.

[25] Vickers, *Metals and their Alloys* (Crosby, Lockwood & Son), 1923, chap. xx.

mercury cathode,[1, 2, 3] or by acting on an ammonium salt with an amalgam of the alkali or alkaline earth metals,[2, 4, 5, 6] has been the subject of much controversy. Ammonium amalgam, as it is called, may be prepared as follows: Sodium amalgam, containing a quantity of sodium equivalent to the concentration of ammonium amalgam required, is cooled in a flask with a long narrow neck to a temperature just above freezing-point. Anhydrous ammonia is then condensed in the flask and excess of ammonium iodide added to it. The mixture is shaken from time to time whilst a low temperature is maintained. After about an hour the ammonia is allowed to evaporate and the liquid amalgam filtered several times through an ordinary folded filter paper with a hole pierced in the bottom.[2, 4, 7] At ordinary temperatures it forms a spongy mass of the consistency of butter, and is very unstable, giving off hydrogen and ammonia in equal volumes, after expanding to approximately thirty times the volume which it occupies at about −60° C.[4]

It appears necessary to have a certain concentration of ammonium ions before the amalgam can be formed, because it is not obtained under conditions where ionisation is only small—for example, in solution in alcohol.[8]

Davy compared ammonium amalgam with the amalgams of the alkali metals and considered that they are closely analogous, and that the radicle NH_4 behaves as a metal.[6] Berzelius was also of the same opinion. Gay-Lussac and Thénard, on the other hand, concluded that it is merely a mixture of mercury, ammonia, and hydrogen.[3] Seely also regarded it as a foam resulting from a mechanical mixture of the same constituents.[9] Landolt [10] tried, but without success, to reduce salts in aqueous solution to the metallic state by means of ammonium amalgam, as can be done with the alkali amalgams. He therefore concluded that the radicle NH_4 has no existence in the product.[11] Coehn [12] showed, however, that Landolt's failure was due to the employment of too high a temperature, and that, at 0° C., copper, cadmium, and zinc may be precipitated. It was found later that barium, potassium, and sodium may also be replaced.[13]

Meanwhile, evidence of a fairly convincing nature in support of the amalgam theory had been produced as a result of electrolytic measurements. Le Blanc [14] electrolysed a solution of an ammonium salt with

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[1] Seebeck, *Ann. Chim.*, 1808, [1], 66, 191; Davy, *Phil. Trans.*, 1808, 353; Berzelius and Pontin, *Gilbert's Annalen*, 1810, 36, 260; Le Blanc, *Zeitsch. physikal. Chem.*, 1890, 5, 467; Coehn, *Zeitsch. Elektrochem.*, 1902, 8, 591; Schroeder, *J. prakt. Chem.*, 1908, [2], 77, 271; Bain and Withrow, *J. Physical Chem.*, 1921, 25, 543.

[2] Moissan, *Compt. rend.*, 1907, 144, 790.

[3] Gay-Lussac and Thénard, *Ann. Chim.*, 1810, [1], 73, 197.

[4] Moissan, *Compt. rend.*, 1901, 133, 803.

[5] Böttger, *J. prakt. Chem.*, 1834, [1], 1, 302; 3, 285. See also Weyl, *Jahresber.*, 1864, 165.

[6] Davy, *Phil. Trans.*, 1810, 55.

[7] Rich and Travers, *Proc. Chem. Soc.*, 1906, 22, 136; *Trans. Chem. Soc.*, 1906, 89, 872.

[8] Proude and Wood, *Proc. Chem. Soc.*, 1895, 11, 236; *Chem. News*, 1896, 73, 54.

[9] Seely, *Chem. News*, 1870, 21, 265. See also Wetherill, *Amer. J. Sci.*, 1865, [2], 40, 160; Pfeil and Lippmann, *ibid.*, 1866, [2], 42, 72; but see, on the contrary, Gallatin, *Phil. Mag.*, 1869, [4], 38, 57; Routledge, *Chem. News*, 1872, 21, 210.

[10] Landolt, *Annalen Suppl.*, 1868, 6, 346.

[11] But see Gunning, *Ber.*, 1870, 3, 19.

[12] Coehn, *Zeitsch. anorg. Chem.*, 1900, 25, 430.

[13] Smith, *J. Amer. Chem. Soc.*, 1907, 29, 844.

[14] Le Blanc, *Zeitsch. physikal. Chem.*, 1890, 5, 467.

a mercury cathode and measured, at the same time, the polarisation potential. It rose in a few minutes to a maximum nearly as great as in the case of a sodium salt. After the current had been cut off, the mercury cathode, which showed the inflation characteristic of ammonium amalgam, was still strongly electro-negative to the solution, and remained so for ten to twenty minutes. This could not be due to hydrogen, because the hydrogen polarisation potential was found to be much smaller, and fell off almost as soon as the current was interrupted.[1]

Determinations of the freezing-point lowering for different amounts of "ammonium" in the amalgam have been made,[2] and they are of the same order as those found for potassium and sodium amalgams.[3] Rich and Travers [2] interpreted their results as indicating that ammonium, NH_4, is present in the free state in solution.[4] Smith,[5] however, maintained that work on the free ammonium radicle shows this to be impossible, and that the existence of a compound NH_4Hg_n, comparable with the compounds between the alkali metals and mercury, must be assumed.

A sodium ammonium amalgam,[6] a copper ammonium amalgam,[7] and a magnesium ammonium amalgam [8] have been described, but Michaud [9] showed that, in general, the presence of another metal decreases the stability, magnesium being an exception in that it apparently produces no effect. In the presence of platinum, on the other hand, it is quite impossible to prepare ammonium amalgam.

The view that a true amalgam is formed may be considered to receive additional support from the behaviour of substituted ammonium compounds, some of which also form amalgams, in certain cases of considerable stability. The most stable of them, tetramethyl ammonium amalgam, may be prepared by electrolysing the chloride, dissolved in absolute alcohol, at $-34°$ C., using a mercury cathode. The semi-solid amalgam is then washed with ice-cold carbon tetrachloride and filtered from excess of mercury through wood fibre. A solid, crystalline, metallic mass remains. Large crystals may be isolated, and these, in cold, dry weather, will remain unchanged in air for several minutes, after which they become coated with an alkaline crust due to oxidation. Tetramethyl ammonium amalgam is lighter than mercury and has a greater electrical resistance. It does not become inflated at or below 10° C. as does ammonium amalgam, but near 20° C. it decomposes rapidly, giving trimethylamine as one of the products. With water a violent reaction takes place, with the evolution of hydrogen and the formation of colloidal mercury. Polarisation potential measurements seem to indicate that two phases may exist, with potentials 2·6 and 2·0 volts respectively, in alcohol, or 2·4 and 1·7 in water, and the reaction with water tends to the same conclusion, one phase being more active than the other. Monomethyl, diethyl, and possibly tetraethyl ammonium amalgam also appear to exist.[1, 2]

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[1] See also Pocklington, *Zeitsch. Elektrochem.*, 1898–99, 5, 139 ; Coehn and Dannenberg, *Zeitsch. physikal. Chem.*, 1901, 38, 627.

[2] Rich and Travers, *loc. cit.*

[3] Tammann, *Zeitsch. physikal. Chem.*, 1889, 3, 440.

[4] See also Travers, *Ber.*, 1907, 40, 3949.

[5] Smith, *loc. cit.* ; *Ber.*, 1907, 40, 2941, 4298, 4893.

[6] Weyl, *Jahresber.*, 1864, 164.

[7] Böttger, *J. prakt. Chem.*, 1834, [1], 3, 278.

[8] Loomis, *J. Amer. Chem. Soc.*, 1922, 44, 8.

[9] Michaud, *Amer. Chem. J.*, 1894, 16, 488.

These amalgams, and also ammonium amalgam, emit charged particles on decomposition, due to the bubbling of the gases produced, in a finely divided form, through the mercury.[1, 3]

COMPOUNDS OF MERCURY.

Mercury is distinct from the other members of the same group in the periodic system, since it forms two well-defined series of salts, mercurous and mercuric. Solutions of mercurous salts contain the ion $Hg_2^{\cdot\cdot}$,[4] and of mercuric, the ion $Hg^{\cdot\cdot}$. It is possible that at high dilution the mercurous ion splits up into two monovalent ions $Hg^{\cdot}$, but probably only to an inappreciable extent.[5]

The mercuric salts are peculiar in that the halides and the thiocyanate are only very slightly dissociated. Those which are dissociated to a normal extent—that is, salts of strong inorganic oxygen acids and also salts of weak acids—are readily hydrolysed and form basic salts. Mercuric salts have a strong tendency to form complex salts with mercury in the anion. Mercurous salts, on the other hand, have very little tendency towards complex formation, are not readily hydrolysed, and are, many of them, only slightly soluble in water. Under the action of heat or light, mercurous salts tend to form a mixture of metallic mercury and the corresponding mercuric salt, especially if mercury be continually removed from the system, whilst mercuric salts, with excess of mercury, form mercurous salts.[6]

Both the mercurous and mercuric ions are colourless.

MERCURY AND HYDROGEN.

Loëw considered that the spongy mass formed by shaking zinc amalgam with its own volume of a 10 per cent. solution of platinum chloride is a hydrogen amalgam.[7] It decomposes very rapidly with the evolution of hydrogen, but is much more stable if freed from zinc by washing with hydrochloric acid and then with water. Platinum chloride may be replaced by gold or palladium chloride.[8] Seely[9] regarded the product as a foam or mechanical mixture of mercury with minute bubbles of hydrogen. Joule tried without success to get hydrogen amalgam.[10]

MERCURY AND THE HALOGENS.

Mercurous Fluoride, Hg_2F_2, may be obtained by dissolving freshly precipitated mercurous carbonate in hydrofluoric acid, or by

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[1] McCoy and West, *J. Physical Chem.*, 1912, 16, 261.

[2] McCoy and Moore, *J. Amer. Chem. Soc.*, 1911, 33, 273. See also Le Blanc, *Zeitsch. physikal. Chem.*, 1890, 5, 477; *Zeitsch. Elektrochem.*, 1902, 8, 801; Pfeil and Lippmann, *Amer. J. Sci.*, 1866, [2], 42, 72; *Chem. News*, 1866, 14, 122.

[3] Aronheim, *Zeitsch. physikal. Chem.*, 1921, 97, 95.

[4] Ogg, *ibid.*, 1898, 27, 285; Abel, *Zeitsch. anorg. Chem.*, 1901, 26, 361.

[5] Linhart, *J. Amer. Chem. Soc.*, 1916, 38, 2356.

[6] Hada, *Trans. Chem. Soc.*, 1896, 69, 1667.

[7] Loëw, *J. prakt. Chem.*, 1870, [2], 1, 307; *Amer. J. Sci.*, 1870, [2], 50, 99.

[8] Walz, *Chem. News*, 1870, 22, 217.

[9] Seely, *ibid.*, 1870, 21, 265.

[10] Joule, *J. Chem. Soc.*, 1863, 16, 378.

the action of a solution of silver fluoride on freshly precipitated mercurous chloride.[1] It forms a pale yellow crystalline powder which can be recrystallised from hydrofluoric acid.[1] The melting-point is 570° C.[2] and the density at 15° C. is 8·73.[2] The salt blackens under the action of light, in the presence of moist air, and when heated above 260° C. in a glass vessel, mercury sublimes and the glass vessel is corroded.[1] Unlike the other mercurous halides, it is partially hydrolysed by water forming mercurous oxide. Potassium hydroxide precipitates mercurous oxide, and ammonia gives a black precipitate containing metallic mercury. It rapidly turns grey, and the filtrate soon deposits a white mass containing mercury, ammonia, and fluorine. Mercurous fluoride slowly absorbs dry ammonia with the formation of a black compound, $Hg_2F_2.NH_3$, which appears to be stable at ordinary temperatures and, even at 100° C., gives an inappreciable amount of ammonia. Water, however, decomposes it, forming mercury and a compound containing mercuric oxide.[3]

An acid salt, $Hg_2F_2.4HF.4H_2O$, in monoclinic crystals, is formed by the action of concentrated hydrofluoric acid on mercurous oxide. When heated it gives water, hydrofluoric acid, and mercuric oxide.[4]

Mercuric Fluoride, HgF_2, may be obtained in long colourless needles as the dihydrate, $HgF_2.2H_2O$, by dissolving mercuric oxide in excess of hydrofluoric acid.[5] According to Finkener,[6] the initial product is an oxyfluoride, $HgF_2.HgO.H_2O$. The fluoride retains its water of crystallisation up to 130° C., but above that temperature it loses hydrofluoric acid, forming oxyfluorides of varying composition. It is decomposed by light and readily hydrolysed by water, forming a reddish-yellow oxyfluoride,[5] although, according to Cox,[7] there is no basic salt, only a mixture of mercuric oxide and mercuric fluoride.

The anhydrous salt is formed by the direct action of fluorine on mercury.[8] It may be prepared by heating mercurous fluoride in a current of dry chlorine at 275° C., or dry bromine at 400° C., or alone at 450° C. under 10 mm. pressure.[9] It forms transparent octahedral crystals of melting-point 645° C. and of boiling-point probably in the neighbourhood of 650° C. The density at 15° C. is 8·95. The salt is very sensitive to moisture, and becomes discoloured by traces of moisture not analytically detectable. On exposure to air, mercuric oxide is ultimately formed. With small quantities of water a white, hydrated oxyfluoride, $Hg_3F_4(OH)_2.3H_2O$, is formed, whilst with larger quantities mercuric oxide is gradually produced. By dissolving the anhydrous salt in 40 per cent. hydrofluoric acid and cautiously evaporating, the hydrated salt, $HgF_2.2H_2O$, is obtained in small colourless crystals. Mixtures of the fluoride with silver, copper, lead, aluminium, magnesium, zinc, tin, chromium, iron, or arsenic react vigorously when strongly heated locally, yielding amalgams and metallic fluorides. When heated with sulphur, sulphur tetrafluoride is formed. The fluoride is not attacked when heated in a stream of chlorine or bromine, but, by passing dry chlorine over mercurous fluoride at 120° C., a pale yellow chlorofluoride, HgClF, is obtained, and, in bromine at 105° C., a bromofluoride.[1] When heated, mercuric fluoride attacks platinum, but not carbon.[1]

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[1] Finkener, *Pogg. Annalen*, 1860, 110, 142.

[2] Ruff and Bahlau, *Ber.*, 1918, 51, 1756.

[3] Finkener, *loc. cit.*

[4] Böhm, *Zeitsch. anorg. Chem.*, 1905, 43, 326.

[5] Frémy, *Ann. Chim. Phys.*, 1856, [3], 47, 38.

[6] Finkener, *Pogg. Annalen*, 1860, 110, 628. See also Poulenc, *Ann. Chim. Phys.*, 1894, [7], 2, 74.

[7] Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 169.

[8] Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 248.

[9] Ruff and Bahlau, *Ber.*, 1918, 51, 1752.

Mercuric fluoride is hydrolysed in solution to the extent of about 80 per cent. The solubility of the red oxide in hydrofluoric acid is proportional to the concentration, and is decreased by the addition of potassium fluoride. This indicates the non-existence of complex fluorides.[2]

By adding concentrated aqueous ammonia, and then alcohol, to a solution of mercuric fluoride, a light yellow amorphous powder, which is the fluorine analogue of infusible white precipitate,[3] and hence has the formula $HgNH_2F$, has been prepared.[4] If a hydrofluoric acid solution of mercuric fluoride be decomposed by aqueous ammonia in slight excess, a gelatinous white mass, which, on washing, forms a white powder, is obtained. On heating it gives ammonia and nitrogen, and Finkener ascribed to it the formula $HgF_2.HgO.NH_3$.[5] Franklin regarded it as a hydrated ammonobasic fluoride, or as a mixture of the compound $HgNH_2F$ with a basic fluoride, and gave to it the formula $(HgF)_2.NH.H_2O$.[6]

Mercurous Chloride, Hg_2Cl_2, occurs naturally, in a white or yellowish-grey crystalline form with a conchoidal fracture, as the mineral *calomel* or *horn mercury*. In Europe it has been employed in medicine since the sixteenth century under a variety of names—sweet sublimate, sweet mercury, and so on. In Japan, however, it was apparently known as far back as the eighth century.[7]

It may be prepared by subliming an intimate mixture of mercury and mercuric chloride, or its equivalent—for example, mercurous sulphate and sodium chloride,[8] or mercury, mercuric chloride, and sodium chloride. The Japanese method consists in heating mercury with a compost of arenaceous red clay and bay salt moistened with bittern.[7] The hydrochloric acid obtained from the magnesium chloride of the bittern, along with the oxygen of the air, reacts with the mercury as follows [9] :—

$$4Hg+4HCl+O_2=2Hg_2Cl_2+2H_2O.$$

Other methods may be employed—for example, precipitation of a dilute solution of mercurous nitrate with a soluble chloride, the action of chlorine on a feebly acid, concentrated solution of mercurous nitrate,[10] or the action of a reducing agent on mercuric chloride. As reducing agents the following have been used: sulphur dioxide,[1] an alkali sulphite,[2] hypophosphorus acid,[3] ferrous sulphate,[4] hypochlorites,[5] potassium binoxalate,[6] and oxalic acid.[7] Electrolytic reduction may also be employed.[8]

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[1] Ruff and Bahlau, *loc. cit.*

[2] Jaeger, *Zeitsch. anorg. Chem.*, 1901, 27, 22.

[3] See Compounds resulting from the Action of Ammonia on Mercuric Chloride.

[4] Böhm, *Zeitsch. anorg. Chem.*, 1905, 43, 332. Böhm describes this as the action of ammonia on mercurous fluoride, but since he prepares the latter by the action of hydrofluoric acid on precipitated mercuric oxide, and the composition of the resulting compound relates it to infusible white precipitate, which is a mercuric chloride derivative, mercuric fluoride must have been actually used.

[5] Finkener, *Pogg. Annalen*, 1860, 110, 628 ; *Jahresber.*, 1860, 197.

[6] Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 58.

[7] Divers, *J. Soc. Chem. Ind.*, 1894, 13, 108.

[8] *British Pharmacopœia* (Constable & Co., Ltd.), 1914, p. 176.

[9] See also Berthelot, *Compt. rend.*, 1897, 125, 746 ; *Ann. Chim. Phys.*, 1898, [7], 13, 73.

[10] Sievers, *Ber.*, 1888, 21, 650.

Both the natural and artificial calomel form crystals belonging to the quadratic system. Prepared by sublimation it forms fibrous masses, and prepared by precipitation it forms a heavy white powder composed of microscopic needles. The density varies according to the conditions of formation, having an average value of about 7.[9] The heat of formation of mercurous chloride from its elements is 62·65 Cal.[10] The specific heat is 0·05019.[11] Pollitzer[12] gives the molecular heat of $HgCl$ as 3·12 at 22·95° abs., and 12·24 at 326° abs. The melting-point is about 302° C.[13] When fused in closed vessels it conducts electricity.[14] The solid salt is also a conductor of electricity, and its conductivity is increased by the addition of a little sodium chloride.[15] Under ultra-violet light an orange fluorescence is observed.[16]

The earlier determinations of the vapour pressure of mercurous chloride were considered to indicate a formula $HgCl$.[17] Other investigators, however, found values indicating Hg_2Cl_2,[18] and still others stated that there is dissociation into mercury and mercuric chloride, as could be shown by the amalgamation of a gold leaf introduced into the vapour.[19] In 1900, Baker found that mercurous chloride vapour, dried as completely as possible, had a vapour density of 217·4, but if dried by sulphuric acid only, the density was 118·4. In the first case no amalgamation of a gold leaf took place, whilst in the second the leaf was readily attacked. This appeared to show that the dry vapour consists of mercurous chloride molecules, whereas the undried is dissociated into mercury and mercuric chloride.[20] Later investigations confirmed this,[1, 2, 3] and it was also shown that dissociation of the undried calomel is complete.[1]

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[1] Vogel, *J. prakt. Chem.*, 1843, [1], **29**, 276; Wöhler, *Annalen*, 1854, **90**, 124; Stein, *ibid.*, 1855, **96**, 335; Zinkeisen, *Zeitsch. Pharm.*, 1855, 8; Muck, *Jahresber.*, 1855, 417; Vitali, *J. Chem. Soc.*, 1894, **68**, Abs. ii, 140.

[2] Meyer, *Zeitsch. anorg. Chem.*, 1905, **47**, 399.

[3] Glückmann, *Jahresber.*, 1896, 2177; Gladstone and Tribe, *Phil. Mag.*, 1875, [4], **49**, 426.

[4] Hempel, *Annalen*, 1858, **107**, 97.

[5] Fairley, *B.A. Reports*, 1875, 42.

[6] Millon, *Ann. Chim. Phys.*, 1846, [3], **18**, 391.

[7] Schoras, *Ber.*, 1870, **3**, 11; Uloth, *Jahresber.*, 1871, 335.

[8] Gladstone and Tribe, *B.A. Reports*, 1874, 58.

[9] Boullay, *Ann. Chim. Phys.*, 1830, [2], **43**, 266; Herapath, *Berzelius' Jahrbuch*, 1876, **5**, 52; Clarke, *Constants of Nature*, Part I (Macmillan & Co.), 1888.

[10] Varet, *Ann. Chim. Phys.*, 1896, [7], **8**, 98. See also Nernst, *Zeitsch. physikal. Chem.*, 1888, **2**, 23.

[11] Brönsted, *Zeitsch. Elektrochem.*, 1912, **18**, 714. See also Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 154.

[12] Pollitzer, *Zeitsch. Elektrochem.*, 1913, **19**, 513.

[13] Ruff and Bahlau, *Ber.*, 1918, **51**, 1756.

[14] Hampe, *Chem. Zeit.*, 1887, **11**, 905.

[15] Fritsch, *Wied. Annalen*, 1897, **60**, 308.

[16] Wolff, *Chem. Zeit.*, 1912, **36**, 1039.

[17] Mitscherlich, *Pogg. Annalen*, 1833, **29**, 223; Deville and Troost, *Compt. rend.*, 1857, **45**, 821; Rieth, *Ber.*, 1870, **3**, 666; Fileti, *Gazzetta*, 1881, **11**, 341; *J. prakt. Chem.*, 1894, [2], **50**, 222; 1895, [2], **51**, 297.

[18] Williamson, *J. Chem. Soc.*, 1864, **17**, 211; Debray, *Compt. rend.*, 1868, **66**, 1339; 1876, **83**, 330.

[19] Odling, *Jahresber.*, 1864, 280; Erlenmeyer, *Annalen*, 1864, **131**, 124; Harris and Meyer, *Ber.*, 1894, **27**, 1482; Meyer, *Ber.*, 1894, **27**, 3143; 1895, **28**, 364.

[20] Baker, *Trans. Chem. Soc.*, 1900, **77**, 646.

The following values have been found for the vapour pressure at different temperatures[4] :—

Temperature, ° C. .	90	100	120	150	180
Pressure, mm. Hg .	0·004	0·0089	0·016	0·07	0·45

The boiling-point is 383·7° C.,[3, 5] but the vapour pressure of the dried material, even at 352° C., is practically zero.[6]

When dissolved in mercury, mercurous chloride has a molecular weight indicating the formula $HgCl$,[1] whilst in mercuric chloride it has the formula Hg_2Cl_2.[7]

On exposure to light, mercurous chloride darkens, probably with decomposition into the metal and mercuric chloride. It is readily oxidised by ozone,[8] by fluorine directly,[9] and by chlorine, bromine, and iodine in acetone solution.[10] It is also readily reduced to mercury by suitable reducing agents—for example, alkali hyposulphites[11] or sulphites,[12] and stannous chloride.[13] Sulphuric acid does not act upon it in the cold, but gives sulphur dioxide when hot and no hydrochloric acid.[14] When heated with concentrated nitric acid it forms mercuric chloride and mercuric nitrate.[15]

According to Meyer,[16] a different modification of mercurous chloride is obtained in lustrous scales, and of density 4·55, by mixing solutions of mercuric chloride and lithium sulphite, filtering off the heavy white precipitate first formed, and heating the clear solution to 70°–80° C. It changes into the ordinary salt on sublimation. It shows no difference of potential, however, when combined in a galvanic chain with ordinary mercurous chloride, and thus can scarcely be an allotropic modification.

Calomel is only very slightly soluble in water, the solubility being about 1×10^{-6} grm.-molecules per litre.[17] It is insoluble in most organic liquids.[18] If calomel be boiled with water it slowly forms mercuric chloride and mercury. With water at 150° C. in the presence of oxygen, mercuric chloride in solution and a precipitate of oxychloride are obtained.[1] In presence of hydrochloric acid or potassium chloride the oxychloride dissolves.[2] Calomel dissolves more readily in solutions of alkali or alkaline earth chlorides or cyanides, or of hydrochloric acid, than in water, and the dissolved mercury is in the mercuric state. As with water alone there is probably a preliminary dissociation into mercury and mercuric chloride. The latter gives a complex ion with the chloride introduced, thus removing the mercuric chloride as such from the system and facilitating further dissociation until an equilibrium is reached. The extent of the action increases with temperature and concentration of chloride.[1, 3] The mercury itself dissolves to a slight extent, in presence of air, when shaken with an alkali chloride.

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[1] Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1541.

[2] Smith and Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 251, 713.

[3] Smith and Calvert, *J. Amer. Chem. Soc.*, 1916, **38**, 801.

[4] Wiedemann, Stelzner, and Niederschulte, *Ber. Deut. physikal. Ges.*, 1905, **7**, 159.

[5] Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 1541) found 382·5° C., Harris and Meyer (*Ber.*, 1894, **27**, 1482), 357° C., and Jonker (*Chem. Weekblad*, 1909, **6**, 1035), 373° C.

[6] Smith and Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 713; but this was not found to be the case by Baker, *loc. cit.*

[7] Beckmann, *Zeitsch. anorg. Chem.*, 1907, **55**, 175.

[8] Mailfert, *Compt. rend.*, 1882, **94**, 860.

[9] Moissan, *Ann. Chim. Phys.*, 1891, [6], **24**, 257.

[10] Naumann, *Ber.*, 1904, **37**, 4328.

[11] Schnauss, *Arch. Pharm.*, 1875, [3], **6**, 411.

[12] St.-Gilles, *Ann. Chim. Phys.*, 1852, [3], **36**, 90.

[13] Divers and Shimidzu, *Trans. Chem. Soc.*, 1886, **49**, 558.

[14] Vogel, *Schweigger's J.*, 1821, **32**, 59.

[15] Boullay, *Ann. Chim.*, 1803, [1], **44**, 187.

[16] Meyer, *Zeitsch. anorg. Chem.*, 1905, **47**, 399.

[17] Ley and Heimbucher, *Zeitsch. Elektrochem.*, 1904, **10**, 301; Sherrill, *Zeitsch. physikal. Chem.*, 1903, **43**, 732. Kohlrausch and Rose (*ibid.*, 1893, **12**, 241) give a much higher value, 6×10^{-6} at 18° C.

[18] Naumann, *Ber.*, 1904, **37**, 3600, 4328; Šulc, *Zeitsch. anorg. Chem.*, 1900, **25**, 399.

Ammonia solution blackens mercurous chloride, forming "black precipitate." This consists of a mixture of metallic mercury with "infusible white precipitate."[4] It is impossible to assign a formula to black precipitate, as part of the white compound goes into solution to an extent determined by the concentration of the ammoniacal liquid.[5] According to Sen,[6] dimercuroammonium chloride, NH_2Hg_2Cl, is formed. This compound is reduced to metallic mercury by arsenic trisulphide.[7] Calomel, especially if prepared in the wet way, rapidly absorbs dry ammonia and forms a black compound $Hg_2Cl_2.2NH_3$.[8] The dissociation pressure increases regularly with temperature.

Calomel is employed in the production of a standard electrode prepared from a normal or more dilute solution of potassium chloride, saturated with mercurous chloride and placed in contact with mercury. Hydrochloric acid may be used instead of potassium chloride. The absolute value of the electromotive force of the normal calomel electrode was formerly considered to be 0·560 volt,[9] but recent work casts considerable doubt on this value.[10] Referred to the hydrogen electrode as zero, the electromotive force of the normal calomel electrode is 0·2828 volt at 25° C., and of the decinormal electrode, 0·3357 volt.[11] A carefully prepared electrode only suffers a very slight variation with time.[12]

Mercurous chloride is also used for various pharmaceutical purposes.

Colloidal Mercurous Chloride. Hydroxylamine hydrochloride reacts with a mercuric salt to give an unstable colloidal solution of mercuric chloride which is decomposed by dialysis.[1] By the addition of chlorine water to a colloidal solution of mercury, a milky liquid, reddish yellow by transmitted light, is obtained.[2] Excess of chlorine gives a solution of mercuric chloride. A solid stable product, capable of giving a colloidal solution with water, has been prepared by precipitating calomel from mercurous nitrate and sodium chloride in the presence of a protective colloid such as albumen, albuminiform substances, or gums, dialysing the resulting liquid, and evaporating to dryness or precipitating by alcohol.[3]

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[1] Hada, *Trans. Chem. Soc.*, 1896, 69, 1667.

[2] See also Boullay, *Ann. Chim. Phys.*, 1827, [2], 34, 343.

[3] Gewecke, *Zeitsch. physikal. Chem.*, 1903, 45, 684; Richards and Archibald, *ibid.*, 1902, 40, 385; Abegg, Immerwahr, and Jander, *Zeitsch. Elektrochem.*, 1902, 8, 688; Ditte, *Ann. Chim. Phys.*, 1891, [6], 22, 559.

[4] See Compounds resulting from the Action of Ammonia on Mercuric Chloride.

[5] Kane, *Pogg. Annalen*, 1837, 42, 380; Barfoed, *J. prakt. Chem.*, 1889, [2], 39, 211; Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1910, 67, 357.

[6] Sen, *ibid.*, 1903, 33, 197. See also Kane, *Phil. Mag.*, 1837, [3], 11, 507.

[7] Reichard, *Ber.*, 1897, 30, 1916.

[8] Rose, *Pogg. Annalen*, 1830, 20, 158; Isambert, *Compt. rend.*, 1868, 66, 1259; Barfoed, *J. prakt. Chem.*, 1889, [2], 39, 217.

[9] Rotté, *J. Physique*, 1900, [3], 9, 543; Sauer, *Zeitsch. physikal. Chem.*, 1904, 47, 146.

[10] Garrison, *J. Amer. Chem. Soc.*, 1923, 45, 37; Bodforss, *Zeitsch. Elektrochem.*, 1923, 29, 121.

[11] Lewis, Brighton, and Sebastian, *J. Amer. Chem. Soc.*, 1917, 39, 2245. See also Loomis and Meacham, *ibid.*, 1916, 38, 2310; Furness, Hardman, and Newbery, *Trans. Chem. Soc.*, 1914, 105, 2302; *Proc. Chem. Soc.*, 1914, 30, 233; Palmaer, *Zeitsch. physikal. Chem.*, 1907, 59, 129; Loomis and Acree, *Amer. Chem. J.*, 1911, 46, 585.

[12] Myers and Acree, *ibid.*, 1913, 50, 396; Loomis and Acree, *loc. cit.*

Lachs has studied mercurous chloride sols ultramicroscopically.[4]

Reinders has observed that colloidal solutions obtained from very dilute solutions of mercurous nitrate and sodium chloride are doubly refracting even in the presence of gelatine, due to the fact that they contain needle-shaped ultramicroscopic particles. In the flowing liquid these set themselves along the line of flow. The solution is a milky bluish white by reflected light and a yellowish brown by transmitted light. If gelatine is not present, a silky-looking suspension of mercurous chloride needles, of length about 10 μ, may be obtained.[5]

Double Salts and Addition Compounds.—The mercurous, unlike the mercuric ion, shows very little tendency to form complex ions. It has been stated, however, that a double salt with silver, $Hg_2Cl_2.2AgCl$, possibly to be regarded as the silver salt of a complex acid, $Ag_2(Hg_2Cl_4)$,[6] and also a chlorostannate, $Hg_2Cl_2.SnCl_2$ or $Hg_2(SnCl_4)$,[7] have been prepared, as well as a compound with sulphur dichloride, $Hg_2Cl_2.SCl_2$.[8] A double salt with aluminium, containing benzene of crystallisation, $AlCl_3.HgCl.C_6H_6$, separates from a benzene solution of the two salts.[9]

Mercuric Chloride, $HgCl_2$.—As far back as the time of Geber, mercuric chloride, or corrosive sublimate, was in use for medicinal purposes. Chlorine apparently combines with mercury directly in the cold to form mercuric chloride, even when a considerable excess of mercury is present.[10] The usual method of preparation of the salt, which is similar to the early methods, is by sublimation of a mixture of mercuric sulphate and sodium chloride. Many variants of this method have been proposed.[11] Mercuric chloride can also be obtained by precipitation of a mercuric salt with a soluble chloride, by treatment of mercuric oxide with hydrochloric acid or a soluble chloride,[12] or by saturation of mercuric nitrate solution with chlorine.[13] The heat of formation of the salt from its elements is 53·3 Cal.[14]

When prepared by sublimation it forms a white mass of octahedral crystals.[1] From aqueous and alcoholic solutions prismatic crystals separate. The behaviour of mercuric chloride in solid solution with mercuric bromide indicates that the former is dimorphous.[2] The density is 5·45,[3] the melting-point 277° C.,[4, 5, 6] and the boiling-point 302·5° C.[5, 6, 7] The salt is readily volatile, and the following values for the vapour pressure at different temperatures have been given[5, 8]:—

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[1] Gutbier, *Zeitsch. anorg. Chem.*, 1902, 32, 353.

[2] Lottermoser, *J. prakt. Chem.*, 1898, [2], 57, 484.

[3] Ellis, Chemische Fabrik von Heyden Akt.-Ges., German Patent, 165282 (1903); English Patent, 19163 (5th September 1903).

[4] Lachs, *J. Physique Radium*, 1922, 3, 125.

[5] Reinders, *Kolloid-Zeitsch.*, 1917, 21, 161.

[6] Jones, *J. Soc. Chem. Ind.*, 1893, 12, 983; *Trans. Chem. Soc.*, 1910, 97, 339.

[7] Capitaine, *J. Pharm. Chim.*, 1839, [2], 25, 549.

[8] Abegg, *Handbuch d. anorg. Chem.* (S. Hirzel, Leipzig), 1905, ii, 2, p. 611.

[9] Gulewitsch, *Ber.*, 1904, 37, 1560.

[10] Bailey and Fowler, *Trans. Chem. Soc.*, 1888, 53, 761.

[11] See Rupp and Klee, *J. Chem. Soc.*, 1910, 98, Abs. ii, 615.

[12] Mailhe, *Ann. Chim. Phys.*, 1842, [3], 5, 177; Wagner, *Dingl. poly. J.*, 1865, 176, 135.

[13] Sievers, *Ber.*, 1888, 21, 649.

[14] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 97. See also Nernst, *Zeitsch. physikal. Chem.*, 1888, 2, 27.

Temperature, °C.	90	100	120	152	195	231	262	275	278	283	302
Pressure, mm. Hg	0·05	0·10	0·38	3	20	82	237	375	421	481	754

Prideaux gives values at less than degree intervals from 286·1° C., pressure 505 mm., to 309° C., pressure 844 mm.[9]

The critical temperature is 976° abs.[10] The specific heat at 12°–98° C. is 0·0689.[11] The electrical conductivity of fused mercuric chloride is small.[12] The solid salt also conducts electricity, but the addition of 1 per cent. of sodium chloride increases the conductivity eighteen times.[13]

On account of its slight dissociation in solution, mercuric chloride is a somewhat inert substance, but it is readily reduced to calomel. By exposure to ultra-violet light, in either the dry or moist condition, mercurous chloride is formed. The action, however, is reversible.[14] The reduction by oxalic acid or oxalates is greatly influenced by light,[15] or by radium rays.[16] The reduction by phosphorous acid,[17] hypophosphorous acid,[18] sodium formate,[19] hydrogen peroxide in alkaline solution, or sodium peroxide,[20] ferrous sulphate,[21] ferrous chloride under the influence of ultra-violet light,[22] and piperidine,[23] has been carefully studied. The reducing action of stannous chloride has long been known.

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[1] Mitscherlich, *Pogg. Annalen*, 1833, **28**, 119; Hiortdahl, *Compt. rend.*, 1879, **88**, 584.

[2] van Nest, *Zeitsch. Kryst. Min.*, 1910, **47**, 263. See also Luczizky, *ibid.*, 1909, **46**, 297.

[3] van Nest, *loc. cit.*, 265. See also Boullay, *Ann. Chim. Phys.*, 1830, [2], **43**, 266; Ortloff, *Zeitsch. physikal. Chem.*, 1896, **19**, 210.

[4] Ruff and Bahlau, *Ber.*, 1918, **51**, 1756.

[5] Johnson, *J. Amer. Chem. Soc.*, 1911, **33**, 777.

[6] Jonker, *Chem. Weekblad*, 1909, **6**, 1035.

[7] See also Freyer and Meyer, *Zeitsch. anorg. Chem.*, 1892, **2**, 1.

[8] Wiedemann, Stelzner, and Niederschulte, *Ber. Deut. physikal. Ges.*, 1905, **7**, 159. See also Arctowski, *Zeitsch. anorg. Chem.*, 1894, **7**, 167.

[9] Prideaux, *Trans. Chem. Soc.*, 1910, **97**, 2038.

[10] Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, **87**, 253. See also Rassow, *Zeitsch. anorg. Chem.*, 1920, **114**, 146.

[11] Regnault, *Ann. Chim. Phys.*, 1841, [3], **1**, 155.

[12] Hampe, *Chem. Zeit.*, 1887, **11**, 904.

[13] Fritsch, *Wied. Annalen*, 1899, **60**, 308.

[14] Pougnet, *Compt. rend.*, 1915, **161**, 348.

[15] Schoras, *Ber.*, 1870, **3**, 11; Uloth, *Jahresber.*, 1871, 335; Eder, *ibid.*, 1880, 198; Roloff, *Zeitsch. physikal. Chem.*, 1894, **13**, 329; Kastle and Beatty, *Amer. Chem. J.*, 1900, **24**, 182.

[16] Becquerel, *Compt. rend.*, 1901, **133**, 709.

[17] Montemartini and Egidi, *Gazzetta*, 1902, **32**, ii, 182; Garner, Foglesong, and Wilson, *Amer. Chem. J.*, 1911, **46**, 361; Garner, *ibid.*, 648; Linhart, *Zeitsch. anorg. Chem.*, 1913, **82**, 1; *Amer. J. Sci.*, 1913, [4], **35**, 353.

[18] Mitchell, *Trans. Chem. Soc.*, 1921, **119**, 1266.

[19] Findlay and Davies, *ibid.*, 1913, **103**, 1550; Linhart, *J. Amer. Chem. Soc.*, 1915, **37**, 70.

[20] Kolb, *Chem. Zeit.*, 1901, **25**, 21; Kohn, *Zeitsch. anorg. Chem.*, 1908, **59**, 271; Kohn and Ostersetzer, *ibid.*, 1913, **80**, 218.

[21] Winther, *Zeitsch. wiss. Photochem.*, 1912, **11**, 60.

[22] Winther, *Zeitsch. Elektrochem.*, 1912, **18**, 138.

[23] Werner and Ferchland, *Zeitsch. anorg. Chem.*, 1897, **15**, 11.

A number of other methods of reduction have been indicated.[1] According to Linhart and Adams,[2] metallic mercury is probably first obtained in the reduction of mercuric compounds, and then, if conditions permit, mercurous compounds are formed.

Mercuric chloride is a powerful poison and is useful as a disinfectant, but the sodium chloride often added to stabilise it reduces also its virulence.[3]

The solubility of mercuric chloride in water at 25° C. is 0·263 grm.-molecules per litre.[4, 5] Etard obtained the following values at different temperatures[5]:—

Temperature, ° C.	0	10	20	30	40	60	80	100	120	150
Percentage of mercuric chloride	3·5	4·5	5·4	7·2	9·3	14·0	23·1	38	59	78·5

The saturated solution freezes at −0·2° C., and has a composition at this temperature of 3·29 per cent. mercuric chloride.[6] The heat of solution is −3,[7] or −3·3 Cal.[8] In solution mercuric chloride only dissociates into ions to a very small extent.[9] The dissociation constant $\frac{[\mathrm{Hg}^{\cdot\cdot}]\times[\mathrm{Cl}']^2}{[\mathrm{HgCl}_2]}$ has been given as $0{\cdot}5\times10^{-14}$,[10] but in reality the ion $\mathrm{HgCl}^{\cdot}$ is also present, and, taking this into account, the following dissociation constants have been found :—

$$K_1=\frac{[\mathrm{Hg}^{\cdot\cdot}]\times[\mathrm{Cl}']^2}{[\mathrm{HgCl}_2]}=1{\cdot}0\times10^{-14};^{11,\,12}\qquad K_2=\frac{[\mathrm{HgCl}^{\cdot}]\times[\mathrm{Cl}']}{[\mathrm{HgCl}_2]}=2{\cdot}8\times10^{-7};$$

$$K_3=\frac{[\mathrm{Hg}^{\cdot\cdot}]\times[\mathrm{Cl}']}{[\mathrm{HgCl}^{\cdot}]}=3{\cdot}5\times10^{-8};\text{ and }K_4=\frac{[\mathrm{Hg}^{\cdot\cdot}]\times[\mathrm{HgCl}_2]}{[\mathrm{HgCl}^{\cdot}]^2}=0{\cdot}13.^{12,\,13}$$

A small amount of hydrolysis takes place in aqueous solution,[14] possibly with the formation of an oxychloride, $(\mathrm{HgCl})_2\mathrm{O}$.[13, 15] The following values for the degree of hydrolysis at 25° C., for different dilutions, have been given[16]:—

Dilution in litres containing equivalent	16	32	64	128	256
Percentage hydrolysis	0·26	0·39	0·58	0·90	1·43

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[1] Moissan, *Traité de Chimie Minérale* (Masson et Cie, Paris), 1906, vol. v, p. 252.

[2] Linhart and Adams, *J. Amer. Chem. Soc.*, 1917, **39**, 948.

[3] Paul and Krönig, *Zeitsch. physikal. Chem.*, 1896, **21**, 414.

[4] Sherrill, *Zeitsch. Elektrochem.*, 1903, **9**, 549; *Zeitsch. physikal. Chem.*, 1903, **43**, 705. See also Morse, *ibid.*, 1902, **41**, 726; Rohland, *Zeitsch. anorg. Chem.*, 1898, **18**, 328; Hannay, *J. Chem. Soc.*, 1873, **26**, 574; Poggiale, *Ann. Chim. Phys.*, 1843, [3], **8**, 463.

[5] Etard, *Ann. Chim. Phys.*, 1894, [7], **2**, 555.

[6] Guthrie, *Phil. Mag.*, 1875, [4], **49**, 266.

[7] Berthelot, *Ann. Chim. Phys.*, 1883, [5], **29**, 236.

[8] Thomsen, *J. prakt. Chem.*, 1875, [2], **11**, 273.

[9] Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 204; Carnegie and Burt, *Chem. News*, 1897, **76**, 174.

[10] Luther, *Zeitsch. physikal. Chem.*, 1901, **36**, 385.

[11] Sherrill, *ibid.*, 1903, **43**, 734. See also Drucker, *Zeitsch. Elektrochem.*, 1912, **18**, 236.

[12] Morse, *Zeitsch. physikal. Chem.*, 1902, **41**, 709; Sherrill, *ibid.*, 1904, **47**, 103.

[13] Luther, *ibid.*, 1904, **47**, 107.

[14] Rohland, *Chem. Zeit.*, 1894, **23**, 581.

[15] See also Arctowski, *Zeitsch. anorg. Chem.*, 1895, **9**, 178.

[16] Ley, *Zeitsch. physikal. Chem.*, 1899, **30**, 249.

Kullgren studied it at higher temperatures by the inversion of cane sugar,[1] and his results are given in the following table :—

Dilution in Litres.	At 100° C. Percentage Hydrolysis.	At 85 5° C. Percentage Hydrolysis.
8	0·60	0·451
32	1·35	1·06
128	2·99	2·31
512	6·91	4·87

The aqueous solution of mercuric chloride is found to contain a number of ultramicroscopic particles attributed to the formation of a colloidal substance produced as the result of hydrolytic decomposition.[2] In the presence of air and light hydrolysis is much more extensive, but the solution may be stabilised to light by the addition of hydrochloric acid.[3] According to Verda,[4] aqueous solutions form the oxide in the dark, but in the light calomel is deposited.

From measurements of the distribution of mercuric chloride between water and benzene, Linhart concludes that the aqueous solution contains Hg_2Cl_4 molecules only,[5] but, from measurements of the boiling-point of aqueous solutions, it appears to associate to treble molecules in water, the formula $Hg[HgCl_3]_2$ being suggested to bring the compound into line with the double alkali salts of general formula $M(HgCl_3)_2$.[6] Measurements of the lowering of freezing-point in urethane indicate that, in this solvent, it apparently forms simple molecules.[7]

Mercuric chloride is readily soluble in alcohol. At 25° C. 100 parts of methyl alcohol dissolve 66·9 parts of mercuric chloride, and 100 of ethyl alcohol 49·5 parts of the salt.[8] According to McIntosh,[9] alcoholates are formed.[10] Below 38·8° C. the compound $HgCl_2.CH_3OH$ may be obtained, and above this temperature pure $HgCl_2$. At this temperature also there is a change in the direction of the solubility curve. The transition temperature is lowered by the addition of water. Another alcoholate, $HgCl_2.2CH_3OH$, has also been mentioned.[11] The solubility of mercuric chloride in mixtures of water and methyl alcohol reaches a maximum at one molecule of water to two of alcohol. In mixtures of ethyl alcohol and water the solubility increases with the proportion of alcohol.[12] Laird, on the contrary, states that there is a minimum at 24 per cent. of alcohol,[13] corresponding with the point of maximum toxicity observed in such solutions by Paul and Krönig.[14] The salt is also soluble in ether,[1, 2] but the solubility is greatly increased by the addition of water.[1, 3] Strömholm concluded from this that the chloride forms a hydrate in the ethereal solution.[4] Investigations have also been made of the solubility in the higher alcohols,[5, 6] mixtures of alcohols,[7] acetone,[5, 8] acetone and water,[9] glycerol,[10] benzene,[11] carbon bisulphide,[12] ethyl acetate,[13] pyridine,[14] formic acid,[15] benzonitrile and other aromatic nitriles,[16, 17] nitrobenzene and other aromatic nitro-compounds,[18] paratoluidine,[16] and various other organic solvents,[5, 19] as well as mixtures of these.[20]

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[1] Kullgren, *Zeitsch. physikal. Chem.*, 1913, **85**, 472.

[2] Fischer and Brieger, *Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 196.

[3] Delépine, *Chem. Zentr.*, 1913, i, 49.

[4] Verda, *ibid.*, 1907, i, 1392.

[5] Linhart, *J. Amer. Chem. Soc.*, 1915, **37**, 258.

[6] Bourion and Rouyer, *Compt. rend.*, 1923, **177**, 54.

[7] Castoro, *Gazzetta*, 1898, **28**, ii, 317.

[8] Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1892, **10**, 783; Rohland, *Zeitsch. anorg. Chem.*, 1898, **18**, 328; Etard, *Compt. rend.*, 1892, **114**, 112; *Ann. Chim. Phys.*, 1894, [7], **2**, 556.

[9] McIntosh, *J. Physical Chem.*, 1897, **1**, 298.

[10] See also Herz and Kuhn, *Zeitsch. anorg. Chem.*, 1908, **58**, 161; Dukelski, *ibid.*, 1907, **53**, 327.

[11] Timofeieff, *Compt. rend.*, 1891, **112**, 1223.

[12] Herz and Anders, *Zeitsch. anorg. Chem.*, 1907, **52**, 164.

[13] Laird, *J. Physical Chem.*, 1920, **24**, 736.

[14] Paul and Krönig, *Zeitsch. physikal. Chem.*, 1896, **21**, 448.

The physical constants of solutions in different solvents have been studied: density in water,[21, 22, 23, 24] alcohol,[22, 23, 25, 26] acetone,[22, 25] and other solvents; specific heat in water [27] and alcohol; [28] vapour pressure in water; [29] boiling-point in water,[30, 31] alcohol,[31] acetone,[32] various nitriles,[33] and alkyl sulphides; [34] freezing-point in water [21, 29] and in urethane; [35] refractive index in water,[36, 25] alcohol,[25, 26] and acetone; [25] magnetic rotation in ethyl and amyl alcohols, acetone, and pyridine; [37] viscosity in water; [38] electrical conductivity in water,[39, 40]

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[1] Linebarger, *Amer. J. Sci.*, 1894, 16, 214.

[2] See also Madsen, *Jahresber.*, 1897, 967.

[3] See also Mylius and Hüttner, *Ber.*, 1911, 44, 1315.

[4] Strömholm, *Zeitsch. physikal. Chem.*, 1903, 44, 63.

[5] Etard, *Ann. Chim. Phys.*, 1894, [7], 2, 555.

[6] Rohland, *Zeitsch. anorg. Chem.*, 1898, 18, 328.

[7] Herz and Kuhn, *ibid.*, 1908, 58, 161; 60, 152.

[8] Naumann, *Ber.*, 1904, 37, 4328.

[9] Herz and Knoch, *Zeitsch. anorg. Chem.*, 1904, 41, 319.

[10] Fairley, *Mon. scient.*, 1879, [3], 9, 685; Moles and Marquina, *Anal. Fis. Quim.*, 1914, 12, 383.

[11] Sherrill, *Zeitsch. physikal. Chem.*, 1903, 43, 705; *Zeitsch. Elektrochem.*, 1903, 9, 549; Franchimont, *Rec. Trav. chim.*, 1882, 1, 55.

[12] Arctowski, *Zeitsch. anorg. Chem.*, 1894, 6, 260.

[13] Naumann, *Ber.*, 1904, 37, 3600; Aten, *Zeitsch. physikal. Chem.*, 1905, 54, 121.

[14] Naumann and Schroeder, *Ber.*, 1904, 37, 4609.

[15] Aschan, *Chem. Zeit.*, 1913, 37, 1117.

[16] Werner, *Zeitsch. anorg. Chem.*, 1897, 15, 1.

[17] Naumann and Kämmerer, *Ber.*, 1914, 47, 1369.

[18] Mascarelli and Ascoli, *Gazzetta*, 1907, 37, i, 125.

[19] Šulc, *Zeitsch. anorg. Chem.*, 1900, 25, 399; Naumann, *Ber.*, 1899, 32, 1000.

[20] Dukelski, *Zeitsch. anorg. Chem.*, 1907, 53, 327; Marden and Dover, *J. Amer. Chem. Soc.*, 1917, 39, 1.

[21] Biltz, *Zeitsch. physikal. Chem.*, 1902, 40, 199.

[22] Schönrock, *ibid.*, 1893, 11, 768.

[23] Schröder, *Jahresber.*, 1886, 469.

[24] Grotrian, *Wied. Annalen*, 1883, 18, 192; Engel, *Ann. Chim. Phys.*, 1889, [6], 17, 362.

[25] Le Blanc and Rohland, *Zeitsch. physikal. Chem.*, 1896, 19, 282.

[26] Röhrs, *Ann. Physik*, 1912, [4], 37, 315.

[27] Blümke, *Wied. Annalen*, 1884, 23, 161.

[28] Timofeieff, *Compt. rend.*, 1891, 112, 1261.

[29] Raoult, *ibid.*, 1878, 87, 167.

[30] Bourion and Rouyer, *ibid.*, 1923, 177, 54; Salvadori, *Gazzetta*, 1896, 26, i, 237; Beckmann, *Zeitsch. physikal. Chem.*, 1890, 6, 453, 460; Skinner, *Trans. Chem. Soc.*, 1892, 61, 339.

[31] Landsberger, *Zeitsch. anorg. Chem.*, 1898, 17, 450.

[32] Dutoit and Friderich, *Bull. Soc. chim.*, 1898, [3], 19, 321.

[33] Kahlenberg, *J. Physical Chem.*, 1902, 6, 45; Werner and Stephani, *Zeitsch. anorg. Chem.*, 1897, 15, 31.

[34] Werner and Stephani, *ibid.*, 30; Werner and Maiborn, *ibid.*, 26.

[35] Castoro, *Gazzetta*, 1898, 28, ii, 317.

[36] Chéneveau, *Compt. rend.*, 1904, 138, 1483.

[37] Schönrock, *Zeitsch. physikal. Chem.*, 1893, 11, 762.

[38] Wagner, *ibid.*, 1890, 5, 39.

[39] Grotrian, *Wied. Annalen*, 1883, 18, 177; Ley, *Zeitsch. physikal. Chem.*, 1899, 30, 247; Ley and Kissel, *Ber.*, 1899, 32, 1358; Kahlenberg, *J. Physical Chem.*, 1901, 5, 339.

[40] Fitzpatrick, *Phil. Mag.*, 1887, [5], 24, 377.

alcohols,[1] ether,[2, 3] acetone,[4, 5] acetamide,[6] ethyl chloride,[7] and other organic solvents;[4, 8] transport number;[9] and electrical endosmose.[10]

Mercuric chloride is soluble in hydrochloric acid, possibly with compound formation.[11, 12] A study of the heat evolved seems to support this view,[13] and solid crystalline compounds of mercuric chloride with hydrochloric acid have been obtained—for example, $HgCl_2.2HCl$, $HgCl_2.HCl$,[14] and, according to Ditte,[11, 15] $HgCl_2.2HCl.7H_2O$, $3HgCl_2.4HCl.14H_2O$, $2HgCl_2.HCl.6H_2O$, $4HgCl_2.2HCl.9H_2O$, and $3HgCl_2.HCl.5H_2O$. It has been suggested that the compounds formed are to be regarded as complex acids of formulæ $H(HgCl_3)$, $H_2(HgCl_4)$, etc.[16] The following values have been given for the solubility in hydrochloric acid solution[12, 17]:—

Milli-equivalents in 10 c.c. of Solution.		Density.	Grm. of Water.
$HgCl_2$.	HCl.		
9·7	4·3	1·117	9·704
19·8	9·9	1·238	9·340
35·5	17·8	1·427	8·816
68·9	32·25	1·811	7·714
85·5	41·5	2·023	7·131
95·675	70·875	2·198	6·481

Double Salts.—Mercuric chloride dissolves more readily in solutions of a number of chlorides than in water, due to the formation of complex salts in which mercury enters into the anion.[18] The evidence obtained from measurements of the distribution ratio of mercuric chloride between sodium chloride solution and benzene,[19] ebullioscopic determinations of the molecular weights of sodium, potassium, or ammonium mercuric chlorides in solution,[1] measurements of the heats of formation of a number of double chlorides in solution,[2] and a study of the absorption spectra of solutions of mercuric chloride along with other chlorides in alcohol or water,[3, 4] indicates that no complex containing a higher proportion of the second chloride than M_2HgCl_4 exists. According to Calzolari and Tagliavini, compounds of double salts of mercury halides with hexamethylene tetramine all show that they are of the type $MHgCl_3$ or M_2HgCl_4.[5] Double salts are formed with the chlorides of lithium,[6, 7, 8] sodium,[6, 7, 9, 10, 11] potassium,[6, 7, 8, 9, 10, 12, 13] ammonium[3, 10, 12, 14]—an aqueous solution of mercuric chloride and ammonium chloride was known by the alchmeists as *sal alembroth*—substituted ammonium compounds,[15] rubidium,[9, 10, 16] cæsium,[17] calcium,[6] strontium,[6, 8, 18, 19] barium,[6, 18, 19, 20] beryllium,[6] magnesium,[6, 18, 19] zinc,[21, 22, 23] thallium,[24] copper[21, 22]—there is also a triple salt with copper and potassium[25]—gold,[26] ferrous iron,[21] cobalt,[21] including complex cobalt salts containing the nitrate or sulphate radicle,[27] nickel,[21] manganese,[21] cerium,[21] lanthanum,[28] didymium,[28] yttrium,[29] and erbium.[30] Mailhe obtained compounds with the oxides of cobalt,[1] nickel,[1] cadmium,[2] lead,[2] and copper.[3] There are two types of chromates of the general formulæ $M_2Cr_2O_7.HgCl_2$, of which the ammonium and potassium salts are known, and $M_4Cr_2O_7Cl_2.HgCl_2.2H_2O$, of which the ammonium, potassium, and rubidium salts have been described.[4] A compound has been obtained with strontium chromate,[5] and has been found to contain also hydrochloric acid.[6]

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[1] Arrhenius, *Zeitsch. physikal. Chem.*, 1892, **9**, 493.

[2] Fitzpatrick, *loc. cit.*

[3] Cattaneo, *Atti R. Accad. Lincei*, 1893, [5], **2**, i, 295.

[4] Shaw, *J. Physical Chem.*, 1913, **17**, 162.

[5] Laszczynski, *Zeitsch. Elektrochem.*, 1895–96, **2**, 55.

[6] Walker and Johnson, *Trans. Chem. Soc.*, 1905, **87**, 1597.

[7] Eversheim, *Ann. Physik*, 1902, [4], 8, 564.

[8] Kahlenberg and Lincoln, *J. Physical Chem.*, 1899, **3**, 12; Bruner, Kozak, and Mariasz, *Ber.*, 1903, **36**, 3297.

[9] Hittorf, *Pogg. Annalen*, 1859, **106**, 524; Morse, *Zeitsch. physikal. Chem.*, 1902, **41**, 728.

[10] von Elissafoff, *ibid.*, 1912, **79**, 399.

[11] Ditte, *Ann. Chim. Phys.*, 1881, [5], **22**, 551.

[12] Engel, *ibid.*, 1889, [6], **17**, 362.

[13] Berthelot, *ibid.*, 1883, [5], **29**, 231.

[14] Neumann, *Monatsh.*, 1889, **10**, 236.

[15] See also Boullay, *Ann. Chim. Phys.*, 1827, [2], **34**, 343.

[16] Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 389.

[17] See also Ditte, *loc. cit.*

[18] Le Blanc and Noyes, *loc. cit.*; Richards and Archibald, *Zeitsch. physikal. Chem.*, 1902, **40**, 385; Sherrill, *ibid.*, 1903, **43**, 705; 1904, **47**, 103; *Zeitsch. Elektrochem.*, 1903, **9**, 549; Abegg, Immerwahr, and Jander, *ibid.*, 1902, 8, 688; Herz and Paul, *Zeitsch. anorg. Chem.*, 1913, **82**, 431.

[19] Linhart, *J. Amer. Chem. Soc.*, 1916, **38**, 1272.

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[1] Bourion and Rouyer, *Compt. rend.*, 1924, **178**, 86.

[2] Varet, *ibid.*, 1896, **123**, 421.

[3] Crymble, *Trans. Chem. Soc.*, 1914, **105**, 658.

[4] Ley and Fischer, *Zeitsch. anorg. Chem.*, 1913, **82**, 329; Shibata, Inouye, and Nakatsuka, *J. Jap. Chem. Soc.*, 1921, **42**, 983, see *Chem. Abs.*, 1922, **16**, 2075.

[5] Calzolari and Tagliavini, *Atti R. Accad. Lincei*, 1915, [5], **24**, i, 925.

[6] Bonsdorff, *Pogg. Annalen*, 1829, **17**, 115.

[7] Linebarger, *Amer. Chem. J.*, 1893, **15**, 337.

[8] Harth, *Zeitsch. anorg. Chem.*, 1897, **14**, 323.

[9] Foote and Levy, *Amer. Chem. J.*, 1906, **35**, 236.

[10] Tourneux, *Ann. Chim.*, 1919, [9], **11**, 225.

[11] Lassaigne, *Ann. Chim. Phys.*, 1837, [2], **64**, 104; Voit, *Annalen*, 1857, **104**, 354; Linebarger, *Amer. Chem. J.*, 1894, **16**, 214.

[12] Rammelsberg, *Pogg. Annalen*, 1853, **90**, 33.

[13] Boullay, *Ann. Chim. Phys.*, 1827, [2], **34**, 343; Berthelot, *ibid.*, 1889, [5], **29**, 202; Ditte, *Compt. rend.*, 1890, **110**, 1330; Tichomiroff, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 731; Benrath, *Zeitsch. anorg. Chem.*, 1908, **58**, 258; Foote, *Amer. Chem. J.*, 1910, **42**, 620.

[14] Kane, *Ann. Chim. Phys.*, 1839, [2], **72**, 380; Holmes, *Chem. News*, 1862, **5**, 351; Hirzel, *Jahresber.*, 1853, 381; Thomson and Bloxam, *Trans. Chem. Soc.*, 1882, **41**, 379; Jones and Ota, *Amer. Chem. J.*, 1899, **22**, 12; Strömholm, *J. prakt. Chem.*, 1902, [2], **66**, 441; Meerburg, *Zeitsch. anorg. Chem.*, 1908, **59**, 136.

[15] Strömholm, *J. prakt. Chem.*, 1902, [2], **66**, 518.

[16] Godeffroy, *Jahresber.*, 1878, 238; *Ber.*, 1875, **8**, 11.

[17] Wells, *Amer. J. Sci.*, 1892, [3], **44**, 221; *Zeitsch. anorg. Chem.*, 1892, **2**, 402; Penfield, *ibid.*, 420; *Amer. J. Sci.*, 1892, [3], **44**, 311; Foote, *Amer. Chem. J.*, 1903, **30**, 339; Foote and Haigh, *J. Amer. Chem. Soc.*, 1911, **33**, 459.

[18] Swan, *Amer. Chem. J.*, 1898, **20**, 613.

[19] Herz and Paul, *Zeitsch. anorg. Chem.*, 1913, **82**, 433.

[20] Foote and Bristol, *Amer. Chem. J.*, 1904, **32**, 246; Schreinemakers, *Chem. Weekblad.*, 1910, **7**, 197.

[21] Bonsdorff, *Pogg. Annalen*, 1829, **17**, 247.

[22] Harth, *Zeitsch. anorg. Chem.*, 1897, **14**, 323.

[23] Drucker, *Zeitsch. Elektrochem.*, 1912, **18**, 236.

[24] Carstanjen, *Jahresber.*, 1867, 280; Jörgensen, *J. prakt. Chem.*, 1873, [2], **6**, 86; Barlot and Pernot, *Compt. rend.*, 1921, **173**, 232.

[25] Bonsdorff, *Pogg. Annalen*, 1834, **33**, 81; Schreinemakers and Thonus, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 472.

[26] Behrens, *ibid.*, 1899, **2**, 163, see *J. Chem. Soc.*, 1900, **78**, Abs. ii, 213.

[27] Blomstrand and Krok, *Ber.*, 1871, **4**, 712.

[28] Marignac, *Ann. Mines*, 1859, [5], **15**, 272.

[29] Bonsdorff, *Pogg. Annalen*, 1829, **17**, 136.

[30] Clève, *Bull. Soc. chim.*, 1874, [2], **21**, 344.

A compound of the composition $HgCl_2.2HgS$ is formed by the action of sulphuretted hydrogen on mercuric chloride in various organic solvents.[7]

Double salts with thallium nitrate,[8] and also with the chloro platinates of amines,[9] have been described.

Compounds resulting from the Action of Ammonia on Mercuric Chloride.—The constitution of the large number of compounds which arise through the interaction of mercury salts and ammonia, in the presence or absence of the corresponding salts of ammonia, has been a much discussed question for the past century. As the interest has centred chiefly round the halides, and especially round the chloride, it seems desirable at this point to give some indication of the theories most generally adopted.

The best known compound obtained by the direct action of ammonia on mercuric chloride is the substance long known as "fusible white precipitate," or "Wöhler's precipitate." The ammonia may be in the gaseous [10] or liquid form; [11, 12] in concentrated aqueous solution, with,[13, 14] or without,[15] ammonium chloride; or, finally, in solution in some organic solvent such as acetone,[16] methyl [17] or ethyl [18] acetate, methylal,[19] or pyridine.[20] The compound may also be obtained by dissolving mercuric oxide in boiling ammonium chloride solution and allowing to cool.[21] Wöhler prepared it by precipitating a solution of

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[1] Mailhe, *Ann. Chim. Phys.*, 1902, [7], **27**, 368; *Compt. rend.*, 1901, **132**, 1273.

[2] Mailhe, *Ann. Chim. Phys.*, 1902, [7], **27**, 371; *Compt. rend.*, 1901, **132**, 1560.

[3] Mailhe, *ibid.*, 1901, **133**, 226.

[4] Strömholm, *Zeitsch. anorg. Chem.*, 1912, **75**, 277. See also Darby, *Annalen*, 1848, **65**, 208; Wyrouboff, *Jahresber.*, 1880, 309; Jäger and Krüss, *Ber.*, 1889, **22**, 2043; Millon, *Ann. Chim. Phys.*, 1846, [3], **18**, 388.

[5] Imbert and Bélugou, *Bull. Soc. chim.*, 1897, [3], **17**, 471.

[6] Bélugou, *ibid.*, 473.

[7] Naumann, *Ber.*, 1899, **32**, 1000; Naumann and Eidmann, *ibid.*, 1904, **37**, 4335; Naumann and Alexander, *ibid.*, 3602; Naumann and Bezold, *ibid.*, 1909, **42**, 3794; Naumann and Henninger, *ibid.*, 1910, **43**, 315.

[8] Bergman, Henke, and Isaïkin, *J. Russ. Phys. Chem. Soc.*, 1923, **54**, 466, see *J. Chem. Soc.*, 1923, **124**, Abs. ii, 764.

[9] Strömholm, *Zeitsch. anorg. Chem.*, 1923, **126**, 129.

[10] Holmes, *Trans. Chem. Soc.*, 1918, **113**, 74.

[11] André, *Compt. rend.*, 1899, **108**, 233, 290.

[12] Weyl, *Pogg. Annalen*, 1867, **131**, 547; Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 300; Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

[13] Mitscherlich, *J. prakt. Chem.*, 1840, [1], **19**, 455.

[14] Strömholm, *Zeitsch. anorg. Chem.*, 1908, **57**, 72.

[15] Gaudechon, *Ann. Chim. Phys.*, 1911, [8], **22**, 167.

[16] Naumann and Müller, *Ber.*, 1904, **37**, 4335.

[17] Naumann and Bezold, *ibid.*, 1909, **42**, 3794.

[18] Naumann and Henninger, *ibid.*, 1910, **43**, 315; Naumann and Alexander, *ibid.*, 1904, **37**, 3603.

[19] Naumann, *ibid.*, 1899, **32**, 1000.

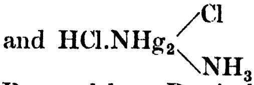
[20] Naumann and Schroeder, *ibid.*, 1904, **37**, 4609; Schroeder, *Zeitsch. anorg. Chem.*, 1905, **44**, 1.

[21] Rammelsberg, *J. prakt. Chem.*, 1888, [2], **38**, 558. See also André, *Compt. rend.*, 1891, **112**, 859.

sal alembroth, that is a double salt of mercuric chloride and ammonium chloride, by potassium hydroxide in the cold.[1]

The first product of the action of water on fusible white precipitate is "infusible white precipitate," ammonium chloride being eliminated.[2, 3] It may be prepared by precipitation of mercuric chloride solution with excess of aqueous ammonia.[4, 5, 6] The presence of ammonium chloride tends to inhibit the reaction, or rather to transform the compound into fusible white precipitate,[7, 8, 9] and Franklin has shown that the two compounds are in equilibrium with a 0·49*N* solution of ammonium chloride.[10, 11] A certain amount is also obtained in the formation of fusible white precipitate by the action of liquid ammonia on mercuric chloride.[12] Another method of preparation of infusible white precipitate is by the action of sodamide on mercuric chloride.[12]

By the prolonged hydrolysing action of water on the white precipitates, a yellow powder is obtained which is known as the chloride of Millon's base.[7, 13] The same compound may also be obtained by the action of dilute hydrochloric acid on Millon's base,[7, 14] or of ammonium chloride on an aqueous solution of mercury acetamide,[15] or, probably, by the action of dry ammonia on the oxychloride $HgCl_2.3HgO$.[16]

According to the views originally put forward by Rammelsberg[7] on the basis of Hofmann's work on the substituted ammonias,[17] and sanctioned by a large number of investigators,[8, 9, 18, 19] all mercury-ammonia compounds are regarded as substituted ammonium compounds of one single type, namely, those in which the four hydrogen atoms in the ammonium group are replaced by two mercury atoms, making the group NHg_2 a constituent of all the compounds. The three compounds mentioned are hence formulated: fusible white precipitate, $NHg_2Cl.3NH_4Cl$; infusible white precipitate, $NHg_2Cl.NH_4Cl$; and the chloride of Millon's base, $NHg_2Cl.H_2O$, Millon's base itself being $NHg_2OH.xH_2O$. The justification for these formulæ is based largely on the fact that fusible and infusible white precipitate lose ammonium chloride when treated with water, or ammonia with potassium hydroxide. Gaudechon[8, 9, 18] also maintained that the thermal relations in the formation of these compounds offer confirmation of Rammelsberg's formulæ, although he preferred to express the white precipitates, not as ordinary double salts, but as complex salts on the analogy of the chloroplatinates, $3HCl.NHg_2\left\langle\begin{matrix}Cl\\3NH_3\end{matrix}\right.$ and  $HCl.NHg_2\left\langle\begin{matrix}Cl\\NH_3\end{matrix}\right.$ respectively.[1] The most serious rival to the Rammelsberg-Pesci theory is that put forward by Franklin.[2] This is in reality a modified and extended form of Kane's old amide theory with regard to the constitution of these compounds.[3] Franklin regards ammonia as behaving, in many circumstances, in a manner exactly analogous to water. Thus we may have ammonia of crystallisation instead of water of crystallisation, and ammonolysed instead of hydrolysed salts. As the result of an ammonolytic action, ammonia acts upon the salt similarly to water, removing the acid radicle to form ammonium salts instead of the free acid, and substituting one of the ammonia residues, $\equiv N$, $=NH$, or $-NH_2$, for the acid radicle removed. On this view all mercury-ammonia compounds are to be divided into three classes: (*a*) Those containing ammonia of crystallisation, of which fusible white precipitate, with a formula $HgCl_2.2NH_3$, is an example; (*b*) ammonolysed or ammonobasic compounds, of which infusible white precipitate may be taken as an example, since, in the presence of water, we get mercury chloroamide or amidochloride from fusible white precipitate,

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[1] See Kane, *Ann. Chim. Phys.*, 1839, [2], 72, 380.

[2] Gaudechon, *loc. cit.*

[3] Franklin, *Amer. Chem. J.*, 1912, 47, 369.

[4] André, *Compt. rend.*, 1899, 108, 233, 290.

[5] Strömholm, *loc. cit.*

[6] Kane, *Phil. Mag.*, 1836, [3], 8, 495; *Annalen*, 1836, 18, 135; 1838, 26, 195; Sen, *Zeitsch. anorg. Chem.*, 1903, 33, 197; Saha and Choudhuri, *ibid.*, 1914, 86, 225; Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 419; Balestra, *Gazzetta*, 1891, 21, ii, 294.

[7] Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 558.

[8] Gaudechon, *Compt. rend.*, 1907, 145, 142.

[9] Gaudechon, *Ann. Chim. Phys.*, 1911, [8], 22, 167.

[10] Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 40.

[11] See also Gaudechon, *loc. cit.*

[12] Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 820; *Zeitsch. anorg. Chem.*, 1905, 46, 25.

[13] Kane, *Annalen*, 1836, 18, 288; *Phil. Mag.*, 1837, [3], 11, 428; André, *Compt. rend.*, 1889, 108, 1108, 1164; Pesci, *Zeitsch. anorg. Chem.*, 1899, 21, 361; Strömholm, *ibid.*, 1908, 57, 72; Hofmann and Marburg, *Annalen*, 1899, 305, 194. For an account of Millon's base, see under Mercuric Oxide.

[14] Hofmann and Marburg, *loc. cit.*, 211.

[15] Fürth, *Monatsh.*, 1902, 23, 1147.

[16] Ullgren, *Annalen*, 1838, 26, 208.

[17] Hofmann, *Jahresber.*, 1856, 408.

[18] Gaudechon, *Compt. rend.*, 1908, 146, 177.

[19] Pesci, *Gazzetta*, 1889, 19, 509; 1890, 20, 485; *Zeitsch. anorg. Chem.*, 1899, 21, 361; Rây, *ibid.*, 1903, 33, 193; *Trans. Chem. Soc.*, 1902, 81, 644; Balestra, *Gazzetta*, 1891, 21, ii, 294; Raffo and Scarella, *ibid.*, 1915, 15, i, 123.

$$HgCl_2+2NH_3=HgNH_2Cl+NH_4Cl;$$

(*c*) compounds which are both ammonolysed and hydrolysed, or mixed ammonobasic-hydrobasic salts, of which there is a large number of examples. For the best known of these, the chloride of Millon's base, Franklin proposes the formula $HO.Hg.NH.HgCl$, since it may be formed by the action of acid on Millon's base, to which he gives the formula $HO.Hg.NH.HgOH$. A strong argument in favour of Franklin's view may be based on the fact of the formation of similar compounds with substituted ammonias, of which a large number have been studied, namely, compounds with hydroxylamine,[4] hydrazine,[5] alkylamines,[6,7] aromatic amines,[7,8] pyridine,[9] quinoline,[10] ethylene diamine,[11] and thiocarbamide,[12] as well as compounds of the double chlorides of mercuric chloride with hexamethylene tetramine.[1] Hofmann and Marburg[2] have pointed out that, considering, for example, the monoethylamine analogue of infusible white precipitate, which, on treatment with hot water, gives a yellow residue comparable with the chloride of Millon's base, it can only be formulated as NHC_2H_5HgCl—that is, in accordance with Franklin's theory. To reduce it to a formula analogous to $NHg_2Cl.NH_4Cl$ would involve too drastic a transformation of the amino group. Further, Strömholm has suggested[3] that, if Rammelsberg's formula holds, it should be possible to prepare double salts similar to fusible and infusible precipitate in which potassium chloride is substituted for ammonium chloride. This is not the case, however, a circumstance which favours Franklin's theory.

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[1] Gaudechon, *Ann. Chim. Phys.*, 1911, [8], 22, 244.

[2] Franklin, *Zeitsch. anorg. Chem.*, 1905, 46, 1; *J. Amer. Chem. Soc.*, 1905, 27, 820; 1907, 29, 35; *Amer. Chem. J.*, 1912, 47, 361.

[3] Kane, *Ann. Chim. Phys.*, 1839, [2], 72, 337.

[4] Adams, *Amer. Chem. J.*, 1902, 28, 198.

[5] Curtius and Schrader, *J. prakt. Chem.*, 1894, [2], 50, 332; Hofmann and Marburg, *Ber.*, 1897, 30, 2019; *Annalen*, 1899, 305, 191.

[6] Strömholm, *Zeitsch. anorg. Chem.*, 1908, 57, 72; Raffo and Scarella, *Gazzetta*, 1915, 45, i, 123.

[7] Rây and Dhar, *Trans. Chem. Soc.*, 1913, 103, 3.

[8] Forster, *Ber.*, 1874, 7, 294; Fürth, *Monatsh.*, 1902, 23, 1147; Pesci, *Zeitsch. anorg. Chem.*, 1897, 15, 225; André, *Compt. rend.*, 1891, 112, 995; Köhler, *Ber.*, 1879, 12, 2208.

[9] Naumann, *Ber.*, 1904, 37, 4609; Schroeder, *Chem. Zentr.*, 1904, ii, 454; Staronka, *J. Chem. Soc.*, 1910, 98, Abs. i, 876; McBride, *J. Physical Chem.*, 1910, 14, 189; Werner, *Zeitsch. anorg. Chem.*, 1897, 15, 1; Monari, *Jahresber.*, 1884, 629; Pesci, *Gazzetta*, 1895, 25, ii, 429; Lang, *Ber.*, 1888, 21, 1586.

[10] Pesci, *Gazzetta*, 1895, 25, i, 394.

[11] Schering, *J. Chem. Soc.*, 1902, 82, Abs. i, 348.

[12] Rosenheim and Meyer, *Zeitsch. anorg. Chem.*, 1906, 49, 13; Claus, *Ber.*, 1876, 9, 226; Maly, *ibid.*, 172.

Saha and Choudhuri[4] find that hydrofluoric acid acts upon infusible white precipitate, giving a mixture of mercuric chloride, mercuric fluoride, and ammonium fluoride, which seems to indicate that the chlorine is combined with the mercury. With platinic chloride it forms a yellow crystalline precipitate which has the composition $NH_2HgCl.PtCl_4$. If infusible white precipitate were a double salt of ammonium chloride, the empirical formula would probably be $2NH_2HgCl.PtCl_4$. These two reactions appear to offer additional evidence in confirmation of Franklin's view.

Franklin's method of preparation of infusible white precipitate,[5] by the action of sodamide on mercuric chloride, is also in favour of the formula NH_2HgCl, since

$$NH_2Na+ClHgCl=NH_2HgCl+NaCl.$$

Further Properties of some of the Mercury-Ammonia Compounds.—Fusible white precipitate melts when heated and decomposes, giving nitrogen, ammonia, calomel, and ammonium chloride.[6] Infusible white precipitate gives nitrogen, ammonia, and calomel, with a little ammonium chloride, but without melting.[7, 8] Infusible white precipitate is soluble in mineral acids.[4, 8, 9] When precipitated from mercuric chloride solution by ammonium phosphate it is soluble in excess of the latter.[10] It is vigorously attacked by the halogens and sulphur,[11] and is reduced by arsenic trisulphide [12] and hypophosphorous acid.[13] The chloride of Millon's base is a yellow powder, which is decomposed by heat into ammonia, water, mercury, calomel, and nitrogen,[14] the water not being given off until 180° C. is reached, when, however, complete decomposition takes place.[15]

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[1] Calzolari and Tagliavini, *Atti R. Acad. Lincei*, 1915, [5], **24**, i, 925; Quercigh, *J. Chem. Soc.*, 1919, **116**, Abs. i, 523.

[2] Hofmann and Marburg, *Annalen*, 1899, **305**, 191; *Zeitsch. anorg. Chem.*, 1900, **23**, 126.

[3] Strömholm, *ibid.*, 1908, **57**, 72.

[4] Saha and Choudhuri, *ibid.*, 1914, **86**, 225.

[5] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820; *Zeitsch. anorg. Chem.*, 1905, **46**, 25.

[6] Kane, *Ann. Chim. Phys.*, 1839, [2], **72**, 380.

[7] Sen, *Zeitsch. anorg. Chem.*, 1903, **33**, 197; Kane, *Phil. Mag.*, 1836, [3], 8, 495.

[8] Fourcroy, *Ann. Chim.*, 1792, [1], **14**, 47.

[9] Kosman, *Ann. Chim. Phys.*, 1848, [3], **27**, 238.

[10] Carnegie and Burt, *Chem. News*, 1897, **76**, 174.

[11] von Schwarzenbach, *Ber.*, 1875, 8, 1231; Flückiger, *ibid.*, 1875, 8, 1619.

[12] Reichard, *ibid.*, 1897, **30**, 1916.

[13] Howard, *J. Soc. Chem. Ind.*, 1904, **23**, 152.

[14] Sen, *loc. cit.*

[15] Hofmann and Marburg, *Annalen*, 1899, **304**, 214.

Many more compounds of all three types have been described, including $HgCl_2.NH_3$,[1] $2HgCl_2.3NH_3$,[2] $3HgCl_2.2NH_3$,[3] $HgCl_2.12NH_3$,[4] and similar compounds of the double salts of mercury with zinc[5] and cobalt,[6] $Hg_2Cl_3NH_2$,[3, 7] NHg_2Cl,[8] and $Hg_4N_2H_2OCl_2$.[9] Still other compounds have been mentioned, but it is probable that many of them are mixtures, especially the basic compounds.[10]

Reactions of Mercuric Chloride with other Compounds of the Ammonia Type.—Hydrogen phosphide reacts with mercuric chloride, forming the compound $PHg_2Cl.HgCl_2$, both anhydrous[11, 12] and hydrated,[13] and possibly other compounds.[14] Similar arsenic compounds have been prepared,[15] and there are also compounds with the alkyl substitution products of phosphine,[11] arsine,[16] and stibine.[17]

Addition Compounds.—Mercuric chloride forms addition compounds with a large variety of other substances besides ammonia. The existence of alcoholates has already been mentioned. There are also compounds with aromatic tellurides,[18] sulphine and thetine chlorides,[19] acetone,[20] aromatic nitro-compounds,[21] ethylene and acetylene or their derivatives,[22] unsaturated ketones,[23] and a number of other organic substances.[24] In many of these cases the double compound is not stable, and a further reaction takes place with the removal of one halogen atom.

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[1] Naumann, *Ber.*, 1899, **32**, 1000 ; Rose, *Pogg. Annalen*, 1830, **20**, 158.

[2] Varet, *Compt. rend.*, 1889, **109**, 941.

[3] Holmes, *Trans. Chem. Soc.*, 1918, **113**, 74.

[4] Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 300.

[5] André, *Compt. rend.*, 1891, **112**, 995.

[6] Werner and Klein, *Zeitsch. anorg. Chem.*, 1897, **14**, 40 ; Claude, *Ann. Chim. Phys.*, 1851, [3], **33**, 491.

[7] Millon, *ibid.*, 1846, [3], **18**, 392 ; Balestra, *Gazzetta*, 1891, **21**, ii, 298 ; Strömholm, *Zeitsch. anorg. Chem.*, 1908, **57**, 72.

[8] Weyl, *Pogg. Annalen*, 1867, **131**, 524 ; Rammelsberg, *J. prakt. Chem.*, 1888, [2], **38**, 558 ; André, *Compt. rend.*, 1889, **108**, 1108.

[9] André, *ibid.*, 1889, **108**, 1110, 1164 ; Sen, *Zeitsch. anorg. Chem.*, 1903, **33**, 206 ; Rây, *Trans. Chem. Soc.*, 1902, **81**, 646.

[10] A descriptive catalogue of the mercury-ammonia compounds has been given by Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 35.

[11] Partheil and van Haaren, *Arch. Pharm.*, 1900, **238**, 28.

[12] Lemoult, *Compt. rend.*, 1907, **145**, 1175.

[13] Rose, *Pogg. Annalen*, 1837, **40**, 75.

[14] Aschan, *Chem. Zeit.*, 1886, **10**, 102.

[15] Partheil and Amort, *Ber.*, 1898, **31**, 594.

[16] Partheil, Amort, and Gronover, *Arch. Pharm.*, 1899, **237**, 127.

[17] Partheil and Mannheim, *ibid.*, 1900, **238**, 166.

[18] Lederer, *Ber.*, 1914, **47**, 277.

[19] Strömholm, *J. prakt. Chem.*, 1902, [2], **66**, 423.

[20] Aten, *Zeitsch. physikal. Chem.*, 1905, **54**, 121.

[21] Mascarelli, *Atti R. Accad. Lincei*, 1908, [5], **17**, i, 29.

[22] Keiser, *Amer. Chem. J.*, 1893, **15**, 537 ; Biginelli, *Ann. Farm. Chim.*, 1898, 16 ; Hofmann and Sand, *Ber.*, 1900, **33**, 1340, 1353 ; Hofmann, *ibid.*, 1904, **37**, 4459 ; Biltz and Mumm, *ibid.*, 1904, **37**, 4417 ; Biltz, *ibid.*, 1905, **38**, 133 ; Manchot, *ibid.*, 1921, **54B**, 571 ; *Annalen*, 1918, **417**, 93 ; Manchot and Haas, *ibid.*, 1913, **399**, 123 : Manchot and Klüg, *ibid.*, 1920, **420**, 170 ; Sand and Breest, *Zeitsch. physikal. Chem.*, 1907, **59**, 424 ; Brame, *Trans. Chem. Soc.*, 1905, **87**, 427 ; Chapman and Jenkins, *ibid.*, 1919, **115**, 847 ; Jenkins, *ibid.*, 1921, **119**, 747.

[23] Vorländer and Eichwald, *Ber.*, 1923, **56B**, 1150.

[24] Sand and Hofmann, *ibid.*, 1900, **33**, 1358 ; Sand and Singer, *ibid.*, 1902, **35**, 3170 ; Biilmann, *ibid.*, 1900, **33**, 1641 ; Dimroth, *ibid.*, 1902, **35**, 2040 ; Hofmann and Seiler, *ibid.*, 1906, **39**, 3187 ; Ville and Astre, *Compt. rend.*, 1900, **130**, 837 ; Bougault, *J. Pharm. Chim.*, 1900, [6], **11**, 97, 165 ; Schering, *J. Chem. Soc.*, 1902, **82**, Abs. i, 348 ; Straus and Blankenhorn, *Annalen*, 1918, **415**, 232 ; Bernardi, *Gazzetta*, 1919, **49**, ii, 318 ; Olivieri-Mandalà, *ibid.*, 1921, **51**, i, 125.

Mercurous Bromide, Hg_2Br_2.—Bromine reacts directly with mercury, even in the dry state,[1] but the reaction finally results in the formation of mercuric bromide.[2] According to Berthelot, hydrobromic acid reacts with mercury, slowly in the cold but more quickly when heated, to form mercurous bromide.[3] It is also obtained by treating mercurous nitrate with liquid bromine,[4] or by subliming a mixture of the theoretical quantities of mercury and mercuric bromide,[5] but it is most readily prepared by precipitating a solution of mercurous nitrate with a soluble bromide.[2, 6, 7]

It forms a white powder similar to calomel,[2] or long needles,[6] or, if dissolved in a hot solution of mercurous nitrate, it separates on cooling as white tetragonal plates.[4] The density is 7·307.[8] It sublimes without decomposition between 340° C. and 350° C., if rapidly heated.[4] According to Carnelley,[9] it volatilises completely at 405° C. without melting. The vapour density of mercurous bromide is 10·11 compared with air, and indicates either the simple formula $HgBr$, or, more probably, decomposition into mercury and mercuric bromide.[10] The molecular weight in fused mercuric bromide, as determined by the freezing-point lowering, corresponds with the formula Hg_2Br_2.[11] The heat of formation from liquid mercury and liquid bromine is 49·1 Cal.[12]

Mercurous bromide shows an orange fluorescence under ultra-violet light,[13] and becomes black, especially if moist.[14] Under direct sunlight it is also partially decomposed.[4]

The conductivity of the solid salt has been determined,[15] and has been found to be greatly increased by the addition of 1 per cent. of potassium bromide.

Hot hydrochloric acid blackens mercurous bromide, due to the separation of mercury.[4] Hot, concentrated sulphuric acid dissolves it with the evolution of sulphur dioxide, and it is also slowly dissolved by hot, fuming nitric acid.[4] Alkalies blacken it, owing to the separation of mercury.

Mercurous bromide is practically insoluble in water, the value for the solubility given by Sherrill [16] being 7×10^{-8} grm.-molecules per litre at 25° C. The values obtained by other investigators, generally by electromotive force determinations, vary considerably.[17] Solutions of the alkali halides have a decomposing effect on the bromide similar to that on calomel.[1]

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[1] Shenstone, *Trans. Chem. Soc.*, 1897, 71, 471.

[2] Balard, *Ann. Chim. Phys.*, 1826, [2], 32, 360.

[3] Berthelot, *ibid.*, 1856, [3], 46, 492. See also Bailey and Fowler, *Trans. Chem. Soc.*, 1888, 53, 760.

[4] Stroman, *Ber.*, 1887, 20, 2822.

[5] Löwig, *Mag. Pharm.*, 1828, 23, 7.

[6] Henry, *J. Pharm. Chim.*, 1829, [2], 15, 55.

[7] Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1912, 77, 41.

[8] Karsten, *Schweigger's J.*, 1832, 65, 417. See Clarke, *Constants of Nature*, Part I (Macmillan & Co.), 1888, p. 22.

[9] Carnelley, *Trans. Chem. Soc.*, 1878, 33, 277.

[10] Mitscherlich, *Pogg. Annalen*, 1833, 29, 224.

[11] Beckmann, *Zeitsch. anorg. Chem.*, 1907, 55, 182 ; Guinchant, *Compt. rend.*, 1909, 149, 479.

[12] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 94. See also Nernst, *Zeitsch. physikal. Chem.*, 1888, 2, 25. From solid bromine and mercury it is 70 Cal. (Berthelot, *Ann. Chim. Phys.*, 1880, [5], 21, 389), or 68·29 Cal. (Thomsen, *J. prakt. Chem.*, 1875, 11, 283).

[13] Wolff, *Chem. Zeit.*, 1912, 36, 1039.

[14] Pougnet, *Compt. rend.*, 1915, 161, 348.

[15] Fritsch, *Wied. Annalen*, 1897, 60, 309.

[16] Sherrill, *Zeitsch. physikal. Chem.*, 1903, 43, 728.

[17] Goodwin, *ibid.*, 1894, 13, 652 ; Bodländer, *ibid.*, 1898, 27, 61 ; de K. Thompson, *J. Amer. Chem. Soc.*, 1906, 28, 762 ; Rolla, *Atti R. Accad. Lincei*, 1913, [5], 22, ii, 104.

When the salt is treated with concentrated ammonia a black mass is formed containing free mercury, whilst the filtrate, evaporated *in vacuo*, leaves a white compound to which the formula $NH_2.HgBr.HgO.2H_2O$ has been given.[2] According to Druce, however, mercury and ammonium bromide are formed, along with the compound NH_2HgBr.[3]

Colloidal Mercurous Bromide may be obtained by the action of bromine water on colloidal mercury.[4] A water-soluble colloid may be prepared by precipitating mercurous nitrate solution with a soluble bromide in the presence of an organic colloid such as albumen or gum, dialysing, and evaporating or precipitating by acid.[5]

Mercuric Bromide, $HgBr_2$, may be obtained by the action of an excess of bromine on mercury or mercurous bromide ;[6] by treating a mixture of mercuric nitrate and potassium bromide in aqueous solution with alcohol ;[7] by subliming a mixture of mercuric sulphate and potassium bromide ;[8] by shaking an excess of bromine with a solution of mercuric nitrate containing a little nitric acid ;[9] or, finally, by treating mercury with bromine under water[10] or alcohol.[11] Easley and Brann prepared pure mercuric bromide for atomic weight determinations by passing bromine vapour in a current of pure nitrogen over mercury.[12]

The crystals are of rhombic form,[11] separating from aqueous solution as glistening plates and from alcoholic solution as white needles.[9] They are isomorphous with yellow mercuric iodide, forming a continuous series of mixed crystals with it, the minimum freezing-point being 216·1° C. at 59 per cent. of mercuric bromide.[10, 13] A second rhombic form, isomorphous with mercuric chloride, has been obtained from alcoholic solution.[14] It has been suggested that a third form exists, isomorphous with the red tetragonal mercuric iodide, since the salt forms mixed crystals with this isomorph,[15] but no transition-point is reached, even at temperatures as low as −83·5° C.[16]

The molecular heat of formation of the solid from the liquid elements is 40·6 Cal., and if the bromine be gaseous, 47·9 Cal.[17] The density at 20° C. is $6{\cdot}064 \pm 0{\cdot}05$,[15] but other values have been given.[18] The density of the molten salt at different temperatures has been determined.[1] Between 240° C. and 340° C. it is expressed by the formula

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[1] Mailhe, *Ann. Chim. Phys.*, 1842, [3], 5, 177 ; Ditte, *Compt. rend.*, 1890, 110, 1330 ; Abegg, Immerwahr, and Jander, *Zeitsch. Elektrochem.*, 1902, 8, 689. See also Löwig, *Mag. Pharm.*, 1828, 23, 7 ; Wittstein, *Repert. Pharm.*, 1838, 63, 322.

[2] Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1912, 77, 41. See also Rammelsberg, *Pogg. Annalen*, 1842, 55, 248.

[3] Druce, *Chem. News*, 1923, 126, 225.

[4] Lottermoser, *J. prakt. Chem.*, 1898, [2], 57, 487.

[5] Ellis (Chemische Fabrik von Heyden Akt.-Ges.), English Patent, 19163 (1903).

[6] Balard, *Ann. Chim. Phys.*, 1826, [2], 32, 360.

[7] Löwig, *loc. cit.*

[8] Henry, *J. Pharm. Chim.*, 1829, [2], 15, 56, 647.

[9] Sievers, *Ber.*, 1888, 21, 648.

[10] Reinders, *Zeitsch. physikal. Chem.*, 1900, 32, 495.

[11] Hjortdahl, *Zeitsch. Kryst. Min.*, 1879, 3, 302.

[12] Easley and Brann, *J. Amer. Chem. Soc.*, 1912, 34, 137.

[13] See also Niggli, *Zeitsch. anorg. Chem.*, 1912, 75, 185.

[14] Luczizky, *Zeitsch. Kryst. Min.*, 1909, 46, 297.

[15] van Nest, *ibid.*, 1910, 47, 263

[16] Reinders, *Zeitsch. physikal. Chem.*, 1900, 32. 528.

[17] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 93. See also Nernst, *Zeitsch. physikal. Chem.*, 1888, 2, 25.

[18] Ortloff, *ibid.*, 1896, 19, 210 ; Clarke, *Constants of Nature*, Part I (Macmillan & Co.), 1888, p. 32 ; *Amer. J. Sci.*, 1878, [3], 16, 201 ; Karsten, *Schweigger's J.*, 1832, 65, 417 ; Biltz, *Zeitsch. anorg. Chem.*, 1921, 115, 241.

$$D_t = 5{\cdot}116 - 0{\cdot}00338(t^\circ - 240),$$

where D_t is the density at the temperature t.[2] The viscosity of the molten salt has also been measured.[1]

Johnson gives 236° C. as the melting-point,[3] but values varying from 235°–236·5° C. have been found.[4, 5, 6] The following values have been obtained for the vapour pressures at different temperatures[3, 7]:—

Temperature, ° C. .	162	206	233	247	276	290	306	318·5
Pressure, mm. Hg .	3	29	88	136	293	413	597	764

The boiling-point is 318° C. at 760 mm. pressure.[3, 8] The latent heat of fusion is 12·8 cal. per grm.[4] or 13·9 cal. per grm.[5] The specific heat of the liquid salt is 0·068 and of the solid 0·052.[4] The critical temperature is 1011° abs.[9]

The electrical conductivity of the compressed solid has been determined.[10] That of the molten salt is practically zero, even with the addition of a little potassium bromide.[10, 11] When exposed to ultraviolet light, whether in the dry or moist state, the salt is very little affected.[12]

If mercuric bromide be heated with concentrated nitric or sulphuric acid, bromine vapour is given off,[13] but in the cold, sulphuric acid precipitates mercuric bromide.[14] The salt is readily reduced to metallic mercury by alkaline hydrogen peroxide.[15]

The solubility of mercuric bromide in water is about 0·017 grm.-molecules per litre at 25° C.[16, 17] Somewhat variable values are actually found, probably due to hydrolysis, especially at higher temperatures.[18] The aqueous solution is said to be decomposed by light, giving mercurous bromide and hydrobromic acid,[19] but Berthelot stated that the action is due to the organic matter present in some pharmaceutical preparations.[20] The ionisation constant[16] of mercuric bromide is $6{\cdot}5 \times 10^{-18}$.

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[1] Beck, *Zeitsch. physikal. Chem.*, 1907, 58, 430.

[2] Prideaux, *Trans. Chem. Soc.*, 1910, 97, 2032.

[3] Johnson, *J. Amer. Chem. Soc.*, 1911, 33, 777.

[4] Guinchant, *Compt. rend.*, 1909, 149, 479.

[5] Beckmann, *Zeitsch. anorg. Chem.*, 1907, 55, 182.

[6] Reinders, *loc. cit.*; Beck, *loc. cit.*; Niggli, *loc. cit.*; Sandonnini, *Atti R. Accad. Lincei*, 1912, [5], 21, i, 211; Carnelley, *Trans. Chem. Soc.*, 1878, 33, 276.

[7] See also Prideaux (*loc. cit.*), who gives a large number of values between 266° C. (*p.* 225 mm.) and 331° C. (*p.* 947 mm.); Wiedemann, Stelzner, and Niederschulte, *Ber. Deut. physikal. Ges.*, 1905, 7, 159.

[8] Freyer and Meyer, *Zeitsch. anorg. Chem.*, 1892, 2, 1.

[9] Rotinjanz and Suchodski, *Zeitsch. physikal. Chem.*, 1914, 87, 253. See also Rassow, *Zeitsch. anorg. Chem.*, 1920, 114, 117.

[10] Fritsch, *Wied. Annalen*, 1897, 60, 308.

[11] See also Hampe, *Chem. Zeit.*, 1887, 11, 904.

[12] Pougnet, *Compt. rend.*, 1915, 161, 348.

[13] Balard, *Ann. Chim. Phys.*, 1826, [2], 32, 361.

[14] Viard, *Compt. rend.*, 1902, 135, 244.

[15] Kohn, *Zeitsch. anorg. Chem.*, 1908, 59, 271.

[16] Sherrill, *Zeitsch. physikal. Chem.*, 1903, 43, 727.

[17] Morse, *ibid.*, 1902, 41, 731; Herz and Paul, *Zeitsch. anorg. Chem.*, 1913, 82, 431; Gaudechon, *Ann. Chim. Phys.*, 1911, [8], 22, 212; Abegg, Immerwahr, and Jander, *Zeitsch. Elektrochem.*, 1902, 8, 688; Abegg and Sherrill, *ibid.*, 1903, 9, 550.

[18] Vicario, *J. Pharm. Chim.*, 1907, [6], 26, 145.

[19] Löwig, *Pogg. Annalen*, 1828, 14, 486.

[20] Berthelot, *Compt. rend.*, 1898, 127, 157.

The solubility in a number of organic solvents has been investigated. The solvents examined include alcohols,[1, 2, 3] benzene,[1, 4] methyl acetate,[5] ethyl acetate,[2, 6] acetone,[7] carbon disulphide,[8] aromatic nitro-compounds,[9] pyridine,[10] and many other substances.[7, 11] The solubility in liquid sulphur dioxide has also been studied.[12] The density of aqueous solutions,[13] and the electrical conductivity of aqueous [13, 14, 15] and alcoholic [15] solutions, have been determined.

An acid salt, $HgBr_2.HBr$, is known, and possibly also $HgBr_2.2HBr$.[16] Berthelot determined the heat evolved when mercuric bromide is dissolved in different quantities of hydrobromic acid solution of constant concentration.[17]

Double Salts.—Like mercuric chloride, mercuric bromide is more soluble in solutions of halide salts than in pure water, due, no doubt, to the formation of a complex ion.[18] This conclusion appears to be confirmed by thermochemical evidence.[19] Double salts are formed with the bromides of lithium,[19, 20] sodium,[19, 21, 22, 23, 24] potassium,[21, 24, 25, 26] ammonium,[19, 23, 27] cæsium,[28] calcium,[19, 21, 24] strontium,[24, 25] barium,[19, 21, 23, 24] magnesium,[19, 20, 24, 29] zinc,[19, 21] cadmium,[19] thallium,[30] lead,[31] ferrous iron,[21] cobalt,[19] nickel,[19] and manganese.[19] There are also chlorobromides with sodium,[22] potassium,[32] ammonium,[33] and cæsium.[34] Mailhe has described compounds with the oxides of

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[1] Dukelski, *Zeitsch. anorg. Chem.*, 1907, 53, 336.

[2] Herz and Anders, *ibid.*, 1907, 52, 164.

[3] Herz and Kuhn, *ibid.*, 1908, 58, 159; 60, 152; Reinders, *Zeitsch. physikal. Chem.*, 1900, 32, 521.

[4] Morse, *loc. cit.*

[5] Naumann and Bezold, *Ber.*, 1909, 42, 3795.

[6] Naumann and Hamers, *ibid.*, 1910, 43, 316.

[7] Reinders, *Zeitsch. physikal. Chem.*, 1900, 32, 504.

[8] Arctowski, *Zeitsch. anorg. Chem.*, 1894, 6, 260.

[9] Mascarelli and Ascoli, *Gazzetta*, 1907, 37, i, 125.

[10] Naumann and Schroeder, *Ber.*, 1904, 37, 4609; Schroeder, *Zeitsch. anorg. Chem.*, 1905, 44, 1.

[11] Šulc, *ibid.*, 1900, 25, 399.

[12] Niggli, *ibid.*, 1912, 75, 187.

[13] Grotrian, *Wied. Annalen*, 1883, 18, 192.

[14] Ley and Kissel, *Ber.*, 1899, 32, 1358.

[15] Cattaneo, *Atti R. Accad. Lincei*, 1895, [5], 4, ii, 63, 73.

[16] Neumann, *Monatsh.*, 1889, 10, 236. See also Löwig, *Mag. Pharm.*, 1831, 33, 7.

[17] Berthelot, *Ann. Chim. Phys.*, 1883, [5], 29, 231.

[18] Abegg, Immerwahr, and Jander, *Zeitsch. Elektrochem.*, 1902, 8, 688; Sherrill, *ibid.*, 1903, 9, 549.

[19] Varet, *Compt. rend.*, 1896, 123, 497.

[20] Calzolari and Tagliavini, *Atti R. Accad. Lincei*, 1915, [5], 24, i, 925.

[21] Bonsdorff, *Pogg. Annalen*, 1830, 19, 340.

[22] Vicario, *J. Pharm. Chim.*, 1907, [6], 26, 145.

[23] Clerici, *Atti R. Accad. Lincei*, 1911, [5], 20, i, 45.

[24] Herz and Paul, *Zeitsch. anorg. Chem.*, 1913, 82, 431.

[25] Löwig, *Mag. Pharm.*, 1831, 33, 7.

[26] Clarke, *Ber.*, 1878, 11, 1504; Berthelot, *Ann. Chim. Phys.*, 1883, [5], 29, 206; van Name and Brown, *Amer. J. Sci.*, 1917, [4], 44, 122.

[27] Thomson and Bloxam, *Trans. Chem. Soc.*, 1882, 41, 379.

[28] Wells, *Amer. J. Sci.*, 1892, [3], 44, 221; *Zeitsch. anorg. Chem.*, 1892, 2, 402; Penfield, *ibid.*, 1892, 2, 420; *Amer. J. Sci.*, 1892, [3], 44, 311.

[29] Bonsdorff, *Pogg. Annalen*, 1829, 17, 136.

[30] Barlot and Pernot, *Compt. rend.*, 1921, 173, 232.

[31] Sandonnini, *Atti R. Accad. Lincei*, 1912, [5], 21, i, 208.

[32] Harth, *Zeitsch. anorg. Chem.*, 1897, 14, 323.

[33] Grossmann, *Ber.*, 1902, 35, 2945; Rây, *Trans. Chem. Soc.*, 1902, 81, 648.

[34] Wells, *loc. cit.*

copper,[1] zinc,[1] cobalt,[2] and nickel.[2] A double salt with thallium nitrate has been prepared.[3]

By the action of sulphuretted hydrogen on mercuric bromide in alcoholic solution, a canary-yellow double salt, of the composition $2HgS.HgBr_2$, is obtained, but with excess of hydrogen sulphide the black sulphide is formed.[4] The same double compound may be precipitated in methyl [5] or ethyl [6] acetate.

Compounds resulting from the Action of Ammonia on Mercuric Bromide.—Compounds formed by the interaction of ammonia with mercuric bromide, similar to those obtained in the case of mercuric chloride, have long been known.[7] The bromine analogue of fusible white precipitate, $HgBr_2.2NH_3$, has been prepared by Pesci,[8] by the action of ammonium bromide on a compound to which he gave the formula $4Hg_2NBr.5NH_4Br$. It may also be obtained by the action of ammonia on a solution of mercuric bromide, either alone or mixed with ammonium bromide,[8, 9, 10, 11] or by the action of ammonia on mercuric bromide in ethyl [6] or methyl [12] acetate, or by boiling mercuric oxide with ammonium bromide solution.[13] It is difficult to obtain in the pure state,[14] melts with decomposition when heated, and dissolves in acid.[8] In accordance with Rammelsberg's theory,[15] Pesci represents it as $Hg_2NBr.3NH_4Br$.[8] A double compound with copper has also been obtained.[16]

By the action of water on the bromine analogue of fusible white precipitate, a bromine infusible white precipitate is formed.[10, 11, 14, 17] The product of further hydrolysis, either by water or alkali, is not the bromide of Millon's base, as might have been expected, but dimercuriammonium bromide, NHg_2Br.[8, 11, 13, 14] It can also be obtained by the action of hydrobromic acid on Millon's base,[18] or of potassamide on mercuric bromide.[19, 20] Hofmann and Marburg have doubted the existence of such salts in the anhydrous form.[21] It is a yellow compound [14, 18, 19] which, by treatment with water, is partially transformed into mercuric oxide, and with ammonium bromide gives the compound $HgBr_2.2NH_3$.[18] Widman [14, 22] has carefully studied the equilibria in solutions containing ammonium bromide, ammonia, and mercuric bromide in varying proportions, and, in addition to the compounds already mentioned, has isolated two others, $NH(HgBr)_2$ and $Hg_9N_4Br_6$.[1] Hydrates of the compound NHg_2Br have also been described, $NHg_2Br.H_2O$ [1, 2] and $2NHg_2Br.H_2O$,[3, 4] and there is a compound with mercuric bromide, $2NHg_2Br.HgBr_2$.[3]

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[1] Mailhe, *Compt. rend.*, 1901, **132**, 1273.
[2] Mailhe, *Ann. Chim. Phys.*, 1902, [7], **27**, 368.
[3] Bergman, Henke, and Isaïkin, *J. Russ. Phys. Chem. Soc.*, 1923, **54**, 466, see *J. Chem. Soc.*, 1923, **124**, Abs. ii, 764.
[4] Franceschi, *Boll. chim. farm.*, 1918, **57**, 221, see *J. Chem. Soc.*, 1918, **114**, Abs. ii, 365.
[5] Naumann and Bezold, *Ber.*, 1909, **42**, 3795.
[6] Naumann and Henninger, *ibid.*, 1910, **43**, 316.
[7] See Rose, *Pogg. Annalen*, 1830, **20**, 160.
[8] Pesci, *Gazzetta*, 1889, **19**, 509.
[9] See also Gaudechon, *Compt. rend.*, 1909, **148**, 1763.
[10] Gaudechon, *ibid.*, 1910, **150**, 467.
[11] Gaudechon, *Ann. Chim. Phys.*, 1911, [8], **22**, 211.
[12] Naumann and Bezold, *Ber.*, 1909, **42**, 3795.
[13] Pesci, *Zeitsch. anorg. Chem.*, 1899, **21**, 374.
[14] Widman, *ibid.*, 1910, **68**, 1.
[15] See Compounds resulting from the Action of Ammonia on Mercuric Chloride.
[16] Anderlini, *Gazzetta*, 1917, **47**, ii, 171.
[17] See also Löwig, *Mag. Pharm.*, 1831, **33**, 7.
[18] Pesci, *Gazzetta*, 1889, **19**, 375.
[19] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820; *Zeitsch. anorg. Chem.*, 1905, **46**, 23.
[20] See also Fitzgerald, *J. Amer. Chem. Soc.*, 1907, **29**, 656.
[21] Hofmann and Marburg, *Zeitsch. anorg. Chem.*, 1900, **23**, 126; *Annalen*, 1899, **305**, 212.
[22] See also Gaudechon, *Ann. Chim. Phys.*, 1911, [8], **22**, 211.

Compounds with hydrazine,[5] hydroxylamine,[6] alkylamines,[7] and pyridine, quinoline, and aniline,[8] have been prepared. There are also compounds of the double bromides with hexamethylene tetramine.[9]

With hydrogen phosphide a compound, $P_2Hg_5Br_4$, has been obtained.[10]

There are various addition compounds with aromatic tellurides,[11] acetylene,[12] and ethylene.[13] As in the case of the chloride, the addition compounds with the hydrocarbons are unstable, and tend to form condensation products with the elimination of an atom of halogen.

Mercuric Polybromides.—Experiments to determine the distribution of bromine between mercuric bromide solution and carbon tetrachloride indicate the existence in solution of a polybromide, $HgBr_4$, and possibly of still more highly brominated compounds.[14] The equilibrium between bromine and the double salt, $HgBr_2.2KBr$, has also been studied.[15]

Mercurous Iodide, Hg_2I_2, may be obtained by the direct union of mercury and iodine, if ground together in a mortar and, preferably, moistened with alcohol or some other iodine solvent.[16, 17, 18, 19] Yvon heated the two constituents together below 250° C.[20] Even with excess of mercury the product is always contaminated with mercuric iodide, which may be extracted by hot alcohol [21] or by a hot solution of sodium chloride.[22] Mercurous iodide may also be obtained by grinding together mercury and mercuric iodide,[16, 17, 23] or calomel, iodine, and water.[24] Various precipitation methods have been employed—for example, the action of potassium iodide on a slightly acid solution of mercurous nitrate,[16, 25, 26, 27, 28] or on a mixture of mercurous acetate and pure sodium pyrophosphate solutions,[1] or the action of a hot solution of potassium iodide on calomel.[2] Mercury reacts directly with gaseous hydriodic acid, producing mercurous iodide,[3] but not with hydriodic acid in solution.

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[1] See also Gaudechon, *Compt. rend.*, 1909, 148, 1763.

[2] Hofmann and Marburg, *Annalen*, 1899, 305, 191.

[3] Rây, *Trans. Chem. Soc.*, 1902, 81, 649.

[4] Sen, *Zeitsch. anorg. Chem.*, 1903, 33, 197.

[5] Hofmann and Marburg, *loc. cit.*, 214.

[6] Adams, *Amer. Chem. J.*, 1902, 28, 198.

[7] Hann, *J. Amer. Chem. Soc.*, 1923, 45, 1763; Staronka, *J. Chem. Soc.*, 1910, 98, Abs. i, 876.

[8] Schroeder, *Chem. Zentr.*, 1904, ii, 454; *Zeitsch. anorg. Chem.*, 1905, 44, 14; Naumann and Schroeder, *Ber.*, 1904, 37, 4609.

[9] Calzolari and Tagliavini, *Atti R. Accad. Lincei*, 1915, [5], 24, i, 925.

[10] Lemoult, *Compt. rend.*, 1907, 145, 1175.

[11] Lederer, *Ber.*, 1915, 48, 1422.

[12] Manchot and Haas, *Annalen*, 1913, 399, 123.

[13] Hofmann and Sand, *Ber.*, 1900, 33, 2692.

[14] Herz and Paul, *Zeitsch. anorg. Chem.*, 1914, 85, 214.

[15] van Name and Brown, *Amer. J. Sci.*, 1917, [4], 44, 105.

[16] Berthemot, *J. Pharm. Chim.*, 1831, [2], 17, 456.

[17] Dublanc, *ibid.*, 1849, [3], 15, 164.

[18] Mailhe, *ibid.*, 1843, [3], 4, 36.

[19] Siller, *ibid.*, 1841, [2], 28, 62; Gautier and Charpy, *Compt. rend.*, 1890, 111, 645.

[20] Yvon, *ibid.*, 1873, 76, 1607.

[21] Soubeiran, *J. Pharm. Chim.*, 1843, [3], 4, 38.

[22] Williams, *Jahresber.*, 1873, 288.

[23] See also Inglis, *Phil. Mag.*, 1836, [3], 8, 19; Rieckher, *Jahresber.*, 1867, 305.

[24] Lichtenberg, *ibid.*, 1856, 407.

[25] François, *J. Pharm. Chim.*, 1897, [6], 6, 529.

[26] Boullay, *Ann. Chim. Phys.*, 1827, [2], 34, 357.

[27] Varet, *ibid.*, 1896, [7], 8, 89.

[28] Stroman, *Ber.*, 1887, 20, 2818.

There was, for long, considerable doubt as to the colour of mercurous iodide, owing to the difficulty of obtaining it pure, since it is readily decomposed into mercury and mercuric iodide by many chemical reagents—for example, halogen acids and alkali halides,[4, 2, 5] aniline,[6] phenol,[7] alcohol,[8] by heat,[9] and by light.[10, 11] The pure product forms yellow tetragonal leaflets, the green colour often ascribed to it being due to finely divided mercury.[10, 12, 13] According to Yvon the crystals are rhombic.[14] Several methods have been given for obtaining the pure yellow iodide: by the action of alkyl iodides on a mercurous salt;[15] by the addition of a concentrated alcoholic solution of iodine in the cold to a saturated mercurous nitrate solution;[10] by the action of hydroxylamine hydriodide on mercuric iodide below 0° C.;[16] by adding alcoholic potassium hydroxide to a boiling alcoholic solution of mercuric iodide;[17] by heating an alcoholic solution of aniline with mercuric iodide and treating the precipitate with ether;[18] and by the action of methylene iodide upon mercury at about 200° C. in a sealed tube.[19] The crystals show a strong double refraction.[13] At higher temperatures, probably above 100° C., the stable form is red, but no definite transition point has been found.[10, 20] It has, in fact, been said to change at temperatures as low as 70° C.,[14, 21] but the change is not complete until about 245° C. is reached.[22] Pressure also brings about the change from yellow to red.

The heat of formation from liquid mercury and solid iodine is given as 28·85 Cal.,[23] but from the solid components 47·6 Cal.[24] The density is approximately 7·7,[25] and the specific heat is 0·0395.[26] The vapour density is rather less than theoretical,[27] but when dissolved in mercuric iodide the salt, according to the freezing-point lowering, appears to have the molecular formula Hg_2I_2.[1] Mercurous iodide melts with partial decomposition at 290° C.,[2, 3, 4] unless mixed with mercuric iodide in the molecular proportions of one to two, when no decomposition takes place.[5] It readily sublimes at lower temperatures.[2]

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[1] Lefort, *Jahresber.*, 1873, 288.

[2] Boullay, *loc. cit.*

[3] Bailey and Fowler, *Trans. Chem. Soc.*, 1888, **53**, 760. See also Berthelot, *Ann. Chim. Phys.*, 1856, [3], **46**, 492; Balard, *ibid.*, 1826, [2], **32**, 353.

[4] Mailhe, *loc. cit.*

[5] François, *J. Pharm. Chim.*, 1899, [6], **10**, 16.

[6] François, *Compt. rend.*, 1895, **121**, 253.

[7] François, *ibid.*, 768.

[8] François, *ibid.*, 888.

[9] François, *ibid.*, 1896, **122**, 190.

[10] Stroman, *loc. cit.*

[11] Artus, *J. prakt. Chem.*, 1836, [1], 8, 63; Eder, *Jahresber.*, 1885, 347.

[12] François, *J. Pharm. Chim.*, 1897, [6], **6**, 529.

[13] des Cloiseaux, *Compt. rend.*, 1877, **84**, 1418.

[14] Yvon, *loc. cit.*

[15] Bodroux, *ibid.*, 1900, **130**, 1622; Rây, *Proc. Chem. Soc.*, 1899, **15**, 239; *Annalen*, 1901, **316**, 254; Neogi, *J. Chem. Soc.*, 1907, **92**, Abs. ii, 772.

[16] Adams, *Amer. Chem. J.*, 1902, **28**, 217.

[17] Fischer and von Wartenberg, *Chem. Zeit.*, 1905, **29**, 308.

[18] François, *J. Pharm. Chim.*, 1894, [5], **29**, 67.

[19] Thomas, *Bull. Soc. chim.*, 1900, [3], **23**, 49.

[20] Houston, *Chem. News*, 1871, **24**, 177.

[21] Bodroux, *loc. cit.*, 1624.

[22] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 89.

[23] Varet, *loc. cit.*, 91. See also Nernst, *Zeitsch. physikal. Chem.*, 1888, **2**, 27.

[24] Berthelot, *Ann. Chim. Phys.*, 1880, [5], **21**, 389. See also Thomsen, *J. prakt. Chem.*, 1875, [2], **11**, 283.

[25] Clarke, *Constants of Nature*, Part I (Macmillan & Co.), 1888, p. 35; Karsten, *Schweigger's J.*, 1832, **65**, 417; Boullay, *Ann. Chim. Phys.*, 1830, [2], **43**, 266.

[26] Regnault, *ibid.*, 1841, [3], **1**, 159.

[27] Troost, *Compt. rend.*, 1882, **95**, 135.

Mercurous iodide is oxidised by hot concentrated nitric acid and by hot sulphuric acid,[6] but is scarcely affected by hydrochloric acid vapour at high temperatures.[7] The decomposing action of alkali halide solutions has already been mentioned.

The solubility in water is extremely small, of the order of 10^{-8} to 10^{-10} grm.-molecules per litre.[8] It is probable that hydrolysis takes place. The presence of alkali iodides increases the solubility, possibly through the formation of complex compounds.[9] Owing to the instability of mercurous iodide, there is much doubt as to its solubility in organic liquids.[10] Aqueous ammonia decomposes Hg_2I_2 with the formation of mercury and the diammoniate of mercuric iodide, the iodine analogue of fusible white precipitate, $HgI_2.2NH_3$.[11] There is probably a separation of mercury in a finely divided state.[12] Rammelsberg obtained a black compound, which, on drying, quickly lost ammonia and became green.[13] In very dilute ammonia solution no action is observed,[14] but with a large excess of ammonia Behrend [14] obtained the compound NH_2Hg_2I. Mercurous iodide is readily soluble in liquid ammonia.[15] It forms double salts with certain substituted ammonium iodides.[16]

Mercurous iodide has a therapeutic value.

Colloidal Mercurous Iodide may be obtained in a stable form similarly to the chloride and bromide by treating a solution of mercurous nitrate with potassium iodide in the presence of a protective colloid, and dialysing.[17] By precipitating from solution by alcohol a solid colloid is obtained, and this may be redissolved in water.

Hausmann precipitated mercurous iodide by diffusion of mercurous nitrate through gelatinised potassium iodide solution, and obtained in the gelatine the banded structure known as Liesegang's rings.[18] At the same time some mercurous iodide was also formed.

Mercuric Iodide, HgI_2, is said to exist in the natural state, but the evidence is not very strong.[19] It is readily formed by triturating together mercury and iodine in the requisite proportions, either alone,[20] or moistened with a little water[1] or alcohol.[2] The union is not quite complete, especially in the dry state, free iodine and mercurous iodide being present in the final product.[3] Mercury in colloidal solution reacts with iodine to form a deep red colloidal solution of mercuric iodide, which rapidly deposits the salt.[4] The salt may also be formed by the action of iodine on the oxides, or on different mercurous or mercuric salts.[1, 5, 6, 7] Hydriodic acid reacts directly with mercury, and, if sufficient excess be present, mercuric iodide is formed.[8] With calomel also hydriodic acid gives mercuric iodide.[6] Solid potassium iodide in contact with solid mercuric chloride will react to give mercuric iodide, unless the materials are perfectly dry.[9] The action of alkyl iodides[5, 10] or methylene iodide[11] on mercuric salts may result in the formation of mercuric iodide.

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[1] Beckmann, *Zeitsch. anorg. Chem.*, 1907, **55**, 183; Beckmann, Hanslian, and Maxim, *ibid.*, 1914, **89**, 167. See also Guinchant, *Compt. rend.*, 1907, **145**, 68.

[2] Stroman, *loc. cit.*

[3] Yvon, *loc. cit.*

[4] Bodroux, *loc. cit.*

[5] François, *Compt. rend.*, 1896, **122**, 190.

[6] Souville, *J. Pharm. Chim.*, 1840, [2], **26**, 474.

[7] Hautefeuille, *Compt. rend.*, 1867, **64**, 704; *Jahresber.*, 1867, 174.

[8] Sherrill, *Zeitsch. physikal. Chem.*, 1903, **43**, 722; Bodländer, *ibid.*, 1898, **27**, 58.

[9] Abegg and Jander, *Zeitsch. Elektrochem.*, 1902, **8**, 688.

[10] Maclagen, *Jahresber.*, 1884, 1606; François, *Compt. rend.*, 1895, **121**, 253, 768, 888; Retgers, *Zeitsch. anorg. Chem.*, 1893, **3**, 343.

[11] François, *J. Pharm. Chim.*, 1897, [6], **5**, 388; Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1912, **77**, 44.

[12] Wittstein, *Repert. Pharm.*, 1833, **63**, 322.

[13] Rammelsberg, *Pogg. Annalen*, 1839, **48**, 184.

[14] Behrend, *Zeitsch. physikal. Chem.*, 1893, **11**, 475.

[15] Franklin and Kraus, *Amer. Chem. J.*, 1898, **20**, 829.

[16] Datta and Sen, *J. Amer. Chem. Soc.*, 1917, **39**, 750.

[17] Ellis (Chemische Fabrik von Heyden Akt.-Ges.), English Patent, 19163 (1903).

[18] Hausmann, *Zeitsch. anorg. Chem.*, 1904, **40**, 120.

[19] del Castillo, *Neues Jahrb. Miner.*, 1866, 411; Moses, *Amer. J. Sci.*, 1901, [4], **12**, 98.

[20] Courtois, *Ann. Chim.*, 1813, [1], **88**, 314.

The ordinary method of preparation is by precipitation from mercuric chloride solution by potassium iodide, preferably in the presence of ammonium chloride.[12] Other mercuric salts may be used.[5, 13]

The existence of two forms of mercuric iodide, red and yellow, is well known. The red, crystallising in quadratic octahedra,[14] is stable at ordinary temperatures, and is apparently obtained when the iodide is formed directly from its elements. It has also been stated that, by crystallising from solution under certain conditions, the red form alone separates—for example, from solutions of potassium iodide,[15] zinc iodide,[16] or hydrochloric acid.[17] According to more recent investigations, however, it is always the yellow, orthorhombic variety, unstable at ordinary temperatures, which separates out from solutions of all kinds, either when formed by precipitation[18, 19] or when simply crystallised from a solvent.[19, 20, 21] It then changes with more or less rapidity to the red form. The change may be retarded to some extent by the presence of a protective colloid, for example, gelatin.[22, 23] Under a viscous solvent, in the dark, the change is also slow.[1] Light accelerates the change from yellow to red.[2, 3, 4, 5] Yellow mercuric iodide, obtained by rapid evaporation of a solution, may be kept unchanged for a very long time if dust be excluded.[6] The yellow variety is always first formed when the vapour of mercuric iodide is condensed at any temperature.[6, 7, 8]

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[1] Vauquelin, *Ann. Chim.*, 1814, [1], **90**, 246.

[2] Berthemot, *J. Pharm. Chim.*, 1831, [2], **17**, 456; Dublanc, *ibid.*, 1849, [3], **15**, 164.

[3] Mohr, *Arch. Pharm.*, 1848, [2], **55**, 29.

[4] Lottermoser, *J. prakt. Chem.*, 1898, [2], **57**, 487.

[5] Schuyten, *Chem. Zeit.*, 1895, **19**, 1683.

[6] Gramp, *Ber.*, 1874, **7**, 1723.

[7] Preuss, *Annalen*, 1839, **29**, 326; Soubeiran, *J. Pharm. Chim.*, 1841, [2], **27**, 744; Sievers, *Ber.*, 1888, **21**, 651.

[8] Bailey and Fowler, *Trans. Chem. Soc.*, 1888, **53**, 760; Norris and Cottrell, *Amer. Chem. J.*, 1896, **18**, 99.

[9] Perman, *Proc. Roy. Soc.*, 1907, [A], **79**, 312.

[10] Bodroux, *Compt. rend.*, 1900, **130**, 1622; de Coninck, *Bull. Soc. chim.*, 1880, [2], **34**, 633.

[11] Thomas, *ibid.*, 1900, [3], **23**, 50.

[12] Williams, *Jahresber.*, 1873, 289.

[13] Boullay, *Ann. Chim. Phys.*, 1827, [2], **34**, 357; Rupp and Goy, *Arch. Pharm.*, 1909, [3], **47**, 100.

[14] Groth, *Ber.*, 1869, **2**, 574.

[15] Mitscherlich, *Pogg. Annalen*, 1833, **28**, 116.

[16] Inglis, *Phil. Mag.*, 1836, [3], **8**, 18.

[17] Köhler, *Ber.*, 1879, **12**, 608.

[18] Warington, *Phil. Mag.*, 1842, [3], **21**, 192; *Ann. Chim. Phys.*, 1843, [3], **7**, 417.

[19] Ostwald, *Zeitsch. physikal. Chem.*, 1897, **22**, 308.

[20] Kastle and Reed, *Amer. Chem. J.*, 1902, **27**, 209.

[21] Kastle and Clark, *ibid.*, 1899, **22**, 473; Mascarelli, *Atti R. Accad. Lincei*, 1906, **15**, ii, 192; Gernez, *Compt. rend.*, 1903, **136**, 1322; *Ann. Chim. Phys.*, 1903, [7], **29**, 417; Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 384. See also Schiff, *Annalen*, 1859, **111**, 371; Selmi, *Jahresber.*, 1855, 417; Šulc, *Zeitsch. anorg. Chem.*, 1900, **25**, 402.

[22] Friend, *Nature*, 1922, **109**, 341.

[23] Ostwald, *Zeitsch. physikal. Chem.*, 1912, **79**, 253.

As regards the isomorphism of mercuric iodide with the other mercuric halides, mixed crystals have been obtained containing iodide, chloride, and bromide, as well as the pairs iodide and bromide, and bromide and chloride, but not iodide and chloride. It is the yellow iodide, however, which enters into the formation of these mixed crystals,[9] although, according to van Nest, it is also possible to obtain mixed crystals of the red iodide and bromide.[10] Reinders obtained a continuous series of mixed crystals of mercuric iodide and bromide.[11]

The red iodide is changed to yellow by heat.[12] Varying values for the transition temperature have been given, but the most probable appears to lie between 127° C. and 128° C.[11, 13, 14, 15, 16, 17, 18, 19] Spring noticed that pressure changes the yellow to the red form.[20] The transition temperature rises to about 180° C. at a pressure of 5000 kgm. per sq. cm., but is lowered by a further increase of pressure.[21] Schwarz calculated that a pressure of 100 atmospheres changes the transition temperature by 1·1° C.[17]

Interesting observations have been made on the effect of extremes of temperature on mercuric iodide. When the red variety is cooled it becomes first orange-red and then yellow at the boiling-point of liquid air,[16, 22] whilst the yellow variety becomes white.[16] On heating yellow mercuric iodide above the transition temperature it begins to assume a reddish or orange tint at about 190° C.,[16] and finally melts to a dark red liquid.[13, 14, 15, 23, 24] A comparison of the more recent results of different investigators indicates that the melting-point is approximately 255° C.[1, 2, 3, 4, 5, 6] Smits,[1, 7] in accordance with his theory of allotropy, ascribes the changes in appearance with temperature to the formation of mixed rhombic crystals containing both yellow and red, or α- and β-modifications, the proportion of the latter first decreasing with rise of temperature until the substance becomes yellow, and then increasing until it becomes red. At all times, therefore, both forms are present, but in varying proportions. In proof of this it is shown that, when mercuric iodide is heated to different temperatures, and then chilled in liquid air, there are more red centres of crystallisation in the solid mass the higher the temperature reached.[2] Damiens[8] contradicts this view, maintaining that the behaviour depends on whether the mercuric iodide is finely powdered or in large masses. In the latter case it all becomes red. In the former the small crystals increase in size with increase in temperature, owing to volatility, and the final product is redder in proportion.

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[1] Kastle and Reed, *loc. cit.*

[2] Friend, *loc. cit.*

[3] Ostwald, *Zeitsch. physikal. Chem.*, 1912, **79**, 253.

[4] Ostwald, *ibid.*, 1897, **22**, 308, footnote.

[5] See also Price, *Chem. Ind.*, 1923, **42**, 292.

[6] Gernez, *Compt. rend.*, 1909, **148**, 1015.

[7] Ostwald, *Zeitsch. physikal. Chem.*, 1897, **22**, 308.

[8] Gernez, *ibid.*, 1899, **128**, 1516; *Ann. Chim. Phys.*, 1900, [7], **20**, 384; Weber, *Pogg. Annalen*, 1857, **100**, 131; Berthelot, *Compt. rend.*, 1893, **117**, 827.

[9] Luczizky, *Zeitsch. Kryst. Min.*, 1909, **46**, 297.

[10] van Nest, *ibid.*, 1910, **47**, 263.

[11] Reinders, *Zeitsch. physikal. Chem.*, 1900, **32**, 494.

[12] Sievers, *Ber.*, 1888, **21**, 651.

[13] Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 703.

[14] Smits and Bokhorst, *Zeitsch. physikal. Chem.*, 1915, **89**, 365, 374.

[15] Rodwell, *Phil. Trans.*, 1882, **173**, 1141.

[16] Gernez, *Compt. rend.*, 1903, **136**, 889.

[17] Schwarz, *Zeitsch. Kryst. Min.*, 1896, **25**, 613.

[18] Bergmann, *J. Russ. Phys. Chem. Soc.*, 1922, **54**, 200.

[19] Smits, *Zeitsch. physikal. Chem.*, 1917, **92**, 345; Steger, *ibid.*, 1903, **43**, 595; Kastle and Reed, *Amer. Chem. J.*, 1902, **27**, 209; Reinders, *Proc. K. Akad. Wetensch. Amsterdam*, 1899, **2**, 146; Sandonnini, *Atti R. Accad. Lincei*, 1912, [5], **21**, i, 208; Guinchant, *Compt. rend.*, 1907, **145**, 68; Kastle and Clark, *Amer. Chem. J.*, 1899, **22**, 473.

[20] Spring, *Ber.*, 1882, **15**, 595, footnote.

[21] Bridgman, *Proc. Amer. Acad.*, 1915, **51**, 104.

[22] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 384; Kastle, *Amer. Chem. J.*, 1900, **23**, 500. See also Dewar, *Chem. News*, 1894, **70**, 252; *Proc. Chem. Soc.*, 1894, **10**, 173.

[23] Köhler, *Ber.*, 1879, **12**, 608.

[24] Bodroux, *Compt. rend.*, 1900, **130**, 1622.

A colourless form of mercuric iodide has been described.[9] It is obtained by heating the salt at about 300°-500° C. and then cooling under a sudden reduction of pressure. It condenses as a white snow-like mass consisting of colourless crystals, but almost immediately, at ordinary temperatures, it begins to form the red variety. At lower temperatures it is somewhat more stable. This is not to be confused with the white form obtained by cooling yellow mercuric iodide in liquid air.

Most of the values given for the density of mercuric iodide lie between 6·2 and 6·3.[10, 11] At the transition-point there is a sudden expansion, the density of the red form being 6·276 and of the yellow 6·225.[11, 12] The molecular heat of formation of red mercuric iodide from liquid mercury and solid iodine is 25·2 Cal., and of the yellow variety 22·1 Cal., giving a heat of transformation from yellow to red of 3·1 Cal.[13] Berthelot found 3·0 Cal.[14] Considerably lower values for the heat of transition have, however, been given by other investigators.[15, 16]

The specific heats of the red, yellow, and fused salts are, respectively, 0·0406, 0·0446, and 0·0554.[15, 17] At low temperatures, between

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[1] Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, 19, 703.

[2] Smits and Bokhorst, *loc. cit.*

[3] Reinders, *Zeitsch. physikal. Chem.*, 1900, 32, 494.

[4] Bergmann, *loc. cit.*

[5] Köhler, *loc. cit.*

[6] Niggli, *Zeitsch. anorg. Chem.*, 1912, 75, 185; Prideaux, *Trans. Chem. Soc.*, 1910, 97, 2032.

[7] Smits, *Zeitsch. physikal. Chem.*, 1911, 76, 435; 1913, 84, 250, 402; but see Hasselblatt, *ibid.*, 1913, 86, 61.

[8] Damiens, *Compt. rend.*, 1923, 177, 816.

[9] Tammann, *Chem. Zentr.*, 1917, i, 1065; *Zeitsch. anorg. Chem.*, 1920, 109, 213.

[10] Karsten, *Schweigger's J.*, 1832, 65, 417; Filhol, *Ann. Chim. Phys.*, 1847, [3], 21, 417; Clarke, *Constants of Nature*, Part I (Macmillan & Co.), 1888, p. 35; *Amer. J. Sci.*, 1878, [3], 16, 401.

[11] Rodwell and Elder, *Proc. Roy. Soc.*, 1879, 28, 284.

[12] Rodwell and Elder, *Phil. Trans.*, 1882, 173, 1143.

[13] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 84.

[14] Berthelot, *ibid.*, 1883, [5], 29, 236. See also Thomsen, *J. prakt. Chem.*, 1875, [2], 11, 266.

[15] Guinchant, *Compt. rend.*, 1907, 145, 68.

[16] Schwarz, *Zeitsch. Kryst. Min.*, 1896, 25, 613; Bridgman, *Proc. Amer. Acad.*, 1915, 51, 110.

[17] See also Regnault, *Ann. Chim. Phys.*, 1841, [3], 1, 161; Schwarz (*loc. cit.*) obtained a higher value for the red than for the yellow variety.

—78·2° C. and —183·3° C., the specific heat is 0·0375.[1] The latent heat of fusion is 12·4 (small) cal. per grm.[2]

The following values have been found for the vapour pressure of mercuric iodide at different temperatures [3] :—

Temperature, ° C. . .	177	231	266	301	318	341
Vapour pressure, mm. Hg	3	32	108	260	390	624

By extrapolation to a vapour pressure of 760 mm. a boiling-point of 351° C. is found. Prideaux gave values for the vapour pressure at higher temperatures [4, 5] :—

Temperature, ° C. .	297·5	321·9	341·3	350·8	353·7	356·8	360·5
Vapour pressure, mm. Hg . .	232	404	598·5	720	760	801	861

According to these determinations the boiling-point is evidently 353·7° C.[4] A certain amount of decomposition of the vapour takes place at high temperatures, with the production of violet iodine vapour. At 665° C. and 750 mm. about one-fifth is dissociated.[6] The molecular latent heat of vaporisation is 15·84 Cal.,[3] or, according to Prideaux,[4] 14·7 Cal. The critical temperature is 797° C.[7]

The cryoscopic constant of mercuric iodide at high dilutions is 550.[8] According to Beckmann,[9] the molecular weight in iodine is normal, but Timmermanns stated that polymerisation takes place.[10]

The glow discharge in mercuric iodide vapour has been studied. By comparison with the other mercury halide vapours it is seen that the cathode fall increases with the molecular weight of the compound.[11]

Ultra-violet light has little or no action on mercuric iodide when dry, but in the moist state a little yellow iodide is formed.[12] Although not so readily affected as silver halides, mercuric iodide is, however, sufficiently sensitive to light to form photographic emulsions.[13]

Mercuric iodide is vigorously attacked by fluorine in the cold, producing a fluoride, or fluoro-iodide.[14] Chlorine also decomposes it with the formation of mercuric chloride,[15] but it is not affected by heating in a current of gaseous hydrochloric acid,[16] and it dissolves in hot, concentrated hydrochloric acid without decomposition.[1] It is decomposed by hot, concentrated nitric acid with the liberation of iodine.[1, 2] It is dissolved by a solution of bleaching powder with the separation of white gelatinous basic calcium periodate.[3] On treatment with pure sulphuric acid, or Nordhausen acid, partial decomposition takes place with the production of various compounds of mercuric iodide with mercuric sulphate.[4] Mercuric iodide reacts with hydrogen sulphide in alcoholic solution, and the compound $Hg(SHgI)_2$ may be obtained as an intermediate stage in the production of mercuric sulphide.[5] Under the action of various reducing agents, such as sodium arsenite,[6] hydrogen peroxide in alkaline solution, or sodium peroxide,[6] or various metals such as zinc, tin, bismuth, antimony,[7] and potassium,[3] metallic mercury is formed. In other cases the reduction tends to stop with the formation of mercurous iodide—for example, in reduction by stannous chloride,[8] hypophosphorous acid,[9] and the metals iron, cadmium, lead, and copper.[7]

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[1] Barschall, *Zeitsch. Elektrochem.*, 1911, 17, 341.

[2] Beckmann, *Zeitsch. anorg. Chem.*, 1907, 55, 183 ; Guinchant (*loc. cit.*) gave 9·79 Cal. at 250° C., this value apparently referring to 1 kgm. of iodide.

[3] Johnson, *J. Amer. Chem. Soc.*, 1911, 33, 777.

[4] Prideaux, *Trans. Chem. Soc.*, 1910, 97, 2032.

[5] For other vapour pressure measurements, see Wiedemann, Stelzner, and Niederschulte, *Ber. Deut. physikal. Ges.*, 1905, 7, 159 ; Ditte, *Compt. rend.*, 1905, 140, 1164.

[6] Troost, *ibid.*, 1884, 98, 807 ; Deville, *ibid.*, 1866, 62, 1157.

[7] Rassow, *Zeitsch. anorg. Chem.*, 1920, 114, 117 ; Rotinjanz and Suchodski (*Zeitsch. physikal. Chem.*, 1914, 87, 253) found 1072° abs., that is 799° C.

[8] Beckmann, Hanslian, and Maxim, *Zeitsch. anorg. Chem.*, 1914, 89, 167. See also Guinchant, *Compt. rend.*, 1907, 145, 68.

[9] Beckmann, *Zeitsch. anorg. Chem.*, 1912, 77, 204.

[10] Timmermanns, *J. Chim. phys.*, 1905, 4, 170.

[11] Matthies, *Ann. Physique*, 1905, 17, 675.

[12] Pougnet, *Compt. rend.*, 1915, 161, 348.

[13] Lüppo-Cramer, *Kolloid-Zeitsch.*, 1913, 13, 151 ; 1915, 15, 13 ; 1917, 21, 77. See also Price, *Chem. Ind.*, 1923, 42, 292.

[14] Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 258.

[15] Filhol, *J. Pharm. Chim.*, 1839, [2], 25, 506.

[16] Hautefeuille, *Compt. rend.*, 1867, 64, 704.

The solubility of mercuric iodide in water is very small, approximately 0·06 grm. per litre at 25° C.[10, 11] Kohlrausch gives the very much smaller value of 0·002 milli-equivalents per litre, as determined by conductivity measurements.[12] Morse finds [10] that, in normal mercuric nitrate solution, its solubility reaches 48 grm. per litre, from which he concludes that most of the halogen is present as the $HgI^{\cdot}$ ion, as is also shown by determinations of the transport number.[11] He obtained for the ionic equilibria the approximate values $\frac{[Hg^{\cdot\cdot}]\times[I']}{[HgI^{\cdot}]}=0{\cdot}4\times10^{-13}$; $\frac{[HgI^{\cdot}]\times[I']}{[HgI_2]}=2{\cdot}5\times10^{-12}$; and $\frac{[Hg^{\cdot\cdot}]\times[I']^2}{[HgI_2]}=10^{-25}$. Thus the degree of ionisation is extremely small.[13] Hydrolysis does not take place until a high temperature is reached, and then only to a very small extent.[14] The solubility in aqueous solutions of various acids, such as hydrochloric, hydriodic, and nitric acid, has been determined.[15]

Mercuric iodide is much more soluble in organic solvents than in water. Ethyl alcohol dissolves about 2 per cent. at 25° C., the solubility being diminished by water.[16, 17, 18, 19, 20] In methyl alcohol the solubility is a little higher.[17, 18, 19, 21, 22, 23, 24] Determinations of the solubility have also been made in the higher alcohols,[1, 2, 3, 4] and in a very large number of other organic solvents.[2, 4, 5, 6, 7, 8] The solubility in certain inorganic liquids has been studied—for example, phosphorus tribromide,[9] phosphoric oxychloride,[9] arsenic tribromide,[10] and also liquid sulphur dioxide.[11]

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[1] Köhler, *Ber.*, 1879, **12**, 608.

[2] Bodroux, *Compt. rend.*, 1900, **130**, 1622.

[3] Rammelsberg, *Pogg. Annalen*, 1842, **56**, 315.

[4] Ditte, *Compt. rend.*, 1905, **140**, 1162.

[5] Franceschi, *Boll. chim. farm.*, 1916, **55**, 481.

[6] Kohn, *Zeitsch. anorg. Chem.*, 1908, **59**, 108; Kohn and Ostersetzer, *ibid.*, 1913, **80**, 218.

[7] Berthemot, *J. Pharm. Chim.*, 1828, [2], **14**, 610.

[8] Labouré, *ibid.*, 1843, [3], **4**, 329.

[9] Howard, *J. Soc. Chem. Ind.*, 1904, **23**, 153.

[10] Morse, *Zeitsch. physikal. Chem.*, 1902, **41**, 731.

[11] Sherrill, *ibid.*, 1903, **43**, 735; *Zeitsch. Elektrochem.*, 1903, **9**, 549. See also Bodländer, *Zeitsch. physikal. Chem.*, 1898, **27**, 58; Bourgoin, *Ann. Chim. Phys.*, 1884, [6], **3**, 429; Rohland, *Zeitsch. anorg. Chem.*, 1898, **18**, 328.

[12] Kohlrausch and Rose, *Zeitsch. physikal. Chem.*, 1893, **12**, 241; Kohlrausch, *ibid.*, 1903, **44**, 224.

[13] This no doubt accounts for Kohlrausch's low value for the solubility.

[14] Arctowski, *Zeitsch. anorg. Chem.*, 1895, **9**, 184.

[15] Colin, *Ann. Chim.*, 1814, [1], **91**, 254; Boullay, *Ann. Chim. Phys.*, 1827, [2], **34**, 340; Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1912, **77**, 46; Köhler, *Ber.*, 1879, **12**, 608.

[16] Herz and Knoch, *Zeitsch. anorg. Chem.*, 1905, **45**, 266.

[17] Beckmann and Stock, *Zeitsch. physikal. Chem.*, 1895, **17**, 130.

[18] Lobry de Bruyn, *ibid.*, 1892, **10**, 784.

[19] Rohland, *loc. cit.*

[20] Bourgoin, *loc. cit.*

[21] Šulc, *Zeitsch. anorg. Chem.*, 1900, **25**, 399.

[22] Herz and Kuhn, *ibid.*, 1908, **58**, 159.

[23] Herz and Anders, *ibid.*, 1907, **52**, 164; **60**, 152.

[24] Orloff, *Chem. Zeit.*, 1906, **30**, 1301.

Mascarelli [8] has stated that both the red and yellow forms have the same solubility at any one temperature, and that the solubility curve shows no break at the transition-point. This seems to support the conclusions of other investigators, namely, that the yellow form is the one in equilibrium with the dissolved salt,[12, 13] which may be interpreted as due to the lowering of the transition-point by the solvent.[12] According to Kastle and Clark,[12] the red modification is not obtained, but only crystals of the yellow, even when a red crystal is added to the supersaturated solution. In general, the solutions of mercuric iodide are yellow,[12] but they may be coloured violet, red, or brown, due to slow decomposition into mercurous iodide and iodine, especially under the influence of light.[14] The molecular weight in different solvents, as determined by freezing-[15] and boiling-point [16] methods, indicates that, as already mentioned in the case of aqueous solutions, there is very little ionisation in these solvents, and that the salt in solution is monomolecular. Results indicating an appreciable degree of ionisation, however, have also been found.[17]

The density and magnetic rotation of solutions of mercuric iodide in different solvents,[18] and the electrical conductivity in water,[19] liquid ammonia,[20] ether,[21] pyridine,[22] methylamine,[23] acetone,[24] epichlorhydrin,[24] and other solvents,[25] have been determined.

An acid salt, in yellow needles of composition $HgI_2.HI$, has been obtained.[26]

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[1] Rohland, *Zeitsch. anorg. Chem.*, 1898, **18**, 328. [2] Šulc, *loc. cit.*

[3] Herz and Kuhn, *loc. cit.* [4] von Laszczynski, *Ber.*, 1894, **27**, 2285.

[5] Beckmann and Stock, *loc. cit.* [6] Herz and Anders, *loc. cit.*

[7] Arctowski, *Zeitsch. anorg. Chem.*, 1894, 6, 260; Dukelski, *ibid.*, 1907, **53**, 336; Werner, *ibid.*, 1897, **15**, 1; Retgers, *ibid.*, 1893, **3**, 252; Schroeder, *ibid.*, 1905, **44**, 1; *Chem. Zentr.*, 1904, ii, 454; Schroeder and Steiner, *J. prakt. Chem.*, 1909, [2], **79**, 62; Naumann and Hamers, *Ber.*, 1910, **43**, 316; Rosenfeld, *ibid.*, 1880, **13**, 1476; Reinders, *Zeitsch. physikal. Chem.*, 1900, **32**, 506, 514, 521; Sherrill, *ibid.*, 1903, **43**, 735; Gautier and Charpy, *Compt. rend.*, 1890, **111**, 647; Méhu, *J. Pharm. Chim.*, 1885, [5], **11**, 249; Gibbs, *J. Amer. Chem. Soc.*, 1906, **28**, 1419; Fairley, *Moniteur Sci.*, 1879, [3], **9**, 685.

[8] Mascarelli, *Atti R. Accad. Lincei*, 1906, [5], **15**, ii, 192; *Gazzetta*, 1906, **36**, ii, 880.

[9] Walden, *Zeitsch. anorg. Chem.*, 1900, **25**, 211. [10] Walden, *ibid.*, 1902, **29**, 374.

[11] Walden and Centnerszwer, *Bull. Acad. St Petersburg*, 1901, [5], **15**, 17; Niggli, *Zeitsch. anorg. Chem.*, 1912, **75**, 176. [12] Kastle and Clark, *Amer. Chem. J.*, 1899, **22**, 473.

[13] Kastle and Reed, *ibid.*, 1902, **27**, 209; Gernez, *Compt. rend.*, 1903, **136**, 1322; *Ann. Chim. Phys.*, 1903, [7], **29**, 417; Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 384.

[14] Beckmann and Stock, *Zeitsch. physikal. Chem.*, 1895, **17**, 130; Šulc, *Zeitsch. anorg. Chem.*, 1900, **25**, 399.

[15] Beckmann, *ibid.*, 1912, **77**, 204; Garelli and Bassani, *Gazzetta*, 1901, **31**, i, 407.

[16] Herz and Knoch, *Zeitsch. anorg. Chem.*, 1905, **46**, 460; Kahlenberg, *J. Physical Chem.*, 1902, **6**, 45. [17] Schroeder and Steiner, *J. prakt. Chem.*, 1909, [2], **79**, 62.

[18] Schönrock, *Zeitsch. physikal. Chem.*, 1893, **11**, 768.

[19] Kohlrausch and Rose, *ibid.*, 1893, **12**, 241; Fritsch, *Wied. Annalen*, 1897, **60**, 309.

[20] Cady, *J. Physical Chem.*, 1897, **1**, 707.

[21] Cattaneo, *Atti R. Accad. Lincei*, 1893, [5], **2**, i, 295.

[22] Lincoln, *J. Physical Chem.*, 1899, **3**, 457; Sachanoff, *Zeitsch. physikal. Chem.*, 1913, **83**, 149. [23] Fitzgerald, *J. Physical Chem.*, 1912, **16**, 621. [24] Shaw, *ibid.*, 1913, **17**, 162.

[25] Lincoln, *Zeitsch. Elektrochem.*, 1900, 6, 384; Cattaneo, *Atti R. Accad. Lincei*, 1895, [5], **4**, ii, 63, 73; Gibbs, *J. Amer. Chem. Soc.*, 1906, **28**, 1419.

[26] Neumann, *Monatsh.*, 1889, **10**, 236. See also Boullay, *Ann. Chim. Phys.*, 1827, [2], **34**, 340; Berthelot, *ibid.*, 1883, [5], **29**, 231.

Double Salts.—Like the other mercuric halides, mercuric iodide dissolves in various iodide solutions with the formation of complex iodides. In fact, among the halides, the tendency to complex formation reaches a maximum in the iodide. The dissociation equilibria have been studied in certain cases.[1, 2, 3, 4] Double salts appear to be formed with the iodides of lithium,[5, 6] sodium,[2, 5, 7, 8, 9, 10] potassium,[1, 2, 3, 4, 7, 8, 9, 11, 12, 13, 14] ammonium,[5, 8, 12, 15] rubidium,[16] cæsium,[17] calcium,[2, 8, 11, 18, 19] strontium,[2, 8, 11, 18] barium,[2, 8, 9, 10, 11, 13, 20] magnesium,[8, 21] zinc,[7, 8, 22, 23] cadmium,[22, 23, 24] aluminium,[25, 26] thallium,[27] cuprous copper[22, 28, 29]—only ammonia compounds of the double salt with cupric iodide are known[29, 30]—silver[31]—this double salt is slightly sensitive to light, but less so than either of its constituents[32]—ferrous iron,[7, 22, 25] cobalt,[33] nickel,[33] manganese,[21, 34] and thorium.[5, 26] There are also double salts with other halides—for example, ammonium and rubidium bromides,[35] and cæsium chloride[36] and bromide.[36, 37] Mercuric iodide also forms compounds with silver nitrate.[38]

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[1] Sherrill, *Zeitsch. physikal. Chem.*, 1903, **43**, 705; 1904, **47**, 103.

[2] Herz and Paul, *Zeitsch. anorg. Chem.*, 1913, **82**, 431.

[3] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 387.

[4] Abegg, Immerwahr, and Jander, *Zeitsch. Elektrochem.*, 1902, **8**, 688.

[5] Duboin, *Ann. Chim. Phys.*, 1909, [8], **16**, 258.

[6] Duboin, *Compt. rend.*, 1905, **141**, 1015; Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 774.

[7] Bonsdorff, *Pogg. Annalen*, 1829, **17**, 266; *Ann. Chim. Phys.*, 1827, [2], **34**, 146.

[8] Boullay, *ibid.*, 1827, [2], **34**, 337.

[9] Clerici, *Atti R. Accad. Lincei*, 1911, [5], **20**, i, 45.

[10] Duboin, *Compt. rend.*, 1906, **143**, 313.

[11] Berthemot, *J. Pharm. Chim.*, 1828, [2], **14**, 185.

[12] François, *Compt. rend.*, 1899, **128**, 1456; **129**, 959.

[13] Peters, *Zeitsch. anorg. Chem.*, 1912, **77**, 156.

[14] Berthelot, *Ann. Chim. Phys.*, 1883, [5], **29**, 211; Thomson and Bloxam, *Trans. Chem. Soc.*, 1882, **41**, 379; Dunningham, *ibid.*, 1914, **105**, 368, 724, 2623; Dawson, *ibid.*, 1909, **95**, 870; Clayton, *Chem. News*, 1894, **70**, 102; Inglis, *Phil. Mag.*, 1836, [3], **8**, 19; Pawlow, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 732; Bredig and Walton, *Zeitsch. Elektrochem.*, 1903, **9**, 116; Rieger, *ibid.*, 1901, **7**, 872; Walton, *Zeitsch. physikal. Chem.*, 1904, **47**, 204; Marsh and Struthers, *Proc. Chem. Soc.*, 1908, **24**, 266; Jander, *Ueber einige Komplexe Mercurisalze* (Breslau), 1902; van Name and Brown, *Amer. J. Sci.*, 1917, [4], **44**, 115.

[15] Duboin, *Compt. rend.*, 1905, **141**, 385; Longi and Mazzolino, *Gazzetta*, 1896, **26**, i, 274; Deville, *Jahresber.*, 1866, 43.

[16] Erdmann, *Arch. Pharm.*, 1894, **232**, 3; Grossmann, *Ber.*, 1904, **37**, 1258.

[17] Wells, *Zeitsch. anorg. Chem.*, 1892, **2**, 402; *Amer. J. Sci.*, 1892, [3], **44**, 221; Penfield, *Zeitsch. anorg. Chem.*, 1892, **2**, 420.

[18] Duboin, *Compt. rend.*, 1906, **142**, 573.

[19] Duboin, *ibid.*, 1906, **142**, 395.

[20] Duboin, *ibid.*, 1906, **142**, 887.

[21] Duboin, *ibid.*, 1906, **142**, 1338.

[22] Berthemot, *J. Pharm. Chim.*, 1828, [2], **14**, 610.

[23] But see Duboin, *Compt. rend.*, 1906, **143**, 40.

[24] Clarke and Kebler, *Amer. Chem. J.*, 1883–84, **5**, 235; *Chem. News*, 1883, **48**, 297.

[25] Duboin, *Compt. rend.*, 1907, **145**, 713.

[26] Duboin, *ibid.*, 1908, **146**, 1027.

[27] Barlot and Pernot, *ibid.*, 1921, **173**, 232.

[28] Lenoble, *Bull. Soc. chim.*, 1893, [3], **9**, 137; Willm and Caventou, *ibid.*, 1870, [2], **13**, 220; Meusel, *Ber.*, 1870, **3**, 123; Hess, *Dingl. poly. J.*, 1875, **218**, 183.

[29] Jörgensen, *J. prakt. Chem.*, 1870, [2], **2**, 350.

[30] Anderlini, *Gazzetta*, 1912, **42**, i, 321.

[31] Roozeboom, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 84, see *J. Chem. Soc.*, 1901, **80**, Abs. ii, 20; Steger, *Zeitsch. physikal. Chem.*, 1903, **43**, 595; Wegelius, *ibid.*, 1911, **77**, 587; Rebenstorff, *Chem. Zentr.*, 1908, ii, 1803.

[32] Price, *Chem. Ind.*, 1923, **42**, 292.

[33] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 303.

[34] Dobroserdoff, *ibid.*, 1900, **32**, 742.

[35] Grossmann, *Ber.*, 1903, **36**, 1600.

[36] Wells, *Zeitsch. anorg. Chem.*, 1892, **2**, 402; *Amer. J. Sci.*, 1892, [3], **44**, 221.

[37] Penfield, *ibid.*, 1892, [3], **44**, 311; *Zeitsch. anorg. Chem.*, 1892, **2**, 420.

[38] Bergmann, *J. Russ. Phys. Chem. Soc.*, 1921, **53**, 181; *J. Chem. Soc.*, 1923, **124**, Abs. ii, 636.

There appears to be a compound mercuric chloro-iodide, $HgCl_2.HgI_2$, formed by the action of mercuric chloride solution on mercuric iodide,[1, 2] or by heating mercuric chloride with iodine in a sealed tube.[2] It apparently exists in two forms, red and yellow, the temperature of transition to the yellow form being 125° C., melting-point 153° C., and boiling-point 315° C.[2] It is affected by ultra-violet light when moist.[3] The formation of this compound has been denied, and mixed crystals only of the chloride and iodide said to be obtained.[4, 5] No such compound is formed with mercuric bromide, but only an unbroken series of mixed crystals.[4, 6]

Boullay[7] described a sesqui-iodide, Hg_4I_6, but it appears to be only a mixture of mercurous and mercuric iodides which can be separated by ether.[8]

Compounds resulting from the Action of Ammonia on Mercuric Iodide.—By the action of ammonia on mercuric iodide in the dry state,[9, 10, 11] in benzene solution,[10] in potassium iodide solution,[12] or in cold aqueous solution,[13, 14] a diammoniate, $HgI_2.2NH_3$, comparable with fusible white precipitate, is obtained. It forms white or yellow crystalline needles,[14] which, on exposure to air, become red owing to loss of ammonia.[10] It is immediately decomposed by excess of water. The compounds $HgI_2.NH_3$[14, 15, 16] and $3HgI_2.4NH_3$[11] have also been mentioned. Compounds of ammonia with various complex mercuric iodides have been described, namely, compounds with potassium,[17] cuprous,[17, 18] cupric,[18, 19] barium,[17, 20] cadmium,[17, 20] and zinc[20] mercuric iodides.

By the action of aqueous ammonia in small quantities at a time on the diammoniate of mercuric iodide, the compound NH_2HgI, analogous to infusible white precipitate, is obtained.[21] The process is reversible, the original compound being obtained by the action of ammonia and ammonium iodide on the product,[21] that is,

$$HgI_2.2NH_3 \rightleftharpoons NH_2HgI+NH_4I.$$

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[1] Boullay, *Ann. Chim. Phys.*, 1827, [2], **34**, 366; Larocque, *J. Pharm. Chim.*, 1843, [3], **4**, 15.

[2] Köhler, *Ber.*, 1879, **12**, 1187.

[3] Pougnet, *Compt. rend.*, 1915, **161**, 348.

[4] Bruni and Padoa, *Gazzetta*, 1902, **32**, ii, 319; *Atti R. Accad. Lincei*, 1902, [5], **11**, 565.

[5] Padoa and Tibaldi, *ibid.*, 1903, [5], **12**, ii, 158.

[6] van Nest, *Zeitsch. Kryst. Min.*, 1910, **47**, 263; Luczizky, *ibid.*, 1909, **46**, 297; Reinders, *Zeitsch. physikal. Chem.*, 1900, **32**, 494; but see Oppenheim, *Ber.*, 1869, **2**, 571; Groth, *ibid.*, 1869, **2**, 574.

[7] Boullay, *Ann. Chim. Phys.*, 1827, [2], **34**, 360.

[8] François, *J. Pharm. Chim.*, 1897, [6], **6**, 443.

[9] Rose, *Pogg. Annalen*, 1830, **20**, 161; François, *J. Pharm. Chim.*, 1897, [6], **5**, 388; Peters, *Zeitsch. anorg. Chem.*, 1912, **77**, 183.

[10] Colson, *Compt. rend.*, 1892, **115**, 658.

[11] François, *ibid.*, 1899, **129**, 296.

[12] Pesci, *Gazzetta*, 1890, **20**, 485; Lemoult, *Compt. rend.*, 1904, **139**, 478.

[13] François, *ibid.*, 1900, **130**, 332; Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1912, **77**, 44; but see Rammelsberg, *Pogg. Annalen*, 1839, **48**, 169; *J. prakt. Chem.*, 1888, [2], **38**, 565.

[14] Nessler, *Jahresber.*, 1856, 408.

[15] Rammelsberg, *loc. cit.*

[16] Caillot and Corriol, *J. Pharm. Chim.*, 1823, [2], **9**, 381; Böttger, *J. prakt. Chem.*, 1836, [1], **8**, 481; but see Pesci, *Gazzetta*, 1890, **20**, 485.

[17] Peters, *Zeitsch. anorg. Chem.*, 1912, **77**, 156.

[18] Anderlini, *Gazzetta*, 1912, **42**, i, 321.

[19] Jörgensen, *J. prakt. Chem.*, 1870, [2], **2**, 351; Ley and Wiegener, *Zeitsch. Elektrochem.*, 1905, **11**, 590.

[20] Ephraim and Mosimann, *Ber.*, 1921, **54B**, 396.

[21] François, *Compt. rend.*, 1900, **130**, 1022.

The compound NH_2HgI is a dirty white powder consisting of microscopic crystals which are insoluble in ether and do not redden in air.

The iodide of Millon's base, or "Nessler's precipitate," which, in accordance with Franklin's views,[1] should be formulated as HO.Hg.NH.HgI, is obtained by the action of ammonia on an alkaline solution of mercuric iodide,[2, 3] or of the double iodide of mercury and potassium.[4, 5] It forms a brown powder which is decomposed on heating at temperatures as low as 160° C., although the action is not rapid until a temperature of about 400° C. is reached. Decomposition is accompanied by a violet luminescence.[5]

By the continued action of concentrated aqueous ammonia, or, better still, of a 25 per cent. solution of sodium or potassium hydroxide, on the diammoniate, dimercuri-ammonium iodide, NHg_2I, is obtained.[6, 7] When slowly formed by the first method it separates as a dark purple mass of crystals which, under the microscope, are a dark reddish brown by transmitted light. According to François,[7] the hydrated compound, the iodide of Millon's base, does not exist, and only this stable anhydrous compound is formed under all conditions. It has also been prepared by the action of liquid ammonia on mercuric iodide, and by the addition of potassamide to an excess of mercuric iodide dissolved in liquid ammonia.[8] Obtained in this way it forms a reddish-yellow precipitate soluble in ammoniacal solutions of ammonium salts. By the further action of potassamide it is converted into the nitride.[8] By the action of a solution of ammonia containing a large proportion of ammonium iodide, the dimercuri-ammonium iodide is partly reconverted to the diammoniate.[6] François [6] has studied the equilibrium conditions.

$$2(HgI_2.2NH_3) \rightleftharpoons NHg_2I + 3NH_4I.$$

Compounds with substituted ammonias and other bases, and with their halides, have also been described, for example with hydrazine,[9] alkylamines,[10, 11, 12] arylamines,[10, 13, 14] pyridine,[10, 11, 13, 14, 15] quinoline,[11, 14, 16] nitriles,[17] thiocarbamide,[18] and others.[11] The double iodides form compounds with hexamethylenetetramine.[19]

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[1] See Compounds resulting from the Action of Ammonia on Mercuric Chloride.

[2] Rammelsberg, *loc. cit.*

[3] See Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 58. See also Weyl, *Pogg. Annalen*, 1867, 131, 524.

[4] Nessler, *Jahresber.*, 1856, 410.

[5] Weiser, *J. Physical Chem.*, 1917, 21, 37.

[6] François, *Compt. rend.*, 1900, 130, 332.

[7] François, *ibid.*, 1900, 130, 571.

[8] Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 838; 1907, 29, 54.

[9] Ferratini, *Gazzetta*, 1912, 42, i, 138.

[10] François, *J. Pharm. Chim.*, 1906, [6], 24, 21.

[11] Datta, *J. Amer. Chem. Soc.*, 1913, 35, 949.

[12] Risse, *Annalen*, 1858, 107, 223; Köhler, *Ber.*, 1879, 12, 2321; François, *Compt. rend.*, 1905, 140, 1697; 1906, 142, 1199; Schmidt and Krauss, *Chem. Zentr.*, 1907, ii, 1593; Gibbs, *J. Amer. Chem. Soc.*, 1906, 28, 1419; Löw, *Zeitsch. Kryst. Min.*, 1912, 51, 138.

[13] François, *Compt. rend.*, 1903, 137, 1069.

[14] Staronka, *Bull. Acad. Sci. Cracow*, 1910, [A], 372; see *J. Chem. Soc.*, 1910, 98, Abs. i, 876.

[15] Groos, *Jahresber.*, 1890, 950; François, *Compt. rend.*, 1905, 140, 861; Mathews and Ritter, *J. Chem. Soc.*, 1917, 112, Abs. ii, 300; Schroeder, *Chem. Zentr.*, 1904, ii, 454; *Zeitsch. anorg. Chem.*, 1905, 44, 15.

[16] Gernez, *Ann. Chim. Phys.*, 1903, [7], 29, 423.

[17] Hartley, *Trans. Chem. Soc.*, 1916, 109, 1300, 1302.

[18] Rosenheim and Meyer, *Zeitsch. anorg. Chem.*, 1906, 49, 13.

[19] Calzolari and Tagliavini, *Atti R. Accad. Lincei*, 1915, [5], 24, i, 925.

Reactions of Mercuric Iodide with other Compounds of the Ammonia Type.—With hydrogen phosphide mercuric iodide forms the compound PHg_3I_3,[1] and similar compounds have been obtained with arsenic and antimony hydrides. There are also addition compounds with alkyl-substituted phosphonium,[2] arsonium,[3] and stibonium[4] iodides.

Other Addition Compounds and Condensation Products.—Mercuric iodide forms compounds with aromatic tellurides,[5] alkyl iodides and sulphides,[6] olefines,[7] camphor,[8] ketones,[9] and other organic compounds.[10]

Mercuric Polyiodides.—The existence of solid polyiodides appears to be rather doubtful, although Jörgensen described a hexa-iodide which he obtained as unstable, brown, rhombic crystals, isomorphous with yellow mercuric iodide, by mixing warm solutions of alcoholic potassium tri-iodide and aqueous mercuric chloride, and slowly cooling. The yellow mercuric iodide first formed gradually changed to the periodide. The crystals strongly absorbed polarised light. They were decomposed by alcohol or aqueous potassium iodide solution almost at once, with the formation of a red tri-iodide in the first case and complete solution in the second. They were even decomposed in time by cold water, and they lost iodine in the air.[11]

A study of the distribution of iodine between mercuric bromide or chloride solutions and carbon tetrachloride indicates the existence of the compound $HgBr_2I_2$ and $HgCl_2I_2$,[12] and equilibria in aqueous solutions of iodine and the double iodide, $HgI_2.2KI$, have also been investigated.[13]

OXYHALOGEN COMPOUNDS OF MERCURY.

Mercuric Oxyfluoride.[14]—By the hydrolytic action of small quantities of water on mercuric fluoride a white hydrated oxyfluoride, $Hg_3F_4(OH)_2.3H_2O$, has been obtained.[15] An oxyfluoride is also said to be produced by the action of light on mercuric fluoride.[16] The compound $HgF_2.HgO.H_2O$ is possibly an intermediate stage in the preparation of the fluoride from mercuric oxide and hydrofluoric acid.[17] According to Cox, however, no true oxyfluorides have been obtained, only mixtures of the oxide and fluoride, and he has discussed the hydrolytic equilibrium between fluoride, acid, and oxide.[18]

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[1] Lemoult, *Compt. rend.*, 1904, 139, 478.

[2] Partheil and van Haaren, *Arch. Pharm.*, 1900, [3], 38, 28.

[3] Partheil, Amort, and Gronover, *ibid.*, 1899, [3], 37, 127; Partheil and Amort, *Ber.*, 1898, 31, 596.

[4] Partheil and Mannheim, *Arch. Pharm.*, 1900, [3], 38, 166.

[5] Lederer, *Ber.*, 1915, 48, 1422.

[6] Smiles, *Trans. Chem. Soc.*, 1900, 77, 160; Smiles and Hilditch, *ibid.*, 1907, 91, 1394; Rây, *ibid.*, 1916, 109, 603; 1919, 115, 548; Rây and Guha, *ibid.*, 1919, 115, 1154.

[7] Sand, *Ber.*, 1901, 34, 1385; Hofmann and Sand, *ibid.*, 1900, 33, 1340, 1353.

[8] Marsh and Struthers, *Proc. Chem. Soc.*, 1908, 24, 266, 267.

[9] Gernez, *Compt. rend.*, 1903, 137, 255; Marsh and Struthers, *Proc. Chem. Soc.*, 1908, 24, 266.

[10] Hofmann and Sand, *Ber.*, 1900, 33, 2692; Sand and Singer, *ibid.*, 1902, 35, 3170.

[11] Jörgensen, *J. prakt. Chem.*, 1870, [2], 2, 357.

[12] Herz and Paul, *Zeitsch. anorg. Chem.*, 1914, 85, 214.

[13] van Name and Brown, *Amer. J. Sci.*, 1917, [4], 44, 105.

[14] See Mercuric Fluoride.

[15] Ruff and Bahlau, *Ber.*, 1918, 51, 1752.

[16] Frémy, *Ann. Chim. Phys.*, 1856, [3], 47, 38.

[17] Finkener, *Pogg. Annalen*, 1860, 110, 628.

[18] Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 169; Abegg and Cox, *Zeitsch. physikal. Chem.*, 1903, 46, 7, footnote.

Mercurous Oxychloride.—The formula $Hg_2O.Hg_2Cl_2$ has been ascribed to the mineral *eglestonite.*[1] The mineral *terlinguaite* appears to be a compound of mercuric oxide with mercurous chloride, $2HgO.Hg_2Cl_2$.[1, 2] A compound of the same composition has also been prepared, in the form of small red prisms, by heating mercurous chloride with mercuric oxide and water in a sealed tube for sixty hours at 180° C.[3]

Mercuric Oxychlorides.—A naturally occurring mercuric oxychloride, of composition $3HgO.HgCl_2$, is said to exist in the mineral *kleinite.*[2, 4] More recent investigations, however, seem to indicate that it has the composition $NHg_2Cl.\frac{1}{2}H_2O$ mixed with some sulphate and oxysulphate.[1, 5]

According to Schoch,[6] ten different compounds may be distinguished, namely, one trimercuric monoxychloride, $2HgCl_2.HgO$, and three isomers of each of the following: trimercuric dioxychloride, $HgCl_2.2HgO$, tetramercuric trioxychloride, $HgCl_2.3HgO$, and pentamercuric tetroxychloride, $HgCl_2.4HgO$.[7] Still other compounds have, however, been described. The heats of formation of some of the compounds have been determined by André.[8]

$2HgCl_2.HgO$ is formed by boiling a solution of mercuric chloride with excess of mercuric oxide, decanting off the liquid, and allowing to crystallise between 40° C. and 50° C. The yellowish-white rhombic prisms obtained are mixed with mercuric chloride.[9] Similar processes have been described by others.[6, 10] According to Driot,[11] the compound formed depends on the concentration of the mercuric chloride, $2HgCl_2.HgO$ being obtained in a 13–20 per cent. solution. It is also formed by the action of marble on a solution of mercuric chloride.[12]

$HgCl_2.HgO$ is formed by the action of a 30 per cent. mercuric chloride solution on mercuric oxide,[11] by evaporating to dryness a solution of sublimate saturated with oxide and dissolving out the mercuric chloride with alcohol,[11] by heating together the dry constituents,[8] by leaving a saturated solution of mercuric chloride in contact with marble,[13] or by acting on mercury with hydrochloric acid vapour in presence of oxygen.[14] It forms thin red crystals [13] or a yellow powder.[11]

$HgCl_2.2HgO$.—Both red and black forms of compound are known. The red, or α-modification is obtained by the action of a cold saturated solution of potassium bicarbonate on six to ten volumes of a solution of mercuric chloride saturated at 15° C.[15] Disodium phosphate [16] or marble [17] may be substituted for the bicarbonate. Schoch [6] prepared it by heating mercuric oxide with mercuric chloride, in the molecular proportions of two to one, in a sealed tube. Similar wet methods are employed for the production of the black or β-variety, but a smaller proportion of mercuric chloride solution is necessary.[1, 2, 3, 4] It is also obtained by the action of a dilute solution of mercuric chloride on excess of mercuric oxide, either red or yellow.[1, 5, 6, 7, 8, 9, 10] According to Schoch, the black variety is formed in slightly alkaline solution and the red in slightly acid. Purple shades between black and red may be obtained by varying the conditions.[7] Volhard obtained the black variety by the action of sodium acetate on a saturated solution of mercuric chloride.[11] It may also be obtained by heating the red form in the dry state.[12]

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[1] Hillebrand and Schaller, *J. Amer. Chem. Soc.*, 1907, **29**, 1180 ; *Amer. J. Sci.*, 1907, [4], **24**, 259 ; *U.S. Geol. Survey*, 1909, Bull. 405.

[2] Moses, *Amer. J. Sci.*, 1903, [4], **16**, 253 ; *Zeitsch. Kryst. Min.*, 1904, **39**, 3.

[3] Fischer and von Wartenberg, *Chem. Zeit.*, 1905, **29**, 308.

[4] Sachs, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 1091.

[5] Hillebrand, *J. Amer. Chem. Soc.*, 1906, **28**, 122 ; *Amer. J. Sci.*, 1906, [4], **21**, 85.

[6] Schoch, *Amer. Chem. J.*, 1903, **29**, 332.

[7] See also Millon (*Ann. Chim. Phys.*, 1846, [3], **18**, 372), who mentions all but the first.

[8] André, *Ann. Chim. Phys.*, 1884, [6], **3**, 116.

[9] Roucher, *ibid.*, 1849, [3], **27**, 353 ; *Compt. rend.*, 1844, **19**, 773.

[10] Thümmel, *Arch. Pharm.*, 1889, [3], **27**, 589.

[11] Driot, *Compt. rend.*, 1911, **152**, 958.

[12] Arctowski, *Zeitsch. anorg. Chem.*, 1895, **9**, 178.

[13] Tarugi, *Gazzetta*, 1901, **31**, ii, 313.

[14] Bailey and Fowler, *Trans. Chem. Soc.*, 1888, **53**, 760.

[15] Millon, *loc. cit.*

[16] Haack, *Annalen*, 1891, **262**, 188.

[17] van Nest, *Zeitsch. Kryst. Min.*, 1910, **47**, 271.

A hemi-hydrate, consisting of an orange and a black variety, is obtained by treating neutral mercurous nitrite solution, which always contains a little mercuric nitrite, with excess of sodium chloride, and allowing the filtered solution to evaporate at room temperature. Sodium hydroxide transforms the black into the orange form.[13]

$HgCl_2.3HgO$ forms three modifications: the α- or amorphous red form, the β- or citron-yellow amorphous form, and the γ- or yellow crystalline variety. These are obtained by varying slightly the previously described methods of preparation.[2, 3, 5, 6, 8, 9, 12, 14, 15, 16, 17] Haack [18] prepared the α-modification by the action of sodium chloride solution on the dry normal mercuric phosphate.

$HgCl_2.4HgO$.—Three varieties of this compound have also been described: a brown or yellow crystalline variety,[2, 6, 9, 12, 15, 16, 19, 20] a brown amorphous form,[2, 7, 12, 16] and a black [6, 10, 16] or dark brown [20] crystalline product.

Other compounds, for example, $2HgCl_2.3HgO$,[21] $4HgCl_2.7HgO$,[22] $HgCl_2.5HgO$,[23] $HgCl_2.6HgO$,[23] and the monohydrate of the latter, $HgCl_2.6HgO.H_2O$,[23] have also been described, but it is doubtful if these are chemical individuals.[24]

André described compounds of mercuric oxide with the chlorides of other metals.[21]

Mercurous Chlorite, $Hg_2(ClO_2)_2$, is formed, by the action of a soluble chlorite on mercurous nitrate solution, as a canary-yellow precipitate which becomes white in the presence of excess of the nitrate.[25] It cannot be obtained quite free from the oxide, and it reddens in air and decomposes spontaneously when dried.[25, 26] A basic salt,

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[1] Philipps, *Phil. Mag.*, 1830, [2], **7**, 130.

[2] Millon, *loc. cit.*

[3] Tarugi, *loc. cit.*

[4] Blaas, *Zeitsch. Kryst. Min.*, 1881, **5**, 283.

[5] Grouvelle, *Ann. Chim. Phys.*, 1821, [2], **17**, 42.

[6] Roucher, *ibid.*, 1849, [3], **27**, 353.

[7] Toda, *J. Chem. Soc.*, 1922, **122**, Abs. ii, 769.

[8] Driot, *loc. cit.*

[9] Schoch, *loc. cit.*

[10] Thaulow, *J. prakt. Chem.*, 1844, [1], **31**, 370.

[11] Volhard, *Annalen*, 1889, **255**, 252.

[12] Thümmel, *loc. cit.*

[13] Rây, *Annalen*, 1901, **316**, 250.

[14] Voit, *ibid.*, 1857, **104**, 349.

[15] Arctowski, *loc. cit.*

[16] André, *loc. cit.*

[17] See also van Nest, *loc. cit.*

[18] Haack, *loc. cit.*

[19] Soubeiran, *J. Pharm. Chim.*, 1830, [2], **16**, 662.

[20] Dukelski, *Zeitsch. anorg. Chem.*, 1906, **49**, 336.

[21] André, *Compt. rend.*, 1887, **104**, 431.

[22] Voit, *Annalen*, 1857, **104**, 349.

[23] Roucher, *loc. cit.*

[24] Tarugi, *loc. cit.*; Toda, *loc. cit.*; Thümmel, *loc. cit.*

[25] Bruni and Levi, *Gazzetta*, 1915, **45**, ii, 161.

[26] Levi, *Atti R. Accad. Lincei*, 1923, [5], **32**, i, 165; *Gazzetta*, 1923, **53**, i, 245.

$Hg_2(ClO_2)_2.HgO.5H_2O$, may also be obtained as a cream-yellow precipitate which is decomposed by heat or shock.[1]

Mercuric Chlorite, $Hg(ClO_2)_2$, may be obtained as a red crystalline precipitate from solutions of potassium or barium chlorite and mercuric nitrate.[1] If kept dry in more than very small amount it undergoes rapid decomposition and sometimes spontaneous ignition, forming mercuric chloride. It explodes slightly on percussion. The precipitate may contain mercuric oxide, and it has been suggested that a basic salt, $3Hg(ClO_2)_2.HgO$, is formed.[2] A highly explosive mercuriammonium chlorite, $NH_2(HgO.Hg)ClO_2$, in an impure state, has been obtained by treatment of an aqueous suspension of the chlorite with ammonia.[1]

Mercurous Chlorate, $Hg_2(ClO_3)_2$, may be obtained by dissolving precipitated mercurous oxide in chloric acid.[3, 4] It forms a white powder, soluble in water or alcohol, when the solution is evaporated over sulphuric acid.[4] When heated carefully to 250° C. it begins to decompose with the formation of oxygen, oxide, and chloride. If heated rapidly, instantaneous decomposition takes place with the evolution of chlorine. A second modification, insoluble in water but soluble in acetic acid, is obtained by evaporating a solution of the first on the water bath.[4]

Mercuric Chlorate.—Neutral mercuric chlorate is not known in the solid state. It is strongly hydrolysed by water, and, from a solution of mercuric oxide in chloric acid,[5] the basic compound, $Hg(ClO_3)_2.HgO.H_2O$, separates out in small, colourless, deliquescent, rhombic plates, isomorphous with the corresponding basic bromate.[6] It is soluble in alcohol, decomposed by sulphuric acid with the evolution of chlorine, and readily decomposed by heat, giving oxygen or chlorine according to whether it is heated quickly or slowly. It has also been prepared by the action of chlorine on mercuric oxide.[7]

Mercurous Perchlorate, $Hg_2(ClO_4)_2$, may be prepared by dissolving mercurous oxide in perchloric acid,[8] or by shaking mercuric perchlorate with mercury.[9] It is soluble, and the solution may be evaporated in a vacuum desiccator.[9] It crystallises in fine needles or flattened prisms [10] with 4 molecules of water,[9, 11] and is deliquescent.[12] At 100° C., in a current of dry air, it loses water very slowly.[9] It is gradually decomposed by water and forms a basic salt.[9] On treatment with cold alcohol part dissolves, and a residue is left of the anhydrous salt, which is completely dissolved if the alcohol be heated.[13] Ammonia blackens it.[8] It has no melting-point, but, if quickly heated, it partially liquefies. At higher temperatures it decomposes and gives mercuric oxide, oxygen, a very little free chlorine, and a sublimate of mercurous and mercuric chlorides.[9]

The solution, although neutral to litmus,[9] is hydrolysed to some extent, the degree of hydrolysis in decinormal solution being about 3–4 per cent., as measured by the sugar-inversion method.[1]

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[1] Levi, *loc. cit.*

[2] Bruni and Levi, *loc. cit.*

[3] Vauquelin, *Ann. Chim.*, 1815, [1], 95, 103.

[4] Wächter, *J. prakt. Chem.*, 1843, [1], 30, 331.

[5] Vauquelin, *loc. cit.*, 107; Wächter, *loc. cit.*, 333.

[6] Topsöe, *Jahresber.*, 1872, 164.

[7] Braamcamp and Oliva, *Ann. Chim.*, 1805, [1], 54, 129.

[8] Sérullas, *Ann. Chim. Phys.*, 1831, [2], 46, 306.

[9] Chikashigé, *Trans. Chem. Soc.*, 1895, 67, 1016.

[10] See also Sérullas, *loc. cit.*

[11] But Roscoe (*Annalen*, 1862, 121, 356) found 6 molecules.

[12] Sérullas found the contrary.

[13] Chikashigé, *loc. cit.*, 1905, 87, 823.

A mercurous perchlorate coulometer may be made, using mercury electrodes in a solution of mercurous perchlorate containing perchloric acid and sodium perchlorate. Without the latter, part of the mercury is deposited as a black powder.[2]

Mercuric Perchlorate, $Hg(ClO_4)_2$, may be obtained by dissolving mercuric oxide in perchloric acid.[3] On evaporation the hexahydrate, $Hg(ClO_4)_2.6H_2O$, separates in long, colourless, rectangular prisms which are very deliquescent.[4] It may also be prepared by treating mercuric nitrate with a slight excess of 70 per cent. perchloric acid, and boiling off the nitric acid and excess of perchloric acid.[5] When treated with cold alcohol the hydrated salt is partially dissolved and a residue of the anhydrous salt is left.[6] Boiling alcohol reacts with mercuric perchlorate, giving aldehyde and mercurous perchlorate. If the solution be diluted with water it is chiefly the hydrated mercurous salt which is obtained.[6]

The acidity of the aqueous solution,[3, 4] and the high electrical conductivity, indicate that, although no basic salt precipitates from aqueous solutions, the salt is hydrolysed to a considerable extent [7]—to a much greater extent, in fact, than the mercurous salt. At a dilution of 1 grm.-molecule in 512 litres the degree of hydrolysis is 37 per cent.[8] Basic compounds have, however, been obtained.[4, 6] If the normal salt be gently heated to 150° C., a compound, $2HgO.Hg(ClO_4)_2$, appears to be formed.[4] A hydrated compound, $HgO.2Hg(ClO_4)_2.12H_2O$, may be prepared by treating excess of mercuric oxide with perchloric acid, filtering, and evaporating the solution.[6] Prismatic crystals are formed similar to those of the normal salt, and soluble in water with only a slight residue of mercuric oxide. When the basic salt is boiled with alcohol a flocculent precipitate, which gradually becomes granular, separates out. The flocculent compound is simply the original basic salt, $HgO.2Hg(ClO_4)_2$, in the anhydrous form.[9] It is insoluble in hydrochloric or nitric acid, but decomposed by a mixture of the two. It remains unchanged by heat up to nearly dull redness, and then burns explosively with a pale violet flame, leaving red mercuric oxide. The granular precipitate has the same composition as the product obtained by heating the normal salt, $2HgO.Hg(ClO_4)_2$, which may be called the α-form, but it is isomeric with it, and behaves differently towards acids and water which decompose the α- but not the β-salt. Both forms are stable up to nearly red heat. The β-compound then detonates with great violence, but the α-salt decomposes without explosion. Borelli failed to prepare the compound $HgO.2Hg(ClO_4)_2.12H_2O$, and only obtained a mixture of the approximate composition $3HgO.2Hg(ClO_4)_2$.[10]

Mercuric perchlorate forms complex salts, of composition $HgX(ClO_4)$, where X is Br, I, or CN, but not Cl.[10, 11]

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[1] Ley and Heimbucher, *Zeitsch. Elektrochem.*, 1904, 10, 302.

[2] Mathers and Germann, *J. Chem. Soc.*, 1911, 100, Abs. ii, 577.

[3] Sérullas, *loc. cit.*

[4] Chikashigé, *Trans. Chem. Soc.*, 1895, 67, 1013.

[5] Smith, *J. Amer. Chem. Soc.*, 1923, 45, 1417.

[6] Chikashigé, *Trans. Chem. Soc.*, 1905, 87, 822.

[7] Ley and Kissel, *Ber.*, 1899, 32, 1362.

[8] Ley, *Zeitsch. physikal. Chem.*, 1899, 30, 249; Ley and Heimbucher, *Zeitsch. Elektrochem.*, 1904, 10, 301.

[9] Chikashigé, *loc. cit.*

[10] Borelli, *Gazzetta*, 1908, 38, ii, 421.

[11] Borelli, *ibid.*, 1908, 38, i, 361.

Mercurous Oxybromide, $2HgO.Hg_2Br_2$, may be prepared as thin, dark, rhombic plates by heating mercuric oxide and mercurous bromide with water in sealed tubes for forty-eight hours at 180° C.[1]

Mercuric Oxybromides.—Several oxybromides have been described, but some of these are probably not chemical individuals. According to Löwig,[2] an oxybromide of unknown composition may be obtained by boiling mercuric oxide with mercuric bromide solution; but this is contradicted by Fischer and von Wartenberg, who found that the mixture must be heated in a closed vessel at 160° C.[3] They thus obtained the oxybromides $HgBr_2.4HgO$ [4, 5] and $2HgBr_2.7HgO$. The same modification of the first compound, but a different one of the second, may be obtained by fusing together the oxide and bromide.[6] A second modification of the compound $HgBr_2.4HgO$ is obtained by the action of sodium carbonate solution on a boiling solution of mercuric bromide.[3, 4] By the action of a cold saturated solution of potassium bicarbonate on a mercuric bromide solution saturated at room temperature, the second modifications of both the oxybromides are formed.[3] The action of marble or magnesia on mercuric bromide solution produces $HgBr_2.4HgO$.[3, 7] Both modifications of each of these basic salts are insoluble in indifferent solvents, but quickly decomposed by acids and alkali hydroxides. They are unaffected by dry ammonia, but give a yellow compound with aqueous ammonia. When heated to about 230° C. they are decomposed.[3]

By the action of dilute potassium hydroxide solution on mercuric bromide in water [8] or alcohol,[3] the compound $HgBr_2.3HgO$ is obtained.[9] This is only decomposed when heated to a very high temperature. It is unaffected by alkalies, but is attacked by both dry and aqueous ammonia.[3] André [4, 5] described the compounds $HgBr_2.HgO$ and $HgBr_2.2HgO$ obtained in the dry way, and determined the heats of formation.

Mercurous Bromate, $Hg_2(BrO_3)_2$, is obtained as a yellowish-white powder when a solution of mercurous nitrate is precipitated with bromic acid or potassium bromate. It may be recrystallised from bromic acid as white, anhydrous leaflets. It is very soluble in hydrochloric acid but not in nitric.[10] By the action of water a basic salt, $Hg_2O.Hg_2(BrO_3)_2$, is obtained as a citron-yellow precipitate which detonates on heating.[10]

Mercuric Bromate, $Hg(BrO_3)_2.2H_2O$, may be obtained by dissolving mercuric oxide in bromic acid.[11] It forms small prismatic crystals, much more soluble in hot water than in cold. It shows only a slight tendency to hydrolyse in aqueous solution, even at a very high temperature.[12] The salt is decomposed by heat, detonating at 130°–140° C. The basic salt, $HgO.Hg(BrO_3)_2.H_2O$, analogous to the chlorate, is obtained when excess of mercuric oxide is employed, or when a hot neutral solution of mercurous nitrate is precipitated by potassium bromate. It forms thin, lustrous leaflets, and is slowly decomposed by cold water, giving a still more basic salt. In hot water the red oxide is rapidly formed.[1] The compound obtained, during the preparation of hypobromous acid from bromine and mercuric oxide, is apparently the anhydrous basic bromate, $Hg(BrO_3)_2.HgO$, and not the oxybromide.[2, 3]

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[1] Fischer and von Wartenberg, *Chem. Zeit.*, 1905, 29, 308.

[2] Löwig, *Pogg. Annalen*, 1828, 14, 485.

[3] Fischer and von Wartenberg, *Chem. Zeit.*, 1902. 26, 983.

[4] André, *Ann. Chim. Phys.*, 1884, [6], 3, 123.

[5] André, *Compt. rend.*, 1884, 98, 515.

[6] Fischer and von Wartenberg, *Chem. Zeit.*, 1902, 26, 966.

[7] See also Arctowski, *Zeitsch. anorg. Chem.*, 1895, 9, 184.

[8] Rammelsberg, *Pogg. Annalen*, 1842, 55, 250.

[9] See also André, *loc. cit.*

[10] Rammelsberg, *Pogg. Annalen*, 1842, 55, 79.

[11] Rammelsberg, *ibid.*, 83.

[12] Arctowski, *Zeitsch. anorg. Chem.*, 1895, 9, 184.

By the action of ammonia on solutions of mercuric bromate, a yellow bulky powder, to which Rammelsberg gave the formula $2NHg_2BrO_3.3H_2O$, has been obtained.[4, 5]

Mercurous Oxyiodide, $6HgO.Hg_2I_2$, has been prepared in the form of brownish-red, rhombic plates, isomorphous with the oxybromide, by heating a mixture of mercurous iodide and mercuric oxide at 160° C. for eighty hours.[6]

Mercuric Oxyiodides.—A compound $HgI_2.3HgO$ has been prepared by fusing together the constituents in the proper proportions.[7] The same formula was ascribed by Rammelsberg to the product of the action of potassium hydroxide on mercuric iodide,[8] but the composition of the compound obtained depends on the concentration of the alkali employed.[9] At 15° C., below concentrations of 0·3 N, there is no action at all. Above this concentration, up to 1·5 N, the double salt, $HgI_2.2KI$, is formed in solution, and it is only at still higher concentrations that oxyiodides begin to appear. The following formulæ have been suggested:[9] $HgI_2.2HgO$, $2HgI_2.HgO$, and $6HgI_2.HgO$. The products are all sensitive to light.

Mercuric Hypoiodite.—By shaking finely powdered iodine and precipitated mercuric oxide with water for a few minutes, and filtering, a solution which gives the reactions for hypoiodites is obtained, but the amount present is only small.[10]

Mercurous Iodate, $Hg_2(IO_3)_2$, may be prepared by precipitating mercurous nitrate with a soluble iodate[11] or iodic acid.[12] It may also be formed, along with the iodide, by the action of iodine on mercuric nitrate.[13] It is an anhydrous white powder unaffected by water, and it decomposes when heated to 250° C. It is also obtained when hot iodic acid acts on metallic mercury.[14] The product contains iodide.

Mercuric Iodate, $Hg(IO_3)_2$, may be obtained by the action of iodic acid on precipitated mercuric oxide,[15] on mercuric chloride in the dry state,[16] or on a solution of a soluble mercuric salt.[17] It may also be prepared by precipitating a soluble mercuric salt, other than the chloride, with sodium iodate,[16, 17] or by the action of nitric acid on mercuric iodide.[18]

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[1] Topsöe, *Jahresber.*, 1872, 164.

[2] Fischer and von Wartenberg, *Chem. Zeit.*, 1902, 26, 983.

[3] According to Löwig (*Pogg. Annalen*, 1828, 14, 486), bromide and bromate are formed.

[4] Rammelsberg, *Pogg. Annalen*, 1842, 55, 83.

[5] Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 568.

[6] Fischer and von Wartenberg, *Chem. Zeit.*, 1905, 29, 308.

[7] Weyl, *Pogg. Annalen*, 1867, 131, 549.

[8] Rammelsberg, *ibid.*, 1839, 48, 183.

[9] Pélabon, *Compt. rend.*, 1924, 178, 1718.

[10] See Mercuric Iodate; Orton and Blackman, *Trans. Chem. Soc.*, 1900, 77, 835. See also Köne, *Pogg. Annalen*, 1845, 66, 302; Lippmann, *Compt. rend.*, 1866, 63, 968.

[11] Rammelsberg, *Pogg. Annalen*, 1838, 44, 570.

[12] Vauquelin, *Ann. Chim.*, 1814, 90, 219.

[13] Vauquelin, *ibid.*, 247.

[14] Ditte, *Ann. Chim. Phys.*, 1870, [4], 21, 28. It is not definitely stated whether mercurous or mercuric iodide is formed.

[15] Rammelsberg, *Pogg. Annalen*, 1838, 44, 571; *J. prakt. Chem.*, 1888, [2], 38, 568.

[16] Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 367.

[17] Cameron, *Chem. News*, 1876, 33, 253.

[18] Kraut, *Ber.*, 1885, 18, 3461.

It is the chief product formed when iodine and mercuric oxide are shaken up together with water,[1, 2] and is also formed along with the iodide if mercurous oxide is substituted for mercuric.[3]

Mercuric iodate is an amorphous white powder almost insoluble in water and nitric acid, but soluble in hydrochloric acid and a number of salt solutions. It dissolves in hydrobromic or hydriodic acid with the evolution of bromine or iodine.[4] Heat decomposes it into oxygen and mercuric iodide.[2, 5] Stannous chloride reduces it to mercuric iodide.[2]

Millon prepared a compound of composition $Hg_2N_3H_{10}O(IO_3)_3$, or $Hg_2N_3H_{12}O_2(IO_3)_3$, by the action of excess of ammonia solution on mercuric iodate.[6] By heating mercuric iodate with ammonia, Rammelsberg obtained a product to which he gave the formula $NHg_2IO_3.2NH_4IO_3$.[7] According to Franklin,[8] both are probably mixtures of mercuric iodate with ammonia of crystallisation, and the ammonobasic salt, NH_2HgIO_3, and may be expressed by the formula $Hg(IO_3)_2.2NH_3.NH_2HgIO_3.xH_2O$.

Mercurous Periodate.—Only basic mercurous periodates are known. By the action of sodium periodate [9, 10] on mercurous nitrate, the compound $4Hg_2O.Hg_2(IO_4)_2$ or, in slightly acid solution, $3Hg_2O.Hg_2(IO_4)_2$,[11] is formed as a light yellow precipitate. It becomes reddish brown on heating [9, 10] and ultimately decomposes. It is soluble in hydrochloric and in nitric acid.[10] Periodic acid on metallic mercury only gives mercurous oxide.[9]

Mercuric Periodate.—The neutral salt has not been prepared, but a basic compound, $4HgO.Hg(IO_4)_2$, is obtained by the action of sodium iodate,[9] or of a basic sodium iodate,[12, 13] on mercuric nitrate, or of excess of periodic acid on mercuric oxide.[11, 14] It forms a deep orange-yellow or red powder.[15] It is readily soluble in hydrochloric acid but only slightly so in nitric.[12] When digested with ammonia it gives a light yellow product, to which Rammelsberg [14] ascribed the formula $2NHg_2IO_4.NHg_2OH.NH_4OH.3H_2O$. Franklin suggests that it was probably a mixture of NH_2HgIO_4 and Millon's base, thus formulating it as $NH_2HgIO_4.NH(HgOH)_2.xH_2O$.[16]

Rammelsberg also obtained a double basic salt with potassium.[17]

MERCURY AND OXYGEN.

Mercurous Oxide.—Alkali hydroxides throw down a black precipitate from solutions of mercurous salts. A similar precipitate results from the action of caustic potash upon freshly precipitated mercurous chloride.[18] This precipitate consists mainly of mercurous

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[1] See Mercuric Hypoiodite; Orton and Blackman, *Trans. Chem. Soc.*, 1900, 77, 835; Colin, *Ann. Chim.*, 1814, [1], 91, 252.

[2] Rammelsberg, *Pogg. Annalen*, 1839, 48, 183.

[3] Brückner, *Monatsh.*, 1906, 27, 341.

[4] Cameron, *Chem. News*, 1876, 33, 253.

[5] Millon, *loc. cit.*

[6] Millon, *loc. cit.*, 410.

[7] Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 568.

[8] Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 63.

[9] Bengieser, *Annalen*, 1836, 17, 259.

[10] Lautsch, *J. prakt. Chem.*, 1867, [1], 100, 86; *Jahresber.*, 1867, 164.

[11] Rammelsberg, *Pogg. Annalen*, 1868, 134, 524.

[12] Lautsch, *Jahresber.*, 1867, 165.

[13] Rammelsberg, *Pogg. Annalen*, 1842, 55, 79.

[14] Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 568.

[15] According to Bengieser (*loc. cit.*), a white powder, which becomes yellowish on warming, is formed.

[16] Franklin, *loc. cit.*, 64.

[17] Rammelsberg, *Jahresber.*, 1868, 169.

[18] Schaffner, *Annalen*, 1844, 51, 181.

oxide, Hg_2O, but it always contains some metallic mercury and mercuric oxide, HgO. These two impurities are present even when the precipitation is done in the dark or in the absence of air.[1] They are also present in small quantities when the precipitate produced by rubbing mercurous acetate with alcoholic potash is washed with alcohol, then with ether, and dried.[2]

Mercurous oxide is unstable,[3] and apparently decomposes, slowly but steadily, into mercury and mercuric oxide. If the black precipitate is freely exposed to air mercury volatilises, and, finally, only mercuric oxide remains.[4] It also seems to oxidise slowly in air, and moisture quickens the oxidation.[2, 4] The absorption of oxygen is rapid at 100° C.[5] Mercurous oxide decomposes into mercury and oxygen at higher temperatures. It is reduced at 80° C. by hydrogen, according to Fay and Seeker,[6] though Colson[5] says that it is not reduced by hydrogen even at 100° C.

Mercurous oxide is practically insoluble in cold water; 150,000 parts of warm water dissolve about 1 part of it.[7] The solubility product $[Hg''_2][OH']^2 = 4{\cdot}8 \times 10^{-24}$.[8] Liquid ammonia does not dissolve it.[9] A hot solution of ammonium thiocyanate dissolves it with separation of mercury.[10] Hydrogen peroxide and mercurous oxide react with explosive violence. Free acid does not prevent the reaction, which ceases after repeated additions of the peroxide. The presence of mercuric peroxydate, HgO_2, imparts a red colour to the residue.[11] Mercurous carbonate is formed by the action of carbon dioxide on the moist oxide; it slowly decomposes into carbon dioxide, mercury, and mercuric oxide.[4]

The heat of formation of mercurous oxide from liquid mercury and gaseous oxygen has been given as 42·2 Cal.[12] and as 22·2 Cal.[3] According to Campbell[13] it is slightly radioactive.

Mercurous Hydroxide.—A small quantity of amber-coloured precipitate slowly forms when solutions of mercurous nitrate and caustic potash in alcohol are cooled to −42° C. and mixed. This may be mercurous hydroxide—it apparently changes with rise of temperature into mercurous oxide, mercuric oxide, and mercury.[14]

Mercuric Oxide.—Alkali hydroxides precipitate yellow HgO from cold solutions of mercuric salts. The dried precipitate may contain a small quantity of mercuric hydroxide,[15] and when it is precipitated by caustic potash from mercuric chloride solution it may be contaminated with potassium and chlorine.[16] Brunck[17] prepared it by treating mercuric nitrate solution with excess of sodium carbonate solution. The precipitate, after hot digestion in the solution and in fresh soda solution, contained neither chlorine nor nitric acid, and left no residue on volatilisation.

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[1] Guibourt, *Ann. Chim. Phys.*, 1816, [2], **1**, 422; Barfoed, *J. prakt. Chem.*, 1888, [2], **38**, 441.

[2] Bruns and Pfordten, *Ber.*, 1888, **21**, 2010.

[3] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 102.

[4] Hada, *Trans. Chem. Soc.*, 1896, **69**, 1677.

[5] Colson, *Compt. rend.*, 1899, **128**, 1105.

[6] Fay and Seeker, *J. Amer. Chem. Soc.*, 1903, **25**, 641.

[7] Bhaduri, *Zeitsch. anorg. Chem.*, 1897, **13**, 411.

[8] Allmand, *Zeitsch. Elektrochem.*, 1910, **16**, 263.

[9] Franklin and Kraus, *Amer. Chem. J.*, 1898, **20**, 829.

[10] Fleischer, *Annalen*, 1875, **179**, 234.

[11] Antropoff, *J. prakt. Chem.*, 1908, [2], **77**, 273.

[12] Thomsen, *ibid.*, 1875, [2], **11**, 283.

[13] Campbell, *Proc. Camb. Phil. Soc.*, 1906, **13**, 282.

[14] Bird, *Amer. Chem. J.*, 1886, 8, 426.

[15] Schoch, *ibid.*, 1903, **29**, 327.

[16] Siewart, *Annalen*, 1863, **125**, 227.

[17] Brunck, *Zeitsch. anorg. Chem.*, 1895, **10**, 243.

When mercuric oxide is precipitated hot from solutions of mercuric salts with alkali carbonates it tends to be red. Dufan prepared the red oxide by precipitating mercuric chloride solution with a solution of potassium carbonate. The originally brown precipitate became red on boiling.[1] The precipitate from hot solutions of mercuric chloride and barium hydroxide is also red.[2]

The red oxide forms slowly when mercury is heated in air just below its boiling-point. According to Echols,[3] mercury begins to unite with oxygen at 450° C. at ordinary pressure, and the oxide decomposes again about 630° C. Taylor and Hulett prepared it by heating purified mercury in oxygen under a pressure of 2–3 atmospheres.[4] It is usually prepared by heating mercuric nitrate without raising the temperature high enough to decompose the oxide.[5] A mixture of finely divided mercury and mercuric oxide is obtained by electrolysing alkalies with a mercury anode. A high yield of finely divided mercuric oxide is secured by distilling off the mercury below 500° C. in a current of air or oxygen.[6]

According to Schoch, when cold saturated mercuric chloride is added to excess of caustic soda solution the yellow precipitate soon turns orange if the solution is allowed to stand. The colour may continue to deepen for one or two weeks. The precipitated yellow oxide is very finely crystallised in square tablets. The minute crystals enlarge in contact with the precipitation mixture or with a solution of sodium or potassium chloride. As the crystals grow the colour changes from pale yellow to red. If the yellow oxide is boiled in aqueous solutions of salts it changes to the prismatic red oxide. Dry samples of the yellow oxide continuously heated for some hours at temperatures from 250° to 600° C. become red, and the crystals change into the prismatic form. A finely ground sample of the red prismatic oxide may be yellower than an originally yellow oxide that has been transformed. Mercuric oxide, therefore, seems to exist in two crystalline forms: in square tabular crystals precipitated at ordinary temperatures, and in monoclinic prisms produced by heating the former, or by preparation at higher temperatures.[7]

Fuseya changed the red oxide into the yellow by shaking it for some hours with a solution of alkali. A litre of water at 25° C. dissolves about 23·4 millimols of HgO.[8] The sudden change of solubility in passing from a neutral to a slightly alkaline solution is probably due to the dispersion of the oxide into finer particles. It seems to be generally considered that the yellow oxide only differs from the red by being more finely divided.[9]

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[1] Dufan, *J. Pharm. Chim.*, 1902, [6], 16, 439.

[2] Kendall and Fuchs, *J. Amer. Chem. Soc.*, 1921, 43, 2022.

[3] Echols, *Chem. News*, 1881, 44, 203.

[4] Taylor and Hulett, *J. Physical Chem.*, 1913, 17, 755.

[5] Fuseya, *J. Amer. Chem. Soc.*, 1920, 42, 368.

[6] *J. Soc. Chem. Ind.*, 1923, 42, 183A.

[7] Schoch, *Amer. Chem. J.*, 1903, 29, 319.

[8] 23·1 according to Hulett, *Zeitsch. physikal. Chem.*, 1901, 37, 406; 23·8 according to Schick, *ibid.*, 1903, 42, 172.

[9] Fuseya, *loc. cit.*

Gay-Lussac[1] attributed the physical and chemical differences between the two oxides to their different fineness of division. Pelouze, however, thought that the yellow oxide was amorphous and the red oxide crystalline.[2] There has always been rivalry between the two types of opinion: experimental results have been constantly adduced to show that the two oxides of mercury differ more essentially than in the fineness of their particles. The red oxide is frequently less active than the yellow. Dry chlorine acts less vigorously upon the red than upon the yellow oxide: the dispute between Gay-Lussac and Pelouze originated in this observation. Oxalic acid attacks the yellow oxide readily, the red oxide only slightly. The yellow oxide is converted into an oxychloride by alcoholic mercuric chloride; the red oxide is hardly attacked at all.[3] There is a similar difference of reactivity towards iodic acid,[4] selenic acid,[5] arsenites,[6] sulphuryl chloride,[7] hydrogen peroxide,[8] and other reagents.

The yellow oxide was often observed to volatilise more rapidly than the red, and, according to Schoch, the dissociation pressure was greater between 300° C. and 320° C. for the yellow than for the red oxide.[9] Taylor and Hulett, however, found identical pressure curves for both oxides—an indication of their absolute identity.[10] Both oxides are also similarly reduced by hydrogen at 100° C., and the yellow oxide simply decomposes five times more quickly than the red, as if it were simply more finely grained.[11] Yellow mercuric oxide, however, can be reduced by either hydrogen or carbon monoxide at lower temperatures than the red, and this greater reactivity, in conjunction with the previous examples, has been supposed to indicate that the yellow and red forms are two different physical varieties of mercuric oxide.[12]

Opinion swayed between different physical modifications and mere different size of grain. Varet, in 1895, observed that, while only the red variety of mercuric iodide is stable at ordinary temperatures, both the yellow and red varieties of the oxide are stable in the cold. Heat, also, is disengaged by the conversion of the yellow mercuric iodide into the red form. He found that, at about 12° C., 31·55 Cal. are evolved by the action of dilute hydrocyanic acid upon the red oxide. Since Berthelot had found 31·6 Cal. for the yellow oxide under similar conditions, the conversion of the one oxide into the other involves no thermal change.[13] Ostwald[14] argued from the equality of their free energies to the identity of the two oxides. He drew the same conclusion from the failure of a galvanic cell of mercury-red oxide-caustic potash-yellow oxide-mercury to give an E.M.F. The exact equivalence between the two oxides in other cells, replacement of one by the other involving no change of E.M.F., had the same implication.

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[1] Gay-Lussac, *Compt. rend.*, 1843, 16, 309.

[2] Pelouze, *ibid.*, 1843, 16, 50.

[3] Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 352.

[4] Rammelsberg, *Pogg. Annalen*, 1838, 44, 570.

[5] Köhler, *ibid.*, 1853, 89, 151.

[6] Reichard, *Ber.*, 1897, 30, 1914.

[7] Spelta, *Gazzetta*, 1904, 34, i, 262.

[8] Antropoff, *J. prakt. Chem.*, 1908, [2], 77, 273.

[9] Schoch, *Amer. Chem. J.*, 1903, 29, 323.

[10] Taylor and Hulett, *J. Physical Chem.*, 1913, 17, 565.

[11] Colson, *Compt. rend.*, 1899, 128, 1105.

[12] Fay and Seeker, *J. Amer. Chem. Soc.*, 1903, 25, 641. See Müller, *Pogg. Annalen*, 1869, 136, 62; Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 10.

[13] Varet, *Compt. rend.*, 1895, 120, 622.

[14] Ostwald, *Zeitsch. physikal. Chem.*, 1895, 18, 159.

Cohen found a small E.M.F. in the cell arranged by Ostwald corresponding to a difference between the free energies of the two oxides of the order represented by the difference between the results of Varet and Berthelot. He therefore affirmed that the two oxides were isomeric.[1] Ostwald explained that the difference in potential only implied the difference in solubility which corresponded to a difference in the size of the grains. The red oxide becomes yellower as it is more finely powdered; the finely precipitated yellow oxide is the more soluble, but the solubility of the red oxide approaches it as it is more finely powdered.[2] Hulett found an increase of solubility at 25° C. from 50 mgm. per litre to 150 with finer powdering of the oxide.[3] Schick believed with Ostwald that the red and yellow oxides only differed in their state of division. A litre of pure water at 25° C. dissolves 0·0518 grm. of yellow oxide and 0·0513 grm. of red; the corresponding quantities at 100° C. are 0·41 and 0·38 grm. The presence of hydroxyl ions increases the solubility.[4] Shortly afterwards Schoch, as noted above, ascribed different crystalline forms to the two oxides. According to Allmand, however, the red and yellow modifications both contain prisms and, apparently, quadratic plates.[5] They only differ in the size of their particles. Prolonged shaking with potassium chloride coarsens the grain by the disappearance of the finer particles, and after this treatment the same potential difference is obtained whether the initial oxide is red or yellow.[6]

Different physical modifications of one substance usually have different densities. Schoch admitted that either there is no difference in density between yellow and red mercuric oxides, or the difference is very small. He obtained for the red oxide a density at 27·5° C. of 11·08–11·11. A sample of yellow oxide had a density at 27·5° C. of 11·03, and another sample a density at 28·5° C. of 11·08. The experimental error was relatively large.[7]

Caustic potash was said to precipitate $HgO.3H_2O$ from solutions of mercuric chloride. This hydrated oxide lost no water at 200° C.[8] According to Carnelley and Walker, caustic soda precipitated the hydroxide $Hg(OH)_2$, which was stable up to about 100° C.[9] The dried precipitate, however, seems to be substantially HgO.[10]

Since the solubility of mercuric oxide in caustic soda distinctly increases with the concentration of the latter, $Hg(OH)_2$ presumably functions as a very weak acid. The ionisation constant of the first hydrogen of mercuric acid, H_2HgO_2, has been determined as $1{\cdot}7 \times 10^{-15}$.[11]

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[1] Cohen, *Zeitsch. physikal. Chem.*, 1900, 34, 69.

[2] Ostwald, *ibid.*, 1900, 34, 495.

[3] Hulett, *ibid.*, 1901, 37, 385.

[4] Schick, *ibid.*, 1902, 42, 155.

[5] For examination of the crystals of the red oxide, see des Cloizeaux, *Ann. Chim. Phys.*, 1870, [4], 20, 201.

[6] Allmand, *Zeitsch. Elektrochem.*, 1910, 16, 254. See Donnan and Allmand, *Trans. Chem. Soc.*, 1911, 99, 845.

[7] Schoch, *Amer. Chem. J.*, 1903, 29, 319. Mercuric oxide also seems to occur in transparent brown needles. See Gaudechon, *Compt. rend.*, 1907, 144, 1268.

[8] Schaffner, *Annalen*, 1844, 51, 181.

[9] Carnelley and Walker, *Trans. Chem. Soc.*, 1888, 53, 80.

[10] Schoch, *Amer. Chem. J.*, 1903, 29, 327; Siewart, *Annalen*, 1863, 125, 227.

[11] Fuseya, *J. Amer. Chem. Soc.*, 1920, 42, 370.

The solubility product $[Hg^{\cdot\cdot}].[OH']^2$ has been given as $2{\cdot}8\times10^{-25}$,[1] as 4×10^{-26},[2] and as $1{\cdot}5\times10^{-26}$.[3] Mercuric hydroxide ionises in solution step by step according to the equations

$$Hg(OH)_2 \rightleftharpoons HgOH^{\cdot}+OH',$$
$$HgOH^{\cdot} \rightleftharpoons Hg^{\cdot\cdot}+OH'.$$[4]

Svedberg obtained a *colloidal solution* by the action of the electric discharge on mercuric oxide under isobutyl alcohol.[5] Paal obtained a yellow solution by adding aqueous sodium hydroxide to mercuric protalbate or lysalbate. A similar solution was prepared by adding mercuric chloride solution to alkaline solutions of protalbic or lysalbic acids. The colloidal mercury compound, which is not dialysable, is easily reduced, especially by light, to metallic mercury.[6] The turbid solution obtained by adding mercuric chloride solution to an aqueous solution of potassium hydroxide and acetone, after filtration and dialysis, does not deposit mercury on immersed copper gauze. A clear transparent jelly gradually separates: raising the temperature increases the speed of separation. Hydrogen sulphide precipitates mercuric sulphide from solutions of the jellies. An alcosol is formed by adding an equal volume of alcohol to a 1 per cent. aqueous solution and evaporating over lime.[7] If the original dialysed solution is carefully evaporated to dryness, it leaves a resinoid residue of composition $\{(CH_3)_2.CO\}_2.3HgO$.[8]

Yellow precipitated mercuric oxide reacts to some extent with a 10 per cent. solution of sodium bicarbonate according to the equation

$$HgO+2NaHCO_3=Na_2CO_3+HgCO_3+H_2O.$$[9]

Sulphur monochloride converts mercuric oxide almost completely into mercuric chloride—

$$2HgO+2S_2Cl_2=2HgCl_2+SO_2+3S.$$[10]

Solutions of silver sulphate, silver nitrate, and silver acetate dissolve yellow mercuric oxide. Pale yellow rhombic tablets of $Ag_2SO_4.HgO$, and acicular crystals of reddish-yellow $AgNO_3.2HgO$, have been isolated from their respective solutions.[11]

The reaction

$$HgO+4KI+H_2O=K_2HgI_4+2KHO$$

has been used to standardise acids for volumetric analysis. About 0·4 grm. of the yellow oxide is treated with 10 c.c. of 60 per cent. potassium iodide solution. As soon as the oxide is dissolved the titration is performed. Methyl orange, or methyl red, or phenolphthalein can be used as indicator. Yellow mercuric oxide, thus used, is a trustworthy alkalimetric standard, because it is non-hygroscopic and can be obtained in a pure, anhydrous condition.[12]

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[1] Allmand, *Zeitsch. Elektrochem.*, 1910, 16, 260.

[2] Grossmann, *Zeitsch. anorg. Chem.*, 1905, 43, 368.

[3] Abegg and Latendzinski, *Zeitsch. Elektrochem.*, 1904, 10, 80.

[4] Kolthoff, *Chem. Weekblad.*, 1917, 14, 1016.

[5] Svedberg, *Ber.*, 1906, 39, 1705.

[6] Paal, *Ber.*, 1902, 35, 2219.

[7] Bunce, *J. Physical Chem.*, 1914, 18, 269.

[8] Emerson and Reynolds, *Proc. Roy. Soc.*, 1870, 19, 431.

[9] Tichborne, *Sci. Proc. Roy. Dubl. Soc.*, 1904, 10, 331.

[10] Oddo and Giachery, *Gazzetta*, 1923, 53, i, 63.

[11] Finzi, *ibid.*, 1911, 41, ii, 543.

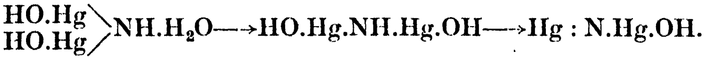
[12] Incze, *Zeitsch. anal. Chem.*, 1907, 56, 177. Rosenthaler and Abelmann (*Pharm. J.*, 1913, 91, 144) also advised the use of mercuric oxide as a volumetric standard. *Cf.* Incze, *Zeitsch. anal. Chem.*, 1918, 57, 176.

Determinations of the heat of formation of mercuric oxide from liquid mercury and gaseous oxygen have varied from 20·7 Cal. to 22·0 Cal.[1]

The yellow product of the action of aqueous ammonia on mercuric oxide, known as *Millon's base*, has the empirical formula $Hg_2NH_5O_3$. When dried over caustic potash in an atmosphere of ammonia it darkens, and loses 1 molecule of water to form $Hg_2NH_3O_2$. The compound Hg_2NHO is formed by the loss of 2 molecules of water when the original base is heated at 125° C. in ammonia : it is a dark brown explosive powder. Absolute alcohol completely dehydrates Millon's base, and mercuric oxide is formed.[2] The explosive dehydrated product is also formed by heating dried yellow mercuric oxide in ammonia at 120° C.[3]

Salts of Millon's base have the formula $Hg_2NH_2O.X$: Soubeiran's salt, for example, which has been prepared by the action of ammonia in slight excess on a dilute solution of mercuric nitrate, and by precipitating a solution of mercury acetamide with ammonium nitrate,[4] is $Hg_2NH_2O.NO_3$. The chloride, $Hg_2NH_2O.Cl$, is well characterised ; it is formed by the action of dilute hydrochloric acid on Millon's base, and by other methods.[5]

Millon's base has been variously formulated,[6] but, according to Franklin,[7] its constitution is better represented by the formula HO.Hg. NH.Hg.OH.H_2O, or by $(HOHg)_2.NH_2OH$, as Hofmann and Marburg expressed it,[8] or by HO.Hg.O.Hg.NH_3OH, as Fürth preferred,[9] than by any other constitutive formula. Franklin also suggested the representation of its successive dehydration thus :—



$$\left.\begin{matrix}HO.Hg\\HO.Hg\end{matrix}\right\rangle NH.H_2O \longrightarrow HO.Hg.NH.Hg.OH \longrightarrow Hg : N.Hg.OH.$$

The chloride would then be HO.Hg.NH.Hg.Cl. Weitz formulated the chloride as $HgO.Hg(NH_2)Cl$.[10, 11]

The brown, amorphous base, $(NHg_2)_2O$, has been prepared by acting on mercuric oxide at 100° C. with gaseous ammonia. The yellow, amorphous tetrahydrate, $(NHg_2)_2O.4H_2O$, has been obtained by acting on freshly precipitated yellow mercuric oxide, either undried or dried at 15° C., with ammonia. This tetrahydrate is stable from 0° C. to 20° C. if the air is saturated with moisture and free from carbon dioxide. It passes into the brown, amorphous monohydrate in dry air containing ammonia. The monohydrate reverts to the tetrahydrate in a moist atmosphere. If the tetrahydrate is heated in an atmosphere of ammonia at 100° C. it dehydrates into the brown, amorphous, anhydrous base. This product, unlike the product of gaseous ammonia on mercuric oxide, absorbs water from a moist atmosphere and becomes the tetrahydrate. The finely ground base slowly decomposes into ammonia and mercuric oxide when boiled with water: the mercuric oxide forms in transparent brown needles.[1] This reaction may be reversible.

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[1] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 100.

[2] Millon, *ibid.*, 1846, [3], 18, 392 ; Hofmann and Marburg, *Annalen*, 1899, 305, 191.

[3] Weyl, *Pogg. Annalen*, 1864, 121, 601.

[4] Soubeiran, *J. Pharm. Chim.*, 1826, [2], 12, 465, 509, 561 ; Fürth, *Monatsh.*, 1902, 23, 1147.

[5] Hofmann and Marburg, *loc. cit.* ; Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 60.

[6] Millon, *loc. cit.* ; Gerresheim, *Annalen*, 1879, 195, 373 ; Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 558.

[7] Franklin, *loc. cit.*, 35.

[8] Hofmann and Marburg, *loc. cit.*

[9] Fürth, *loc. cit.*

[10] Weitz, *Annalen*, 1915, 410, 162.

[11] For various other compounds, see Mitscherlich, *Pogg. Annalen*, 1827, 9, 97; Kane, *Ann. Chim. Phys.*, 1839, [2], 72, 242 ; Millon, *loc. cit.* ; Weyl, *loc. cit.* ; Gerresheim, *loc. cit.* ; Rammelsberg, *loc. cit.* ; Pesci, *Gazzetta*, 1890, 20, 485 ; 1891, 21, ii, 571 ; *Zeitsch. anorg. Chem.*, 1899, 21, 363 ; Hofmann and Marburg, *loc. cit.* ; Franklin, *loc. cit.* ; Stromholm, *Zeitsch. anorg. Chem.*, 1908, 57, 86 ; Gaudechon, *Compt. rend.*, 1907, 144, 1268 ; *Ann. Chim. Phys.*, 1911, [8], 22, 148.

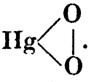
The heat of formation of solid $(NHg_2)_2O$ from liquid mercury, gaseous ammonia, and gaseous oxygen is —75·5 Cal. Its endothermic nature corresponds to its explosive character. A pentahydrate probably exists.[2]

Mercuric Peroxide.—Hydrogen peroxide decomposes in contact with mercury with a periodically varying rate of decomposition.[3] Slightly alkaline solutions of the peroxide react in this periodic way. The decomposition is more rapid and continuous in strongly alkaline solutions, and the mercury is slowly oxidised when the solution is acid.[4] A yellowish or brownish-black skin remains after the evolution of oxygen during the periodic contact catalysis of hydrogen peroxide by mercury. This substance decomposes too violently and too easily into mercury and oxygen to be analysed. It may be mercurous peroxydate, or the mercurous salt of hydrogen peroxide, Hg_2O_2.

Concentrated hydrogen peroxide converts this skin into an explosive, brownish-red compound that has the composition HgO_2. Hydrogen peroxide acts explosively on mercurous oxide, even when free acid is present. The violence ceases, however, after repeated additions of the peroxide, and dark red HgO_2 is formed. Hydrogen peroxide, therefore, oxidises both mercury and mercurous oxide into mercury peroxide.

The brownish-red mercury peroxide can be more readily prepared by the action of hydrogen peroxide on red mercuric oxide. If the oxide is finely powdered till its colour is yellow the product is paler and more unstable. Some samples of the red oxide decompose hydrogen peroxide with the evolution of oxygen, but the addition of a little nitric acid induces the formation of the mercury peroxide. Yellow mercuric oxide cannot be substituted for the red.

Mercury peroxide is also formed by interaction between an alcoholic solution of mercuric chloride and hydrogen peroxide in the presence of alcoholic potassium hydroxide solution. This precipitated compound is less stable than the other.

The red peroxide appears to be mercuric peroxydate, the mercuric salt of hydrogen peroxide, . Acids dissolve it to form mercuric salts and hydrogen peroxide. It also reacts with potassium iodide and potassium permanganate like a true peroxide.

Water hydrolyses it slowly at 0° C.: the washings contain hydrogen peroxide, and mercuric oxide is ultimately formed. Hydrolysis is more vigorous at higher temperatures; traces of alkali accelerate it; traces of acid are retardive.

The compound is comparatively stable at ordinary temperatures when dry. It explodes, however, when struck, and the product from the finely powdered oxide will even explode if it is rubbed when still moist. It can leave a grey residue by rapid decomposition, as during drying, or decompose slowly into oxygen and red mercuric oxide. It does not seem to be affected by light. Since mercury is more feebly positive than magnesium, zinc, and cadmium, its peroxide is much less stable than the peroxides of these metals.

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[1] Gaudechon, *loc. cit.* [2] Gaudechon, *loc. cit.*, 1419.

[3] Bredig and Weinmayr, *Zeitsch. physikal. Chem.*, 1903, 42, 601.

[4] Bredig and Wilke, *Chem. Zentr.*, 1905, i, 64.

Hydrogen peroxide will not convert red oxide of mercury into the peroxide unless the solution is sufficiently concentrated : a 30 per cent. solution gives good results ; a 15 per cent. solution is ineffective.[1]

MERCURY AND SULPHUR.

Mercurous and Mercuric Sulphides.—Mercuric sulphide, HgS, occurs naturally as vermilion-coloured *cinnabar* which crystallises rhombohedrally in the hexagonal system. It has a hardness of 2·0–2·5 and a density (D^{25}_{4}) of 8·176.[2] Some specimens from Serbia and Austria are radioactive.[3] Cinnabar is the stable form of mercuric sulphide up to its sublimation point at about 580° C.[4] This σ-HgS is readily prepared by digesting any other form of mercuric sulphide with a solution of alkali sulphide.[2]

A crystalline powder, coloured like cinnabar, of β'-HgS, is obtained by precipitating solutions of sodium mercuric chloride, of suitable concentration, with sodium thiosulphate. Its density at 25° C. is 7·20.[2]

Metacinnabar, which occurs naturally as a black crystalline mineral, apparently iosmetric, represents a form α'-HgS. It has been prepared by the action of an excess of sodium thiosulphate on sodium mercuric chloride in dilute solution containing a little sulphuric acid. The density of the artificial product at 25° C. was 7·60,[2] which corresponds closely to determinations of the density of the mineral.[5]

The action of sodium thiosulphate upon sodium mercuric chloride in solution produces white mercuric chlorosulphide, $HgCl_2.2HgS$, or amorphous black HgS, or the red β'-HgS, or the black α'-HgS, or admixtures of these, according to conditions.[6]

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[1] Antropoff, *Zeitsch. Elektrochem.*, 1906, **12**, 585 ; *J. prakt. Chem.*, 1908, [2], **77**, 272 ; Pellini, *Atti R. Accad. Lincei*, 1907, [5], **16**, ii, 408.

[2] Allen and Crenshaw, *Amer. J. Sci.*, 1912, [4], **34**, 367.

[3] Losanitsch, *Ber.*, 1904, **37**, 2904.

[4] According to Pélabon (*Compt. rend.*, 1905, **140**, 1391), mercuric sulphide sublimes at about 590° C.

[5] Moore, *Amer. J. Sci.*, 1872, [3], **3**, 36 ; Genth and Penfield, *Amer. J. Sci.*, 1892, [3], **44**, 383. Spring (*Zeitsch. anorg. Chem.*, 1894, **7**, 371) obtained a black form, of density 8·0395 at 17° C., by subliming ordinary mercuric sulphide in an inert gas. It was converted into cinnabar by pressure or ammonium sulphide.

[6] Allen and Crenshaw, *Amer. J. Sci.*, 1912, [4], **34**, 369. According to Sander (*Zeitsch. angew. Chem.*, 1916, **29**, 11), mercuric thiosulphate is formed when sodium thiosulphate acts on mercuric chloride solution, which decomposes, under hydrolysis, into mercuric sulphide and sulphuric acid. White mercuric chlorosulphide is then formed by interaction between the sulphide and chloride of mercury. Feld (*Zeitsch. angew. Chem.*, 1911, **24**, 290, 1161) said that the mercuric chloride is converted into black mercuric sulphide or reduced to calomel. Herschel (*Edin. Philos. J.*, 1819, **1**, 28) obtained a yellow precipitate with calcium thiosulphate. Rose (*Pogg. Annalen*, 1834, **33**, 240) obtained a white precipitate with thiosulphate, which became yellow, then brown, and finally black on standing. Kessler (*J. prakt. Chem.*, 1849, **47**, 42) obtained a white precipitate by the action of trithionate on mercuric chloride, and a yellow by the action of tetra- or pentathionate. Vortmann (*Ber.*, 1889, **22**, ii, 2307) obtained black HgS by the action of sodium thiosulphate on mercuric salts. The filtrate contained sulphate, a little tetrathionate, and no pentathionate. Hausmann (*Ber.*, 1874, **7**, 1746) prepared cinnabar by warming a solution of mercuric chloride with dilute ammonia solution and sodium thiosulphate.

Yellow $HgCl_2.2HgS$ was said to be obtained by passing chlorine into freshly precipitated mercuric sulphide, and bright yellow $HgCl_2.2HgS$, $HgCl_2.3HgS$, and $HgCl_2.4HgS$ by the action of mercuric chloride solution on mercuric sulphide,[1] but, according to Jolibois and Bouvier, the series of colours, from white to black, observed when a solution of mercuric chloride is precipitated by hydrogen sulphide, is due to the formation of $HgCl_2.2HgS$ only, which is converted into black HgS by excess of the gas.[2]

If mercuric iodide in alcoholic solution is first reduced by hydrogen sulphide to mercurous iodide, which is then converted into tobacco-coloured $HgI_2.2HgS$, and finally into HgS, the action of hydrogen sulphide on mercuric salts may be represented by the stages (*a*) mercuric salt, (*b*) mercurous salt, (*c*) $Hg({\cdot}S{\cdot}HgR)_2$, (*d*) HgS.[3]

The black precipitate produced by hydrogen sulphide with mercurous salts was said to be a mixture of mercuric sulphide and mercury,[4] though some *mercurous sulphide* may be simultaneously obtained when the gas acts on mercurous chloride under pressure.[5] Mercurous sulphide was said to be produced by covering mercury with pure concentrated sulphuric acid and allowing the mixture to stand for five years in a stoppered bottle. The brownish-black plates went white when heated in a closed tube, then yellow, and finally melted to a dark orange-coloured liquid that cooled to a white solid.[6] Hg_2S has been obtained by the action of dry hydrogen sulphide and carbon dioxide on pure, dry mercurous chloride at $-10°$ C., or of dry hydrogen sulphide alone on dry mercurous acetate at the same temperature. It is a black powder, oxidised by fuming nitric acid but not affected by alkali hydroxides, ammonia, ammonium sulphide, and dilute nitric or hydrochloric acid below 0° C. It decomposes above 0° C. into mercuric sulphide and mercury.[7]

Black mercuric sulphide can be precipitated by hydrogen sulphide from solutions of mercuric salts containing half their volume of concentrated hydrochloric acid.[8] According to Linder and Picton, the precipitate from the chloride, with or without slight acidification, contains a small quantity of combined hydrogen sulphide. The washed sulphide dissolves in a solution of hydrogen sulphide to a dark brown solution. This solvent effect does not occur if the mercuric sulphide is previously boiled with water or heated to 100° C.[9] The concentrated *colloidal solution* of mercuric sulphide is black and opaque; more dilute solutions are brown, with a slightly greenish tint by reflected light.[10]

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[1] Poleck and Goercki, *Ber.*, 1888, **21**, 2412.

[2] Jolibois and Bouvier, *Compt. rend.*, 1920, **170**, 1497.

[3] Franceschi, *Boll. Chim. farm.*, 1916, **45**, 481. $HgBr_2$ behaves analogously (Franceschi, *Boll. Chim. farm.*, 1918, **47**, 221). Bernardi and Rossi (*Gazzetta*, 1922, **52**, i, 139) obtained silky needles of $S(Hg{\cdot}CO_2{\cdot}CH_3)_2$ by the action of carbon disulphide on a cold saturated solution of mercuric acetate.

[4] Guibourt, *Ann. Chim. Phys.*, 1816, [2], **1**, 424; Barfoed, *J. prakt. Chem.*, 1864, [1], **93**, 230.

[5] Weinschenk, *Zeitsch. Kryst. Min.*, 1890, **17**, 498.

[6] Baskerville, *J. Amer. Chem. Soc.*, 1903, **25**, 799.

[7] Antony and Sestini, *Gazzetta*, 1894, **24**, i, 193.

[8] Clarens, *Bull. Soc. chim.*, 1916, [4], **19**, 154.

[9] Linder and Picton, *Trans. Chem. Soc.*, 1892, **61**, 123.

[10] Wenssiger, *Bull. Soc. chim.*, 1888, [2], **49**, 452. For properties, see Picton, *Trans. Chem. Soc.*, 1892, **61**, 138. For precipitation by electrolytes, see Freundlich and Schucht, *Zeitsch. physikal. Chem.*, 1913, **85**, 643. For adsorbtive properties, see Freundlich and Hase, *ibid.*, 1915, **89**, 417.

A colloidal solution of mercuric sulphide also results when hydrogen sulphide is passed through very dilute solutions of mercuric chloride containing formic or citric acid,[1] and a stable hydrosol is obtained by the action of hydrogen sulphide on mercuric cyanide solution and carefully distilling off the hydrogen cyanide.[2]

Sufficiently dilute colloidal solutions of mercuric sulphide in hydrogen sulphide solution can be boiled till the hydrogen sulphide is expelled or kept for more than a month without alteration.[3]

A deep dark brown colloidal solution is obtained by passing hydrogen sulphide through a saturated solution of mercuric cyanide in 97 per cent. alcohol. This alcosol is fairly stable, especially in the presence of hydrogen sulphide.[4]

Colloidal solutions of mercuric sulphide in various organic media have been prepared.[5]

The insolubility of mercuric sulphide precipitated by hydrogen sulphide in hydrochloric or nitric acid is used in analysis.[6] It is usually separated from soluble sulphides by mixing either acid with its own volume of water. Concentrated hydrochloric acid appears to have some action.[7] Ordinary, pure, boiling nitric acid (density 1·42) appears to have no action,[8] but it converts the sulphide into sulphate if the heating is done in a sealed tube at 120° C.[9] The compound $Hg(NO_3)_2.2HgS$ was obtained by prolonged boiling of HgS with nitric acid of density 1·52, and white crystalline $2Hg(NO_3)_2.HgO.6HgS.12H_2O$ by heating either the black sulphide or cinnabar to 120° C. in a sealed tube with acid of density 1·2.[9] According to Howe, yellowish-white $Hg(NO_3)_2.2HgS$ is produced by the action of concentrated boiling nitric acid on mercuric sulphide if a little hydrochloric acid is present, which dissolves in a rather larger quantity of the latter acid.[8]

Mercuric sulphide dissolves readily in aqua regia or hydrobromic acid.[10] Hydrogen sulphide will only precipitate a very dilute solution of mercuric iodide in hydriodic acid, and mercuric sulphide, crystalline or amorphous, dissolves in concentrated hydriodic acid when cold and in more dilute acid when warm.[11]

A mixture of equal volumes of potassium sulphide and potassium hydroxide dissolves precipitated mercuric sulphide,[12] and all mercuric sulphides dissolve easily in concentrated solutions of sodium or potassium sulphide.[13] A solution containing 1·52 molecule per litre of sodium sulphide dissolves 0·7832 molecule per litre of the red sulphide and 0·8561 of the black. With more concentrated solutions the solubility of the black sulphide cannot be determined, because it changes too rapidly into the red variety.[1]

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[1] Proctor and Seymour-Jones, *J. Soc. Chem. Ind.*, 1911, 30, 404.

[2] Lottermoser, *J. prakt. Chem.*, 1907, [2], 75, 293.

[3] Wenssinger, *Bull. Soc. chim.*, 1888, [2], 49, 452.

[4] Ostwald, *Trans. Faraday Soc.*, 1921, 16, 90.

[5] Lefort and Thibault, *J. Pharm. Chim.*, 1882, [5], 6, 169; Hausmann, *Zeitsch. anorg. Chem.*, 1904, 40, 122; Pieroni, *Gazzetta*, 1913, 43, i, 197; Lewis and Waumsley, *J. Soc. Chem. Ind.*, 1912, 31, 518.

[6] Antony and Niccoli, *Gazzetta*, 1892, 22, ii, 408.

[7] Berthelot, *Jahresber.*, 1874, 119.

[8] Howe, *Amer. Chem. J.*, 1886, 8, 75.

[9] Gramp, *J. prakt. Chem.*, 1876, [2], 14, 299.

[10] Rising and Lenher, *J. Amer. Chem. Soc.*, 1896, 18, 96.

[11] Kekulé, *J. prakt. Chem.*, 1862, [1], 87, 471. See Gutman, *Biochem. Zeitsch.*, 1918, 89, 199.

[12] Polstorff and Bülow, *Arch. Pharm.*, 1891, 229, 292.

[13] Allen and Crenshaw, *Amer. J. Sci.*, 1912, [4], 34, 368.

The predominant complex in solutions of mercuric sulphide in sodium sulphide is $Na_2S.HgS$, though yellow crystals of $2Na_2S.5HgS.3H_2O$ have been obtained.[2]

The *double sulphides* of potassium and mercury, $K_2S.HgS$,[3] $K_2S.HgS.H_2O$,[3] $K_2S.HgS$ $5H_2O$,[3, 4] $K_2S.HgS.7H_2O$,[3] $K_2S.2HgS$,[4] $K_2S.5HgS.5H_2O$,[3] have been described.

In the wet process for preparing vermilion, in which black mercuric sulphide is digested with potassium sulphide at a temperature not exceeding 45° C., the compound $K_2S.5HgS$, according to Ditte,[5] is successively formed and decomposed with the formation of the red sulphide until the original sulphide is all transformed.

Though the slight solubility of mercuric sulphide in ammonia may affect toxicological estimations of small amounts of mercury,[6] mercuric sulphide is virtually insoluble in ammonia, ammonium sulphide, sodium or potassium hydroxide. Cinnabar is slightly soluble in sodium carbonate solution[7] and dissolves in sulphur monochloride.[8]

Mineral cinnabar has probably been deposited from alkali sulphide solutions of mercury,[9] and metacinnabar is probably a characteristic secondary mineral deposited from acid solutions.[10]

Mercuric sulphide, red or black, is not acted upon by sulphuric acid at ordinary temperatures. Sulphur dioxide is perceptible at 115° C., freely evolved at 150° C., and sulphur sensibly sublimes at 175° C. with the black sulphide. Cinnabar reacts similarly but less readily.[11] The boiling acid converts the sulphide largely into mercuric sulphate but partly into sulphato-sulphide, probably $HgSO_4.2HgS$, which apparently decomposes on prolonged action.[12]

The heat of reaction from black amorphous mercuric sulphide to the red amorphous form is, according to Varet,[13] 0·240 Cal., and from red amorphous to red crystalline 60 Cal. When hydrogen sulphide acts upon mercuric oxide suspended in water the heat of reaction is 24·350 Cal.[14]

Mercuric sulphide fuses at 1450° C. under a pressure of 120 atmospheres, and a steel-grey matt solid results that goes red when rubbed,[15] and, in addition to the production of cinnabar by treatment, under various conditions, of other mercuric sulphides with ammonium or alkali sulphides,[16] various organic compounds, containing mercury and sulphur, form red mercuric sulphide when shaken with ammonium sulphide.[1] Small red crystals of cinnabar were also obtained by heating mercury at 70°–90° C. on a water-bath for six days in an atmosphere of hydrogen sulphide.[2]

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[1] Knox, *Zeitsch. Elektrochem.*, 1906, **12**, 477.

[2] Knox, *Trans. Faraday Soc.*, 1908, **4**, 29. According to Allen and Crenshaw (*Amer. J. Sci.*, 1912, [4], **34**, 368), $2Na_2S.HgS$ also exists.

[3] Ditte, *Ann. Chim. Phys.*, 1907, [8], **12**, 229.

[4] Schneider, *J. prakt. Chem.*, 1866, [1], **98**, 238.

[5] Ditte, *Compt. rend.*, 1884, **98**, 1380.

[6] Ghigliotto, *Ann. Chim. anal.*, 1923, **5**, 326.

[7] Ippen, *J. Chem. Soc.*, 1896, **70**, Abs. ii, 108.

[8] Smith, *J. Amer. Chem. Soc.*, 1898, **20**, 291.

[9] Becker, *Amer. J. Sci.*, 1887, [3], **33**, 199.

[10] Allen and Crenshaw, *ibid.*, 1912, [4], **34**, 367.

[11] Berthelot, *Ann. Chim. Phys.*, 1898, [7], **14**, 198. He observed no hydrogen sulphide.

[12] Divers and Shimidzu, *Chem. News*, 1885, **51**, 193.

[13] Varet, *Compt. rend.*, 1895, **120**, 1114.

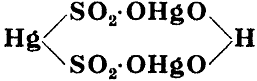
[14] Berthelot, *ibid.*, 1874, **78**, 1175.

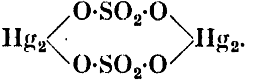
[15] Tiede and Schleede, *Ber.*, 1920, **53B**, 1717.

[16] Ippen, *J. Chem. Soc.*, 1896, **70**, ii, 108; Allen and Crenshaw, *Amer. J. Sci.*, 1912, [4], **34**, 367.

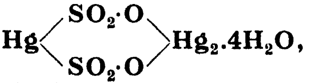
Vermilion has been commercially prepared by many modifications of the wet process in which alkali sulphides act upon amorphous mercuric sulphide. Chinese vermilion, famous for its fine colour, is said to be prepared by the direct combination of sulphur and mercury under heat[3] or by purifying fine cinnabar by sublimation.[4] Picton and Linder[5] advised the preparation of a colloidal solution by suspending precipitated mercuric sulphide in water and passing in hydrogen sulphide. Pure vermilion is deposited when this solution is heated for several hours in a closed vessel at 160°–170° C.

Light has a darkening effect on the surface of cinnabar,[6] and the substance dissociates into mercury and sulphur above a red heat.[7]

Mercuric Oxysulphite,  $\mathrm{Hg}\left\langle\begin{matrix}\mathrm{SO_2{\cdot}OHgO}\\ \mathrm{SO_2{\cdot}OHgO}\end{matrix}\right\rangle\mathrm{Hg.H_2O}$, is precipitated as a faintly yellow, curdy, or granular salt from solutions of normal mercuric nitrate, slightly acid with nitric acid, by solutions of normal sodium sulphite or mercuric sodium sulphite. Silver sulphite also precipitates it from a solution of mercuric nitrate, and an alkaline solution of sodium sulphite or mercuric sodium sulphite from mercuric sulphate solution.

Even when rendered anhydrous *in vacuo* over sulphuric acid it gradually changes into mercurous sulphate,  $\mathrm{Hg_2}\left\langle\begin{matrix}\mathrm{O{\cdot}SO_2{\cdot}O}\\ \mathrm{O{\cdot}SO_2{\cdot}O}\end{matrix}\right\rangle\mathrm{Hg_2}$. The change is more rapid when moisture is present.

Mercuric oxysulphite is explosive, and decomposes on heating with water. The action of aqueous hydrochloric acid, which converts it into mercuric chloride and sulphurous acid, indicates that it is a sulphite.

Mercurosic Sulphite,  $\mathrm{Hg}\left\langle\begin{matrix}\mathrm{SO_2{\cdot}O}\\ \mathrm{SO_2{\cdot}O}\end{matrix}\right\rangle\mathrm{Hg_2.4H_2O}$, is temporarily formed during the gradual addition of hydrochloric acid to mercuric oxysulphite. Mercurosic sulphite also results from the action of aqueous sulphurous acid on mercuric oxide, or mercuric nitrate solution, or mercuric sulphate solution. It is also formed when a warm solution of mercuric sodium sulphite acts on mercuric oxide. It is produced by the action of mercuric sodium sulphite solution on mercurous sulphate or mercurous nitrate solution, and when hypomercurosic sulphite acts on a solution of either mercuric nitrate or mercuric sulphate.

It is amorphous or crystalline according to conditions, and may apparently be pale buff as well as white. It is insoluble in water, very efflorescent, and, though subject to discoloration, fairly stable when dry. It decomposes at 80° C., and is tumultuously converted into mercury and sulphuric acid by treatment with water. Since hydrochloric acid decomposes it into sulphurous acid and the two chlorides of mercury, it is a sulphite and both a mercuric and mercurous salt.

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[1] Alvisi, *Real. Accad. dei Linc.*, 1898, 7, 97.

[2] Doelter, *Zeitsch. Kryst. Min.*, 1885, 11, 29.

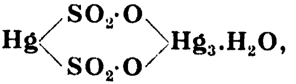
[3] *J. Soc. Chem. Ind.*, 1882, 1, 95.

[4] *Ibid.*, 1890, 9, 1047.

[5] English Patent, 5120 (1892).

[6] Heumann, *Ber.*, 1874, 7, 750.

[7] V. and C. Meyer, *ibid.*, 1879, 12, 1112. Pélabon (*Compt. rend.*, 1901, 132, 1411) has studied the reaction (reversible) between mercuric sulphide and hydrogen.

Hypomercurosic Sulphite,  $\mathrm{Hg}\left\langle\begin{matrix}\mathrm{SO_2{\cdot}O}\\ \mathrm{SO_2{\cdot}O}\end{matrix}\right\rangle\mathrm{Hg_3.H_2O}$, is formed when aqueous sulphurous acid acts upon mercuric oxysulphite, or mercurosic sulphite, or mercurous sulphate, or mercurous nitrate solution, when sodium sulphite solution acts upon mercuric oxysulphite, or mercurosic sulphite, or mercurous sulphate, or mercurous nitrate solution, or mercurous chloride, and when silver sulphite reacts with an aqueous solution of either mercurous nitrate or mercurous sulphate.

It is a greyish-black, amorphous substance, voluminous and flocculent. It is fairly stable when dry, but sensitive to moisture and readily decomposed by water. A temperature of 80° C. rapidly decomposes the dry salt. Its behaviour with reagents indicates that it is a mercuric hypomercurous salt.

The mercury sulphites resemble the sulphonates in not suffering atmospheric oxidation, and their acid radicle has a partly haloid character.[1]

If precipitated mercuric oxide is added, finely divided and suspended in water, to aqueous sulphurous acid that does not contain much sulphuric acid, the solution reacts as if it were mercuric sulphite dissolved in sulphurous acid. Only a weak solution can be prepared which probably contains mercuric hydrogen sulphite, $Hg(SO_2.OH)_2$. The solution is very unstable and hydrolyses readily. Mercuric oxysulphite can be substituted for mercuric oxide, and several other methods of preparation are possible.

The reactions of the double sulphites of mercury and the alkalies, such as $Na_2SO_3.HgSO_3.H_2O$, indicate that they should be considered as salts of mercury sulphonic acid and be formulated as $Hg(SO_2.OR)_2.XH_2O$.[2] This is confirmed by the electrolytic and cryoscopic behaviour of their solutions.[3] Solutions of sodium mercuric sulphite, either on warming or standing, also decompose into sodium sulphate, sulphur dioxide, and mercury without any sign of dithionic acid.[4] Unstable $Ag_2SO_3.HgSO_3$[5] seems to have been prepared.

Mercurous Sulphate, Hg_2SO_4, is a white powder that may be amorphous and pulverulent[6] or crystalline. It can be prepared by treating mercury dissolved in nitric acid, or a solution of mercuric nitrate, with sulphuric acid,[7] or a solution of sodium sulphate.[6] By adding a solution of mercury in nitric acid to an excess of sulphuric acid diluted with four volumes of water, drop by drop, the precipitated salt is said to be free from nitrate.[1] The commercial product can be purified from nitrate by heating with a little mercury and concentrated sulphuric acid at 150° C. and pouring into dilute sulphuric acid,[1] or by heating with a little mercury and dilute sulphuric acid in a sealed tube.[2] White crystalline mercurous sulphate can also be obtained by acting upon excess of mercury with sulphuric acid at moderate temperatures,[3] but mercury is preferably allowed to stand in the cold in contact with fuming sulphuric acid rich in sulphur trioxide. The excess of sulphur trioxide can be subsequently expelled by warming.[4] The product may be finally added to dilute sulphuric acid.[1] Pure crystals of mercurous sulphate are obtained by electrolysing sulphuric acid with a mercury anode. No mercuric salt contaminates the salt deposited on the mercury. Wolff used a mercury cathode and 5 per cent. acid.[5] Carhart and Hulett used a platinum sheet cathode, acid diluted with six volumes of water, and a current of 0·3 amp. Some finely divided mercury, according to them, deposits with the mercurous sulphate and prevents the formation of mercuric sulphate.[6]

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[1] Divers and Shimidzu (*Trans. Chem. Soc.*, 1886, 49, 533; *Proc. Chem. Soc.*, 1886, 2, 139), who made a lengthy study of the mercury sulphites, decided that other sulphites described by various chemists do not seem to exist. Péan de Saint-Gilles (*Ann. Chim. Phys.*, 1852, [3], 36, 80. See also *Annalen*, 1852, 84, 264) investigated the mercury sulphites. Also see Rammelsberg, *Pogg. Annalen*, 1846, 67, 405; Wicke, *Annalen*, 1855, 95, 176.

[2] Divers and Shimidzu, *Trans. Chem. Soc.*, 1886, 49, 533; *Proc. Chem. Soc.*, 1886, 2, 139.

[3] Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 176.

[4] Baubigny, *Compt. rend.*, 1912, 155, 833.

[5] Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 195.

[6] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 117.

[7] Wackenroder, *Annalen*, 1842, 41, 319; Städeler, *ibid.*, 1853, 87, 132.

Mercurous sulphate is also obtained when mercuric sulphate and mercury are rubbed and moistened with alcohol or water or a little sulphuric acid.[7]

The solubility of mercurous sulphate in water is 0·055 per cent. at 16·5° C. and 0·092 at 100° C.:[8] it is depressed in the presence of sulphuric acid or potassium sulphate.[8, 9] The deposition of mercury on the platinum cathode when the electrolytic preparation of mercurous sulphate has been proceeding for some time indicates the slight solubility of the salt.[6] Since washing with pure water converts it into a basic salt, it should be washed with water acidified with sulphuric acid.[6] The yellow *basic sulphate* produced by the action of water has a greenish tinge, has the composition $Hg_2O.Hg_2SO_4.H_2O$, and dissolves in 25,000 parts of water at 20° C. Water containing 0·08 grm. sulphuric acid per litre does not convert the normal into the basic salt, and with higher proportions of acid the basic salt is converted into the normal.[10]

The crystals of mercurous sulphate are monoclinic,[11] and isomorphous with mercurous nitrate.[12] Those taken from a dismantled mercury furnace at Idria had a density of 8·353.[13] The specific heat of the substance between 18·5° C. and 22·5° C. is 0·06400,[1] and its molecular heat varies from 16·74 at −190° C. to 25·9 at −70° C.,[2] and 31·83 at +18·5°–22·5° C.[1] The heat of formation of the solid from liquid mercury, gaseous oxygen, and solid sulphur is 175·0 Cal., and from solid mercurous oxide and sulphur trioxide 49·0 Cal.[3]

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[1] Smith, *Brit. Assoc. Report*, 1905, 100.

[2] Fox, *Brit. Assoc. Report*, 1909, 457.

[3] Baskerville and Miller, *J. Amer. Chem. Soc.*, 1897, 19, 873.

[4] Divers and Shimidzu, *Trans. Chem. Soc.*, 1885, 47, 639.

[5] Wolff, *Trans. Amer. Electrochem. Soc.*, 1904, 5, 56.

[6] Carhart and Hulett, *Trans. Amer. Electrochem. Soc.*, 1904, 5, 61. For methods of preparation, also see Smith, *Proc. Roy. Soc.*, 1908, 80A, 75.

[7] Hada, *Trans. Chem. Soc.*, 1896, 69, 1672.

[8] Barre, *Ann. Chim. Phys.*, 1911, [8], 24, 145. Slightly lower values have been given. See Wright, *Phil. Mag.*, 1884, [5], 17, 288; Wilsmore, *Zeitsch. physikal. Chem.*, 1900, 35, 305.

[9] Drucker, *Zeitsch. anorg. Chem.*, 1901, 28, 361. (Solubility in water=0·58 grm. per litre at 25° C.)

[10] Gouy, *Compt. rend.*, 1900, 130, 1399. Cox confirmed $Hg_2O.Hg_2SO_4.H_2O$, and found no other basic phase (*Zeitsch. anorg. Chem.*, 1904, 40, 179). According to Hada (*Trans. Chem. Soc.*, 1896, 69, 1672), boiling with water effects a slight conversion into mercuric sulphate, mercury, and sulphuric acid. Barre (*Ann. Chim. Phys.*, 1911, [8], 24, 145) suggested that the effect of washing with water is rather more complicated than represented by Gouy, since some metallic mercury is also produced.

[11] de Schulten, *Bull. Soc. franç. Min.*, 1903, 26, 113.

[12] Carhart and Hulett, *loc. cit.*

[13] Seyfriedsberger, *Zeitsch. Kryst. Min.*, 1890, 17, 433.

Light soon turns mercurous sulphate grey, and the discoloration was referred to the formation of an oxy-salt.[4] Though the substance may become dark brown or black on exposure, the change seems to be superficial,[5] and mercurous sulphate need not be classed among the unstable compounds.[6] Buchner advised that mercurous sulphate should be kept moist and in contact with metallic mercury. He thought that water reversed the change into mercuric sulphate and mercury effected by light,[6] but Skinner, who found that the ultra-violet rays were responsible for the darkening, thought that either a sub-salt was formed or polymerisation occurred. The rays from radium bromide act on the substance like light.[7] The discoloration can be removed by heating with mercury and dilute sulphuric acid in a sealed tube.[8]

Fourcroy obtained a grey product by the action of ammonia on mercurous sulphate,[9] and various compounds have been said to result from this action;[10] but, according to Saha and Choudhury, the product is $(NH_2Hg)_2SO_4.2HgO.2H_2O$.[11]

The properties of mercurous sulphate are important for its use in the Weston standard cell.

The *acid salt*, $Hg_2SO_4.H_2SO_4$, was obtained in rhombic prisms by covering mercury for two years with sulphuric acid containing a little nitric acid. The crystals remained transparent only as long as they were well covered with sulphuric acid, and exposure rapidly transformed them into a deliquescent white powder.[12] The existence of $Hg_2SO_4.H_2SO_4$ has been confirmed by a study of the system $Hg_2SO_4-H_2SO_4$.[13]

There is no evidence for the existence of the *double salt*, $Hg_2SO_4.K_2SO_4$,[14] but $Hg_2SO_4.HgSO_4$ has been reported.[15]

Mercuric Sulphate, $HgSO_4$, is a white opaque mass [16] of rhombic crystals that are sometimes four-sided plates.[17] Some rhombic crystals from a dismantled mercury furnace at Idria had a density of 5·995.[18]

It can be prepared by heating mercury with sulphuric acid [19] and expelling the excess of acid.[1] A little nitric acid may be added before driving off the sulphuric acid.[2] The separated sulphate can be washed with 7 *N* sulphuric acid and dried.[3]

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[1] Cohen, Kruisheer, and Moesveld, *Zeitsch. physikal. Chem.*, 1920, 96, 437.

[2] Pollitzer, *Zeitsch. Elektrochem.*, 1911, 17, 6.

[3] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 117.

[4] Städeler, *Annalen*, 1853, 87, 132.

[5] Hada, *Trans. Chem. Soc.*, 1896, 69, 1672. He found that mercurous sulphate is partly oxidised into mercuric sulphate by heating in a sealed tube at 150° C. for six hours with dilute sulphuric acid in the presence of oxygen.

[6] Buchner, *Chem. Zeit.*, 1886, 10, 759, 790.

[7] Skinner, *Proc. Camb. Phil. Soc.*, 1904, 12, 260.

[8] Fox, *Brit. Assoc. Report*, 1909, 457.

[9] Fourcroy, *Ann. Chim.*, 1791, 10, 311.

[10] Pesci, *Gazzetta*, 1890, 20, 485; 1891, 21, ii, 569.

[11] Saha and Choudhury, *Zeitsch. anorg. Chem.*, 1914, 86, 239.

[12] Braham, *Chem. News*, 1880, 42, 163.

[13] Kendal and Davidson, *J. Amer. Chem. Soc.*, 1921, 43, 985.

[14] Barre, *Ann. Chim. Phys.*, 1911, [8], 24, 202.

[15] Brooks, *Pogg. Annalen*, 1845, 66, 63. See Baskerville and Miller, *J. Amer. Chem. Soc.*, 1897, 19, 875.

[16] Eissfeldt, *Arch. Pharm.*, 1853, [2], 76, 16.

[17] Hoitsema, *Zeitsch. physikal. Chem.*, 1895, 17, 655.

[18] Seyfriedsberger, *Zeitsch. Kryst. Min.*, 1890, 17, 433.

[19] Excess of sulphuric acid and high temperature favour the production of the *ic* salt (Baskerville and Miller, *J. Amer. Chem. Soc.*, 1897, 19, 873).

Cameron obtained it by the evaporation *in vacuo* of a solution of either the basic sulphate in selenic acid or the basic selenate in sulphuric acid.[4]

The *monohydrate*, $HgSO_4.H_2O$, separates in colourless rhombic plates when a solution of mercuric sulphate in sulphuric acid, with appropriate concentrations of HgO and SO_3, is evaporated over sulphuric acid.[1]

The prolonged action of a *small* quantity of water on mercuric sulphate produces colourless crystals of $HgO.2HgSO_4.2H_2O$,[5] but the usual hydrolytic product when water acts upon the salt is the familiar *turpeth mineral*[6] that has been prepared by treating mercuric sulphate with warm water, washing the yellow-orange product till free from acid and drying at 110° C.[2] Fourcroy, in 1791, realised that it was a *basic salt*,[7] and the composition of the small yellow tetragonal crystals is $2HgO.HgSO_4$.[1] The hydrolysis, during which sulphuric acid is formed, is reversed by excess of acid, and the mercury salt in solution is the normal salt.[8] Though other basic sulphates have been reported,[9] apparently only the compounds $HgSO_4$, $HgSO_4.H_2O$, $3HgO.SO_3$, and $3HgO.2SO_3.2H_2O$ occur in the system $HgO-SO_3-H_2O$.[1, 10]

According to Rây,[11] *turpeth mineral* occurs as the hemihydrate in an α-form and a β-form, as well as in an anhydrous γ-form. It has frequently been prepared by precipitating a hot solution of mercuric nitrate with sodium sulphate,[11] and it is also precipitated when mercuric oxide is added to ferric sulphate solution.[12]

According to Cameron,[13] it dissolves in 32,258 parts of water at 16° C. when freshly precipitated, and in 43,478 parts after drying at 100° C.

When it is heated the mercuric oxide is given up as mercury and oxygen, and some of the mercuric sulphate decomposes into mercury, sulphur dioxide, and oxygen. At about 400° C. the remaining mercuric sulphate fuses to a brown liquid and volatilises as mercurous sulphate:

$$2HgSO_4 = Hg_2SO_4 + SO_2 + O_2.$$[11]

Mohr[14] noted that mercuric sulphate became yellow and then red on heating, and Lavoisier observed that it gave off sulphur dioxide, oxygen, and the larger proportion of its mercury when strongly heated.[1] When heated with carbon it is reduced to mercury, and, according to Gay-Lussac,[2] sulphur dioxide and carbon dioxide are evolved in about equal volumes.

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[1] Hoitsema, *Zeitsch. physikal. Chem.*, 1895, 17, 655.

[2] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 105.

[3] Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 165.

[4] Cameron, *Analyst*, 1880, 5, 144.

[5] Hoitsema, *loc. cit.* Eissfeldt (*Arch. Pharm.*, 1853, [2], 76, 16) mistook them for a monohydrate.

[6] Phillips, *Phil. Mag.*, 1831, [2], 10, 206.

[7] Fourcroy, *Ann. Chim.*, 1791, 10, 305.

[8] Ditte, *Compt. rend.*, 1874, 79, 915; le Chatelier, *ibid.*, 1884, 98, 675; 1885, 100, 737; Varet, *loc. cit.*; Cox, *loc. cit.*

[9] Hopkins, *Amer. J. Sci.*, 1836, [1], 18, 264; Athanesco, *Compt. rend.*, 1886, 103, 271; Chateau, *Bull. Soc. chim.*, 1915, [4], 17, 121.

[10] Kendall and Davidson (*J. Amer. Chem. Soc.*, 1921, 43, 986) found no indication of an acid salt.

[11] Rây, *Trans. Chem. Soc.*, 1897, 71, 1098.

[12] Mailhe, *Compt. rend.*, 1901, 132, 1560.

[13] Cameron, *Analyst*, 1880, 5, 144. This differs greatly from Fourcroy (*Ann. Chim.*, 1791, [1], 10, 307), who said it dissolved in 2000 parts of water at 10° C. and in 600 parts at boiling-point.

[14] Mohr, *Annalen*, 1839, 31, 184.

The heat of formation of solid mercuric sulphate from liquid mercury, solid sulphur, and gaseous oxygen is 165·1 Cal., and of turpeth mineral 218·9 Cal.[3]

The *double salts*, $K_2SO_4.3HgSO_4.2H_2O$,[4] $(NH_4)_2SO_4.3HgSO_4.2H_2O$,[4] and $Hg_2SO_4.HgSO_4$,[5] also the compounds $HgS.3HgSO_4$,[6] $HgS.2HgSO_4$,[6, 7] $HgO.HgS.HgSO_4$,[8] $2HgS.2HgSO_4$,[6] $2HgS.HgSO_4$,[9] and $3HgS.HgSO_4$,[6] have been reported.

Mercuric sulphate is insoluble in liquid ammonia,[10] but white or yellowish *ammonia turpeth* results with aqueous ammonia.[11] A number of mixed *hydro-basic-ammonobasic sulphates* have been prepared.[12] The most definitely established compound, according to Franklin,[13] may be formulated as the sulphate of Millon's base, $(HO.Hg.NH.Hg)_2SO_4$. This ammonia turpeth is formed by the action of sulphuric acid on Millon's base, which may be regarded as dihydroxymercuriammonium hydroxide, $NH_2(Hg.OH)_2.OH$,[14] though it has been very variously formulated.[15]

The diammino-sulphate, $HgSO_4.2NH_3$, seems to result from the saturation of aqueous ammonia with mercuric sulphate and evaporation to dryness. Its monohydrate was obtained crystalline by dissolving mercuric oxide in ammonium sulphate solution and evaporating.[16]

The sulphate $(NHg_2)_2SO_4.H_2O$ has been prepared.[17]

Compounds of mercuric sulphate with hydroxylamine, $HgSO_4.NH_2OH.H_2O$,[18] and hydrazine, $HgSO_4.N_2H_4$,[19] have been prepared.

Mercurous Thiosulphate, $Hg_2S_2O_3$, is only known as cuprous mercurous thiosulphate, $5Cu_2S_2O_3.3Hg_2S_2O_3$, which separates as a brownish-red precipitate when copper sulphate is added to a solution of $5K_2S_2O_3.3HgS_2O_3$.[20]

Mercuric Thiosulphate, HgS_2O_3, is only known in double salts.[21] Prismatic colourless crystals of $5K_2S_2O_3.3HgS_2O_3$ have been obtained by the action of warm potassium thiosulphate solution on freshly precipitated mercuric oxide. The salt was crystallised by evaporating the alkaline liquid on the water-bath.[1] It does not darken in the light.[2] If the solution is evaporated over concentrated sulphuric acid with an excess of potassium thiosulphate, small colourless crystals of $3K_2S_2O_3.HgS_2O_3.3H_2O$ separate. They are stable in light but become opaque in contact with water. Small prismatic crystals of $5K_2S_2O_3.HgS_2O_3.H_2O$ are obtained by evaporation at about 35° C. with a great excess of potassium thiosulphate.[3]

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[1] See Fourcroy, *Ann. Chim.*, 1791, [1], 10, 295.

[2] Gay-Lussac, *Ann. Chim. Phys.*, 1836, [2], 63, 438.

[3] Varet, *ibid.*, 1896, [7], 8, 140.

[4] Wirzel, *Jahresber.*, 1850, 332.

[5] Brooks, *Pogg. Annalen*, 1845, 66, 63. See Baskerville and Miller, *J. Amer. Chem. Soc.*, 1897, 19, 875.

[6] Spring, *Annalen*, 1879, 199, 116.

[7] Palm, *Jahresber.*, 1862, 221.

[8] Jacobson, *Pogg. Annalen*, 1846, 68, 410.

[9] Barfoed, *J. prakt. Chem.*, 1864, [1], 93, 230; Kessler, *Ann. Phys. Chem.*, 1879, [2], 6, 615.

[10] Franklin and Krauss, *Amer. Chem. J.*, 1898, 20, 829.

[11] Fourcroy, *Ann. Chim.*, 1792, [1], 14, 34; Kane, *Ann. Chim. Phys.*, 1839, [2], 72, 225.

[12] Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 402; Schmieder, *J. prakt. Chem.*, 1858, [1], 75, 129; Rammelsberg, *ibid.*, 1888, [2], 38, 565, Pesci, *Gazzetta*, 1890, 20, 485; Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1914, 86, 239. Franklin (*J. Amer. Chem. Soc.*, 1907, 29, 61) tabulates them.

[13] Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 62.

[14] Hofmann and Marburg, *Annalen*, 1899, 305, 191.

[15] Franklin, *loc. cit.*, 40.

[16] Franklin, *loc. cit.*, 49.

[17] Rây, *Proc. Chem. Soc.*, 1904, 20, 250; *Trans. Chem. Soc.*, 1905, 87, 9.

[18] Adams, *Amer. Chem. J.*, 1902, 28, 209.

[19] Hofmann and Marburg, *loc. cit.*, p. 216.

[20] Rammelsberg, *Pogg. Annalen*, 1842, 56, 319.

[21] Dammer, *Handbuch der Anorganisch. Chem.* (Enke, Stuttgart), 1894, 2, ii, 887.

The double salts, $Na_2S_2O_3.HgS_2O_3$, $4(NH_4)_2S_2O_3.HgS_2O_3.2H_2O$, $CaS_2O_3.HgS_2O_3$, $SrS_2O_3.HgS_2O_3$, and $BaS_2O_3.HgS_2O_3$, have also been reported.[2]

Mercurous Dithionate, $Hg_2S_2O_6$, appears to have been prepared by the action of the acid on freshly precipitated mercurous oxide, but the mercuric salt could not be analogously prepared.[4]

Yellow $Hg_4S_4O_4$ was obtained from the action of tetrathionic acid on mercurous nitrate. It has a density of 6·4159 at 20° C., is insoluble in water, and decomposes, with the formation of black mercuric sulphide, in the light at 50° C.[5]

MERCURY AND SELENIUM.

Mercuric Selenide.—Tiemannite, HgSe, occurs as a blackish-grey mineral. It crystallises tetragonally in the isometric system with a density of 8·2 and a hardness of 2·5. It is readily volatile.

Mercuric selenide is precipitated by hydrogen selenide from solutions of mercuric salts,[6] and is decomposed by hydrogen above 400° C. into hydrogen selenide and mercury. This action is reversible.[7]

The heat of formation of the amorphous form is 6·66 Cal., and of the crystalline form 2·20 Cal.[8]

Mercurous Selenite, Hg_2SeO_3, is obtained as a white powder, stable to light, by precipitating a solution of mercurous nitrate with sodium selenite. By heating above its melting-point, 180° C., it is converted into the acid salt, $3Hg_2O.4SeO_2$, which is a dark red, opaque, crystalline mass of density 7·350 at 13·5° C.[9]

Mercurous selenite is not decomposed by potassium selenite into mercuric salt and mercury.[10] The basic salt, $3Hg_2O.2SeO_2.5H_2O$, is probably partly converted into mercuric selenite at temperatures above 150° C. Yellow crystals of $HgSeO_3$ also appear to be formed by the action of nitric acid on the basic salt.[11]

Mercuric Selenite, $HgSeO_3$, is precipitated as a white crystalline powder by interaction between solutions of mercuric nitrate and sodium selenite, or by adding mercuric oxide to a solution of sodium hydrogen selenite. It is insoluble in water or cold dilute nitric acid, but dissolves readily in hydrochloric acid.[1] The action of selenious acid on precipitated mercuric oxide seems to result in the formation of an insoluble basic salt.[2]

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[1] Fock and Klüss, *Ber.*, 1891, 24, 1351.

[2] Rammelsberg, *Pogg. Annalen*, 1842, 56, 315.

[3] Dammer, *loc. cit.*

[4] Rammelsberg, *loc. cit.*, 1843, 59, 472.

[5] Spring, *Annalen*, 1879, 199, 116; Wackenroder, *ibid.*, 1846, 60, 190.

[6] Reeb, *J. Pharm. Chim.*, 1869, [4], 9, 173.

[7] Pélabon, *Bull. Soc. chim.*, 1900, [3], 23, 211.

[8] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 127.

[9] Köhler, *Pogg. Annalen*, 1853, 89, 146.

[10] Divers and Shimidzu, *Trans. Chem. Soc.*, 1886, 49, 585.

[11] Boutzoureano, *Ann. Chim. Phys.*, 1889, [6], 18, 323.

Mercuric selenite apparently results from the action of selenic acid on excess of mercury. Some selenate, perhaps by decomposition of the selenite, is produced if the acid is in excess, and the usual product when selenic acid acts upon mercury is a mixture of the two salts. There seems to be no acid mercuric selenite.[3]

Mercuric selenite dissolves in a solution of potassium selenite. Neither this solution nor a solution of mercuric oxide in the same solvent is precipitated by potassium hydroxide.[4] The *double salt*, $Na_2SeO_3.HgSeO_3$, has been prepared.[1]

Mercurous Selenate.—According to Köhler, interaction between solutions of sodium selenate and mercurous nitrate produces a white precipitate that goes yellow on washing and dissolves slightly. The colour becomes deeper on drying at 100° C., and light quickly turns the salt grey. Köhler regarded it as a mixture of the normal selenate, Hg_2SeO_4, and a basic selenate, $Hg_2O.Hg_2SeO_4$. The substance, whose composition approximated to $6Hg_2O.5SeO_3$, was only slightly soluble in hot nitric acid. Selenium separated when it was heated with hydrochloric acid.[2]

According to Cameron and Davy, selenic acid or an alkali selenate precipitates a greyish-white substance from a solution of mercurous nitrate. It is almost insoluble in water or hydrochloric acid, but is converted into mercuric selenate, with evolution of nitrogen peroxide, by boiling with nitric acid. It is very sensitive to light.[3]

Mercuric Selenate.—White mercuric selenate can be obtained by heating freshly precipitated mercuric oxide or mercuric acetate with excess of selenic acid and expelling, by heat, the acetic acid or selenic acid. It can be obtained in small crystals from its solution in selenic acid. It dissolves in sulphuric, nitric, and hydrochloric acids.[3] The *monohydrate*, $HgSeO_4.H_2O$, was said to deposit on careful evaporation of the solution of mercuric oxide in selenic acid.[2]

The *basic salt*, $3HgO.SeO_3$, is precipitated from mercuric acetate solution by soluble selenates or selenic acid. It has a fine red colour and is soluble in selenic and mineral acids. 10,330 parts of water dissolve it.[2] Water also converts the normal selenate into a red basic salt which, according to Köhler, is $6HgO.2SeO_3.H_2O$.[2]

Ammonia dissolves the neutral or moist basic salt. This gives a white precipitate of $(NHg_2)_2SeO_4.2H_2O$ with water. This substance dissolves in hydrochloric acid or strong ammonia and, when strongly heated, evolves nitrogen, ammonia, and water, and leaves a residue of basic mercuric selenate. It blackens in light.[3]

MERCURY AND TELLURIUM.

Mercuric Telluride, HgTe, occurs as the mineral coloradoite. It usually occurs massive, with an iron-black colour, and is soluble in boiling nitric acid with the separation of tellurous acid. Its hardness is 3 and its density 8·63.

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[1] Rosenheim and Pritze, *Zeitsch. anorg. Chem.*, 1909, 63, 277.

[2] Köhler, *Pogg. Annalen*, 1853, 89, 146.

[3] Cameron and Davy, *Chem. News*, 1881, 44, 63.

[4] Divers and Shimidzu, *Trans. Chem. Soc.*, 1886, 49, 585.

MERCURY AND CHROMIUM.

Mercurous Chromate.—The brown amorphous mercurous chromate, Hg_2CrO_4, precipitated from solutions of mercurous salts by alkali chromates, changes into the red crystalline modification. Prolonged washing with water converts the amorphous variety into $4Hg_2O.3CrO_3$,[1] which Gmelin erroneously supposed to be first precipitated.[2] Mercurous chromate is slightly soluble in cold water or dilute nitric acid, and more readily in hot water, concentrated nitric acid, or potassium cyanide solution.[3]

When the precipitate with an excess of mercurous nitrate was left in contact with, or boiled in, the solution, red needles of $Hg_2O.2Hg_2CrO_4$ were obtained.[1] A dark substance, corresponding in composition to $3Hg_2O.CrO_3$, was obtained by the action of alkali on mercurous chromate.[2]

A dark green unstable mercurous cyanide forms when mercurous chromate is treated with a little potassium cyanide solution. With excess of the reagent, mercuric cyanide and metallic mercury are produced, and the compound $3Hg(CN)_2.2K_2CrO_4$ can be crystallised from the solution.[2]

Mercuric Chromate.—Berzelius reported the normal chromate, $HgO.CrO_3$, but it was apparently a basic salt. $3HgO.CrO_3$ was obtained by boiling yellow mercuric oxide with potassium dichromate solution, and $4HgO.CrO_3$ by using the red oxide.[4] Geuther[5] obtained red rhombic prisms of $2HgO.CrO_3$ and also $7HgO.2CrO_3$ by treating yellow mercuric oxide with pure chromic acid. According to Freese[6] the latter does not exist.

When ammonium chromate solution is added to a solution of mercuric chloride a yellow precipitate is obtained of mercurammonium chloride mercurichromate, $2(NH_2HgCl)HgCrO_4$. It dissolves in hydrochloric or nitric acid, and when boiled with water produces orange-yellow $5HgO.CrO_3$. This is sparingly soluble in warm nitric acid, freely in hydrochloric acid, and by prolonged digestion with water is converted into bright yellow $6HgO.CrO_3$.[7]

Jäger and Krüss recognised the existence of $2HgO.CrO_3$, $3HgO.CrO_3$, $4HgO.CrO_3$, $5HgO.CrO_3$, $6HgO.CrO_3$, and $7HgO.CrO_3$.[7] According to Cox, the dark red $3HgO.CrO_3$ is the only chemically individual basic salt, and since mercuric chromate hydrolyses into this and finally into mercuric oxide, all the others that have been described are mixtures either of $HgCrO_4$ and $3HgO.CrO_3$, or of $3HgO.CrO_3$ and HgO. He obtained the orange normal chromate, apparently contaminated with about 2·5 per cent. of CrO_3, by digesting mercuric oxide and chromium trioxide with water, and also the red dichromate.[8]

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[1] Fichter and Oesterheld, *Zeitsch. anorg. Chem.*, 1912, 76, 347. See Freese, *Ber.*, 1869, 2, 477.

[2] P. and M. M. Richter, *Ber.*, 1882, 15, 1489.

[3] Rose, *Pogg. Annalen*, 1841, 53, 124.

[4] Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 333.

[5] Geuther, *Annalen*, 1858, 106, 244.

[6] Freese, *loc. cit.*

[7] Jäger and Krüss, *Ber.*, 1889, 22, 2048.

[8] Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 147; 1906, 50, 226.

The yellow double salt, $2HgCrO_4.HgS$, was prepared by digesting freshly precipitated mercuric sulphide with a saturated solution of newly precipitated mercuric oxide in chromic acid, and drying at 30° C. The salt is explosive.[1]

A dense, orange-red, basic mixture, corresponding to $Hg_8N_2H_4O_3.4CrO_3$, was obtained by treating mercuric oxide with ammonium dichromate solution. The chromate of Millon's base, analogous to ammonia turpeth, was obtained from this by the action of aqueous ammonia. This light yellow amorphous powder,[2] which may be formulated $(HO.Hg.NH.Hg)_2CrO_4$, has also been prepared by the action of ammonia or potash on ammoniated mercuric dichromate.[3]

MERCURY AND MOLYBDENUM.

Mercurous Molybdate.—When the yellowish-white flocculent precipitate from mixed solutions of mercurous nitrate and an alkali trimolybdate is washed it becomes yellowish-white $Hg_2O.2MoO_3$, which is converted into gold-yellow microscopic needles of the normal salt, $Hg_2O.MoO_3$, by the prolonged action of water.[4]

MERCURY AND TUNGSTEN.

Mercurous Tungstate.—The yellow normal tungstate, $Hg_2O.WO_3$, was obtained by adding a solution of a mercurous salt to an alkali tungstate solution.[5] Lefort prepared it by dissolving mercurous nitrate in the presence of glycerine and precipitating with sodium tungstate. It cannot be washed or dried without decomposition into mercury and mercuric tungstate. He precipitated the yellow acid salt, $2Hg_2O.3WO_3.8H_2O$, by adding mercurous nitrate solution to a solution of bitungstate of sodium.[6]

The acid salt, $Hg_2O.4WO_3$, highly hydrated (perhaps with $25H_2O$), is said to have been prepared.[7]

Mercuric Tungstate.—The normal tungstate, $HgO.WO_3$, is precipitated as a pale yellow compound by adding a concentrated solution of mercuric acetate to a saturated solution of sodium tungstate. It is not very stable in the presence of water and is difficult to obtain pure.

The compounds $HgO.3WO_3.7H_2O$, $2HgO.3WO_3$, $3HgO.2WO_3$, and $3HgO.5WO_3.5H_2O$ have been obtained by precipitation of solutions of mercuric salts with solutions of sodium tungstates.[8]

MERCURY AND NITROGEN.

Mercuric Nitride.—When potassamide solution is added to excess of mercuric iodide dissolved in liquid ammonia, a reddish-yellow precipitate of NHg_2I is formed. This is converted into mercuric nitride, Hg_3N_2, by excess of potassamide.

Mercuric nitride is a very explosive chocolate-coloured solid that is readily soluble in aqueous acids or in solutions of ammonium salts in liquid ammonia.[9]

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[1] Palm, *Jahresber.*, 1862, 221.

[2] Hirzel, *ibid.*, 1852, 421.

[3] Hensgen, *ibid.*, 1886, 478.

[4] Struve, *J. prakt. Chem.*, 1854, [1], 61, 449.

[5] Anthon, *ibid.*, 1836, [1], 9, 344.

[6] Lefort, *Ann. Chim. Phys.*, 1878, [5], 15, 353.

[7] Scheibler, *J. prakt. Chem.*, 1861, [1], 83, 319.

[8] Lefort, *loc. cit.* See Anthon, *J. prakt. Chem.*, 1836, [1], 9, 344.

[9] Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 820

Mercuric Azide.—The calomel-like HgN_3 is rapidly discoloured in sunlight.[1]

It can be prepared by leading gaseous hydrazoic acid into a boiling aqueous suspension of mercuric oxide, or precipitated as a powdery mass by mixing concentrated solutions of sodium azide and mercuric nitrate. The product of the second method is less sensitive to shock than lead azide, but becomes more explosive by solution and crystallisation. Crystals exceeding 1 mm. in length are extremely sensitive, and the formation of large crystals in the former method should be avoided. They remain sensitive under water.[2]

Mercurous Hyponitrite, $Hg_2N_2O_2$, can be prepared by precipitating mercurous nitrate with neutralised sodium hyponitrite or with acid potassium hyponitrite. It is also precipitated from mercuroso-mercuric nitrite[3] by crude alkali hyponitrite.

The salt is obtained with a bright yellow colour, in a physical condition that varies according to the method of preparation, by washing rapidly and drying under diminished pressure over sulphuric acid. It dissolves readily in dilute nitric acid, partially dissociating into mercury and mercuric hyponitrite,

$$Hg_2N_2O_2 = Hg + HgN_2O_2,$$

and can be precipitated from this solution by sodium carbonate.[4, 5]

It begins to decompose slowly at 80° C., becomes black at a higher temperature, and reddish yellow at 150° C. Mercury, mercuric oxide, nitric oxide, and nitrous oxide are the principal products, and decomposition is apparently complete at 150° C. Small quantities of mercurous nitrate and nitrogen are also formed.[5, 6]

It is blackened by even very dilute alkali, and also, though it is on the whole a stable salt, by bright sunlight.[5]

Mercuric Hyponitrite.—The hydrate $2HgN_2O_2.3H_2O$ is obtained as a flocculent, cream-coloured precipitate by precipitating a solution of mercuric nitrate with a solution of sodium hyponitrite. It dries to a light, buff-coloured powder, probably because of a partial conversion into the mercurous salt, and becomes anhydrous in a desiccator. Since it is sensitive to light it should be dried in the dark.

It decomposes readily into mercurous hyponitrite and nitric oxide; heat decomposes it mainly into mercuric oxide and nitrous oxide, but partly into metal and nitric oxide.[7]

Mercurous Nitrite.—Nitrous acid is probably an important agent during the dissolution of mercury in nitric acid,[8] and mercurous nitrite and nitrate seem to be produced in equimolecular proportions when nitric acid of density 1·11 at 15° C. acts on mercury at 35° C.[9] When diluted nitric acid is poured over an excess of mercury, thin yellow needles and prisms of $Hg_2(NO_2)_2$ separate out, and can be dried on a porous surface after pouring off the mother-liquor from the salt and residual mercury.[1] Colourless nitric acid acts as well as yellow, and acid containing 13–14 per cent. of N_2O_5 appears to give the best growth of crystals.[2] According to Rây,[3] the mercurous nitrite is produced by the combined action of nitrous and nitric acids on the metal.

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[1] Wöhler and Krupko, *Ber.*, 1913, 46, 2050.

[2] Stettbacher, *J. Chem. Soc.*, 1921, 120, Abs. ii, 48.

[3] See Râу, *Trans. Chem. Soc.*, 1902, 81, 644.

[4] Râу, *ibid.*, 1907, 91, 1404.

[5] Divers, *ibid.*, 1899, 75, 120.

[6] Râу and Gañgul, *ibid.*, 1907, 91, 1399.

[7] Divers, *ibid.*, 1899, 75, 119.

[8] Russell, *J. Chem. Soc.*, 1874, 27, 3; Divers, *Trans. Chem. Soc.*, 1883, 43, 465; Veley, *Proc. Roy. Soc.*, 1890, 48, 458

[9] Divers, *J. Soc. Chem. Ind.*, 1904, 23, 1183.

Mercurous nitrite was said to be very insoluble in water, and its aqueous suspension to be very resistant to decomposition by hydrogen sulphide,[4] but excess of water partly hydrolyses it into mercury and mercuric nitrite:[1] in hot water about 78 per cent. is thus resolved, and nearly 22 per cent. of the original salt remains in solution.[5]

By the spontaneous evaporation of a diluted aqueous solution in a shallow dish, lemon-yellow prisms of $Hg_2(NO_2)_2.2H_2O$ were obtained. This *monohydrate* is decomposed by water similarly to the anhydrous nitrite, and effloresces in a desiccator over sulphuric acid.[2]

Mercurous nitrite crystallises in the monoclinic system and is not very stable under ordinary conditions.[6] Its density at 21°–29° C. is 5·925.[7]

Heat first decomposes it thus :—

$$(HgNO_2)_2 = 2Hg + (NO_2)_2.$$

Mercuric nitrate is then secondarily produced :—

$$2(NO)NO_3 + 2Hg = (HgNO_3)_2 + 2NO.^8$$

Mercuric Nitrite.—A pale yellow solution of mercuric nitrite is obtained by rubbing pure silver nitrite and mercuric chloride, in molecular proportions, in a mortar with water. The salt crystallises in tufts of fine needles by concentrating the solution *in vacuo* over sulphuric acid. It is only slightly contaminated with silver nitrite.

The light yellow crystals dissolve partially in boiling water, but they decompose largely into mercuric oxide and nitrous acid. The salt slowly liquefies in air with the evolution of nitrous fumes, and is transformed into white basic mercuric nitrate by exposure over sulphuric acid in a desiccator. It can be kept without changing by prompt exposure in a vacuum, but decomposition cannot be arrested after it has begun.

It decomposes at 100° C. according to the two equations

$$\begin{gathered} Hg(NO_2)_2 = HgO + N_2O_3, \\ Hg(NO_2)_2 = HgNO_3 + NO. \end{gathered}$$

The second reaction predominates.[9]

When diluted nitric acid acts on mercury, mercuric nitrite occurs in the solution—being apparently formed from the initially produced mercurous nitrite,

$$Hg_2(NO_2)_2 + HNO_2 + HNO_3 = 2Hg(NO_2)_2 + H_2O.$$

The mercuric nitrite is remarkably stable in the acid mother-liquor, but it is much less so in the absence of acid.[10]

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[1] Rây, *Zeitsch. anorg. Chem.*, 1896, **12**, 365.

[2] Rây, *Trans. Chem. Soc.*, 1897, **71**, 337.

[3] Rây, *ibid.*, 1905, **87**, 171. According to Palit and Dhar (*Zeitsch. anorg. Chem.*, 1924, **134**, 208), mercurous nitrite is the first product when nitric acid acts on mercury below 52° C. Sodium mercurinitrite is formed if sodium nitrite is present. Urea tends to inhibit solution, ferric nitrate retards it, and mercurous nitrate accelerates it.

[4] Divers and Haga, *Trans. Chem. Soc.*, 1887, **51**, 48.

[5] Rây, *ibid.*, 1904, **85**, 523.

[6] Holland, *ibid.*, 1897, **71**, 346.

[7] Rây, *ibid.*, 1908, **93**, 999.

[8] Rây and Sen, *ibid.*, 1903, **83**, 491; *Proc. Chem. Soc.*, 1903, **19**, 78.

[9] Rây, *Trans. Chem. Soc.*, 1904, **85**, 523.

[10] Rây, *ibid.*, 1905, **87**, 174.

Mercuric nitrite forms additive and substitutive compounds with some organic thio-derivatives.[1]

If to the solution that has undergone the dissociation

$$Hg_2(NO_2)_2 = Hg + Hg(NO_2)_2$$

till about 22 per cent. of the original salt remains,[2] an excess of potassium, sodium, or silver nitrite is added, the residual mercurous nitrite dissociates.[3] The relatively stable *mercuroso-mercuric nitrite*, $HgNO_2.4Hg(NO_2)_2$, is first formed,[4] and when the alkali nitrite is added it forms a stable *double nitrite* with the mercuric nitrite. The displaced mercurous nitrite then dissociates. By applying this method the double salts, $LiNO_2.Hg(NO_2)_2.H_2O$, $4LiNO_2.Hg(NO_2)_2.4H_2O$, $1{\cdot}5NaNO_2.Hg(NO_2)_2$, $2NaNO_2.Hg(NO_2)_2.2H_2O$, $2KNO_2.Hg(NO_2)_2$, $3KNO_2.Hg(NO_2)_2.H_2O$, have been prepared.[5] The double salts, $Ca(NO_2)_2.Hg(NO_2)_2.5H_2O$, $2Sr(NO_2)_2.3Hg(NO_2)_2.5H_2O$, $2Ba(NO_2)_2.3Hg(NO_2)_2.5H_2O$, have been obtained analogously.[6]

The salts, $2NaNO_2.Hg(NO_2)_2$,[7, 8] $KNO_2.Hg(NO_2)_2$,[7] $2KNO_2.Hg(NO_2)_2$,[9, 10] and $3KNO_2.Hg(NO_2)_2.H_2O$,[7, 8] have been prepared from solutions of the mixed salts.

Insoluble *dimercurammonium nitrite*, $NHg_2.NO_2.\frac{1}{2}H_2O$, is precipitated by aqueous ammonia from mercuric-sodium nitrite solution as a cream-coloured, flocculent, dense powder.[4] Heat readily decomposes it.[11]

Mercurous Nitrate.—When cold dilute nitric acid, of 10–23 per cent. concentration, acts upon excess of mercury, mercurous nitrite is formed which slowly dissolves in the mother-liquor with the formation of mono-hydrated mercurous nitrate and the basic nitrate known as "Marignac's salt." [12] If nitric acid of density 1·135–1·14 is used, a crystalline crust of large isolated crystals of $HgNO_3.H_2O$ slowly forms.[13] Varet obtained the monohydrate in transparent prismatic crystals by digesting excess of mercury for some days with pure nitric acid containing half of its own volume of water.[14] A solution of mercurous nitrate free from nitrous acid, which is apparently stable if kept in a closed bottle in the dark, can be prepared by shaking a solution of mercuric nitrate with mercury,[15] and a practically neutral solution is obtained by shaking finely powdered mercuric nitrate and mercury with water and filtering from basic salts.[16]

The crystals are isomorphous with the monoclinic crystals of mercurous sulphate.[17] In the presence of nitric acid the salt is slowly and completely oxidised by ozone into mercuric nitrate.[1] Though mercurous nitrate often becomes yellow on keeping and the purified effloresced salt has an ozone-like odour when kept in a bottle, the thoroughly dried salt is very stable.[2]

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[1] Rây, *Proc. Chem. Soc.*, 1914, 30, 140.

[2] Rây, *Zeitsch. anorg. Chem.*, 1896, 12, 365; *Trans. Chem. Soc.*, 1897, 71, 337; 1904, 85, 523.

[3] Rây, *Proc. Chem. Soc.*, 1899, 15, 103.

[4] Rây, *Trans. Chem. Soc.*, 1902, 81, 645.

[5] Rây, *ibid.*, 1907, 91, 2031.

[6] Rây, *ibid.*, 1910, 97, 326.

[7] Rosenheim and Oppenheim, *Zeitsch. anorg. Chem.*, 1901, 28, 171.

[8] Kohlschutter, *Ber.*, 1902, 35, 489.

[9] Lang, *J. prakt. Chem.*, 1862, [1], 62, 295.

[10] Fock, *Zeitsch. Kryst. Min.*, 1890, 17, 177.

[11] Rây and Ghosh, *Trans. Chem. Soc.*, 1910, 97, 323.

[12] Rây, *ibid.*, 1897, 71, 344.

[13] Rây, *ibid.*, 1905, 87, 174.

[14] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 127. The ordinary hydrate seems to be $HgNO_3.H_2O$ (Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 174), though Lefort (*J. Pharm. Chim.*, 1845, [3], 8, 5) found otherwise. See also Mitscherlich, *Pogg. Annalen*, 1827, 9, 387; Marignac, *Ann. Chim. Phys.*, 1849, [3], 27, 321.

[15] Hada, *Trans. Chem. Soc.*, 1896, 69, 1667.

[16] Ogg, *Zeitsch. physikal. Chem.*, 1898, 27, 288.

[17] Carhart and Hulett, *Trans. Amer. Electrochem. Soc.*, 1904, 5, 61; de Schulten, *Bull. Soc. franç. Min.*, 1903, 26, 113.

Mercurous nitrate is soluble in benzonitrile[3] and very soluble in liquid ammonia.[4] It is decomposed by hydrogen at 100° C. according to the equation

$$2HgNO_3+2H_2=2NO+2HgO+2H_2O,$$[5]

and its heat of formation from liquid mercury, gaseous nitrogen and oxygen, and liquid water is 69·4 Cal.[6]

The *basic double nitrates*, $2SrO.2Hg_2O.3N_2O_5$, $2BaO.2Hg_2O.3N_2O_5$, $2Hg_2O.2PbO.3N_2O_5$, have been obtained.[7]

Heat and light change mercurous nitrate in solution to mercuric salt—the change being apparently connected with a reduction of nitric to nitrous acid.[2] When it is boiled with water it is converted into mercury and mercuric nitrate.[2, 8]

The hydrolysis of the colourless monohydrate may result in white $5Hg_2O.3N_2O_5.2H_2O$, yellow $5Hg_2O.3N_2O_5$, and a yellowish-green basic salt that may have the formula $3Hg_2O.N_2O_5.2H_2O$. There may also be $3Hg_2O.N_2O_5$ and $2Hg_2O.N_2O_5$, but it is doubtful whether hydrolysis takes place completely to mercurous oxide.[9]

When, during the action of diluted nitric acid on mercury, the nitrite first formed is slowly transformed into nitrate, the basic salt, $5Hg_2O.3N_2O_5.2H_2O$, separates as hard colourless crystals that are stable in air and do not lose water *in vacuo* over sulphuric acid. This "Marignac's salt" results from the hydrolysis of mercurous nitrate and forms freely when well-diluted nitric acid acts on mercury.[10]

The following salts may also form during the prolonged action of dilute nitric acid upon mercury:[11] $Hg_2NO_3.OH$, $Hg_2(NO_3)_2.Hg_2NO_3.OH$,[12] $Hg_2(NO_3)_2.4Hg_2NO_3(OH)$,[12] $Hg''O.2Hg_2NO_3.(OH)$, $Hg''O.Hg''NO_3(OH).Hg_2NO_3(OH)$.[13]

Kane, in 1839, considered that $2Hg_2O.N_2O_5.H_2O$ was the only basic nitrate. He represented "Marignac's salt," which he had apparently obtained, as a mixture of the above basic salt with the normal monohydrate.[14]

Mercurous salts react with ammonia to form mercurammonium salts and metallic mercury.[15] Mercurous nitrate and concentrated aqueous ammonia react to form[16] a black mixture of metallic mercury and $Hg_2N_2H_4O_5$.

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[1] Yamanchi, *Amer. Chem. J.*, 1913, 49, 65. According to Mailfert (*Compt. rend.*, 1882, 94, 860), mercurous nitrate is entirely decomposed by ozone into mercuric nitrate and a basic salt.

[2] Hada, *loc. cit.*

[3] Naumann, *Ber.*, 1914, 47, 1369.

[4] Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 829.

[5] Colson, *Compt. rend.*, 1899, 128, 1106.

[6] Varet, *Ann. Chim. Phys.*, 1896, [7], 8, 127.

[7] Städeler, *Annalen*, 1853, 87, 129.

[8] Rose, *ibid.*, 1841, 39, 106.

[9] Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 174.

[10] Rây, *Trans. Chem. Soc.*, 1897, 71, 342; Marignac, *Ann. Chim. Phys.*, 1849, [3], 27, 515.

[11] Rây, *loc. cit.*

[12] Marignac, *loc. cit.*

[13] Lefort, *Compt. rend.*, 1845, 20, 1300; Gerhardt, *ibid.*, 1848, 26, 432.

[14] Kane, *Ann. Chim. Phys.*, 1839, [2], 72, 250.

[15] Pesci, *Gazzetta*, 1891, 21, 569.

[16] Saha and Choudhuri, *Zeitsch. anorg. Chem.*, 1911, 71, 309.

Mercuric Nitrate.—A solution of mercuric nitrate is obtained by dissolving mercuric oxide or mercury in excess of nitric acid. The liquid, which tends to become syrupy on evaporation, deposits crystals of mercuric nitrate on concentration.[1] Varet obtained transparent hygroscopic crystals of the *hemihydrate*, $2Hg(NO_3)_2.H_2O$, by boiling mercury with an excess of concentrated acid, evaporating, and concentrating over lime.[2] Millon obtained it similarly.[1] The *monohydrate*, $Hg(NO_3)_2.H_2O$, was prepared by saturating 50 per cent. nitric acid with the commercial nitrate and evaporating the solution at 18° C. under diminished pressure. The crystals, which deliquesced in air, after drying on filter paper, resembled the hemihydrate that had been described as very soluble in water and forming a syrupy saturated solution.[3] Millon thought he obtained a syrupy *dihydrate*,[1] and Kane referred to a non-crystallisable *trihydrate*.[4] An *octahydrate* was said to occur.[5]

When a mixture of silver nitrate and mercuric chloride is rubbed in a mortar it becomes moist: deliquescent $Hg(NO_3)_2$ is probably produced.[6] The molecular weight of mercuric nitrate dissolved in methyl acetate corresponds closely to the formula $Hg(NO_3)_2$,[7] and Raoult[8] deduced the same formula from the freezing-points of solutions in nitric acid.

The heat of formation of the hemihydrate from its elements and liquid water is 57·4 Cal., and 9·9 Cal. are evolved when mercuric nitrate becomes mercurous nitrate.[9]

Mercuric nitrate is hydrolysed by water into the heavy white pulverulent basic salt, $3HgO.N_2O_5$. Its limits of existence at 25° C. are with solutions varying from 18·715 $N.HNO_3$ and 0·159 $N.HNO_3$. The corresponding solutions at 15° C. are 17·930 N and 0·136 N.[3] The monohydrate, $3HgO.N_2O_5.H_2O$, was obtained as a white precipitate by the action of water on mercuric nitrate.[1, 2, 4]

The hydrolysis of mercuric nitrate has also been said to result in the formation of $2HgO.N_2O_5.H_2O$,[1, 10] $2HgO.N_2O_5.2H_2O$,[4] $4HgO.N_2O_5$,[4] and $6HgO.N_2O_5$.[4]

A number of ammonium mercury nitrates have been described.[11] The nitrate, $NH_2.Hg.NO_3$, corresponding to infusible white precipitate, $NH_2.Hg.Cl$, which had not been prepared previously,[12] was obtained in small white octahedral crystals in 1908.[13] Strömholm prepared it by the action of aqueous ammonia and ammonium nitrate solution on mercuric nitrate dissolved in nitric acid.

Rây obtained $2(NHg_2.NO_3).H_2O$ by stirring the corresponding nitrite into concentrated nitric acid.[14] Anhydrous dimercuriammonium nitrate, $NHg_2.NO_3$, was prepared, as an insoluble pale yellow powder, by the action of aqueous ammonia on a solution of mercuric nitrate,[1] and by the action of dilute nitric acid on Millon's base.[2] The nitrate of Millon's base, or Soubeiran's salt, $HO.Hg.NHHg.NO_3$, has been prepared by precipitating a solution of mercury acetamide with ammonium nitrate.[3]

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[1] Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 355.

[2] Varet, *ibid.*, 1896, [7], 8, 120.

[3] Cox, *Zeitsch. anorg. Chem.*, 1904, 40, 159.

[4] Kane, *Ann. Chim. Phys.*, 1839, [2], 72, 236.

[5] Ditte, *ibid.*, 1879, [5], 18, 342.

[6] See *J. Chem. Soc.*, 1882, 42, Abs., 451.

[7] Schroeder and Steiner, *Zeitsch. prakt. Chem.*, 1909, [2], 79, 65.

[8] Raoult, *Ann. Chim. Phys.*, 1886, [6], 8, 335.

[9] Varet, *ibid.*, 1896, [7], 8, 140.

[10] Mailhe, *ibid.*, 1902, [7], 27, 374.

[11] Fourcroy, *Ann. Chim.*, 1792, [1], 14, 37; Soubeiran, *Ann. Chim. Phys.*, 1827, [2], 36, 220; Mitscherlich, *Pogg. Annalen*, 1827, 9, 27; Kane, *Ann. Chim. Phys.*, 1839, [2], 72, 242; Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 558; Barfoed, *ibid.*, 1889, [2], 39, 201; Pesci, *Gazzetta*, 1890, 20, 485; 1891, 21, 569; Hofmann and Marburg, *Zeitsch. anorg. Chem.*, 1900, 23, 131; Rây, *ibid.*, 1902, 33, 209; Fürth, *Monatsh.*, 1902, 23, 1147; Strömholm, *Zeitsch. anorg. Chem.*, 1908, 57, 98. Franklin (*J. Amer. Chem. Soc.*, 1907, 29, 59) gives a list.

[12] Franklin, *loc. cit.*

[13] Strömholm, *Zeitsch. anorg. Chem.*, 1908, 57, 98.

[14] Rây, *ibid.*, 1902, 33, 209.

Mitscherlich's salt, $Hg_3N_2H_4O.2NO_3$, was obtained as a white precipitate by treating dilute mercuric nitrate solution, barely acid with nitric acid, with dilute aqueous ammonia.[4]

MERCURY AND PHOSPHORUS.

Mercurous Phosphates.—Yellow or white mercurous orthophosphate, Hg_3PO_4, is precipitated by adding a solution of mercurous nitrate in nitric acid to an excess of sodium phosphate solution. The double salt, $HgNO_3.Hg_3PO_4.H_2O$ or $2HgNO_3.Hg_2O.5Hg_3PO_4.H_2O$, is obtained by adding sodium phosphate to excess of the mercurous nitrate solution. The normal mercurous orthophosphate is converted by heat into mercury and the corresponding mercuric salt.[5]

Silver dimercurous phosphate, $AgHg_2PO_4$, is obtained by precipitating a solution of mercurous and silver nitrates in very dilute nitric acid with disodium hydrogen phosphate. The precipitate is crystallised by dissolving in a minimum of nitric acid and diluting with water. The yellowish-white rhombic prisms or tablets are blackened by ammonia with the liberation of free mercury.[6]

Solutions of mercurous salts give a white precipitate with a solution of sodium or ammonium *pyrophosphate* that is soluble in excess of the reagent. The precipitate becomes dark grey when treated with ammonia or ammonium carbonate or warmed with water.[7] The original white crystalline *mercurous pyrophosphate*, $Hg_4P_2O_7.H_2O$, also darkens when dried at 100° C. and is then insoluble in soda.[8]

Mercuric Phosphates.—*Normal mercuric phosphate*, $Hg_3(PO_4)_2$, is precipitated from an acid solution of mercuric nitrate by disodium hydrogen phosphate solution.[9] It was originally obtained by adding mercuric nitrate solution to an excess of sodium phosphate solution.[10] Co-precipitation of mercuric nitrate occurs if sodium phosphate is added to an excess of mercuric nitrate,[10] and either normal or basic mercuric nitrate is co-precipitated if a neutral or nearly neutral solution of the mercury salt is used.[9] The normal phosphate is also precipitated from mercuric nitrate by NaH_2PO_4, and when phosphoric acid is dropped into excess of mercuric nitrate solution.[9]

It is a heavy white crystalline powder. Hot water partially dissolves it, and, as the solution cools, the salt crystallises in small shining needles.[1] Brandes[2] prepared it in a white pulverulent form by adding potassium phosphate that reacted neutral to nitric acid saturated with mercuric oxide.

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[1] Pesci, *Gazzetta*, 1890, 20, 485.
[2] Hofmann and Marburg, *Zeitsch. anorg. Chem.*, 1900, 23, 131.
[3] Fürth, *Monatsh.*, 1902, 23, 1147.
[4] Mitscherlich, *Pogg. Annalen*, 1827, 9, 97.
[5] Gerhardt, *Jahresber.*, 1849, 288; Haack, *Annalen*, 1891, 262, 192.
[6] Jacobsen, *Bull. Soc. chim.*, 1909, [4], 5, 947.
[7] Brand, *Zeitsch. anal. Chem.*, 1889, 28, 592.
[8] Schwarzenberg, *J. prakt. Chem.*, 1849, [1], 46, 247.
[9] Haack, *Annalen*, 1891, 262, 181.
[10] Gerhardt, *Jahresber.*, 1849, 288.

Hydrochloric acid dissolves it readily, nitric acid only slightly, and phosphoric acid not at all. Brine solution converts the dried salt into the amorphous reddish-brown basic chloride $HgCl_2.3HgO$.[1] It is yellow when hot and white when cold.[3]

Solutions of mercuric salts give a white precipitate with sodium pyrophosphate solution that is soluble in ammonia or ammonium carbonate. The precipitate with ammonium pyrophosphate is soluble in great excess of the reagent.[4] The white precipitate thrown down by sodium pyrophosphate becomes yellowish red by further action of the sodium salt, and when dried at 100° C. has the composition $2HgO.P_2O_5$, corresponding to *mercuric pyrophosphate*.[5]

A white crystalline salt is obtained by treating dimercurammonium nitrite, $NHg_2.NO_2$, with phosphoric acid.[6] It has been formulated as $NHg_2.H_2PO_4$[6] and as $Hg_2NH_2.PO_4$.[7] Millon's base has been formulated as $HO.Hg.NH.Hg.OH.H_2O$ or $(HOHg)_2NH_2OH$ or $HO.Hg.O.Hg.NH_3OH$ and in other ways.[8] Rammelsberg's product, obtained by treating Millon's base with excess of phosphoric acid,[9] may be a mixture of $NHg_2.H_2PO_4$ with unchanged base.[10] A white powder, corresponding to the composition $Hg_3NH_2O.PO_4$, was obtained by acting on mercuric oxide with a solution of ammonium phosphate.[10]

MERCURY AND ARSENIC.

Mercurous Arsenate.—The orange-yellow normal mercurous arsenate, Hg_3AsO_4, precipitates from mixed solutions of mercurous nitrate and excess of sodium arsenate. If the mercury salt is in excess, the double salt, $3Hg_3AsO_4.2(HgNO_3.Hg_2O)$, separates, which, when freshly precipitated and washed, is converted by disodium arsenate solution into the normal arsenate. This double salt is white and soluble in hydrochloric acid. Hydrochloric acid converts the normal salt into calomel and arsenic acid.[11]

Rhombic prisms of the normal arsenate are also obtained by heating mercury with arsenic acid solution at 230° C.[12]

Orange-red crystals of *silver dimercurous arsenate*, $AgHg_2AsO_4$, have been prepared analogously to the corresponding phosphate. Ammonia solution blackens it with the liberation of metallic mercury.[13]

Mercuric Arsenate.—The normal arsenate, $Hg_3(AsO_4)_2$, is obtained by precipitating a solution of mercurous nitrate with a solution of disodium arsenate or monosodium arsenate, and by dropping arsenic acid solution into excess of mercuric nitrate solution.

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[1] Haack, *Annalen*, 1891, 262, 181.
[2] Brandes, *Arch. Pharm.*, 1853, [2], 73, 174.
[3] Gerhardt, *Jahresber.*, 1849, 288.
[4] Brand, *Zeitsch. anal. Chem.*, 1889, 28, 592.
[5] Schwarzenberg, *J. prakt. Chem.*, 1849, [1], 46, 247.
[6] Rây, *Trans. Chem. Soc.*, 1905, 87, 10.
[7] Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 65.
[8] Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 558.
[9] Franklin, *loc. cit.*
[10] Franklin, *loc. cit.*
[11] Haack, *loc. cit.*
[12] Coloriano, *Compt. rend.*, 1886, 103, 273.
[13] Jacobsen, *Bull. Soc. chim.*, 1909, [4], 5, 947.

It is a heavy citron-yellow powder. Hot water dissolves it slightly without decomposition, and shining crystals may separate from the cooled solution. Hydrochloric acid dissolves it freely, nitric acid less readily, and arsenic acid not at all. Brine solution converts it into red-brown mercury oxychloride. Potassium bromide solution colours it brown, and a yellow residue is ultimately left. Potassium iodide solution forms mercuric iodide.

Monosodium arsenate or arsenic acid do not precipitate mercuric chloride solution. Mercuric chloride interacts with normal silver arsenate to form normal mercuric arsenate and silver chloride. Yellow precipitates containing normal mercuric arsenate, mercuric chloride, and mercuric oxide are thrown down from mercuric chloride solution by a solution of disodium arsenate.

Basic mercuric sulphate is converted into normal mercuric arsenate and mercuric oxide by warming with disodium arsenate solution. Hot acetic acid will extract the oxide.[1]

When ammonium arsenate solution acts upon mercuric oxide, $Hg_2NH_2AsO_4$ is produced.[2]

MERCURY AND CARBON.

Mercurous Carbonate, Hg_2CO_3, is a yellow powder[3, 4, 5] that darkens in light with the formation of metallic mercury.[5] The dried salt decomposes into mercury, mercuric oxide, and carbon dioxide at 130° C.,[5] and the same decomposition is effected by warm or hot water.[4] According to Barthélemy[6] it is unstable even in the dark, impossible to dry without decomposition, and cannot be formed at temperatures above 36° C.

It has been prepared, more or less pure, by the action of alkali carbonates or bicarbonates on mercurous nitrate. The nitrate solution has been mixed with an excess of potassium bicarbonate solution, and the precipitate, after frequent agitation for some days with the mother-liquor, to ensure removal of basic nitrate, quickly washed and dried *in vacuo* over sulphuric acid.[3] Rose triturated crystalline mercurous nitrate with potassium bicarbonate and water.[4] Lefort added the nitrate solution to a cold saturated solution of potassium bicarbonate, washed with water containing carbonic acid, and dried over sulphuric acid.[5]

Mercuric Carbonate.—Basic carbonates of mercury are precipitated from mercuric nitrate solution by alkali carbonates or bicarbonates. If the mercuric nitrate is added to the dilute alkali in great excess, brown $3HgO.CO_2$ results from the bicarbonate, and ochre-yellow $4HgO.CO_2$ from the carbonate. The precipitate is contaminated with a basic nitrate in both instances if the alkali is added to the mercury salt. The amorphous precipitates are stable to cold water, and, when dry, at temperatures not exceeding 130° C. An excess of potassium hydroxide converts them into yellow mercuric oxide.[1]

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[1] Haack, *loc. cit.*

[2] Hirzel, *Jahresber.*, 1852, 420; Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 65.

[3] Setterberg, *Pogg. Annalen*, 1830, 19, 59.

[4] Rose, *ibid.*. 1841, 53, 117.

[5] Lefort, *J. Pharm. Chim.*, 1845, [3], 8, 5.

[6] Barthélemy, *Ann. Chim. Phys.*, 1868, [4], 13, 80.

If carbon dioxide is passed through a solution of mercuric chloride partially precipitated by potassium hydroxide, the yellow mercuric oxide, first precipitated, is transformed into a dark brown powder. This is normal mercuric carbonate, $HgCO_3$, mixed with a little mercuric bicarbonate.[2]

The compound $Hg_8N_4H_{10}O_5.2CO_3$ was obtained by the action of carbon dioxide on Millon's base and by treating the base with ammonium carbonate or potassium bicarbonate solution.[3] $Hg_4N_2H_6O_3.CO_3$ was prepared by digesting mercuric oxide in the cold with ammonium carbonate solution,[4] and $Hg_8N_4H_{10}O_5.CO_3$ by boiling Millon's base with a solution of sodium carbonate.[5] Franklin suggested that these compounds are not essentially different.[6]

Mercuric Cyanide, $Hg(CN)_2$, occurs in white or colourless quadratic prisms[7] that are moderately soluble in water. Scheele obtained it by boiling Prussian blue with mercuric oxide and water, and it is also formed when alkali cyanides or ferrocyanides are similarly treated.

Mercuric oxide absorbs gaseous hydrogen cyanide in the cold and very freely in the heat. Aqueous hydrocyanic acid acts vigorously on the oxide, and the action may be explosively violent if the acid is concentrated. Hydrocyanic acid acts upon mercurous oxide or mercurous salts to form mercuric cyanide, not mercurous cyanide. Various mercuric salts are also converted into mercuric cyanide by hydrocyanic acid, and reactions like

$$2KCN+HgCl_2=Hg(CN)_2+2HCl$$

occur in the warmth.[8]

Though mercurous cyanide appears to result as a dark green amorphous precipitate when potassium cyanide acts on mercurous chromate, it is very unstable.[9] Potassium cyanide also acts on other mercurous salts with the final formation of the double mercuric cyanide, $2KCN.Hg(CN)_2$, and mercuric cyanide is the only cyanide of mercury that has been isolated.[10]

It is conveniently prepared by the action of sodium cyanide on mercuric sulphate. The mercuric sulphate, acidified with dilute sulphuric acid, is added, in portions, to the sodium cyanide dissolved in about eight or ten times its own weight of water. The solution becomes very warm and clear, and pure mercuric cyanide crystallises out at about 33° C. When the whole has cooled to a solid mass the mercuric cyanide can be extracted with alcohol and recrystallised from water.[11]

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[1] Millon, *Ann. Chim. Phys.*, 1846, [3], 18, 368.

[2] Raikow, *Chem. Zeit.*, 1907, 31, 57.

[3] Millon, *loc. cit.*, 333.

[4] Hirzel, *Jahresber.*, 1852, 421.

[5] Rammelsberg, *J. prakt. Chem.*, 1888, [2], 38, 558.

[6] Franklin, *J. Amer. Chem. Soc.*, 1907, 29, 64.

[7] de la Provostaye, *Ann. Chim. Phys.*, 1842, [3], 6, 159. See Groth, *Ber.*, 1869, 2, 574.

[8] Dammer, *Handbuch der Anorganisch. Chem.* (Enke, Stuttgart), 1894, ii, 2, 925; Plugge, *Zeitsch. anal. Chem.*, 1879, 18, 408. Mohr (*Annalen*, 1839, 31, 187) observed that *turpeth mineral*, $2HgO.HgSO_4$, was converted into mercuric cyanide by aqueous hydrocyanic acid.

[9] P. and M. M. Richter, *Ber.*, 1882, 15, 1489.

[10] Ditte, *Compt. rend.*, 1890, 110, 191.

[11] Rupp and Goy, *Apoth. Zeit.*, 1908, 23, 373; *Chem. Zentr.*, 1908, ii, 773; *J. Chem. Soc.*, 1908, 94, Abs. i, 863.

The density of mercuric cyanide is about 4 at ordinary temperatures.[1]

Hardin prepared mercuric cyanide for atomic weight determinations by dissolving pure mercuric oxide in pure, warm hydrocyanic acid. The solution was filtered, evaporated to the crystallising point, and the separated crystals recrystallised. They were then quickly rinsed with cold water and warmed for six hours in an air-bath at 50° C. After being finely ground they were again heated in an air-bath for twenty-four hours at 55° C. The powder was kept in a desiccator, enclosed in a weighing tube and over sulphuric acid.[2]

The mercury in mercuric cyanide has been supposed by some to be linked with the nitrogen[3] and by others with the carbon.[4] The great transparency of the compound to light favours the formula $Hg=(C\equiv N)_2$ more than $Hg=(N=C)_2$.[5] The carbon linking is also indicated by the slight reactiveness of mercuric cyanide with acids. In dilute solutions hydrocyanic acid completely decomposes mercuric chloride.[6] Gaseous hydrogen chloride, however, readily decomposes mercuric cyanide in the cold, concentrated aqueous hydrochloric acid acts effectively in the warmth,[6] and hydrochloric acid is better adapted for liberating hydrogen cyanide from mercuric cyanide than any other acid.[7]

Dry hydrogen cyanide reduces heated mercuric sulphate to a grey mass with the formation of mercuric cyanide, though the products vary with conditions.[8] The decomposition

$$2Hg(CN)_2+2H_2O+H_2SO_4=Hg_2SO_4+3HCN+CO_2+NH_3$$

is effected by heating mercuric cyanide with sixty to eighty times its weight of a mixture of equal volumes of sulphuric acid and water to about 130° C., but the decomposition of the cyanide is not even then complete, and a further reduction, during which metallic mercury separates, occurs on raising the temperature above 140° C.[9] But diluted sulphuric acid, as well as weaker acids like tartaric or oxalic, under ordinary conditions, only liberates hydrogen cyanide from mercuric cyanide very imperfectly. Plugge advised distilling, in toxicological estimations, the mercuric cyanide with oxalic acid and sodium chloride to secure decomposing effect of hydrochloric acid without the disintegrating action of hydrochloric acid on the tissues.[10]

At a dark red heat gaseous hydrogen iodide acts on mercuric cyanide to form mercuric iodide, methane, and ammonium iodide.[11]

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[1] 3·77 at 13° C. according to Bödeker, *Jahresber.*, 1860, 17. Other determinations are: 4·0262 at 12° C., 4·0036 at 14·2° C., 4·0026 at 22·2° C. (Clarke, *Ber.*, 1878, **11**, 1504).

[2] Hardin, *J. Amer. Chem. Soc.*, 1896, **18**, 1010.

[3] Kieseritzky, *Zeitsch. physikal. Chem.*, 1899, **28**, 406.

[4] Ley and Schaefer, *ibid.*, 1903, **42**, 704.

[5] Ley and Fischer, *Zeitsch. anorg. Chem.*, 1913, **82**, 336.

[6] Berthelot, *Ann. Chim. Phys.*, 1873, [4], **30**, 494.

[7] Plugge, *Zeitsch. anal. Chem.*, 1879, **18**, 408.

[8] Mohr, *Annalen*, 1839, **31**, 186.

[9] Marsh and Struthers, *Proc. Chem. Soc.*, 1902, **18**, 249. Mohr (*Annalen*, 1839, **31**, 187) noted a reduction to mercurous sulphate by heating with sulphuric acid.

[10] Plugge, *Zeitsch. anal. Chem.*, 1879, **18**, 408. Prussia (*Gazzetta*, 1898, **28**, ii, 113) used tartaric acid. According to Fabre and Josset (*J. Pharm. Chim.*, 1923, **28**, 81), 10 per cent. sulphuric acid and weaker acids of similar concentration liberate very appreciable proportions of hydrogen cyanide. The amount formed attains a maximum and then decreases because ammonium formate is produced.

[11] Berthelot, *Bull. Soc. chim.*, 1867, [2], **7**, 53.

Chlorine gas acts vigorously on mercuric cyanide, and the action may be explosive.[1] Cyanogen chloride, CNCl, can be prepared by passing chlorine into a saturated aqueous solution of the salt[2] or into an alcoholic solution.[3]

Mercuric cyanide decomposes on heating into mercury and cyanogen. The brown powdery polymer of cyanogen, known as paracyanogen, $(CN)_n$, may be simultaneously produced.[4] The reaction at 320°-400° C. is represented by the equations

$$4Hg(CN)_2 = Hg_3 + Hg(CN)_8,$$
$$Hg(CN)_8 = Hg + 4(CN)_2.$$

At higher temperatures ordinary cyanogen is evolved.[5]

When mercuric cyanide is heated with water in a sealed tube the reaction, which begins below 230° C., may be expressed by the equation

$$Hg(CN)_2 + 4H_2O = Hg + CO + (NH_4)_2CO_3.^6$$

It dissolves in water, alcoholic ammonia, pyridine,[7] readily in acetone,[8] and is very soluble in aqueous ammonia.[9] Carbon tetrachloride, bromoform, ethyl bromide, and ethylene bromide only dissolve it very slightly.[10] One hundred parts of water dissolve 53·8 parts of the salt at 101·1° C.,[11] and 1 part of mercuric cyanide dissolves in from 8 to 11 parts of cold water.[12]

Cryoscopic determinations indicate that mercuric cyanide in aqueous solution is not an electrolyte.[13] Since aqueous solutions of the salt give no precipitate with solutions of potassium iodide, silver nitrate, ammonia, or alkaline hydroxides,[14] they contain no appreciable amount of mercury ions. Cryoscopic and conductivity experiments on complex salts containing $Hg(CN)_2$ indicate that the cyanomercury ion $HgCN^{\cdot}$ is very stable and very slightly ionised, according to the equation

$$HgCN^{\cdot} \rightleftharpoons Hg^{\cdot\cdot} + CN'.^{15}$$

Yellow mercuric oxide is usually precipitated from solutions of mercuric salts by sodium hydroxide, but if mercuric cyanide is present it unites with it to form mercuric oxycyanide, $HgO.Hg(CN)_2$, and no precipitation occurs.[16] A slight reaction takes place in solutions containing mercuric cyanide and alkali hydroxides if small amounts of halogen salts are present.[13] The salt is reduced to metallic mercury by heating with a concentrated solution of potassium hydroxide,[1] and, if finely divided, it gives yellow mercuric oxide with it, though dilution gives a clear solution. Mercuric cyanide is much more soluble in caustic potash solution than in water, and the alkaline solution acts as an oxidising agent to alcohol and other organic substances. Crystals of $Hg(CN)_2.KOH.H_2O$ have been isolated from the solution. Silver cyanide is precipitated from aqueous solutions of mercuric cyanide by silver acetate or nitrite, but the action is reversible and precipitation is incomplete. Precipitation is less complete still with silver sulphate, and concentrated solutions of silver nitrate form $Hg(CN)_2.AgNO_3.2H_2O$.[2]

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[1] Sérullas, *Ann. Chim. Phys.*, 1827, [2], 35, 293; Bonis, *Annalen*, 1845, 56, 267.

[2] Wöhler, *ibid.*, 1850, 73, 220. See Sérullas, *loc. cit.*, 339; Bonis, *loc. cit.*, 1847, 64, 305; Cahours and Cloëz, *ibid.*, 1854, 90, 97.

[3] Stenhouse, *ibid.*, 1840, 33, 72.

[4] Johnston, *ibid.*, 1837, 22, 280; Troost and Hautefeuille, *Compt. rend.*, 1868, 66, 735, 795.

[5] Maumené, *Bull. Soc. chim.*, 1881, [2], 35, 597.

[6] Marsh and Struthers, *Proc. Chem. Soc.*, 1902, 18, 249.

[7] Varet, *Compt. rend.*, 1892, 114, 224.

[8] Krug and McElroy, *Zeitsch. anal. Chem.*, 1893, 32, 70.

[9] Brinkley, *J. Amer. Chem. Soc.*, 1922, 44, 1210.

[10] Šulc, *Zeitsch. anorg. Chem.*, 1900, 25, 401.

[11] Griffiths, *Zeitsch. anal. Chem.*, 1887, 26, 427.

[12] Comey, *Dict. Chem. Sols. Inorg.* (Macmillan, London and New York), 1896, p. 143.

[13] Prussia, *Gazzetta*, 1898, 28, ii, 113. A few cryoscopic data are given by Raoult (*Compt. rend.*, 1878, 87, 167) and Skinner (*Trans. Chem. Soc.*, 1892, 61, 340). It electrolyses in the presence of a little sulphuric acid (Hardin, *J. Amer. Chem. Soc.*, 1896, 18, 1010).

[14] Plugge, *Zeitsch. anal. Chem.*, 1879, 18, 408.

[15] Borelli, *Gazzetta*, 1908, 38, i, 361.

[16] Rupp and Goy, *Arch. Pharm.*, 1908, 246, 367.

Hydrogen sulphide precipitates mercuric sulphide from solutions of the cyanide, and, since precipitated mercuric sulphide does not dissolve appreciably in potassium cyanide solution, from solutions of the double cyanide $2KCN.Hg(CN)_2$.[3]

Aluminium acts upon aqueous mercuric cyanide to form alumina, hydrocyanic acid, hydrogen, and mercury.[4]

The *heat of formation* of mercuric cyanide from mercury and cyanogen is 10·280 Cal., and the *heat of solution* is −2·965 Cal.[5]

Mercuric cyanide has antiseptic properties.[6] The symptoms of poisoning by this salt resemble those by hydrogen cyanide itself: proteins, especially if acid is present, liberate much hydrogen cyanide from it.[7]

The *ammoniates*, $Hg(CN)_2.NH_3$, $Hg(CN)_2.2NH_3$, $Hg(CN)_2.NH_3.\frac{1}{2}H_2O$, and $Hg(CN)_2.2NH_3.\frac{1}{2}H_2O$, were reported by Varet.[8] He prepared the first by heating aqueous ammonia with a large excess of mercuric cyanide in a closed vessel at 40° C. It was obtained in small, hard, transparent crystals. He obtained transparent, prismatic needles of the second by the action of ammonia gas on a saturated solution of mercuric cyanide in alcoholic ammonia. Franklin and Kraus also prepared it by dissolving mercuric cyanide in liquid ammonia and allowing the excess of liquid to evaporate.[9] These two anhydrous compounds appear to be the only two addition products formed at 0° C. in the system ammonia-mercuric cyanide. They lose ammonia rapidly on exposure to air.[10]

The stable *double salt*, $2KCN.Hg(CN)_2$, is deposited in crystals by evaporating a solution of mercuric cyanide in aqueous potassium cyanide. It can also be prepared by adding the calculated quantity of mercuric sulphate, in successive portions, to a slight excess of aqueous potassium cyanide.[11] When potassium mercuric cyanide is precipitated by zinc sulphate,[12] or potassium zinc cyanide by mercuric chloride, the precipitate is mainly zinc cyanide with varying amounts of mercuric cyanide. There seems, however, to be a double salt, $4Zn(CN)_2.Hg(CN)_2$.[11]

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[1] Marsh and Struthers, *Proc. Chem. Soc.*, 1902, **18**, 249.

[2] Hofmann and Wagner, *Ber.*, 1908, **41**, 317.

[3] Berthelot, *Compt. rend.*, 1899, **128**, 709. For action of sodium thiosulphate and polythionates, see Gutman, *Ber.*, 1916, **49**, 949.

[4] Varet, *Compt. rend.*, 1892, **114**, 224.

[5] Thomsen, *Thermochem. Untersuch.* (ed. Traube, Enke, Stuttgart), 1906, p. 244. See Berthelot, *Ann. Chim. Phys.*, 1873, [4], **30**, 494.

[6] Chibret, *Compt. rend.*, 1888, **107**, 119.

[7] Fabre and Josset, *J. Pharm. Chim.*, 1923, [7], **28**, 81.

[8] Varet, *Bull. Soc. chim.*, 1891, [3], **6**, 220; *Compt. rend.*, 1889, **109**, 903; 1891, **112**, 313.

[9] Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 49.

[10] Brinkley, *ibid.*, 1922, **44**, 1210.

[11] Dunstan, *Trans. Chem. Soc.*, 1892, **61**, 666.

[12] Rammelsberg, *Pogg. Annalen*, 1837, **42**, 1317.

Mercuric cyanide also forms a number of double and complex salts.[1]

Mercuric Oxycyanide.—Johnston obtained a basic mercuric cyanide, to which he ascribed the formula $HgO.Hg(CN)_2$, by agitating an excess of red mercuric oxide with 10–20 per cent. aqueous hydrocyanic acid. The substance crystallised in white four-sided acicular prisms.[2]

This basic salt was said to be superior to mercuric chloride in antiseptic power,[3] though it was also said to prevent bacteria from developing without killing them,[4] and it has been suggested that the antiseptic power is due to impurities.[5] Surgeons use it as a disinfectant, especially for the hands,[6] but commercial preparations have been said to vary in surgical value and rarely to correspond to the formula $HgO.Hg(CN)_2$.[7]

The basic cyanide, $HgO.3Hg(CN)_2$, was said to be formed by the action of aqueous mercuric cyanide on freshly precipitated mercuric oxide[8] or on the former oxycyanide,[9] and, according to Barthe, many pharmaceutical preparations correspond closely to this formula.[10]

$HgO.Hg(CN)_2$ seems, however, to be the only oxycyanide formed by dissolving mercuric oxide in mercuric cyanide, though it is not possible to convert the mercuric cyanide quantitatively by this method.[11] Since the mercuric oxide acts as hydroxide, hydroxyl ions will accelerate the reaction, and the preparation of the oxycyanide can be effected by stirring 27 grm. of mercuric cyanide (a slight excess) into 22·2 grm. of mercuric oxide, 60 c.c. of water, and 4 c.c. of 10 per cent. sodium hydroxide till the mixture is colourless.[12] The reaction

$$HgCl_2+Hg(CN)_2+2KOH=HgO.Hg(CN)_2+2KCl+H_2O$$

can be applied to obtain a 1 per cent. solution of the oxycyanide by mixing aqueous solutions of the reacting substances in appropriate molecular proportions. Analysis indicates that the salt in such a solution (which contains a little potassium chloride, or sodium chloride if caustic soda is used) corresponds closely to $HgO.Hg(CN)_2$ after keeping for three months.[13]

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[1] Bloxam, *Chem. News*, 1883, **48**, 161; *Ber.*, 1883, **16**, 2669; Varet, *Compt. rend.*, 1889, **109**, 941; 1890, **110**, 147; **111**, 679; 1891, **112**, 535, 1312; 1895, **121**, 348; *Ann. Chim. Phys.*, 1896, [7], **8**, 240; 1897, [7], **10**, 5; Vitali, *Chem. Zentr.*, 1889, ii, 391; Prussia, *Gazzetta*, 1898, **28**, ii, 113; Borelli, *ibid.*, 1908, **38**, i, 361; Rupp and Goy, *Chem. Zentr.*, 1908, ii, 773; Strömholm, *Zeitsch. anorg. Chem.*, 1914, **90**, 370; Gupta, *Trans. Chem. Soc.*, 1920, **117**, 67.

[2] Johnston, *Phil. Trans.*, 1839, 113; Schlieper, *Annalen*, 1846, **59**, 9.

[3] Chibret, *Compt. rend.*, 1888, **107**, 119.

[4] von Pieverling, *Arch. Pharm.*, 1906, **244**, 35.

[5] Holdermann, *ibid.*, 1905, **243**, 600. According to Kühl (*ibid.*, 1913, **251**, 341), the presence of salt may increase the bactericidal value, and the disinfectant action is not apparently impaired by substituting considerable quantities of the normal cyanide for the oxycyanide.

[6] Tagliavini, *Boll. chim. farm.*, 1917, **56**, 297.

[7] von Pieverling, *J. Chem. Soc.*, 1899, **76**, Abs. ii, 698.

[8] Holdermann, *Arch. Pharm.*, 1904, **242**, 32.

[9] Joannis, *Ann. Chim. Phys.*, 1882, [5], **26**, 510; he investigated the thermochemistry of $HgO.3Hg(CN)_2$.

[10] Barthe, *J. Pharm. Chim.*, 1896, [6], **3**, 182; he considered both oxycyanides unsuitable for surgical purposes.

[11] Holdermann, *Arch. Pharm.*, 1905, **243**, 600. There may be a compound Hg(OCN)CN (Langhans, *J. Soc. Chem. Ind.*, 1922, **41**, 234A).

[12] Rupp and Goy, *Arch. Pharm.*, 1908, **246**, 367.

[13] Rupp and Lehmann, *Chem. Zentr.*, 1908, ii, 816.

The crystalline salt can be prepared by dissolving 125 grm. of mercuric acetate and 105 grm. of mercuric cyanide in about 1 litre of boiling water, filtering if necessary, and stirring in approximately normal sodium hydroxide till the liquid is alkaline to phenolphthalein. The oxycyanide crystallises suddenly near the end-point. After remaining a day in the cold, the crystals are filtered, washed with cold water, and dried in the air.[1] Jones grinds 40 grm. of mercuric cyanide, 30 grm. of yellow mercuric oxide, and 15 c.c. of water together, adds 0·5 c.c. of 20 per cent. caustic soda, and stirs the whole during the addition of water. After making acid to phenolphthalein with acetic acid, the whole is added to 200 c.c. of boiling water with 20 grm. of mercuric cyanide, boiled to nearly complete solution, filtered, and cooled. The crystals are washed with a little cold water and dried over sulphuric acid. If the crystals are separated from more concentrated solutions they are liable to decompose, and explosions have occurred during preparation.[2] Johnston noted that mercuric oxycyanide exploded when heated, and detonated mildly if it was heated in a closed tube. He also said that it does not explode under the hammer,[3] but it is apparently liable to explode when ground in a mortar, or even when mixed with indifferent substances with a wooden spatula on a wooden board.[4] According to Kast and Haid,[5] it blackens and smokes when strongly triturated. It ignites at 170° C., and is more sensitive to shock than gunpowder or picric acid.

The density of $HgO.Hg(CN)_2$ has been given as 4·437 at 19·2° C., and from 4·428 to 4·419 at 23·2° C.[6] Light apparently does not decompose it,[7] but it darkens on heating. There may be a preliminary reduction to mercurous salt at 100° C.[8] before it finally blackens and explodes.[3]

It is sparingly soluble in cold water but more freely soluble in hot: the solution has an alkaline reaction.[3] The solution acts towards potassium iodide like a mixture of mercuric cyanide and mercuric oxide. The reaction

$$HgO.Hg(CN)_2+2KI+H_2O=HgI_2+Hg(CN)_2+2KOH$$

occurs with lower proportions of the iodide, and complex salts are produced when the proportions are greater. It also behaves like a mixture towards iodine and the halogen acids:[9] when decinormal hydrochloric acid is added to the oxycyanide in presence of sodium chloride, the reaction

$$HgO.Hg(CN)_2+2HCl=HgCl_2+Hg(CN)_2+H_2O$$

occurs.[10] The solution smells of hydrogen cyanide when it is heated with dilute hydrochloric acid. Hydrogen sulphide precipitates mercuric sulphide from it.[3]

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[1] Holdermann, *Arch. Pharm.*, 1906, 244, 133.
[2] Jones, *Pharm. J.*, 1920, 105, 87.
[3] Johnston, *Phil. Trans.*, 1839, 113.
[4] Merck, *Pharm. Zentr.-h.*, 1922, 63, 232.
[5] Kast and Haid, *J. Soc. Chem. Ind.*, 1922, 41, 789A.
[6] Clarke, *Ber.*, 1878, 11, 1504.
[7] Chibret, *Compt. rend.*, 1888, 107, 119.
[8] Schlieper, *Annalen*, 1846, 59, 9.
[9] Rupp and Goy, *Arch. Pharm.*, 1909, 247, 100.
[10] Tagliavini, *Boll. chim. farm.*, 1917, 56, 297.

The solution of the oxycyanide also behaves like a mixture of cyanide and oxide with aqueous ammonia—giving precipitates of mercuriammonium compounds while mercuric cyanide remains dissolved. Stout needles of $Hg(CN)_2.HgSO_4.5H_2O$, hydrolysed by water into mercuric cyanide and basic mercuric sulphate, are obtained by evaporating a solution of the oxycyanide in dilute sulphuric acid. The behaviour of the solid oxycyanide is represented by the formula HgO. $Hg(CN)_2$, and its molecular weight in solution corresponds cryoscopically to OH.Hg.CN.[1] It has been supposed to ionise slightly into OH′ and HgCN˙,[2] but the existence of evidence for the latter ion has been denied.[1]

The heat of formation of the solid oxycyanide from solid mercuric cyanide and oxide is 2·4 Cal.[3]

Mercuric Fulminate.—Howard obtained mercuric fulminate, $Hg(CNO)_2$, by adding a solution of mercury, or mercuric oxide, in nitric acid to alcohol.[4] This method was used by subsequent experimenters,[5] and is still the method of preparation. If the nitric acid solution of mercury is stood and the alcohol added to it (with warming), the fulminate is not the product.[6]

The usual materials are clean mercury, nitric acid of density 1·36, and 90 per cent. alcohol. The operation is performed in a flask. The proportions of acid and alcohol are varied somewhat, but they must be in large excess to ensure a good yield. A vigorous reaction soon begins when the nitric acid solution is added to the spirit, and crystals of the fulminate deposit. About a pound of mercury is usually employed. When the reaction is over the contents of the flask are poured into water and washed free from acid by decantation.[7] The temperature of the alcohol before adding the mercuric nitrate solution is varied in different processes. In the Chandelon process the temperature is about 55° C. In Chavalier's modification of Liebig's process the initial temperature is ordinary room temperature or a few degrees above it. If the reaction becomes too energetic, as it may do in the Chandelon process, it can be circumspectly checked by adding more alcohol.

The washed precipitate is often stored under water in linen bags, so that it can be handled without serious risk of explosion. It is obtained dry by spreading it out on trays and driving off the moisture with warm air at a temperature not above 40° C. or by means of a vacuum drier.[8]

Mercury fulminate can also be prepared by adding oximinoacetic acid to mercuric nitrate dissolved in nitric acid,[9] and it separates in crystals when malonic acid and a little sodium nitrite are added to a solution of mercury in excess of dilute nitric acid.[10] Methyl alcohol cannot be substituted for ethyl alcohol,[1] but various other substances give mercuric fulminate when the nitric acid solution of mercuric nitrate is added to them.[2]

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[1] Rupp and Goy, *Arch. Pharm.*, 1912, **250**, 280. See Rupp, *ibid.*, 1906, **244**, 1. According to Borelli (*Gazzetta*, 1908, **38**, i, 361), the properties of the oxycyanide are expressed by the formula $O(HgCN)_2$ and the formation of the hydroxide OH.Hg.CN in water. See also Holdermann, *Arch. Pharm.*, 1906, **244**, 133.

[2] Holdermann, *Arch. Pharm.*, 1906, **244**, 133.

[3] Joannis, *Compt. rend.*, 1881, **93**, 271.

[4] Howard, *Phil. Trans.*, 1800, 204.

[5] Liebig, *Annalen*, 1855, **95**, 284.

[6] Cowper, *Trans. Chem. Soc.*, 1881, **39**, 242.

[7] Marshall, *Explosives* (Churchill, London), 1917, vol. ii, 700.

[8] Williams, *The Chemistry of Cyanogen Compounds* (Churchill, London), 1915, 315.

[9] Wieland, *Ber.*, 1910, **43**, 3362.

[10] Angelico, *Chem. Zentr.*, 1901, ii, 404.

Pure fulminate of mercury is white, but grey varieties occur commercially, and the product from the above process is often brown—apparently from the presence of resinous substances formed in the reaction when methylated spirit is used. White fulminate is obtained by adding some metallic copper and hydrochloric acid to the nitric acid solution before pouring it into the alcohol, but the whiteness seems to be due to the bleaching, not to the destruction, of the coloured bodies.[3] Solonina advises the addition of cuprous chloride instead of copper and hydrochloric acid.[4]

Howard's product was a dark precipitate that altered into white acicular crystals.[5] A litre of water dissolves 0·693–0·710 grm. at 12° C., 1·7381–1·7835 grm. at 49° C.,[6] and about 8 grm. at 100° C.[4] It crystallises from its aqueous solution in white or yellowish gleaming needles.[7] Its density has been given as 4·42.[8]

Mercuric fulminate is decomposed by nitric or hydrochloric acid and by many other reagents.[9]

It explodes in contact with concentrated sulphuric acid [10] or under shock,[11] and is used as a detonator.

Both grey and white fulminates of mercury are converted into a non-explosive substance by heating at 90° C. for 100 hours in the dry or wet condition. The yellowish-brown product (pyrofulmin) retains the original crystalline form of the fulminate.[12]

Mercurous Thiocyanate, $Hg_2(CNS)_2$, is precipitated from mercurous nitrate solution by potassium thiocyanate.[13] The solutions should be very dilute.[14] Hermes states that the white precipitate is only obtained if mercuric salt is also present in the solution, and he doubted the existence of mercurous thiocyanate.[15] The white precipitate of $Hg_2(CNS)_2$ decomposes readily into mercuric thiocyanate, $Hg(CNS)_2$, and metallic mercury, even when precipitated from dilute solutions of mercurous nitrate and potassium thiocyanate. If, however, the solution is sufficiently acid, the grey or dark precipitate becomes white again on standing, as though the mercurous thiocyanate were reformed.[1]

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[1] Stahlschmidt, *Pogg. Annalen*, 1860, 110, 547.

[2] Wöhler and Theodorovits, *Ber.*, 1905, 38, 1345.

[3] Marshall, *loc. cit.*

[4] Solonina, *Zeitsch. Ges. Schiess u. Sprengstoffwesen*, 1910, 41, 67.

[5] Howard, *loc. cit.*

[6] Hollemann, *Rec. Trav. chim.*, 1896, 15, 159.

[7] Schischkoff, *Annalen*, 1856, 97, 53. He said that his crystals contained a half molecule of water of crystallisation.

[8] Berthelot and Vieille, *Ann. Chim. Phys.*, 1880, [5], 21, 569.

[9] For reactions and constitution of mercury fulminate, see Howard, *Phil. Trans.*, 1800, 204; Kekulé, *Annalen*, 1857, 101, 213; Steiner, *Ber.*, 1875, 8, 520, 1177; 1876, 9, 787; 1883, 16, 1484, 2419; Carstanjen and Ehrenberg, *J. prakt. Chem.*, 1882, [2], 25, 232; Ehrenberg, *ibid.*, 1883, [2], 28, 56; 1884, [2], 30, 38; Scholvien, *ibid.*, 1884, [2], 30, 91; Brownsdon, *J. Soc. Chem. Ind.*, 1905, 24, 381; Rathsburg, *Ber.*, 1921, 54, 3185; Langhans, *J. Soc. Chem. Ind.*, 1923, 42, 120A.

[10] Howard, *Phil. Trans.*, 1800, 204.

[11] For studies of explosive properties of mercury fulminate, see Howard, *Phil. Trans.*, 1800, 204; Berthelot and Vieille, *Ann. Chim. Phys.*, 1880, [5], 21, 564; Hoitsema, *Zeitsch. physikal. Chem.*, 1896, 21, 137; Robertson, *Trans. Chem. Soc.*, 1921, 119, 18; Farmer, *ibid.*, 1922, 121, 174.

[12] Langhans, *J. Soc. Chem. Ind.*, 1922, 41, 234A; 1923, 42, 120A. The pyrofulmin may be a mixture of mercuric oxide and Hg(OCN)CN.

[13] Wöhler, *Gilbert's Annalen*, 1821, 69, 272.

[14] Claus, *J. prakt. Chem.*, 1838, [1], 15, 406.

[15] Hermes, *ibid.*, 1866, [1], 97, 465.

Mercurous thiocyanate is insoluble in water, darkened by alkalies, and dissolved by hot hydrochloric acid with separation of metallic mercury.[1] It decomposes at a red heat.[2]

Some mercurous thiocyanate may be formed by the action of light upon the precipitated mercuric salt.[1]

Mercuric Thiocyanate, $Hg(CNS)_2$, has been crystallised in small white plates from a hot solution of mercuric oxide in thiocyanic acid.[1] It falls as a white precipitate by mixing solutions of a mercuric salt and potassium thiocyanate, and dissolves in excess of either reagent.[1, 3] Joannis prepared it by precipitating a solution of mercuric chloride with potassium thiocyanate solution,[4] and a solution obtained by dissolving mercuric chloride in excess of ammonium thiocyanate has been used as a photographic intensifier.[5] Mercuric thiocyanate dissolves in cold hydrochloric acid, in metallic chlorides, and, with more difficulty, in hot water, alcohol, or ether. It crystallises in needles from water or alcohol,[3] and was also said to crystallise from boiling water in shining plates.[1]

" Pharaoh's serpents " are prepared by rubbing up the dried precipitate of mercuric thiocyanate with gum-water to a thick plastic mass, making short cones of the mixture, and drying them. When these cones are ignited they burn with a sulphur-like flame, and the ash extends as a long twining filament.

The *heat of formation* of mercuric thiocyanate from liquid mercury, octahedral sulphur, and cyanogen gas is 18·0 Cal.[4]

Mercuric thiocyanate appears to be somewhat sensitive to light, and a little mercurous thiocyanate may be formed.[1]

Fleischer obtained small yellow tabular crystals of $2Hg(CNS)_2.4NH_3.H_2O$ (or $2Hg(CNS)_2.3NH_3.H_2O$) by dissolving yellow mercuric oxide in a hot solution of ammonium thiocyanate.[6] When this salt is boiled with water a citron-yellow powder results which, according to Fleischer, is the *basic salt*, $3HgO.Hg(CNS)_2$, but, according to Philipp,[7] is $HgO(NH_2Hg).CNS$. Claus[8] said he obtained the basic salt, $2HgO.Hg(CNS)_2$, by ammoniating a solution of mercuric thiocyanate in potassium thiocyanate.

Yellow needles of the *acid salt*, $Hg(CNS)_2.2HCNS$, were obtained by diluting a solution of mercuric thiocyanate in thiocyanic acid.[3]

The following double salts have been prepared: $KCNS.Hg(CNS)_2$,[1, 8] $2NH_4CNS.Hg(CNS)_2$,[6] $Hg(CNS)_2.Zn(CNS)_2$.[9]

Mercuric thiocyanate also unites with pyridine to form colourless, transparent, monoclinic crystals of $Hg(CNS)_2.C_5H_5N$.[10]

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[1] Philipp, *Pogg. Annalen*, 1867, 131, 86.
[2] Wöhler, *Gilbert's Annalen*, 1821, 69, 272.
[3] Hermes, *J. prakt. Chem.*, 1866, [1], 97, 465.
[4] Joannis, *Ann. Chim. Phys.*, 1882, [5], 26, 543.
[5] Eberhard, *J. Soc. Chem. Ind.*, 1901, 20, 387.
[6] Fleischer, *Annalen*, 1875, 179, 225.
[7] Philipp, *ibid.*, 1875, 180, 341.
[8] Claus, *J. prakt. Chem.*, 1838, [1], 15, 401.
[9] Clève, *ibid.*, 1864, [1], 91, 227.
[10] Grossmann and Hünseler, *Zeitsch. anorg. Chem.*, 1905, 46, 364.

DETECTION AND ESTIMATION OF MERCURY.

Detection of Mercury.—Most mercury compounds sublime when they are heated alone in a closed tube. The sulphide gives a black sublimate and mercuric iodide a yellow, which turns red on rubbing.[1] All compounds of mercury, when mixed with sodium carbonate and heated in a closed tube, give a grey mirror consisting of small globules of mercury. The reduction is assisted by mixing a reducing agent, such as charcoal, with the sodium carbonate. The deposition of a grey film of mercury on bright copper-foil is characteristic of mercury solutions. On drying and rubbing the deposit becomes bright like silver.

Mercurous salts, which are readily hydrolysed in dilute aqueous solution, are usually recognised by the precipitate of mercurous chloride given with hydrochloric acid or chloride solutions. Mercurous chloride is easily distinguished by blackening with ammonia or caustic alkali. It also dissolves in nitric acid, aqua regia, and chlorine water. A similar white precipitate is given by mercurous solutions with hydrobromic acid or soluble bromides.

Potassium iodide solution gives an olive-green precipitate of mercurous iodide with solutions of mercurous salts. Caustic potash precipitates black mercurous oxide, and alkali carbonates give a yellow precipitate of carbonate that rapidly becomes grey through the separation of metallic mercury. Ammonia and ammonium carbonate produce a black precipitate of mercuric ammino salt and metallic mercury. Brown mercurous chromate is precipitated from solutions of mercurous salts by potassium chromate that becomes red on boiling. Potassium cyanide forms mercuric cyanide and metallic mercury, and stannous chloride reduces mercurous salts to metallic mercury. Hydrogen sulphide, under ordinary conditions, throws down a black precipitate of mercur*ic* sulphide from mercurous salt solutions, and mercury is simultaneously separated.

Solutions of mercuric salts give a black precipitate of mercuric sulphide with hydrogen sulphide. Yellow mercuric oxide is precipitated by caustic potash. Ammonia produces white $Hg(NH_2)Cl$ when it acts on mercuric chloride. Potassium iodide gives a red precipitate of mercuric iodide, which is yellow when it first precipitates and dissolves in excess of the reagent.[1] Alkali carbonates precipitate reddish-brown basic carbonates. Potassium cyanide forms complex salts without giving any precipitate, though concentrated mercuric nitrate solution may precipitate some mercuric cyanide that dissolves in excess of potassium cyanide. Alkali chromates give yellow precipitates that go red on boiling. Ferrous sulphate reduces mercuric nitrate on boiling to metallic mercury. Stannous chloride reduces mercuric salts to mercurous, and finally to metallic mercury. Aluminium, copper, zinc, and iron precipitate mercury from its solutions. Potassium thiocyanate throws down white mercuric thiocyanate, soluble in excess of either the potassium thiocyanate or the mercuric salt.

Browning detects very small quantities of mercury by precipitating the metal electrolytically on a gold cathode and examining spectroscopically.[1] Artmann [2] soaks filter paper in some of the mercury salt solution, treats with cuprous iodide, and dries. A bright red colour indicates mercury. Two mgm. in 1000 c.c. may be thus detected.

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[1] See Slater Price, *J. Soc. Chem. Ind.*, 1923, 42, 292.

Denigès applied the characteristic crystals obtained with potassium iodide or bromide microchemically.[3]

If diphenylcarbazide, in benzene or alcoholic solution, is shaken with solutions of mercury salts, a bluish-violet coloration is given with very small quantities of mercury.[4]

Determination as Metal.—The volatility of mercury and the ready reducibility of its compounds were applied to its estimation by distilling it over for collection and weighing.[5] Since most compounds of mercury are quantitatively decomposed by heating with lime, mercuric oxide being first formed which then decomposes into metal and oxygen, the method is usually applied by heating a mixture of the substance under analysis with quicklime. A layer of lime, then a layer of the substance mixed with the quicklime, and another layer of lime are commonly introduced into a long combustion tube of glass. Wads of asbestos at either end keep the material in position. During the heating a current of carbon dioxide or, preferably, according to Treadwell,[6] of illuminating gas, is passed through. The exit end of the tube is drawn out. Rose bent this drawn-out end under water to condense the volatilised mercury for weighing.[7] Instead of collecting the mercury under water, drying, and weighing, Treadwell [6] prefers to collect it in a bulb tube—placing gold leaf at the exit to retain mercury vapours. The tube containing the condensed mercury is weighed, and then again after volatilising the mercury. Dry air should be led through the tube, after condensing the mercury, before the first weighing.

If finely divided copper is added to the mixture of mercury salt and lime, the method can be used for mercuric iodide.[7]

This dry method of analysis can be applied to ores and minerals without the previous removal of other metals. They can be heated with lime alone, but if sulphur is present, iron filings [8] or copper oxide [9] should be mixed with the lime. Accurate results can be obtained with both mercuric sulphide and iodide by using a mixture of quicklime (one part), iron filings (two parts), and powdered lead chromate (one part).[10]

The mercury, instead of being weighed, can be dissolved in nitric acid and estimated by a wet method.[8, 9] It can also be collected on a cooled silver plate that has been previously weighed.[11] Rubiers [12] heats the mineral, mixed intimately with fine iron powder, in a porcelain crucible. A closely covering gold or silver crucible serves to condense the volatilised mercury. This cover is cooled during the heating of the mineral, and, when the decomposition is completed, is washed with alcohol and weighed.

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[1] Browning, *Trans. Chem. Soc.*, 1917, 111, 236.

[2] Artmann, *Zeitsch. anal. Chem.*, 1921, 60, 81.

[3] Denigès, *Ann. Chim. anal.*, 1919, [2], 1, 383.

[4] Cazeneuve, *Compt. rend.*, 1900, 131, 346; Ménière, *ibid.*, 1908, 146, 754.

[5] Erdmann and Marchand, *J. prakt. Chem.*, 1844, [1], 31, 385; König, *ibid.*, 1857, [1], 70, 64.

[6] Treadwell, *Analytical Chemistry* (translated by Hall) (Chapman & Hall, London; Wiley, New York), 1913, 2, 171.

[7] Rose, *Pogg. Annalen*, 1860, 110, 529.

[8] Heinzelmann, *Chem. Zeit.*, 1921, 45, 657.

[9] Bouton and Duschak, *U.S. Bureau of Mines, Techn. Paper* 277, 1920.

[10] Cumming and Macleod, *Trans. Chem. Soc.*, 1913, 103, 513.

[11] Heinzelmann, *loc. cit.*, 1226.

[12] Rubiers, *Anal. Fis. Quim.*, 1918, 16, 661; *J. Chem. Soc.*, 1919, 116, Abs. ii, 80.

Salts of mercury can also be reduced to metal by hydrazine salts,[1] by zinc filings and sulphuric acid,[2] by formaldehyde in the presence of an alkali hydroxide,[3] or by formaldehyde in the presence of sodium hydroxide and potassium iodide.[4] The separated metal can be weighed as such or dissolved and estimated by a volumetric method.

Gordon estimates very small quantities of mercury by rotating a coil of copper gauze in the solution, in the presence of hydrochloric acid, and weighing before and after heating in hydrogen.[5]

Mercury can also be quantitatively precipitated from nitric acid solution by calcium hypophosphite.[6]

Gravimetric Estimation.—Solutions of mercuric salts that contain no oxidising substances can be saturated with hydrogen sulphide in the cold, and the precipitated *sulphide* weighed after drying at 105°–110° C. If oxidising substances are present, the acid solution is almost neutralised with pure sodium carbonate, and treated with a slight excess of ammonium sulphide. Pure caustic soda solution is then added, with rotation, till the dark liquid lightens. It is then heated to boiling and more caustic soda added till the liquid is clear. The sulphosalt, $Hg(SNa)_2$, is decomposed by boiling with ammonium nitrate until the ammonia is almost expelled. The settled HgS is filtered off, dried at 110° C., and weighed. Free sulphur can be removed from the precipitate by extraction with carbon disulphide, or by boiling with sodium sulphite before filtering.[7]

Solutions of mercurous salts can be determined as *mercurous chloride* by treating with sodium chloride, diluting considerably with water, and filtering after standing for twelve hours. The precipitate is then dried at 105° C. and weighed.[8] Hulett precipitated with a slight excess of dilute sodium chloride solution, and dried the mercurous chloride in a vacuum desiccator.[9] Solutions of mercuric salts are heated with hydrochloric acid, diluted with water, and reduced by adding an excess of phosphorous acid [10] before precipitating with the chloride solution.

The precipitated mercurous chloride may be estimated volumetrically by treating with iodine solution and hydrochloric acid,

$$2HgCl+I_2+2HCl=2HgCl_2+2HI.$$

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[1] Duccini, *Gazzetta*, 1913, 43, ii, 693. Struve (*Chem. Zeit.*, 1914, 38, 320) completes the estimation by titrating the excess of hydrazine.

[2] François, *Compt. rend.*, 1918, 166, 950.

[3] Adanti, *Boll. chim. farm.*, 1916, 55, 553. Since some mercurous chloride is liable to form (Kolthoff and Keijzer, *Pharm. Weekblad.*, 1920, 57, 913), the reduction is best performed in the presence of barium hydroxide (Kolthoff and Keijzer, *Pharm. Weekblad.*, 1923, 60, 18).

[4] François, *J. Pharm. chim.*, 1921, 24, 369.

[5] Gordon, *Analyst*, 1920, 45, 41. For estimation of small quantities, also see Böttger and Heinze, *Zeitsch. Elektrochem.*, 1916, 22, 69.

[6] Winkler, *Zeitsch. anal. Chem.*, 1924, 64, 262.

[7] Treadwell, *Analytical Chemistry* (translated by Hall) (Chapman & Hall, London; Wiley, New York), 1919, 2, 168.

[8] Treadwell, *loc. cit.*, 170.

[9] Hulett, *Zeitsch. physikal. Chem.*, 1904, 49, 483.

[10] Treadwell, *loc. cit.*, 171. For investigation of reduction of mercuric chloride by phosphorous acid, see Linhart, *Amer. J. Sci.*, 1913, [4], 35, 353. Hypophosphorous acid reduces mercuric chloride to mercurous chloride more rapidly than phosphorous acid (Mitchell, *Trans. Chem. Soc.*, 1921, 119, 1266).

The estimation is completed by titrating the excess of iodine with sodium thiosulphate.[1]

In estimating mercury as *zinc mercuric thiocyanate,* the solution of the mercuric salt, containing about 0·14 grm. of mercury, is treated with 25 c.c. of a solution containing 39 grm. of ammonium thiocyanate and 0·29 grm. of zinc sulphate per litre. The precipitate of $Zn(CNS)_2.Hg(CNS)_2$ is collected, washed with a solution prepared by diluting 5 c.c. of the thiocyanate reagent with 450 c.c. of water, dried at 105° C., and weighed. The moist precipitate may also be treated with 35 c.c. of concentrated hydrochloric acid, 10 c.c. of water, 7 c.c. of chloroform, and titrated with standard potassium iodate solution.[2]

Neutral solutions of mercuric salts are not precipitated by excess of ammonium thiocyanate solution in the presence of pyridine. The formation of white crystalline cadmium pyridine thiocyanate under these conditions provides a separation of mercury from cadmium. After precipitating the cadmium the mercury can be estimated in the filtrate as sulphide.[3]

Volumetric Methods.—The volumetric estimation by standard thiocyanate solution has been often recommended. Low[4] boils precipitated mercuric sulphide with concentrated sulphuric acid and a solution of potassium permanganate. After destroying manganese dioxide with oxalic acid the whole is heated to fuming and diluted with 100 c.c. of water. Ferric indicator is then added and the titration performed with decinormal thiocyanate. Metallic mercury, as obtained in the dry method, may be dissolved in nitric acid with a few drops of potassium permanganate solution,[5] or in potassium permanganate with an excess of hydrogen peroxide,[6] and titrated as before. Electrometric titration is said to give a sharper end-point. The mercury is dissolved in hot concentrated nitric acid, and the nitric oxide oxidised by potassium permanganate. The slight excess of the permanganate is removed by adding ferrous sulphate ; the small amount of ferric salt formed serves as indicator.[7]

Rupp[8] utilised the fact that potassium cyanide, when added to neutral solutions of mercuric chloride, produces non-ionised mercuric cyanide. The excess of potassium cyanide can then be titrated with standard hydrochloric acid. Mitchell found this method to be more reliable than most volumetric methods published, and to be applicable to very dilute solutions. The solution is exactly neutralised by caustic soda, using bromophenol-blue as indicator. A slight excess of decinormal potassium cyanide is added, and the excess titrated with decinormal hydrochloric acid to the tint of the indicator before adding the cyanide. Methyl-orange can be used, but is less effective in artificial light.[9]

Mercuric salts can also be estimated by precipitation as hydroxide, solution in standard potassium cyanide, and titration of the excess with standard silver nitrate—using potassium iodide as indicator.[1] Bauer,[2] after destroying organic matter with sulphuric acid and hydrogen peroxide, adds a slight excess of ammonia, then an excess of standard potassium cyanide, and titrates as before.

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[1] Riesser, *Zeitsch. physiol. Chem.*, 1915, 96, 355.
[2] Jamieson, *J. Ind. Eng. Chem.*, 1919, 11, 296.
[3] Rotter, *Zeitsch. anal. Chem.*, 1924, 64, 102.
[4] Low, *Analyst*, 1920, 29, 13.
[5] Heinzelmann, *Chem. Zeit.*, 1921, 45, 657.
[6] Boulton and Duschak, *U.S. Bureau of Mines, Techn. Paper* 227, 1920.
[7] Müller and Benda, *Zeitsch. anorg. Chem.*, 1924, 134, 102.
[8] Rupp, *Chem. Zeit.*, 1908, 32, 1077.
[9] Mitchell, *Trans. Chem. Soc.*, 1921, 119, 1272.

The mercury obtained by a reduction method can be dissolved in standard iodine solution,[3] or in standard iodine solution containing some dilute acetic acid,[4] and the excess of iodine over the amount required to convert the mercury into iodide titrated with sodium thiosulphate.

Sasse [5] estimates mercuric chloride volumetrically by titration with potassium iodide solution.

Electrolytic Estimation.—Mercury can be estimated electrolytically in acid, neutral, or alkaline solutions. It separates in fluid drops from acid solutions of either mercurous or mercuric salts, and can be collected in a platinum basin that acts as cathode.[6] The mercury deposited from nitric acid solutions spreads out as a mirror on the platinum cathode as the cathode potential rises, and from ammoniacal or cyanide solutions the fine drops of metal are sufficiently adherent to the cathode.[7] Gold cathodes have been employed,[8] and de Mecus says that the mercury deposit thus obtained can be washed with alcohol and ether. He uses a solution containing about 0·3 grm. metal and a little nitric acid in 125 c.c. The electrolysis is performed at 30°-40° C., the electrolyte is well stirred, and a current of 4–4·5 amp. is employed.[9]

Stirring the electrolyte seems to promote an adherent mirror of mercury on the cathode, and rotating anodes have been used by many experimenters.[10] The cathode has also been rotated,[11] and its surface may be matt with advantage.[12]

Brand washed the separated mercury with water, alcohol, and ether, and then dried it in a desiccator over sulphuric acid.[13] But when the metal is dried over sulphuric acid some mercury vapour is absorbed by the acid.[14] Borelli dried his mercury, after deposition in a platinum capsule, over fused caustic potash ; [15] Losanitsch washes the cathode, with its deposit of mercury, with water and alcohol, and dries over caustic potash in an atmosphere of mercury.[11]

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[1] Clennell, *Eng. and Mining J.*, 1914, 787.

[2] Bauer, *Ber.*, 1921, 54B, 2079.

[3] Adanti, *Boll. chim. farm.*, 1916, 55, 553.

[4] François, *J. Pharm. chim.*, 1921, 24, 369.

[5] Sasse, *Chem. Zeit.*, 1920, 65, 559.

[6] Luckow, *Zeitsch. anal. Chem.*, 1869, 8, 24 ; Hannay, *J. Chem. Soc.*, 1873, 26, 568 ; Clarke, *Ber.*, 1878, 11, 1409.

[7] Sand, *Trans. Chem. Soc.*, 1907, 91, 388. Smith and Knerr (*Amer. Chem. J.*, 1886, 8, 206) obtained shining deposits by electrolysing mercuric nitrate in the presence of free nitric acid.

[8] de la Escosura, *J. Pharm. chim.*, 1886, [5], 13, 411. See Hargreaves and Rowe, *J. Soc. Chem. Ind.*, 1907, 26, 813.

[9] de Meeus, *Bull. Soc. chim. Belg.*, 1922, 31, 302.

[10] Exner, *J. Amer. Chem. Soc.*, 1903, 25, 901 ; Fischer and Boddert, *Zeitsch. Elektrochem.*, 1904, 10, 949.

[11] Losanitsch, *Monatsh.*, 1914, 35, 307.

[12] Classen, *Ber.*, 1894, 27, 2060 ; Bindschedler, *Zeitsch. Elektrochem.*, 1902, 8, 329.

[13] Brand, *Zeitsch. anal. Chem.*, 1889, 28, 592.

[14] Treadwell, *Analytical Chemistry* (translated by Hall) (Chapman & Hall, London ; Wiley, New York), 1919, 2, 173.

[15] Borelli, *Gazzetta*, 1907, 37, i, 425.

Fischer considered that the electrolytic estimation of mercury is best performed in nitric acid solution,[1] and, though other electrolytes can be used satisfactorily, the nitric acid electrolyte is very suitable.[2]

Treadwell[3] advises the following conditions: 150 c.c. electrolyte containing 2 or 3 c.c. of concentrated nitric acid, ordinary temperature, platinum gauze cathode, current of 0·055–0·10 amp. The voltage under these conditions corresponds to 3·5–5·0 volts. With a current of 0·6–1·0 amp., 1 grm. of mercury can be deposited in two or three hours. Guzman and Poch[4] suggest a graphite anode and a copper cathode plated with silver. Mercury electrodes have also been suggested.[5]

Mercury, present as mercuric chloride, for example, can also be electrolytically estimated in the presence of some sulphuric acid.[6]

Insoluble mercury compounds can be electrolysed by suspending them in water slightly acidified with hydrochloric acid, or in a 10 per cent. solution of sodium chloride.[7] Mercury can also be electrolysed in solutions containing chlorine ions by acidifying with a little nitric acid and adding some alcohol.[8]

Good results can be obtained with cyanide solutions,[9] though the method has been criticised.[10] Hardin[11] determined the atomic weight of mercury by electrolysing a solution of mercuric chloride or mercuric bromide in potassium cyanide. He also electrolysed a solution of mercuric cyanide slightly acid with sulphuric acid. Classen advises the following conditions: volume of solution, containing 2–3 grm. of potassium cyanide, 175 c.c., ordinary temperature, a current of 0·03–0·08 amp., voltage 1·65–1·75. He advises that the deposit from cyanide solutions should not be washed with alcohol, since peeling is likely to occur. Water only should be used for washing.[7] Guzman and Poch suggest an iron anode and a copper cathode plated with nickel and finally covered with silver.[4] Potassium cyanide tends to have an action on the platinum cathode.[12]

Mercury can be estimated in cinnabar by solution in hydrobromic acid, nearly neutralising with caustic potash, and treatment with enough potassium cyanide to redissolve the first formed precipitate. The solution is then electrolysed with a platinum dish as cathode.[13]

Mercury can also be electrolytically estimated in solutions containing ammonium oxalate or ammonium tartrate, and in alkaline solutions of potassium mercuric iodide.[14]

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[1] Fischer, *Zeitsch. angew. Chem.*, 1907, **20**, i, 135.

[2] Treadwell, *Analytical Chemistry*, 1919, **2**, 172; Böttiger, *Zeitsch. Elektrochem.*, 1920, **26**, 445.

[3] Treadwell, *loc. cit.*, 173.

[4] Guzman and Poch, *J. Chem. Soc.*, 1919, **116**, Abs. ii, 247.

[5] Gee, *Trans. Faraday Soc.*, 1905, i, 241.

[6] Kollock, *J. Amer. Chem. Soc.*, 1899, **21**, 927; Bindschedler, *Zeitsch. Elektrochem.*, 1902, **8**, 329.

[7] Classen, *Quantitative Chemical Analysis by Electrolysis* (translated by Boltwood) (Chapman & Hall, London; Wiley, New York), 1903, 204.

[8] Böttger, *Zeitsch. angew. Chem.*, 1921, **34**, 120.

[9] Bindschedler, *Zeitsch. Elektrochem.*, 1902, **8**, 329.

[10] Böttger, *Zeitsch. Elektrochem.*, 1920, **26**, 445.

[11] Hardin, *J. Amer. Chem. Soc.*, 1896, **18**, 1003.

[12] Glaser, *Zeitsch. Elektrochem.*, 1903, **9**, 11.

[13] Rising and Lenher, *J. Amer. Chem. Soc.*, 1896, **18**, 96.

[14] Vortmann, *Ber.*, 1891, **24**, 274. For electrolytic estimation of mercury in mercury oleates and salicylates, see Murray, *J. Ind. Eng. Chem.*, 1916, **8**, 257, 258.

Alkali sulphide solutions give good results.[1] Smith and Wallace[2] used a solution containing 0·1913 grm. of mercury and 20 c.c. of a sodium sulphide solution (density 1·22) in 125 c.c. The electrolysis was carried out at 65° C. with a current of 0·13 amp. Guzman and Poch[3] suggest the use of an iron anode and an amalgamated copper cathode.

Mercury can be electrolytically separated from copper,[4, 5] the alkaline earths,[6] zinc,[7] cadmium,[4, 6, 7] aluminium,[6] tin,[8] arsenic,[4, 8, 9] antimony,[4, 8] bismuth,[4] chromium.[6] molybdenum,[9] tungsten,[9] uranium,[6, 10] manganese,[6] iron,[6, 7] cobalt,[6, 7] nickel,[6, 7] palladium,[9] platinum.[11]

Mercury in an organic non-electrolyte may be estimated by first decomposing the compound by heating in a closed tube with concentrated nitric acid. The mercury can then be precipitated as sulphide[12] or otherwise estimated. Bauer destroys organic matter with concentrated sulphuric acid and hydrogen peroxide.[13]

Mercury can be separated from many other elements by distilling mercuric chloride over from phosphoric acid solution.[14]

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[1] Kollock, *J. Amer. Chem. Soc.*, 1899, **21**, 923.

[2] Smith and Wallace, *ibid.*, 1896, **18**, 169.

[3] Guzman and Poch, *loc. cit.*

[4] Freudenberg, *Zeitsch. physikal. Chem.*, 1893, **12**, 111.

[5] Spare and Smith, *J. Amer. Chem. Soc.*, 1901, **23**, 579.

[6] Classen and Ludwig, *Ber.*, 1886, **19**, 323.

[7] Kollock, *loc. cit.*, 916.

[8] Schmucker, *Zeitsch. anorg. Chem.*, 1894, **5**, 208.

[9] Smith and Frankel, *Amer. Chem. J.*, 1890, **12**, 428.

[10] Fernberger and Smith, *J. Amer. Chem. Soc.*, 1899, **21**, 1006.

[11] Smith and Muhr, *Amer. Chem. J.*, 1891. **13**, 421.

[12] Treadwell, *Analytical Chemistry* (translated by Hall) (Chapman & Hall, London; Wiley, New York), 1919, **2**, 170.

[13] Bauer, *Ber.*, 1921, **54B**, 2079.

[14] Strecker and Conradt, *ibid.*, 1920, **53B**, 2113.

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