

CHAPTER XXIX

MAGNESIUM

§ 1. The History of Magnesium

IN 1695, N. Grew examined the mineral water of Epsom, and, in his *Tractatus de salis cathartici amari in aquis Ebeshamensibus et hujusmodi aliis contenti natura et usu* (London, 1695), he reported his discovery of magnesium sulphate. The medicinal virtues of this salt soon afterwards became widely known, and it came to be called *Epsom salts*, *sal anglicum*, *English salts*, *sal catharticum*, *bitter salt*, etc. The presence of the same substance was detected in other mineral springs, and in 1700, G. and F. Moulton established a works for extracting the salt from the waters of a spring at Shooter's Hill, near London. H. Kopp¹ says that in 1710, Mr. Hoy discovered that the same salt could be extracted from the mother liquor remaining after the evaporation of sea-water. Ferrous sulphate (colcothar of vitriol) was added, and crystallizable "bitter salt" was produced. In 1717, F. Hoffmann showed that the salt was present in the mineral waters of Seidlitz, and that derived from this source was called *Seidlitz salt*; others soon found the salt in the waters from numerous other springs.

About this time, too, T. Bergman told us, in his essay *De magnesia* (Upsala, 1775), that Count di Palma, a citizen of Rome, prepared a white powder which he claimed was a panacea for all diseases; and he induced an ecclesiastic of the Church to dispose of it for him. The powder was called *magnesia alba* or *Count Palma's powder*; and its nature was solicitously concealed as a profound secret, until M. B. Valentini disclosed the method of preparation in his *Relatio de magnesia alba, novo, genuino, polychresto et innixio pharmaco purgante Roma nuper advecto* (Giessa Hassoram, 1707), namely, by calcining the residue remaining after evaporating to dryness the mother liquor from the preparation of nitre. We are also told that two years later J. H. Slevogt² showed how *magnesia alba* could be more easily obtained by precipitation from the mother liquors by treating them with a fixed alkali. Works by B. J. Lembeken,³ H. Smith, S. Glass, D. Ingram, J. Schaeffer, C. Norell, P. J. Macquer, and T. Henry are of historical interest.

It is not known why the name *magnesia alba* was given to the product in contrast with *magnesia nigra*, as the black oxide of manganese was then called. Dioscorides used the terms μάγνης λίθος or μάγνης, and Pliny *magnes*, for magnetic iron ore and pyrolusite. According to the latter:

It received its name *magnes*, Nicander informs us, from the person who was the first to discover it upon Ida. (Isidorus, in his *Origines*, said India.) It is said that Magnes made this discovery when, upon taking his herds to pasture, he found that the nails of his shoes and the iron ferrule of his staff adhered to the ground.

Others refer the terms to the place where the stone was found—e.g. *Magnesia in Asia*. Pliny distinguished between what he called the male and female sex of *magnes*—*magnes qui niger est femine sexus ideoque sine viribus*, and he described five different kinds of *magnes*, all but one of which were nearly black. The *magnes* from *Magnesia in Asia* was said to be white, and to resemble pumice in appearance, but to have no attractive influence on iron. From the early writings it is evident that at least three minerals of a totally different nature were called *magnesia*—(i) *magnesium lapis*, which is now represented by magnetite, was magnetic;

stated that the quantity obtained was insufficient for proof, but he said that the metal alloyed with copper formed a brass.

In 1808, H. Davy definitely proved that magnesia is the oxide of a metal which he named *magnium*, and added that this word "is undoubtedly objectionable, but magnesium was employed by T. Bergman for metallic manganese, and would consequently have been an equivocal term." The term magnesium was soon afterwards reserved for the metal in magnesia alba, and manganese for that in pyrolusite. For a time some chemists called magnesium, *calcium*. J. B. Trommsdorff discussed the metal derived from Talkerde in 1828.

REFERENCES.

- ¹ J. Beckmann, *Beiträge zur Geschichte der Erfindungen*, Leipzig, 1805; *A History of Inventions*, London, 1846; H. Kopp, *Geschichte der Chemie*, Braunschweig, 4, 52, 1847.
- ² J. H. Slevogt, *Dissertatio qua magnesia alba novum et innocuum purgans polychrestum que medicamentum exhibetur*, Jena, 1709.
- ³ B. J. Lembecken, *Magnesia alba, novum et innocuum purgans polychrestum que medicamentum*, Jenæ, 1709; S. Glass, *An essay on magnesia alba; wherein its history is attempted and its virtues pointed out, and the use of it recommended*, Oxford, 1764; D. Ingram, *An inquiry into the origin and nature of Epsom waters, demonstrating that magnesia made with those exceeds all others*, London, 1767; J. Schaeffer, *De magnesia*, Argentorati, 1774; C. Norell, *De magnesia alba*, Upsalix, 1775; P. J. Macquer, *Réflexions sur la magnésie du sel d'Epsom*, Paris, 1779; H. Smith, *De magnesia alba*, Edinburgi, 1752; T. Henry, *Experiments and Observations on Magnesia Alba, Calcined Magnesia, Quick Lime, Absorbents as promoting or retarding Putrefaction; Vegetable Infusions prepared with Lime; on the Sweetening Properties of Fixed Air*, London, 1773.
- ⁴ A. E. Waite, *Hermetic and Alchemical Writings of Paracelsus*, London, 1894; J. Beckmann, *Beiträge zur Geschichte der Erfindungen*, Leipzig, 1805; *A History of Inventions*, London, 1846.
- ⁵ C. Leonard, *Speculum lapidum*, Paris, 1610; M. Mercati, *Metallothea*, Romæ, 1719; H. Cardan, *De subtilitate*, Basel, 1580.
- ⁶ A. S. Marggraf, *Mém. Acad. Berlin*, 3, 1759; 3, 1764; 3, 1773; T. Bergman, *De magnesia*, Upsala, 1775; B. G. Sage, *Éléments de minéralogie docimastique*, Paris, 2, 142, 1777; H. Davy, *Phil. Trans.*, 98, 1, 333, 1808; W. P. Jorissen, *Chem. Weekb.*, 16, 1579, 1919; E. Nauck, L. C. Marquart, and J. J. Nöggerath, *Rheinl. Westphal. Corresp.*, 15, 46, 1858; J. B. Trommsdorff, *Trommsdorff's Journ.*, 17, 50, 1828.

§ 2. The Occurrence of Magnesium

Magnesium metal does not occur free in nature. This element is considered to be abundantly distributed on the earth's crust. According to F. W. Clarke's estimate,¹ it occupies 8th place in the list of elements arranged in the order of decreasing abundance in the earth's lithosphere, and there is 2.24 per cent. of that element present. The distribution of magnesia in the lithosphere is:

	Igneous (95%)	Shale (4%)	Sandstone (0.75%)	Limestone (0.25%)	Average
MgO . . .	3.74	2.44	1.16	7.89	3.74

N. Ljubavin has also made an estimate of the relative distribution of magnesium on the earth's crust. F. Cornu, and C. A. Young have reported the lines of magnesium in the solar spectrum. G. Rayet, C. Fievez, W. N. Hartley, and A. Secchi found the lines of magnesium in the spectra of the solar protuberances; also in the spectrum of Hercules.

Magnesium occurs as the oxide, *periclase*, MgO; and as the hydroxides *brucite*, Mg(OH)₂; *hydrotalcite* or *völkerite*, 3Mg(OH)₂.Al(OH)₃.3H₂O; and *pyroaurite*, 3Mg(OH)₂.Fe(OH)₃.3H₂O. There is also the aluminate: *spinel*, Mg(AlO₂)₂; *magnesioferrite*, Mg(FeO₂)₂; as well as the aluminoferrites: *pleonaste* or *iron spinel*, (Mg,Fe){(Al,Fe)O₂}₂; *picotite* or *chromospinel*, (Mg,Fe){(Al,Fe,Cr)O₂}₂; and *mangunospinel*, (Mg,Mn){(Fe,Mn)O₂}₂. Magnesium is widely distributed among the silicate minerals (*q.v.*), the commonest of which are *talc*, *chlorite*, and *serpentine*. It is represented by amphiboles, pyroxenes, micas, and olivine in the igneous rocks. There are enormous deposits of the carbonate: *magnesite*, MgCO₃; and *dolomite* or *bitter spar*, (Mg,Ca)CO₃. In addition there are: *brown spar* or *ankerite*, (Ca,Mg,Fe,Mn)CO₃; *breunerite*, (Mg,Fe)CO₃; and *naquehonite*, MgCO₃.3H₂O;

and the basic carbonates: *hydromagnesite*, $Mg_3(OH)_2(CO_3)_3 \cdot 3H_2O$; and *lanfordite*, $Mg_3(OH)_2CO_3 \cdot 21H_2O$. The haloid salts are represented by *sellaite*, MgF_2 ; *bischofite*, $MgCl_2 \cdot 6H_2O$; *carnallite*, $MgCl_2 \cdot KCl \cdot 6H_2O$; *nocerite*, $(Mg, Ca)_2OF_2$; *raletonite*, $(Na, Mg)F_2 \cdot 3Al(F, OH)_3 \cdot 2H_2O$; and *tachhydrite*, $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$. Some mineral springs in Java contain magnesium iodide, MgI_2 , eq. to 0.012 grm. per litre. The sulphates are represented by; *astrakanite*, *blödite* or *simonyite*, $Na_2Mg(SO_4)_2 \cdot 4H_2O$; *botryogen*, $(FeOH)_4(Mg, Fe, Mn, Ca)_6(SO_4)_6 \cdot 36H_2O$; *cupromagnesite*, $(Cu, Mg)SO_4 \cdot 7H_2O$; *dumreicherite*, $Mg_2Al_2(SO_4)_7 \cdot 36H_2O$; *epsom salts* or *epsomite*, $MgSO_4 \cdot 7H_2O$; *fauserite*, $(Mg, Mn)SO_4 \cdot 7H_2O$; *kamite*, $MgSO_4 \cdot KCl \cdot 3H_2O$; *kieserite*, $MgSO_4 \cdot H_2O$; *clinophaeite*, $(Fe, Al)_2(Fe, Mg, Ni, Ca)(K, Na)_2(OH)_6(SO_4)_3 \cdot 5H_2O$; *krugite*, $K_2Ca_2Mg(SO_4)_6 \cdot 2H_2O$; *lovite*, $Na, Mg(SO_4)_2 \cdot 2\frac{1}{2}H_2O$; *magnesia alum*, or *pickeringite*, $MgAl_2(SO_4)_4 \cdot 22H_2O$; *melanterite*, $(Mg, Fe)SO_4 \cdot 7H_2O$; *picromerite*, or *schönite*, $K_2Mg(SO_4)_2 \cdot 6H_2O$; *plagiocitrite*, $(Al, Fe)_2(Fe, Mg, Ni, Ca)(K, Na)(OH)_6(SO_4)_3 \cdot 21H_2O$; *polyhalite*, $K_2Ca_2Mg(SO_4)_6 \cdot 2H_2O$; *sonomaiite*, $Mg_2Al_2(SO_4)_6 \cdot 33H_2O$; *volaitite*, $(Fe, Al)(Mg, Fe, K, Na)_2(OH)_2(SO_4)_{10} \cdot 14H_2O$; *watervilleite*, $(Na, K)_2(Ca, Mg)(SO_4)_2 \cdot 2H_2O$. There is the nitrate, *nitromagnesite*, $Mg(NO_3)_2$; and a series of phosphates, arsenates, borophosphates, and borates: *Berzeliuite*, $(Ca, Mg, Mn, Na)_3(AsO_4)_2$; *bobierite*, $Mg_3(PO_4)_2 \cdot 8H_2O$; *boracite*, $Mg, Cl_2B_{10}O_{30}$; *boromagnesite*, $4Mg(BO_2)OH \cdot Mg(OH)_2$; *cabrerite*, $(Ni, Mg, Co)_2(AsO_4)_2 \cdot 8H_2O$; *hammayite*, $Mg_3(NH_4)_5H_4(PO_4)_8 \cdot 8H_2O$; *hörnesite*, $Mg_3(AsO_4)_2 \cdot 8H_2O$; *hydroboracite*, $MgCaB_6O_{11} \cdot 6H_2O$; *karyinite*, or *caryinite*, $(Mn, Ca, Pb, Mg)_3(AsO_4)_2$; *lazulite*, $(AlOH)_2(Mg, Fe, Ca)(PO_4)_2$; *lüneburgite*, $2MgHPO_4 \cdot Mg(BO_2)_2 \cdot 7H_2O$; *martinite*, $Ca_2H_2(PO_4)_4 \cdot \frac{1}{2}H_2O$; *neuberyite*, $MgHPO_4 \cdot 3H_2O$; *picroparmacolite*, $(CaMg)_2(AsO_4)_2 \cdot 6H_2O$; *pinnoite*, $Mg(BO_2)_2 \cdot 3H_2O$; *roselite*, $(Ca, Mg, Co)_3(AsO_4)_2 \cdot 2H_2O$; *rösslerite*, $MgHAsO_4 \cdot \frac{1}{2}H_2O$; *struvite*, $Mg(NH_4)PO_4 \cdot 4H_2O$; *sussexite*, $(Mg, Zn, Mn)(OH)BO_2$; *wagnerite*, $Mg(MgF)PO_4$; *wapplerite*, $(Ca, Mg)HPO_4 \cdot 3\frac{1}{2}H_2O$. There is also a number of silicates (*q.v.*).

The waters of numerous springs as a rule contain small quantities of magnesium compounds which appear in the analyses as magnesium sulphate, chloride, or hydrocarbonate; sea-water also contains magnesium which appears in F. W. Clarke's average analysis of oceanic salts as magnesium chloride, 10.88; magnesium sulphate, 4.74; magnesium bromide, 0.22; together with sodium chloride, 77.76; calcium sulphate, 3.60; calcium carbonate, 0.34; and potassium sulphate, 2.46 per cent. The waters of the Dead Sea contain more magnesium chloride than sodium chloride. F. W. Clarke estimates that on the average 0.14 per cent. of magnesium is contained in the waters of the earth.

According to R. Willstätter,² magnesium is an integral part of chlorophyll; and J. Kacher considered it to be an indispensable constituent of plants, saccharomyces, etc.; the ashes of plants usually contain more calcium than magnesium, although the reverse is true for seeds. It is not known how the magnesium is distributed in the organs of plants, but it occurs in the cambium sap of pines as oxalate. R. Kayser found that the amount of magnesium in wine is proportional to the phosphoric acid, and that the smallest amount—0.001 per cent. MgO —was found in Pfälzer wine, and the greatest amount—0.040 per cent. MgO —in Malaga wine. Magnesium compounds also accompany the calcium compounds in animal bodies; and magnesium salts occur in the skeleton, blood, and milk of animals. F. W. Clarke and W. C. Wheeler found it very exceptional for the inorganic parts of sea organisms to be non-magnesian. They found the following percentage amounts in the inorganic matter: Foraminifera, 3.67–11.22; calcareous sponges, 5.37–8.00; madreporian corals, 0.09–0.77; alcyonarians, 6.03–15.73; hydroids, 0.22–1.28; annelids, 0.00–9.72; echinoderms, 5.99–14.08; brachiopods, 0.49–8.63; bryozoans, 0.63–11.08; molluscs, 0.00–2.58; barnacles, 0.79–2.49; and other crustaceans, 4.84–15.99.

A comparison of rock and other analyses makes it probable that the solid crust of the earth contains more calcium than magnesium. Analyses of meteorites reveal more magnesium than calcium; the same remark applies to sea-water, most mineral waters, and lakes in Central and North-Western Asia. Calcium prevails in river waters, in most plants and in animals; some cereals contain more magnesium.

REFERENCES.

- ¹ F. W. Clarke, *The Data of Geochemistry*, Washington, 33, 1920; *Chem. News*, 61, 31, 1890; N. Ljubavin, *Journ. Russ. Phys. Chem. Soc.*, 24, 389, 1892; F. Cornu, *Compt. Rend.*, 86, 101, 983, 1878; C. A. Young, *Amer. Journ. Science*, (3), 20, 353, 1880; G. Rayet, *Ann. Chim. Phys.*,

(4), 24, 58, 1871; C. Fievez, *ib.*, (5), 23, 366, 1881; W. N. Hartley, *Journ. Chem. Soc.*, 43, 392, 1883; A. Secchi, *Le Soleil*, 2, 91, 1877; *Compt. Rend.*, 63, 621, 1866.
² R. Willstätter, *Liebig's Ann.*, 350, 48, 1907; J. Kacher, *Monatsh.*, 7, 410, 1886; R. Kayser, *Bep. Anal. Chem.*, 2, 1881; F. W. Clarke and W. C. Wheeler, *Prof. Paper, U.S. Geol. Sur.*, 90, 1914; F. W. Clarke, *The Data of Geochemistry*, Washington, 564, 1920.

§ 3. The Preparation of Magnesium

Magnesium is usually obtained by the action of sodium on the anhydrous chloride, or by the electrolysis of fused alkali-magnesium chloride. The magnesium chloride was formerly obtained from Stassfurt, but during the 1914-18 war, it was recovered as a by-product at various salt works. It is used as a powder and ribbon for flash-lighting; as a deoxidizer of other metals and alloys; and in making certain alloys—principally Mg-Al alloys. Magnesium occurs in commerce as powder, ribbon, and as ingots or rods. The ribbon is made by pressing the metal in the semi-fluid state into wire; and afterwards flattening it into ribbon by rolling.

The reduction of magnesium oxide.—H. Davy passed the vapour of potassium over red-hot magnesium oxide, and removed the magnesium produced by mercury. J. Walter¹ tried to reduce magnesium oxide by carbon under the conditions which obtain in the manufacture of zinc. The experiments were conducted at low redness and at a white heat, and precautions were taken to isolate the metal, if formed, whether distilled or volatilized. His results were negative, although he considered it would be possible to prepare a kind of *magnesium brass*, i.e. a Mg-Zn alloy, by substituting some dolomite for the zinc ore ordinarily used in the manufacture of zinc. E. von Püttner, however, claimed to have made magnesium by heating burnt magnesite, dolomite, or other magnesian mineral mixed with coal and ferric oxide, and by exposing to a strong white heat in a muffle furnace as in the process for zinc extraction. The vapour of magnesium was condensed in suitable receivers. E. D. Clarke said that when magnesia is mixed with oil, and exposed to the oxy-hydrogen flame, a slag is obtained which crumbles to white pulverulent magnesia when exposed to the air. It will be observed that the possible products of the deoxidation in the reduction of magnesia by carbon: $n\text{MgO} + (n - \frac{1}{2}m)\text{C} = n\text{Mg} + (n - m)\text{CO} + \frac{1}{2}m\text{CO}_2$, are both reduced by the magnesium at a high temp. H. Moissan claimed that "magnesia can be fused, and kept liquid in a carbon crucible without being reduced." P. Lebeau considers that a reaction occurs only between the vapours of carbon and magnesia at the high temp. of the electric arc. R. E. Slade found that the metal can be isolated from a mixture of carbon and magnesia provided the reoxidation of the magnesium by the carbon monoxide is prevented by rapidly removing this gas, say, by working in vacuo, or by absorbing the magnesium by another metal, or by a rapid stream of hydrogen. The condensed magnesium is always associated with a little carbide which gives off acetylene when treated with a dil. acid or water. O. P. Watts also volatilized carbon from a bed of magnesia, and obtained sublimates consisting of mixtures of carbon and magnesium oxide. O. P. Watts found that at very high temp. magnesia and carbon react: $\text{MgO} + \text{C} \rightleftharpoons \text{CO} + \text{Mg}$, and at a lower temp. the reaction is reversed. O. L. Kowalke and D. S. Grenfell found the reduction of magnesia by carbon begins slowly at 1950°, and becomes violent at 2030°. C. Matignon studied the preparation of magnesium by reducing magnesium oxide, magnesium chloride or oxychloride with calcium carbide. O. Knöfler and H. Ledderboge made rods of magnesia and carbon, and used them as the electrodes of an electric arc. To avoid the action of the products of combustion of carbon on the metal, the arc was developed in vacuo, or in an indifferent gas. J. Malovich mixed the oxide, or a salt of magnesium with sulphur and the sulphate or sulphite of another metal, and heated the mass to a temp. above the m.p. but below the volatilization temp. of the metal or alloy to be obtained.

The reduction of magnesium halides by the alkali metals.—A. A. B. Bussy first prepared magnesium as a coherent metal in 1829 by decomposing red-hot anhydrous magnesium chloride by potassium vapour, following the process previously employed by F. Wöhler for aluminium. J. von Liebig employed the same process. According to R. Bunsen, magnesium reduced with potassium retains a little of the latter metal very tenaciously, and the resulting metal is more malleable than magnesium free from potassium. H. St. C. Deville and H. Caron improved the process, substituting sodium for potassium. They heated the mixture: magnesium chloride, 7 parts; calcium fluoride, 4·8 parts; and sodium, freed from oil, 2·3 parts to bright redness in a clay crucible—E. Sonstadt used an iron crucible. The magnesium which separated in globules was heated nearly to whiteness in a carbon boat placed in an inclined tube of the same material and through which a stream of dry hydrogen was passed. The magnesium which condensed in the upper portion of the tube was melted into large globules with a flux made of calcium fluoride and sodium and magnesium chlorides. They obtained a yield of 45 grms. of magnesium from 100 grms. of sodium. According to H. St. C. Deville and H. Caron, and E. Sonstadt, the metal prepared by the sodium reduction process contains carbon and silicon as impurities, and, if ammonium chloride is present, some magnesium nitride, Mg_3N_2 , as well. To remove carbon, silicon, and nitrogen, H. St. C. Deville and H. Caron distilled the metal in a current of hydrogen at a high temp. According to J. B. A. Dumas, the metal usually contains two-thirds of its volume of occluded hydrogen and a little carbon monoxide, which are removed by heating it in vacuo at a red heat. E. Sonstadt improved the distillation apparatus. The crude metal was placed in an iron crucible fitted with an iron tube passing through the bottom to within an inch of the lid. The crucible was nearly filled with the crude metal; the lid screwed and luted down; and the air displaced by coal gas or hydrogen. When the crucible was heated, the vapour of magnesium passed into the upright tube and, by a process of *distillation per descensum*, collected as a coherent mass in a box placed below. The metal was then melted and cast into ingots. F. Wöhler applied the sodium reduction process to a fused mixture of sodium and magnesium chlorides; A. Matthiessen, to a mixture of magnesium and potassium chlorides with a little ammonium chloride; H. Schwarz, to tachhydrite; C. Tissier, to sodium magnesium fluoride; and E. Reichardt, to carnallite. The latter used a mixture of equal parts of previously fused carnallite, calcium fluoride, and sodium; and he said that ferruginous mica in the carnallite does no harm, but the presence of kieserite is to be avoided since an explosion may be produced when it is present.

F. Lauterborn heated magnesium ferrocyanide with sodium carbonate so as to produce a double cyanide of magnesium and sodium from which the magnesium was obtained by heating it with zinc. T. Petitjean proposed to reduce magnesium sulphide by iron, or by hydrocarbon vapours at a red heat. M. Basset patented a modification of this process.

The electrolysis of aqueous solutions of magnesium salts.—H. Davy tried to make magnesium by the electrolysis of moistened magnesium hydroxide or sulphate with a mercury cathode and subsequently distilling off the mercury, but the results were bad. A. C. Becquerel electrolyzed a conc. soln. of magnesium chloride in the cathode compartment, and a conc. soln. of sodium chloride in the anode compartment of an electrolytic cell. Octahedral crystals deposited on the cathode. F. W. Gerhard and J. Smith electrolyzed a soln. of 228 parts of magnesium sulphate and 132 parts of ammonium sulphate in 35,000 parts of water between 65° and 100°. For an alloy of magnesium and nickel, a nickel anode was used; for magnesium bronze, a copper anode was used and potassium cyanide and ammonium carbonate were added to the electrolytes. M. Rietz and M. Herold prepared a soln. of magnesium oxide or carbonate in an organic acid, to which was added starch or gum, the soln. boiled with sugar, and neutralized with alkali. This was electrolyzed. If alloys of magnesium are required, a cyanide of the required metal is added to the electrolyte, and an anode of that metal used. G. Nahnsen and J. Pfleger have patented a

special electrolysis cell; and H. Decker, the use of a mercury cathode. The production of magnesium by the electrolysis of aq. soln. has not been successful; nor has the electrolysis of soln. of magnesium salts in non-aq. solvents yet proved of practical utility.

The electrolysis of fused magnesium salts.—In 1852, R. Bunsen² prepared magnesium by the electrolysis of magnesium chloride fused in a porcelain crucible. The carbon of the negative electrode was cut to form pockets in which the metal collected, otherwise, the metal, being lighter than the fused chloride, rose to the surface and burned. There is a difficulty in preparing magnesium chloride, for, when an aq. soln. of the salt is evaporated to dryness and fused, the residue contains magnesium oxide, owing to the hydrolysis of the salt and the escape of hydrogen chloride. A. Matthiessen preferred, as electrolyte, a fused mixture of $3\text{KCl} + 4\text{MgCl}_2$, with a little ammonium chloride. The magnesium in this case is largely present as a complex anion, and hydrolysis does not occur so readily. A great deal of commercial magnesium is obtained by the electrolysis of fused carnallite. F. Fischer first recommended the use of an electrolyte of fused carnallite, and showed that the combustion of the magnesium can be prevented by passing a current of a reducing gas over the electrolyte. In R. Grätzel's apparatus, Fig. 1, the iron vessel *A* contains the fused electrolyte, heated externally, and sealed by a lid through which pass the tubes *TT'*, which allow a stream of a reducing or inert gas to be passed over the molten electrolyte, thus protecting the magnesium from oxidation. The vessel *B* has openings *CC* to allow the circulation of the molten electrolyte, and is fitted with a carbon anode, from which chlorine is liberated during the electrolysis. W. Borchers, F. Hornung and F. W. Kasmeyer, E. Haag, etc., have investigated this mode of preparation. According to R. Bunsen, the metal prepared by electrolysis usually contains a very small proportion of aluminium and silicon.

Magnesium melts at about 633° ; magnesium chloride at about 708° ; and carnallite at a lower temp. S. A. Tucker and F. L. Jouard attempted to work at 500° , when the metal is produced in a spongy form which is subsequently melted under a flux of calcium chloride and electrolyzed. According to A. Oettel, the best working temp. is about 650° , for then the efficiency of the process is greatest; but by working at that temp. it is difficult to keep the temp. sufficiently constant to prevent the solidification of the magnesium, and therefore A. Oettel recommended 700° – 750° ; and W. Borchers, 700° . A. Oettel worked at 4–8 volts, W. Borchers at 5–8 volts—depending on the current density and temp. The decomposition voltage of magnesium chloride is estimated to be less than 3.2 volts at 700° , and, assuming that this number represents the value for carnallite, the energy efficiency for a current efficiency of 75 per cent. and 6 volts, is $75 \times \frac{1}{3}$ of $3.2 = 40$ per cent.; and a kilogram of metal requires $(1000 \times 2 \times 96540 \times 100 \times 6) \div (24.3 \times 75 \times 3600 \times 1000)$ or 17.7 kilowatt-hrs. A. Oettel showed that the presence of calcium fluoride as a flux favours the coalescence of the globules of magnesium formed at the cathode. If the globules do not coalesce, but pass into the electrolyte, they form a metal fog about the anode, when they are reoxidized. If the carnallite is contaminated with ferric chloride, losses occur owing to the continuous reduction of this salt at the cathode and its reoxidation at the anode. If too high a voltage is used, or if the magnesium chloride content of the bath becomes too low, the magnesium may contain some potassium, and it is then liable to catch fire during the electrolysis. E. Hohler studied the electrolysis of a molten mixture of equi-molar proportions of magnesium, potassium, and sodium chlorides, along with calcium fluoride and a little alkali to keep the electrolyte sufficiently basic. The best working temp. was 750° – 800° , and a 70 per cent. current efficiency was obtained. The cathodic

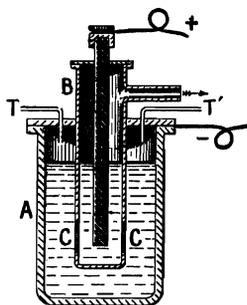


FIG. 1.—R. Grätzel's Electrolytic Cell for Magnesium (Diagrammatic).

current density of 27–30 amps. per sq. dm. was used; W. Borchers used 10 amps. per sq. dm.; and A. Oettel, 30–40 amps. per sq. dm. The subject has been discussed by S. T. Allen, and by K. S. Boynton and co-workers.

According to R. Lorenz and F. Kaufler, some magnesium is produced by the contact electrode process—*vide* Fig. 1 in connection with the preparation of calcium. A. Oettel has shown that the resulting rod of magnesium is somewhat brittle; and, owing to the need for high current densities, the potassium content is liable to rise. M. Sprenger removed the chlorine under reduced press. H. M. A. Berthaut used an electrolyte of magnesium and sodium chlorides; A. Feldmann, a mixture of alkali magnesium chloride mixed with some calcium oxide; F. von Kügelgen and G. O. Seward, magnesium oxide dissolved in fused magnesium fluoride and an alkali fluoride; and the latter also used a bath of fused magnesium and calcium chloride with some calcium fluoride; J. T. Morehead, magnesium fluoride or fluoride and chloride mixed with one, two, or more chlorides of the alkali metals. Magnesium alloys can be made directly by electrolyzing a fused bath of magnesium chloride and fluoride with a carbon anode, and an aluminium cathode. This forms a magnesium-aluminium alloy which can be used as a stock in making alloys of any desired composition—*e.g.* F. von Kügelgen and G. O. Seward's process.

T. Svedberg³ prepared **colloidal magnesium** by connecting a glass condenser of 225 sq. cm. surface with the induction coil and attaching the secondary poles to the electrodes, which are immersed in propyl or isobutyl alcohol contained in a porcelain dish. The magnesium was used in a granular form or as wire clippings. When the current is passed, sparks play between the metal particles, and in the course of a few minutes dark-coloured soln. are obtained. These contain no large particles, and hence need not be filtered. The magnesium sol in absolute ether is olive-green, and very readily coagulated; the coagulum is greenish-black, and very vigorously dissolved by dil. acids with the evolution of hydrogen. D. Zavrieff used a modification of T. Svedberg's process, and obtained a colloidal soln. which could be kept two days without flocculation.

REFERENCES.

¹ J. Walter, *Dingler's Journ.*, **252**, 337, 1884; H. Schwarz, *ib.*, **169**, 442, 1863; E. Sonstadt, *ib.*, **169**, 444, 1863; *Journ. Pharm. Chim.*, (3), **44**, 463, 1863; *Journ. prakt. Chem.*, (1), **90**, 307, 1863; H. Davy, *Phil. Trans.*, **98**, 1, 333, 1808; E. D. Clarke, *Ann. Phil.*, **17**, 421, 1821; O. Knöfler and H. Ledderboge, *German Pat.*, *D.R.P.* 49329, 1889; F. Lauterborn, *ib.*, 39915, 1886; G. Nahnsen and J. Pfleger, *ib.*, 46753, 1888; M. Rietz and M. Herold, *ib.*, 58136, 1890; H. Decker, *ib.*, 184516, 1905; J. Malovich, *ib.*, 159632, 1902; 161428, 1903; E. von Püttner, *ib.*, 31319, 1884; *Brit. Pat. No.* 1031, 1885; F. W. Cerhard and J. Smith, *ib.*, 16651, 1884; A. A. B. Bussy, *Journ. Pharm. Chim.*, (1), **15**, 30, 1829; (1), **16**, 142, 1830; *Journ. Chim. Méd.*, **6**, 141, 1830; *Pogg. Ann.*, **18**, 140, 1830; J. von Liebig, *ib.*, **19**, 137, 1830; C. Tissier, *Compt. Rend.*, **56**, 848, 1863; H. St. C. Deville and H. Caron, *Compt. Rend.*, **44**, 394, 1857; *Ann. Chim. Phys.*, (3), **67**, 340, 1863; A. C. Bequerel, *ib.*, (2), **48**, 344, 1831; A. Matthiessen, *Journ. Chem. Soc.*, **8**, 107, 1855; E. Reichardt, *Jenaer Zeit.*, **1**, 499, 1863; T. Petitjean, *Dingler's Journ.*, **148**, 371, 1858; F. Wöhler, *Liebig's Ann.*, **101**, 362, 1857; R. Bunsen, *ib.*, **82**, 137, 1852; M. Basset, *French Pat. No.* 256931, 1896; *Monit. Scient.*, (4), **11**, 101, 1897; J. B. A. Dumas, *Compt. Rend.*, **90**, 1027, 1880; P. Lebeau, *ib.*, **144**, 799, 1907; J. E. Reynolds, *Pharm. Journ.*, **6**, 543, 1865; C. Matignon, *ib.*, **172**, 381, 1921; H. Moissan, *The Electric Furnace*, London, 224, 1904; R. E. Slade, *Journ. Chem. Soc.*, **93**, 327, 1908; O. P. Watts, *Trans. Amer. Electrochem. Soc.*, **11**, 279, 1907; O. L. Kowalke and D. S. Grenfell, *ib.*, **27**, 221, 1915.

² R. Bunsen, *Liebig's Ann.*, **32**, 137, 1852; A. Matthiessen, *Journ. Chem. Soc.*, **8**, 107, 1856; F. Fischer, *Dingler's Journ.*, **251**, 28, 418, 1884; R. Grützel, *German Pat.*, *D.R.P.* 26962, 1883; 58600, 1890; F. Hornung and F. W. Kasemeyer, *ib.*, 46334, 1888; M. Sprenger, *ib.*, 39554, 1886; A. Feldmann, *ib.*, 50370, 1888; Aluminium- und Magnesiumfabrik, *ib.*, 115015, 1899; A. Martens, *Stahl Eisen*, **8**, 122, 1888; K. S. Boynton, V. Langford, and J. F. G. Hicks, *Journ. Ind. Eng. Chem.*, **14**, 146, 1922; Anon., *Metal Ind.*, **18**, 426, 1921; *Chem. Met. Eng.*, **19**, 525, 1918; *Journ. Franklin Inst.*, **170**, 185, 1910; R. Bunsen, *Pogg. Ann.*, **82**, 137, 1852; W. Borchers, *Zeit. Elektrochem.*, **1**, 261, 420, 1895; E. Haag, *ib.*, **12**, 243, 1906; F. Oettel, *ib.*, **2**, 394, 1895; R. Lorenz, *ib.*, **7**, 252, 1901; R. Lorenz and F. Kaufler, *Elektrochemie geschmolzener Salze*, Leipzig, 70, 1909; E. Hohler, *Beiträge zur Kenntnis der elektrolytischen Abscheidung des Magnesiums und Darstellung einer geeigneten Schmelze*, Zürich, 1904; A. Oettel, *Zeit. Elektrochem.*, **7**, 252, 1901; *Dissertation*,

Dresden, 1908; S. A. Tucker and F. L. Jouard, *Trans. Amer. Electrochem. Soc.*, **17**, 244, 1910; H. M. A. Berthaut, *Brit. Pat. No* 4087, 1879; F. von Kügelgen and G. O. Seward, *U.S. Pat. No.* 880489, 881934, 900961, 1908; J. T. Morehead, *ib.*, 778270, 1904; S. T. Allen, *Electrician*, **88**, 90, 1922; *Chem. Met. Eng.*, **26**, 987, 1922.

³ T. Svedberg, *Ber.*, **38**, 3616, 1905; D. Zavriff, *Zeit. phys. Chem.*, **87**, 507, 1914.

§ 4. The Physical Properties of Magnesium

The magnesium prepared by A. A. B. Bussy¹ was a brilliant silver-white metal, and that by H. St. C. Deville and H. Caron had a bluish or violet tinge. According to A. W. Wright, the metal volatilized in an evacuated tube by means of an electric discharge, produces a metallic film which is silvery-white in reflected light, and greyish-blue by transmitted light. R. Bunsen noted that the metal has a crystalline fracture. S. Kalischer could detect no crystals structure by etching the rolled metal, and he found that although most metals naturally have a crystalline structure, some readily lose this structure by mechanical processes, but assume it again under the influence of heat. According to C. Hlawatsch, and A. des Cloizeaux, the **crystals** prepared by J. B. A. Dumas, by sublimation in a stream of hydrogen, are hexagonal prisms, $a : c = 1 : 1.6242$. These crystals have also been studied by E. Bamberger, and L. Ditscheiner. Regular hexagons were obtained by etching with dil. sulphuric acid, or with chlorine. Z. Jeffries and R. S. Archer give 150° as the lowest temp. at which the recrystallization of the cold-worked metal has been observed. G. T. Beilby showed that the crystalline structure of the metal is hidden when the surface is polished owing to the formation of an amorphous glass-like film which can be removed by an etching liquid. L. Hamburger made an ultra-microscopic examination of these films of the metal. **X-ray spectrograms**, by A. W. Hull, and H. Bohlin, showed a structure in agreement with the holoedral hexagonal crystals. The arrangement of the atoms is that of hexagonal close packing, that is, the arrangement which equal hard spheres assume when closely packed, except that the structure is shortened by about 0.5 per cent. in the direction of the hexagonal axis. The side of the hexagonal lattice is 3.22 A., height 5.23 A., and the closest approach of the atoms is 3.22 A. As in the face-centred cubic lattice, each atom has twelve equidistant near neighbours, but in a slightly different arrangement. G. Jäger made an estimate of the **molecular diameter** of magnesium; W. L. Bragg gave $0.142\mu\mu$ or 1.42 A. for the radius of the atomic spheres; M. N. Saha, 0.95 A.; K. F. Slotte estimates the edge of the molecular cube of the liquid and solid to be 7.3×10^{-9} cm. C. T. Heycock and F. H. Neville estimated the **molecular weight** of magnesium in soln. in lead, and tin. K. Honda and S. Konno gave 1.61×10^8 for the coeff. of normal **viscosity** of hammered magnesium at 20° ; and 0.722×10^8 for the metal annealed at 400° . G. P. Seaman studied the torsional oscillations of magnesium wire between -180° and 500° , and found very little change. C. E. Guye and co-workers measured the effect of temp. on the viscosity of magnesium.

L. Playfair and J. P. Joule's value 2.24 (3.9°) for the **specific gravity** of magnesium is too high, and must have been made on an impure sample. R. Bunsen's value is 1.7430 at 5° ; H. Kopp's, 1.70 at 17° ; H. St. C. Deville and H. Caron's value, 1.75; and H. Wurtz's value, 1.77 at 0° . T. M. Lowry and R. G. Parker found the sp. gr. of purified magnesium was raised from 1.7381 to 1.7429 on filing. This is not usual, the filings, like worked metals, usually have the lower sp. gr. When partially annealed at 180° , they expand, but contract if further annealed at 240° . The at. vol. of magnesium does not fit very well in series with the other elements of the magnesium family, and in this respect, this element fits in better with the calcium family. R. Bunsen found the **hardness** of magnesium to be almost equal to that of calcite. C. A. Edwards gave 38.3 for Brinell's hardness. The subject has been discussed by P. Ludwik, and A. Kürth. A. A. B. Bussy said the metal can be hammered into thin sheets; J. von Liebig, and R. Bunsen found that it can be filed,

and bored, and that at ordinary temp. the **ductility** is scarcely as great as that of zinc. H. St. C. Deville and H. Caron stated that while the crude metal is brittle, purified magnesium is very ductile, and while it cannot be drawn into wire, it can be converted into wire by press. through a die. W. Böhm obtained magnesium foil by rolling the metal at a temp. just below its m.p. J. W. Buchanan found the linear **compressibility** to be 1.054×10^{-6} dynes per sq. cm., or 3.2 kgrms. per sq. cm., per atm. press. between 7° and 12°. T. W. Richards and co-workers found the average compressibility, that is, the fractional change of volume caused by one megabar press. between 100 and 500 megabars, to be 2.7×10^{-7} . W. Sutherland gave 390×10^{-6} grms. per sq. cm. or 3900 kgrms. per sq. mm. for **Young's modulus** or the **modulus of elasticity** at 15°, with the extremes 3520 and 4310 kgrms. per sq. mm. W. Voigt's value for the modulus of elasticity of cast magnesium is 4260 kgrms. per sq. mm. P. Ludwik made some observations on the tensile strength of magnesium. C. J. Burton and W. Marshall observed a rise of 0.00047° per atm. increase of press.

According to W. Sutherland, the ratio of the **rigidity** or torsion modulus at 100° to the value at zero is 0.943, and his value for the absolute value in kgrms. per sq. mm. is 1300; H. Tomlinson's, 1720; C. Schäfer's, 1181; W. Voigt's value for the cast metal is 1710, with a change of -30 per cent. per 100° rise of temp. F. Melde found the **velocity of sound** in magnesium to be 4602 metres per second.

E. Grüneisen² found the **coefficient of linear expansion**, α , of magnesium between -190° and 17° to be 0.00002130; and from 17° to 100°, 0.00002610, or 0.0000250 at 18°; and for the expansion from absolute zero to the m.p., T_s ° K., he gave 0.0248 or $0.00000277T_s^{1.337}$, where $T_s = 903$ ° K. K. Scheel found the linear expansion of magnesium between 0° and θ ° to be

	0°	100°	200°	300°	400°	500°
δl	0	2.60	5.39	8.36	11.53	14.88 mm. per metre

and he represented the results by $\delta l = 0.02507\theta + 0.00000936\theta^2$. J. Desch made some observations on the expansion of magnesium at temp. down to -190°. R. Bunsen said magnesium melts at a red heat, and H. St. C. Deville and H. Caron that it melts near the m.p. of zinc. The reported values for the **melting point** of magnesium range from the 500° of A. Ditte to the 800° of V. Meyer; C. T. Heycock and F. H. Neville gave 632.5°-632.8°; G. Grube, 650.9°; S. F. Schemtschuschny, and R. Vogel, 649°; C. H. Mathewson, G. G. Urasoff, and P. Sahmen, 650°; G. Voss, and N. S. Kurnakoff and N. J. Stephanoﬀ, 651°; N. Beer, 632.6°. According to W. Guertler and M. Pirani, the best representative value is 651°. F. Wöhler noted the **volatility** of magnesium, and H. St. C. Deville estimated that the **boiling point** is near that of zinc, A. Ditte said about 1100°. H. C. Greenwood gave 1120° for the b.p., while H. von Wartenberg gave a value over 1200°. V. and A. Meyer stated that the metal does not volatilize at a white heat in an atm. of carbon monoxide; while H. Cretier said that volatilization begins below the m.p.; and W. C. Roberts-Austen said that the metal has an appreciable vap. press. at ordinary temp. G. Bartha obtained a partial evaporation of magnesium in vacuo at 580°. H. St. C. Deville and H. Caron purified the metal by distillation, and obtained a black crystalline residue of magnesium nitride. J. B. A. Dumas obtained good crystals by sublimation in vacuo at a red heat. A. Schuller noted that the molten metal attacks glass, and C. Margot found that the adhesion of molten magnesium to glass is due to the formation of a film of oxide on the metal, and that the film can be removed by rubbing. M. Knudsen found that the condensation of the vapour of magnesium on a clean glass or mica surface, has a critical temp., -183° to -78°, below which all the vapour is retained, and above which a fraction is repelled. J. W. Richards estimated the latent **heat of fusion** to be 58 cal.; and the latent **heat of vaporization** 31.580 cal. per mol., or 1315 cal. per kilogram. E. van Aubel, and A. Wehnelt and C. Musceleanu observed 1700 cal. per mol. H. V. Regnault gave 0.2499 for the **specific heat** of magnesium, containing 0.06 per

cent. of silicon and 0.08 per cent. of aluminium and iron. H. Schimpff found over the range -190° to 100° , and N. Stücker, over the range 20° to 650° :

	-190° to 17°	-79° to 17°	17° to 100°	20° to 100°	20° to 350°	20° to 650°
Sp. ht.	0.2046	0.2284	0.2475	0.24922	0.28081	0.32996

E. Grüneisen found 0.2068 between -190° and 17° , and 0.2485 between 17° and 100° ; T. W. Richards and F. G. Jackson gave 0.208 between -188° and -20° , and for the **atomic heat** between -188° and 20° , they gave 5.06, and between 20° and 100° , 6.0. P. Nordmeyer and A. L. Bernoulli, etc., have also made determinations of the sp. ht. of magnesium at different temp. R. J. Brunner gave for magnesium at θ° :

	-273°	-200°	-100°	0°	100°	200°	400°	500°
Sp. ht.	0.1104	0.1622	0.2101	0.2386	0.2557	0.2691	0.3171	0.3673
At. ht.	2.689	3.949	5.116	5.810	6.226	6.554	7.721	8.944

P. Schübel obtained 0.2475 at 100° ; 0.2526 at 197° ; 0.2605 at 304° ; 0.2631 at 400° ; and 0.2680 at 500° . E. D. Eastman and W. H. Rodebush also determined values for C_p and C_v at temp. ranging from 74.9° K. to 288.5° K. W. Nernst and F. Schwes found $C_p=4.558$ at 93.8° K., and 0.335 at 27.2° K. G. N. Lewis and co-workers, and E. D. Eastman found the **atomic entropy** at 25° and one atm. to be 8.3 cal. per degree. L. Lorenz found the **thermal conductivity** in cal. per cm. per sec. per degree difference of temp. to be 0.3760 at 0° , and 0.3760 at 100° . The **heat diffusivity** of magnesium is 0.883 computed from $h^2=k/CD$, where k is the conductivity, C , the sp. ht., and D , the sp. gr.

P. Drude³ estimated the **index of refraction** of magnesium to be 0.37 for $\lambda=0.589\mu$; the corresponding **absorption index** was 4.42; and the percentage **reflecting power**, 93. W. W. Coblenz found the reflecting power of magnesium for light of wave length λ to be:

Wave length, λ	0.5	0.6	0.8	1.0	2.0	4.0	7.0μ
Reflecting power	72	73	74	74	77	84	91 per cent.

Plane polarized light reflected from a polished surface is generally elliptically polarized, and for a certain angle, the **angle of principal incidence**, ϕ , $77^{\circ} 57'$, the change is 90° , and if the plane polarized incident beam has a certain azimuth, **angle of principal azimuth**, ψ , $42^{\circ} 42'$, circular polarized light results. The **refraction equivalent** of magnesium in salts for rays of infinite wave length is 6.51, according to J. Kanonnikoff, and 6.7, according to J. H. Gladstone, when calculated by J. H. Gladstone and T. P. Dale's formula. W. J. Pope gave 8.81 for the eq. refraction of magnesium for the D -ray. S. Procopiu found that the birefringence of toluene is positive, but negative when finely divided magnesium is suspended therein. Similarly with benzene, etc.

R. Bunsen and H. E. Roscoe measured the **actinic value of the magnesium light** compared with that of the sun. The visible brightness of the sun's disc, as measured by the eye, is 524.7 times as great as that of burning magnesium when the sun's zenith distance is $67^{\circ} 22'$, while at the same zenith distance, the sun's chemical brightness is only 36.6 times as great. This emphasizes the value of the magnesium light as a source of chemically active rays. The intensity of the magnesium flame was also studied by L. Troost, J. M. Eder, and H. Vogel. The combustion of 0.1 grm. of the metal can theoretically furnish as much light as 74 stearin candles burning for 10 hrs. A magnesium wire, 0.297 mm. diameter, burning in air gives as much light as 74 stearin candles each weighing 100 grms. K. Heumann found that the magnesium flame in sunlight gives an intense shadow, and he assumed that the flame of magnesium is non-luminous, and that the luminosity of the burning metal is really due to the magnesium oxide suspended in the flame. A. R. von Schrötter also studied the nature of the magnesium light. E. L. Nichols found that the efficiency of the **light-energy** of burning magnesium is 10 per cent. of the heat

of combustion, a value unapproached among the known transformations of energy used in the production of light.

According to T. Tommasina, magnesium becomes **fluorescent** when used as electrode in an inductorium, under water or alcohol, but not under vaseline or petroleum. W. Ramsay and J. F. Spencer⁴ gave the order Al, Mg, Zn, Sn, Cd, Pb, . . . for the **photoelectric effect** with polished metal surfaces and a mercury vapour lamp with uviolet glass; K. Herrmann gave Al, Zn, Mg, Sn, Bi, Cd, Pb, . . . with a carbon arc-lamp; R. A. Millikan and G. Winchester gave Al, Mg, Sb, Zn, Pb, . . .; the latter also gave 0.839 volt at 26° for the positive potential of magnesium in vacuo in ultra-violet light. T. C. Sutton, and A. E. Henning and W. H. Kadesch have also studied the phenomenon with magnesium. A. Nodon found a sheet of magnesium is opaque to the penetrating solar photogenic radiations, but a metal of high valency is not. The absorption coefficient, μ , for the β -rays is approximately proportional to the sp. gr. D , and for magnesium $\mu/D=5.1$. W. Duane, and E. Hjalmar measured the absorption frequencies for the X-rays.

W. A. Miller⁵ first examined the spectrum of magnesium as obtained by introducing the chloride in the alcohol flame. The **spectrum** of burning magnesium has three green lines—5184, 5173, and 5167—and is very rich in the chemically active rays at the violet end of the spectrum. The light causes the detonation of a mixture of hydrogen and chlorine; it colours silver chloride dark blue in a few seconds, and, according to A. Schrötter, and H. Lallemand, it causes numerous bodies to phosphoresce. Magnesium salts do not impart any colour to the flame. The spark spectrum of the chloride shows an intense line, 5184; and a strong double line, 5173–5167, at 76 on the scale of Fig. 2. The double line is really a triplet, and

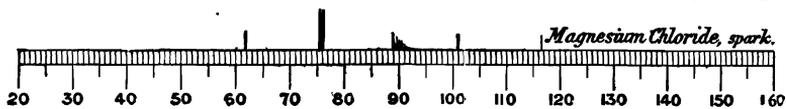


FIG. 2.—Spark Spectrum of Magnesium Chloride.

it coincides with the dark "little b " line of the solar spectrum. There is a shaded band beginning at 83.8, and fading away towards the blue end of the spectrum; and a feeble line at 4705, and another indigo line at 4481. The blue band in the spectrum is supposed to be due to magnesium oxide, and it is very bright in the spectrum of burning magnesium; the other lines are due to the metal itself. C. Cappel claims that 2×10^{-6} mgrms. of magnesium can be detected by the spark spectra; and W. N. Hartley found 10^{-7} mgrms. by photographing the ultra-violet spark spectrum. G. Kirchhoff identified the three green lines in the spectrum of magnesium with the "little b " lines in the solar spectrum. E. Carter examined the vacuum spark spectrum. R. W. Wood and D. V. Guthrie, F. Exner and E. Haschek, G. D. Liveing and J. Dewar, J. C. McLennan and co-workers, A. Cornu, and W. A. Miller examined the **ultra-violet spectrum**. J. Meunier found in the ultra-violet region the band composed of the rays $\lambda=3810, 3829, 3833, 3838, 3851, 3858, 3861$, and another band consisting of the rays $\lambda=3885, 3912, 3940, 3960, 3980$. Nine other rays between $\lambda=3700$ and 3780 have been noticed and their wave lengths approximately determined. Of the salts of magnesium, the chloride, oxychloride, sulphate, nitrate, oxide, and carbonate gave the above spectrum. The pyrophosphate is not, apparently, reduced under these conditions and does not give the above spectrum, since incandescence phenomena, corresponding with the continuous spectrum, are produced. F. Paschen, H. Lehmann, and H. Becquerel examined the **ultra-violet spectrum** of magnesium; W. W. Coblentz, R. A. Millikan and H. Becquerel, the **infra-red spectrum**; J. Stark and G. von Wundt, the effect of the **canal rays**; F. L. Mohler and P. D. Foote studied the **X-ray spectrum** of magnesium; W. Miller and T. Royds investigated the **Zeeman effect**. T. Takamine and N. Kokubu studied the effect of an *electric field* on the spectrum of magnesium. C. Olmsted studied the spectra of *magnesium fluoride, chloride, bromide, and iodide*; W. N. Hartley,

and E. E. Brooks, the spectrum of *magnesium nitride*; W. N. Hartley, *magnesium sulphate*; G. D. Liveing and J. Dewar, G. L. Ciamician, J. N. Lockyer, W. N. Hartley and H. Ramage, E. E. Brooks, A. Fowler and H. Payn, R. A. Porter, and O. H. Basquin, *magnesium hydride*; E. E. Brooks, W. N. Hartley and H. Ramage, J. M. Eder, E. Demarçay, L. de Boisbaudran, A. Gouy, W. M. Watts, H. Crew and O. H. Basquin, C. Olmsted, etc., the spectrum of *magnesium oxide*. G. A. Hemsalech showed that the spectral lines excited thermo-electrically and chemically are of the same type. E. Gehrcke and L. C. Glaser examined the *band spectrum* of magnesium. A. de Gramont and G. A. Hemsalech studied the effect of electric charge on the spectral lines of magnesium.

The spectra of magnesium, zinc, and cadmium are characterized by the presence of triplets repeated over and over again; the triplets are close in magnesium, wider in zinc, and still wider in cadmium. H. Kayser and C. Runge arrange the triplets of magnesium in two series which they believe to be subordinate series, and represent the oscillation frequencies by the formulæ:

FIRST SERIES.

$$10^8\lambda^{-1} = 39796 \cdot 10 - 130398n^{-2} - 1432090n^{-4}$$

$$10^8\lambda^{-1} = 39836 \cdot 79 - 130398n^{-2} - 1432090n^{-4}$$

$$10^8\lambda^{-1} = 39857 \cdot 00 - 130398n^{-2} - 1432090n^{-4}$$

SECOND SERIES.

$$10^8\lambda^{-1} = 39836 \cdot 74 - 125471n^{-2} - 518781n^{-4}$$

$$10^8\lambda^{-1} = 39877 \cdot 95 - 125471n^{-2} - 518781n^{-4}$$

$$10^8\lambda^{-1} = 39897 \cdot 91 - 125471n^{-2} - 518781n^{-4}$$

which agree with 39 lines in the arc-spectrum of magnesium, with very small differences, except in the red, when the difference between the observed and calculated

λ	6000				5000				4000				3500				3000				2500							
$\frac{1}{\lambda}$	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	
Mg									4								5				6				7	8	9	10
					3												4								5	6	7	8
Zn																												
Cd													4								5				6	7	8	
Hg																												
					3																							

FIG. 3.—Series in Spectra of Magnesium, Zinc, Cadmium, and Mercury.

values is about one per cent. The coeff. of n^{-2} and n^{-4} in each series are the same, meaning that the spacing of the lines in the successive triplets are the same within the limits of experimental error. The arrangement of the lines in the series in the spectra of magnesium, zinc, cadmium, and mercury is shown in Fig. 3, the numbers of the lines represent the values assigned to n in the above formulæ. This subject has been discussed by A. Fowler. J. C. McLennan found that the vapour of magnesium gives a single line spectrum $\lambda=2852 \cdot 22$, when the heated vapours are bombarded by electrons whose energy is acquired by an arcing potential of 8.2 volts with Wehnelt's cathode and positive terminal. The **ionization potential** of magnesium vapour calculated by J. C. McLennan is 4.28 volts; M. N. Saha gave 7.65 volts or 1.76×10^5 cal.; F. L. Mohler and co-workers, 8.0 volts; and J. C. McLennan and J. F. T. Young, 7.65 volts; K. T. Compton gave 3.63-4.28 for the minimum ionization potential. F. L. Mohler and co-workers gave 2.65-4.42 volts for the **resonance potential**. E. Rutherford and J. Chadwick obtained little, if any, evidence of the emission of long-range particles detached by scintillations on a zinc sulphide screen when α -particles pass through magnesium; and H. R. von Traubenberg found the range of the α -particles in magnesium to be 57.8×10^{-4} cms. M. N. Saha estimated the **temperature of complete ionization** to be 24,000° K., **luminescence** of the vapour to begin at 7500° K., and the temp. of maximum luminescence to be 11,000° K. B. E. Moore studied the excitation stages in the arc spectrum of magnesium.

According to A. Matthiessen,⁶ the **electrical conductivity** of magnesium is a little less than that of zinc. L. Lorenz gave 24.47×10^{-5} for the electrical conductivity at 0° , and 17.5×10^{-5} at 100° ; J. R. Benoit gave 24×10^{-4} for the cold hammered metal at 0° ; and H. Ihle, 20.8×10^{-4} at 19° . J. Dewar and J. A. Fleming, and H. Dickson gave for zinc-free magnesium at -183° , 99.9×10^{-4} mhos; at -78° , 33.7×10^{-4} ; at 0° , 23×10^{-4} ; at 98.5° , 16.7×10^{-4} ; and at 142.2° , 13.5×10^{-4} ; in addition, G. Niccolai gave :

	-189°	-100°	0°	100°	400°
Conductivity .	78.4×10^{-4}	37.8×10^{-4}	23.2×10^{-4}	16.9×10^{-4}	8.41×10^{-4}

E. F. Northrup measured the electrical resistance of magnesium between 20° and 100° . L. Cailletet and E. Bouty, and P. W. Bridgman gave 0.00390 for the *temperature coefficient* of the electrical conductivity between -88.31° and 0° . J. Dewar and J. A. Fleming gave 0.00381 between 0° and 100° . P. W. Bridgman found -0.0555 for the *pressure coefficient* of magnesium at 0° ; and later, with a purer sample, he obtained 0.05390 between 0 and 12,000 kgrms. per sq. cm. press. The results are :

Electrical resistance	0°	50°	100°
0 kgrm.	1.0000	1.1975	1.3900
Press. coeff. $\left\{ \begin{array}{l} 12 \times 10^3 \text{ kgrms.} \\ \text{Average} \end{array} \right.$	-0.05477	-0.05462	-0.05473
	-0.05311	-0.05348	-0.05341
	-0.054080	-0.054065	-0.054018

It was further found that the purer the sample, the smaller the temp. coeff. This is not usual, although L. Holborn found it to be the case with aluminium. W. P. Davey gave 0.90 A. for the **ionic radius** of the magnesium ion in magnesium oxide.

Magnesium is electrically negative against the metals of the alkalis and alkaline earths. According to J. F. Daniell and F. Exner, the **electromotive force** of an element $\text{Mg}|\text{Br}$ is 2.36 volts, and of an element $\text{Mg}|\text{I}$, 1.57 volts. W. R. Mott measured the potential difference between magnesium and some of its salt soln., at 20° against a normal electrode -0.5 volt, and found with $\text{Mg}-\text{NaCl}$ (2 mols per litre), +1.163 volts; $\text{Mg}-\text{NaOH}$ (one mol per litre), +1.111 volts; $\text{Mg}-\text{KOH}$ (one mol per litre), +1.140 volts; $\text{Mg}-\text{KOH}$ (0.1 mol per litre), +1.105 volts; and $\text{Mg}-\text{MgSO}_4$ (one mol per litre), +1.366 volt. According to C. M. van Deventer, magnesium, when immersed in a mixture of alcohol and water, may become cathodic to zinc, immersed in dil. sulphuric acid. The change of potential is due to the formation of a layer of insoluble badly conducting salt on the magnesium. N. R. Dhar studied the e.m.f. of magnesium against aq. soln. of magnesium and potassium chlorides, and gave 0.81 volt for the potential against water. The e.m.f. in water or a neutral electrolyte is less than in a soln. of its own salt. W. Kistiakowsky measured the potential of cells of the type $\text{Mg}|N-\text{Mg-ions}|N-\text{H-ions}|\text{H}_2$ on Pt. The maximum potential of the **magnesium electrode** agrees with the assumption that the heat evolved by the reaction is $\frac{1}{2}\text{Mg} + \text{H}_2\text{O} = \frac{1}{2}\text{Mg}(\text{OH})_2 + \frac{1}{2}\text{H}_2 + 40.28$ Cals.; and it is inferred that the potential of the magnesium electrode is fixed by the free energy of the reaction $\frac{1}{2}\text{Mg} + \text{OH}' - \ominus = \frac{1}{2}\text{Mg}(\text{OH})_2$, just as the potential of the hydrogen electrode is fixed by the free energy of the reaction $\text{H}_2\text{O} + \ominus = \frac{1}{2}\text{H}_2 + \text{OH}'$. The fact that the potential of the magnesium electrode is independent of the conc. of the Mg-ions, and that it reaches a maximum in reducing soln., and a minimum in oxidizing soln., is taken to support the hypothesis. J. Heyrovsky found the decomposition potential of magnesium to be -1.903 volts. L. Cambi found evidence of the **passivity of magnesium** and its amalgams during his measurements of the e.m.f. of this metal in pyridine soln. of magnesium chloride or iodide, but not when methyl alcohol was used as solvent.

The electric current generated by heating a junction of two different metals, or the same metal in two different conditions, is called a thermoelectric current, or the **Seebeck effect**. If the two junctions of a couple be initially at T° , and the temp. of one be raised by a small increment dT , when dE is the corresponding e.m.f., the ratio dE/dT is the thermoelectric power

of the two metals at T° . When an electric current flow passes in a closed circuit containing different metals, heat is absorbed at the junction which would have to be heated in order to give a thermoelectric current in the same direction as that given by the battery, and conversely for the other junction. The phenomenon is called the **Peltier effect**. Again, if a current passes in a closed circuit containing different metals with hot and cold junctions, there is an absorption or evolution of heat. Thus, heat is absorbed when a current flows from the cold to the hot junction in copper, and conversely; heat is evolved when a current flows from cold to hot in iron, and conversely. This phenomenon is called the **Thomson effect**. The Thomson effect with copper, silver, zinc, cadmium, and antimony is said to be positive; with iron, bismuth, cobalt, nickel, and platinum it is said to be negative; and with lead, the effect is neutral.

J. Dewar and J. A. Fleming's value for the **thermoelectric force**, or the **Seebeck effect**, of magnesium at 100° is 0.42 millivolt; K. Noll's 0.40 millivolt; and E. Wagner's, 0.43 millivolt; and the current goes to the platinum from the junction, at 0° . P. G. Tait represents the thermoelectric powers, E , of a circuit of magnesium and lead with one degree difference of temp. as $dE/d\theta = 2.22 - 0.0094\theta$ microvolts, when θ represents the mean temp. of the two junctions; when θ is 20° and 50° , the respective thermoelectric powers are 2.03 and 1.75 microvolts; the neutral point is 236° , when $dE/d\theta$ is zero. P. W. Bridgman found the thermal effect, E , of magnesium against lead at atm. press. to be very small, $E = (-0.095\theta + 0.00004\theta^2) \times 10^{-6}$ volts; the Peltier effect, P , against lead is $P = (-0.095 + 0.00008\theta)(\theta + 273) \times 10^{-6}$ volts; and the Thomson effect, σ , against lead is $\sigma = 0.00008(\theta + 273) \times 10^{-6}$ volts per degree. The thermal e.m.f. of a couple composed of one branch of the uncompressed metal and the other compressed at p kgms. per sq. cm., with the junctions at 0° , are in volts $\times 10^6$,

p	10°	20°	40°	60°	80°	100°
2,000	-0.17	-0.33	-0.67	-1.00	-1.34	-1.67
6,000	-0.57	-1.04	-2.18	-3.43	-4.57	-5.71
12,000	-1.30	-2.59	-5.18	-7.78	-10.37	-12.96

The curves of e.m.f. at constant temp. against press. are concave upwards corresponding with an increasing proportional effect at higher press.; at constant press., the e.m.f. against temp. is linear. For the **Peltier effect** between the compressed and uncompressed metals, in joules per coulomb $\times 10^6$, P. W. Bridgman found:

p	0°	20°	40°	60°	80°	100°
2,000	-4.56	-4.91	-5.24	-5.56	-5.89	-6.23
6,000	-15.6	-13.7	-17.9	-19.0	-20.1	-21.1
12,000	-35.4	-33.0	-40.6	-43.2	-45.8	-48.4

The Peltier effect is thus negative and increases numerically with both temp. and press. The **Thomson effect** was found to be everywhere zero. According to M. E. Verdet, magnesium and its salts are diamagnetic; S. Meyer gave $+0.57 \times 10^{-6}$ for the **magnetic susceptibility** of crystalline magnesium at 20° ; and K. Honda gave $+0.55 \times 10^{-6}$ at 18° . P. Pascal found the at. coeff. of magnetization to be -113×10^{-7} units. A. Günther-Schulze⁷ studied the **electrolytic valve action** of magnesium in aq. salt soln.

REFERENCES.

- ¹ S. Kalischer, *Ber.*, 15, 702, 1882; R. Bunsen, *Pogg. Ann.*, 82, 137, 1852; H. St. C. Deville and H. Caron, *Compt. Rend.*, 44, 394, 1857; *Ann. Chim. Phys.*, (3), 67, 340, 1863; A. A. B. Bussy, *Journ. Chim. Méd.*, 6, 141, 1830; *Journ. Pharm. Chim.*, (1), 15, 30, 1829; (1), 16, 142, 1830; A. W. Wright, *Amer. Journ. Science*, (3), 13, 49, 1877; E. Bamberger, *Monatsh.*, 19, 114, 1898; C. Hlawatsch, *Zeit. Kryst.*, 32, 497, 1900; A. des Cloizeaux, *Bull. Soc. Min.*, 3, 111, 1880; L. Ditscheiner, *Sitzber. Akad. Wien*, 105, 597, 1896; T. M. Lowry and R. G. Parker, *Journ. Chem. Soc.*, 107, 1005, 1915; G. P. Seaman, *Proc. Roy. Soc. Edin.*, 32, 247, 1912; K. F. Slotte, *Acta Soc Fennicae*, 40, 3, 1910; K. Honda and S. Konno, *Science Rep. Tohoku Univ.*, 11, 435, 1922; *Phil. Mag.*, (6), 42, 112, 1921; C. T. Heycock and F. H. Neville, *Journ. Chem. Soc.*, 61, 895, 1892; W. Guerther and M. Pirani, *Zeit. Metallkunde*, 11, 1, 1919; C. J. Burton and W. Marshall, *Proc. Roy. Soc.*, 50, 130, 1891; H. Wurtz, *Amer. Chemist*, 6, 321, 1876; H. Kopp, *Liebig's Ann.*, 36, 1, 1840; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, 3, 73, 1848; A. W. Hull, *Proc. Nat. Acad.*

Sciences, **3**, 470, 1917; Z. Jeffries and R. S. Aroher, *Chem. Met. Eng.*, **26**, 343, 1922; M. N. Saha, *Nature*, **107**, 682, 1921; J. B. A. Dumas, *Compt. Rend.*, **90**, 1027, 1880; K. Scheel, *Zeit. Physik*, **5**, 167, 1921; P. Schübel, *Zeit. anorg. Chem.*, **87**, 81, 1914; W. Nernst and F. Schwern, *Sitzber. Acad. Berlin*, 355, 1914; P. Ludwik, *Zeit. Ver. deut. Ing.*, **59**, 657, 1915; A. Kürth, *ib.*, **53**, 85, 1909; J. von Liebig, *Pogg. Ann.*, **19**, 137, 1830; G. Jager, *Monatsh.*, **8**, 498, 1887; J. W. Buchanan, *Proc. Roy. Soc.*, **73**, 296, 1904; H. Tomlinson, *ib.*, **40**, 343, 1886; W. Sutherland, *Phil. Mag.*, (5), **32**, 215, 524, 1891; W. L. Bragg, *ib.*, (6), **20**, 169, 1920; W. Voigt, *Wied. Ann.*, **48**, 674, 1893; F. Melde, *ib.*, **45**, 568, 729, 1892; C. Schäfer, *Ann. Physik*, (4), **5**, 220, 1901; (4), **9**, 665, 1124, 1902; H. Bohlin, *ib.*, (4), **61**, 421, 1920; L. Hamburger, *Koll. Zeit.*, **23**, 117, 1918; T. W. Richards, W. N. Stull, F. N. Brink, and F. Bonnet, *Journ. Amer. Chem. Soc.*, **31**, 154, 1909; G. N. Lewis, G. E. Gibson, and W. M. Latimer, *ib.*, **44**, 1008, 1922; G. T. Beilby, *B.A. Rep.*, 604, 1901; *Chem. News*, **84**, 163, 1903; C. A. Edwards, *Metal Ind.*, **17**, 221, 1921; C. E. Guye and S. Mintz, *Arch. Sciences Genève*, (4), **26**, 136, 263, 1908; C. E. Guye and V. Freidericks, *ib.*, (4), **29**, 49, 157, 261, 263, 1908; C. E. Guye and H. Schapper, *ib.*, (4), **30**, 133, 1910; J. Desch, *Zeit. Physik*, **5**, 173, 1921; W. Pöhm, *Brit. Pat. No.* 186253, 1921.

¹ G. Bartha, *Ueber die Siedepunkte der Alkalimetalle und Alkalihalogenide im Vacuum des Kathodenlichts*, Heidelberg, 1912; E. Grüneisen, *Ann. Physik*, (4), **33**, 33, 65, 1910; H. St. C. Deville and H. Caron, *Ann. Chim. Phys.*, (3), **67**, 340, 1863; *Compt. Rend.*, **44**, 394, 1857; J. B. A. Dumas, *ib.*, **90**, 1027, 1880; E. van Aubel, *ib.*, **156**, 456, 1913; S. Procopiu, *ib.*, **174**, 1170, 1922; A. Ditte, *ib.*, **73**, 108, 1871; R. Bunsen, *Pogg. Ann.*, **82**, 137, 1852; F. Wöhler, *Liebig's Ann.*, **73**, 369, 1851; C. T. Heycock and F. H. Neville, *Journ. Chem. Soc.*, **87**, 160, 1895; H. Cretier, *Zeit. anal. Chem.*, **13**, 2, 1874; W. C. Roberts-Austen, *Proc. Roy. Soc.*, **63**, 447, 1898; J. Dewar, *ib.*, **76**, A, 325, 1905; A. Schuller, *Naturwiss. Ber. Ungarn*, **1**, 64, 1884; *Wied. Ann.*, **13**, 317, 1883; L. Lorenz, *ib.*, **13**, 422, 582, 1881; P. Nordmeyer and A. L. Bernoulli, *Ber. deut. phys. Ges.*, **5**, 175, 1907; P. Nordmeyer, *ib.*, **6**, 202, 1908; A. Wehnelt and C. Musceleanu, *ib.*, **14**, 1032, 1912; V. and A. Meyer, *Ber.*, **20**, 497, 1887; G. Grube, *Zeit. anorg. Chem.*, **49**, 80, 1906; G. G. Urasoff, *ib.*, **64**, 375, 1909; R. Vogel, *ib.*, **61**, 50, 1909; G. Voss, *ib.*, **57**, 64, 1908; C. H. Mathewson, *ib.*, **48**, 194, 1906; S. F. Schemtschuschny, *ib.*, **49**, 400, 1906; N. S. Kurnakoff and N. J. Stephanoff, *ib.*, **46**, 184, 1905; P. Sahmen, *ib.*, **57**, 31, 1908; N. Beer, *ib.*, **70**, 364, 1911; H. von Wartenberg, *ib.*, **56**, 320, 1908; J. W. Richards, *Metallurgical Calculations*, New York, **64**, 1906; M. Knudsen, *Ann. Physik*, (4), **50**, 472, 1916; N. Stücker, *Sitzber. Akad. Wien*, **114**, 657, 1905; H. Schimpff, *Zeit. phys. Chem.*, **71**, 257, 1910; T. W. Richards and F. G. Jackson, *ib.*, **70**, 414, 1910; E. D. Eastman and W. H. Rodebush, *Journ. Amer. Chem. Soc.*, **40**, 489, 1918; W. Guertler and M. Pirani, *Zeit. Metallkunde*, **11**, 1, 1919; H. C. Greenwood, *Proc. Roy. Soc.*, **82**, A, 396, 1909; R. J. Brunner, *Die Abhängigkeit der spezifischen Wärme des festen Calciums und Magnesiums von der Temperatur*, Zürich, 1906; H. V. Regnault, *Ann. Chim. Phys.*, (3), **63**, 10, 1861; C. Margot, *Arch. Sciences Genève*, **33**, 161, 1895; E. D. Eastman, *Journ. Amer. Chem. Soc.*, **45**, 80, 1923; K. Scheel, *Zeit. Physik*, **5**, 167, 1921; P. Schübel, *Zeit. anorg. Chem.*, **87**, 81, 1914; W. Nernst and F. Schwern, *Sitzber. Akad. Berlin*, 355, 1914; G. N. Lewis and G. E. Gibson, *Journ. Amer. Chem. Soc.*, **39**, 2555, 1917; G. N. Lewis, G. E. Gibson, and W. M. Latimer, *ib.*, **44**, 1008, 1922.

² P. Drude, *Wied. Ann.*, **36**, 885, 1889; **39**, 481, 1890; **42**, 186, 1891; **64**, 159, 1898; L. Troost, *Pogg. Ann.*, **125**, 664, 1865; J. M. Eder, *Sitzber. Akad. Wien*, **112**, 249, 1903; H. Vogel, *Wied. Ann.*, **25**, 92, 1885; W. J. Pope, *Journ. Chem. Soc.*, **69**, 1530, 1896; W. W. Coblenz, *Bull. Bur. Standards*, **2**, 457, 1906; **7**, 197, 1911; J. H. Gladstone, *Phil. Trans.*, **159**, 13, 1869; *Proc. Roy. Soc.*, **18**, 49, 1870; K. Heumann, *Liebig's Ann.*, **184**, 227, 1876; J. Kanonnikoff, *Journ. Russ. Phys. Chem. Soc.*, **16**, 119, 1884; R. Bunsen and H. E. Roscoe, *Phil. Trans.*, **149**, 920, 1859; *Pogg. Ann.*, **108**, 266, 1859; T. Tommasina, *Compt. Rend.*, **129**, 957, 1899; A. R. von Schrötter, *Anz. Akad. Wien*, **2**, 77, 1865; E. L. Nichols, *Trans. Amer. Illum. Eng. Soc.*, **16**, 331, 1921; S. Procopiu, *Compt. Rend.*, **174**, 1170, 1922.

⁴ W. Ramsay and J. F. Spencer, *Phil. Mag.*, (6), **12**, 397, 1906; R. A. Millikan and G. Winchester, *ib.*, (6), **14**, 188, 1907; T. C. Sutton, *ib.*, (6), **47**, 679, 1915; O. Stuhlmann, *ib.*, (6), **22**, 854, 1911; K. Herrmann, *Beiträge zum Hallwacheffekt*, Berlin, 1908; W. Duane, *Proc. Nat. Acad. Sciences*, **7**, 260, 267, 1921; E. Hjalmar, *Zeit. Physik*, **7**, 341, 1921; A. Nodon, *Compt. Rend.*, **174**, 1061, 1922; A. E. Henning and W. H. Kadesch, *Phys. Rev.*, (2), **8**, 209, 1916; M. N. Saha, *Phil. Mag.*, (6), **41**, 267, 1921.

⁵ A. Schrötter, *Journ. prakt. Chem.*, (1), **95**, 190, 1865; H. Lehmann, *Die ultrarothten Spectren der Alkalien*, Freiburg i. Br., 1900; E. Demarçay, *Spectres électriques*, Paris, 1895; L. de Boisbaudran, *Spectres lumineux*, Paris, 1874; H. Lallemand, *Bull. Soc. Chim.*, (2), **3**, 178, 1865; E. Rutherford and J. Chadwick, *Nature*, **107**, 41, 1921; G. Kirchhoff, *Abhand. Akad. Berlin*, **63**, 227, 1863; F. A. Saunders, *Phys. Rev.*, (1), **20**, 117, 1905; W. W. Coblenz, *ib.*, (1), **22**, 1, 1906; L. Troost, *Coemos*, (2), **1**, 533, 1865; *Pogg. Ann.*, **125**, 644, 1865; R. Bunsen, *Zeit. anal. Chem.*, **15**, 91, 1876; *Pogg. Ann.*, **155**, 230, 366, 1875; *Phil. Mag.*, (4), **50**, 417, 725, 1875; W. M. Watts, (4), **50**, 81, 1875; G. A. Hemsalech, *ib.*, (6), **40**, 296, 1920; J. N. Lockyer, *Chem. News*, **40**, 101, 1879; *Compt. Rend.*, **89**, 514, 1879; E. Mascart, *ib.*, **69**, 337, 1869; H. Becquerel, *ib.*, **99**, 374, 1884; **96**, 1215, 1883; **97**, 71, 1883; *Ann. Chim. Phys.*, (5), **30**, 5, 1883; A. E. Nordenskjöld, *ib.*, **105**, 988, 1887; A. de Gramont, *ib.*, **144**, 1101, 1907; **170**, 31, 1920; A. Gouy, *ib.*, **84**, 231, 1877; A. Cornu, *ib.*, **73**, 332, 1871; *Arch. Sciences Genève*, (3), **2**, 119, 1879; J. L. Sorot, *ib.*, (2), **42**, 82, 1871; H. W. Vogel, *Phot. Mitt.*, **16**, 187, 1879; E. Gehrcke and L. C. Glaser, *Ann. Physik*, (4), **65**, 605, 1921; A. de Gramont and G. A. Hemsalech, *Compt. Rend.*, **173**, 505, 1921; **174**, 356, 1922; *Phil. Mag.*, (6), **43**, 834, 1922; J. Frank and G. Hertz, *Verh. deut. phys. Ges.*, **11**, 512.

- 1914; G. D. Liveing and J. Dewar, *Proc. Roy. Soc.*, **27**, 132, 350, 494, 1878; **30**, 93, 1880; **32**, 189, 1881; A. Schuster, *ib.*, **31**, 337, 1881; W. N. Hartley and W. E. Adeney, *ib.*, **35**, 148, 1883; *Phil. Trans.*, **175**, 325, 1884; J. N. Lockyer, *Proc. Roy. Soc.*, **46**, 35, 1889; W. N. Hartley, *ib.*, **49**, 448, 1891; **64**, 5, 1893; *Phil. Trans.*, **175**, 63, 1884; **185**, A, 161, 1894; A. Fowler, *Proc. Roy. Soc.*, **71**, 419, 1903; A. Fowler and H. Payn, *ib.*, **72**, 253, 1903; G. L. Ciamician, *Sitzber. Akad. Wien*, **79**, 8, 1879; F. Exner and E. Haschek, *ib.*, **106**, 54, 1897; J. M. Eder, *Denkschr. Akad. Wien*, **74**, 1903; C. A. Young, *Amer. Journ. Science*, (3), **20**, 353, 1880; J. C. McLennan, *Journ. Franklin Inst.*, **181**, 191, 1916; C. Fievez, *Bull. Acad. Belgique*, (3), **7**, 245, 348, 1884; *Ann. Chim. Phys.*, (5), **23**, 366, 1881; W. N. Hartley, *Journ. Chem. Soc.*, **41**, 84, 1882; *Trans. Roy. Soc. Dublin*, (2), **9**, 85, 1908; *Proc. Roy. Soc. Dublin*, (2), **11**, 243, 1907; J. H. Pollok and A. G. G. Leonard, *ib.*, (2), **11**, 227, 1907; W. N. Hartley and H. Ramage, *Trans. Roy. Soc. Dublin*, (3), **7**, 339, 1901; A. Grünwald, *Monatsh.*, **8**, 650, 1887; *Phil. Mag.*, (5), **24**, 354, 1887; M. N. Saha, *Nature*, **107**, 682, 1921; *Phil. Mag.*, (6), **40**, 807, 1920; (6), **41**, 267, 1921; W. A. Miller, *ib.*, (3), **27**, 81, 1845; *Phil. Trans.*, **152**, 861, 1862; A. Fowler, *ib.*, **209**, A, 447, 1909; T. R. Robinson, *ib.*, **152**, 393, 1862; H. Kayser and C. Runge, *Wied. Ann.*, **43**, 385, 1891; C. Cappel, *Pogg. Ann.*, **136**, 628, 1870; A. Mitscherlich, *ib.*, **121**, 459, 1864; A. S. King, *Amer. Physik*, (4), **16**, 360, 1905; W. Miller, *ib.*, (4), **24**, 105, 1907; T. Royds, *ib.*, (4), **30**, 1024, 1909; C. Runge and F. Paschen, *Sitzber. Akad. Berlin*, **380**, 1902; J. Hartmann and G. Eberhard, *ib.*, **40**, 1903; J. Hartmann, *ib.*, **234**, 1903; *Phys. Zeit.*, **4**, 427, 1903; J. Barnes, *ib.*, **6**, 148, 1905; *Astrophys. Journ.*, **21**, 74, 1905; E. Carter and A. S. King, *ib.*, **49**, 224, 1919; R. A. Porter, *ib.*, **15**, 274, 1902; C. Olmsted, *Zeit. Wiss. Phot.*, **4**, 255, 1907; R. Thalen, *Om Spectralanalyse*, Upsala, 1866; *Nova Acta Upsala*, (3), **6**, 9, 1868; W. W. Strong and O. H. Basquin, *ib.*, **14**, 1, 1901; H. Crew and O. H. Basquin, *ib.*, **2**, 100, 1895; *Astrophys. Journ.*, **22**, 119, 1905; E. E. Brooks, *ib.*, **29**, 177, 1909; *Nature*, **78**, 198, 1908; *Proc. Roy. Soc.*, **80**, A, 218, 1908; J. C. McLennan, J. F. T. Young, and H. J. C. Ireton, *ib.*, **98**, A, 95, 1920; F. Brasack, *Abhand. Nat. Ges. Halle*, **9**, 1, 1864; H. C. Vogel, *Astron. Nachr.*, **161**, 365, 1903; J. Scheiner, *ib.*, **161**, 263, 1903; W. and Mrs. Huggins, *Astrophys. Journ.*, **17**, 145, 1903; H. Crew, *ib.*, **16**, 246, 1902; R. W. Wood and D. V. Guthrie, *ib.*, **28**, 211, 1909; A. Fowler, *Report on Series in Line Spectra*, London, 1922; H. Kayser has given a bibliography of the spectrum of magnesium in his *Handbuch der Spectroscopie* (Leipzig, 5, 698, 1910); J. Meunier, *Bull. Soc. Chim.*, (4), **25**, 562, 1919; J. Stark and G. von Wendt, *Ann. Physik*, (4), **38**, 669, 690, 1912; R. Seeliger and D. Thaeer, *ib.*, (4), **65**, 423, 1921; F. L. Mohler and P. D. Foote, *Journ. Washington Acad.*, **11**, 273, 1921; R. A. Millikan, *Proc. Nat. Acad. Sciences*, **7**, 289, 1921; H. R. von Traubenberg, *Zeit. Physik*, **2**, 268, 1890; T. Takamine and N. Kokubu, *Mem. Coll. Science Kyoto*, **3**, 173, 1918; J. C. McLennan and J. F. T. Young, *Proc. Roy. Soc.*, **95**, A, 273, 1919; K. T. Compton, *Phys. Rev.*, (2), **8**, 412, 1916; J. C. McLennan, J. F. T. Young, and H. J. C. Ireton, *Trans. Roy. Soc. Canada*, **13**, iii, 67, 1919; F. L. Mohler, P. D. Foote, and W. F. Meggers, *Journ. Amer. Optical Soc.*, **4**, 364, 1920; *Phil. Mag.*, (6), **42**, 1002, 1921; B. E. Moore, *Astrophys. Journ.*, **54**, 191, 1921; E. Carter, *ib.*, **55**, 162, 1922; E. Fues, *Zeit. Physik*, **13**, 211, 1923.
- ^a A. Matthiessen, *Pogg. Ann.*, **103**, 428, 1858; L. Caillaet and E. Bouty, *Compt. Rend.*, **100**, 1188, 1885; F. Exner, *Sitzber. Akad. Wien*, **84**, 511, 1881; *Wied. Ann.*, **15**, 412, 1881; L. Lorenz, *ib.*, **13**, 422, 582, 1881; **25**, 1, 1885; S. Meyer, *ib.*, **68**, 325, 1899; **69**, 236, 1899; K. Neill, *ib.*, **53**, 874, 1894; E. Wagner, *Ann. Physik*, (4), **27**, 955, 1908; K. Honda, *ib.*, (4), **32**, 1027, 1910; S. Meyer, *ib.*, (4), **1**, 664, 1900; G. Niccolai, *Atti Accad. Lincei*, (5), **16**, 757, 906, 1907; M. E. Verdet, *Ann. Chim. Phys.*, (3), **52**, 161, 1858; W. R. Mott, *Journ. Amer. Chem. Soc.*, **25**, 380, 1903; J. F. Daniell, *Phil. Trans.*, **132**, 145, 1842; P. W. Bridgman, *Proc. Amer. Acad.*, **52**, 573, 1917; **53**, 269, 1918; **56**, 61, 1921; H. Ihle, *Jahresber. Gymn. Dresden-Neustadt*, **22**, 3, 1896; P. Pascal, *Compt. Rend.*, **173**, 144, 1921; L. Holborn, *Ann. Physik*, (4), **59**, 146, 1919; L. Cambi, *Atti Accad. Lincei*, (5), **24**, i, 932, 1915; N. R. Dhar, *Zeit. anorg. Chem.*, **118**, 75, 1921; J. R. Benoit, *Compt. Rend.*, **76**, 342, 1873; *Phil. Mag.*, (4), **45**, 314, 1873; J. Dewar and J. A. Fleming, *ib.*, (5), **36**, 271, 1893; (5), **40**, 95, 1895; H. Dickson, *ib.*, (5), **45**, 525, 1898; P. G. Tait, *Trans. Roy. Soc. Edin.*, **27**, 125, 1873; W. P. Davey, *Phys. Rev.*, (2), **19**, 248, 1922; E. F. Northrup, *Met. Chem. Eng.*, **15**, 193, 1916; C. M. van Deventer, *Zeit. phys. Chem.*, **91**, 687, 1916; W. Kistiakowsky, *ib.*, **70**, 206, 1910; J. Heyrovsky, *Phil. Mag.*, (6), **45**, 303, 1923.
- ⁷ A. Günther-Schulze, *Ann. Physik*, (4), **21**, 929, 1906; (4), **22**, 543, 1907; (4), **23**, 226, 1907; (4), **24**, 43, 1907; (4), **25**, 775, 1908; (4), **26**, 372, 1908; (4), **28**, 787, 1909; (4), **31**, 1053, 1910; (4), **34**, 657, 1911; (4), **41**, 593, 1913; (4), **44**, 1106, 1914; (4), **65**, 223, 1921; *Zeit. Elektrochem.*, **14**, 333, 1908; **17**, 510, 1911; **18**, 22, 326, 1912; **19**, 122, 1913; **20**, 307, 592, 1914.

§ 5. The Chemical Properties of Magnesium

Magnesium is used for making illuminating powders for flash-light photography; and for star-shells for illumination in warfare; it is used as a deoxidizer in making bronzes, nickel-silver, and other alloys; it is used in conjunction with aluminium for making light alloys—e.g. magnalium; and it is used in dehydrating oils—e.g. aniline oil—etc. The compounds of magnesium are used medicinally; in making

cements; and magnesia is employed for making the so-called magnesite bricks for lining basic steel furnaces, and electric steel furnaces.

According to J. B. A. Dumas,¹ magnesium absorbs about two-thirds of its vol. of hydrogen, which is evolved in vacuo at a red heat. C. Winkler stated that hydrogen is not absorbed by hot magnesium, but a slow absorption does occur if the metal be mixed with magnesia, and heated to redness in a stream of hydrogen for 4 hrs., and he believed that 6.42 per cent. of the metal has been converted into **magnesium hydride**. No other chemical evidence of the existence of magnesium hydride has been adduced. According to A. Fowler, the dark grey deposit formed by the passage of the arc in hydrogen probably contains magnesium oxide, since, when dissolved in acids, it gives less hydrogen than would be furnished by an equal weight of magnesium; there is no chemical evidence of the formation of a hydride. O. H. Basquin noted that the spectrum, in hydrogen, with the rotating metallic arc with aluminium, copper, magnesium, silver, or sodium, has characteristic lines not found with the arc spectrum in air, and "in lieu of a better hypothesis," he assumed that the lines are due to the formation of metal hydrides. W. N. Hartley did not favour the hypothesis because, in the case of sodium, the dissociation at barometric press. is complete at 422°. G. D. Liveing and J. Dewar attributed the line at $\lambda=5210$, and the attendant series to "a mixture of magnesium and hydrogen rather than to a chemical compound, because this expresses the facts, and we have not yet obtained independent evidence of any chemical compound of these elements"; but in a later paper, they stated that "the lines just indicated are due to a combination of hydrogen and magnesium, and are not dependent solely upon the temp." A. Fowler likewise assumed that magnesium hydride is concerned in the production of the flutings in the spectrum of a mixture of hydrogen and magnesium, and that the combination appears to take place directly under the influence of the arc, especially at low press., or with some forms of the spark discharge, or by the combustion of the metal in an atm. containing hydrogen either free or in combination. E. E. Brooks suggested that the compound is in most experiments decomposed as quickly as it is formed, and A. Fowler added that "a perfectly definite conclusion does not at present seem to be possible."

A. A. B. Bussy,² and R. Bunsen found that magnesium does not change in dry air, but, in moist air, it is soon covered by a white film of magnesium hydroxide, and H. St. C. Deville and H. Caron found that in ordinary air it is attacked superficially. E. Sonstadt also stated that magnesium contaminated with nitrogen (nitride) is not stable in air. The metal inflames when heated just above its m.p. in air, and burns with an intense white dazzling flame, and a white cloud of magnesium oxide is formed. W. Muthmann and K. Kraft give 540° for the ignition temp. of magnesium in oxygen. According to F. J. Rogers, the temp. of the magnesium flame is 1335°. According to A. K. Christomanos, and W. French, when a cold solid is introduced into the magnesium flame, a black spot surrounded by a white halo of magnesium oxide is formed; according to A. K. Christomanos, and G. Baborovsky, the black deposit may be a suboxide; and A. K. Christomanos, J. W. Mallet, and J. Pinnow say that an appreciable quantity of magnesium nitride is formed in the *smothered combustion* of magnesium, *i.e.* the combustion of the metal in a quantity of air insufficient to burn all the metal. H. Kämmerer observed the formation of appreciable quantities of nitric oxide when magnesium burns in a cylinder filled with air; P. L. Aslanoglou noted the formation of ammonia in the oxidation of magnesium in moist air. According to S. Kappel, if air be passed over magnesium in contact with potassium hydroxide, nitrous acid, ozone, and hydrogen peroxide are formed; if the metal is in contact with aq. ammonia, magnesium nitride and suboxide are formed. In oxygen, magnesium burns quantitatively to the oxide. N. B. Pilling and R. E. Bedworth found that magnesium at 500° in oxygen produces a discontinuous film of oxide which offers no impediment to further oxidation. The oxidation is at the rate of about 0.00052 grm. per sq. cm. per hour, a value about one-third as great as that for calcium at the

same temp. O. Ohmann found magnesium-wool burns with explosive violence when ignited with a Bunsen's burner.

According to A. A. B. Bussy, cold, recently boiled **water** is without action on magnesium, while with boiling water, some hydrogen is developed: $\text{Mg} + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{H}_2$. On the other hand, J. von Liebig stated that boiling water is without action on the metal. R. Bunsen observed that the metal he prepared slowly decomposed cold water. It is not clear if all these samples of metal were free from the alkali metals or the water free from carbon dioxide. D. Vitali found water free from carbon dioxide gives no hydrogen in contact with magnesium. According to C. F. Roberts and L. Brown, magnesium has no action on distilled water which has been freed from gases by boiling and afterwards cooled out of contact with air. It reacts, however, with undistilled water, with unboiled distilled water, or with water which has been boiled and afterwards charged with oxygen or carbon dioxide, varying amounts of hydrogen being liberated. H. T. Barnes and G. W. Scherer showed that some hydrogen peroxide is formed in the reaction. W. Hughes found that the reaction between magnesium and water is very slow at the ordinary temp., but is greatly accelerated in presence of neutral and alkaline salts, such as sodium chloride, sodium hydrocarbonate, sodium carbonate, and magnesium sulphate. Experiments with sodium chloride soln. at 25° have shown that the initial rate at which hydrogen is evolved depends on the concentration of the dissolved salt. The reaction velocity has a maximum value for a soln. containing 32 mols of water per mol of sodium chloride. This maximum cannot be satisfactorily interpreted in terms of the physical properties of sodium chloride soln., and is regarded as evidence in favour of the specific nature of the catalytic action of the electrolyte present. According to A. Ditte, magnesium decomposes water at a temp. exceeding 70° . Water vapour, at not particularly high temp., is decomposed by magnesium; and the phenomenon is used as a lecture experiment—*vide* A. Duboin, H. Leffmann, G. T. Moody, M. Rosenfeld, etc. According to F. Kessler, burning magnesium is not extinguished when plunged into steam.

According to C. Weltzien, and G. Giorgis, a soln. of **hydrogen peroxide** dissolves magnesium; if atm. carbon dioxide be not excluded, the soln. becomes alkaline, and furnishes on evaporation needle-like crystals of magnesium carbonate, soluble in water; while if carbon dioxide be excluded, the metal is dissolved much more slowly, the water becomes alkaline, and on evaporation gives a flocculent residue, not soluble in water. H. T. Barnes and G. W. Scherer showed that with magnesium and aluminium electrodes in contact with water containing dissolved air, the e.m.f. slowly rises to about one volt, although the metals are close together in the electrochemical series; this is due to the formation of hydrogen peroxide by the action of water containing dissolved air on aluminium. When free hydrogen peroxide is added to the aluminium compartment, the e.m.f. rises to about two volts, and then gradually falls as the hydrogen peroxide is decomposed.

H. Moissan³ found that magnesium burns vigorously in **fluorine** *avec beaucoup d'éclat*, forming the fluoride. In 1830, J. von Liebig found moist **chlorine** gas inflames magnesium; and in 1852, R. Bunsen said that the warm metal burns in chlorine, and J. A. Wanklyn and E. T. Chapman said that magnesium remains bright for a long time in cold chlorine. R. Cowper found that dry chlorine gas does not attack magnesium. H. Gautier and G. Charpy kept liquid chlorine for 15 months in contact with magnesium without any appreciable action. R. Bunsen said that warm magnesium does not burn so readily in **bromine** vapour as it does in chlorine; and H. Gautier and G. Charpy, and J. A. Wanklyn and E. T. Chapman found that dry liquid bromine could be kept for a year in contact with magnesium without any appreciable action; bromine water, on the other hand, gives a regular development of hydrogen, and an oxybromide is formed. R. Bunsen said that magnesium burns vigorously when heated in **iodine** vapour, and T. L. Phipson distilled iodine from magnesium without appreciable action. F. J. Faktor stated that a soln. of iodine colours magnesium green, and a film of the iodide is formed,

and J. A. Wanklyn and E. T. Chapman, that an ethereal or alcoholic soln. of iodine acts very slowly on magnesium when warmed. R. Bunsen noted in 1852 that magnesium is readily attacked by **hydrochloric acid**—*vide* action of acids on copper, and also on zinc. P. T. Austen noted that when burning magnesium is introduced into gaseous **hydrogen iodide**, it continues burning for a moment, and is then extinguished. A soln. of bleaching powder, sp. gr. 1.04, was shown by A. D. White to act slowly on magnesium with the evolution of hydrogen; with hypochlorous acid, hydrogen is rapidly evolved and magnesium hypochlorite is formed. According to W. S. Hendrixson, when magnesium reacts with **chloric acid**, about 95 per cent. is converted into chlorate, and the remainder is spent in the reduction of the acid. C. Kippenberger reduced soln. of the chlorates to chlorides by means of magnesium. According to A. Ditte, with a cold aq. soln. of **iodic acid** iodine is liberated, and hydrogen evolved; and a very dil. soln. of the acid is coloured yellow by the iodine. According to D. Vitali, a soln. of iodic acid is first coloured yellow by magnesium, and a brown precipitate is formed containing magnesium iodate, while the colourless soln. contains iodide and iodate.

According to K. Seubert and A. Schmidt, the **alkali chlorides** are reduced to the metals when heated with magnesium in an atm. of hydrogen, lithium chloride being reduced most readily; the **alkaline earth chlorides** are also reduced in a similar way, and the reduction is more readily effected the smaller the at. wt. of the metal. Most **metal chlorides**—*e.g.* the chlorides of copper, silver, gold, zinc, cadmium, mercury, aluminium, thallium, lead, tin, arsenic, antimony, bismuth, chromium, tungsten, molybdenum, uranium, manganese, iron, cobalt, nickel, and platinum—are also reduced when heated with magnesium. According to S. Möller, *chemiluminescence* occurs when an **alkyl halide** in ethereal soln. reacts with powdered magnesium.

According to J. von Liebig,⁴ molten **sulphur** reacts with magnesium, and, according to R. Bunsen and J. Parkinson, the reaction is vigorous with the red-hot metal, and the metal burns vigorously in sulphur vapour, forming magnesium sulphide. A. Orłowsky found that the reaction between magnesium and sulphur or a soln. of sulphur in carbon disulphide is exceedingly slight at ordinary temp. According to T. L. Phipson, and F. G. Reichel, the sulphur can be volatilized by heat from an admixture with magnesium filings without reaction. According to W. Spring, a mixture of sulphur and finely divided magnesium forms a polysulphide when subjected to a press. of 6500 atm. L. Kessler found that burning magnesium continues burning in an atm. of **hydrogen sulphide**, and also in an atm. of **sulphur dioxide**. In the latter case J. Parkinson found that there is a separation of sulphur, and the formation of a residue which gives off red fumes when treated with nitric acid, and magnesium sulphate being formed. According to J. Uhl, the residue after the combustion in sulphur dioxide contains sulphate, sulphite, and sulphide. With sulphurous acid, P. Schweitzer obtained sulphite, thiosulphate, and trithionate; and M. Billy obtained magnesium tetrathionate with a soln. of sulphur dioxide in absolute alcohol. C. Brückner found that when **sulphur trioxide** vapour is passed over red-hot magnesium powder, magnesia, sulphur dioxide, and magnesium sulphide are formed. R. Bunsen stated that magnesium dissolves with difficulty in conc. **sulphuric acid**, and J. von Liebig observed the development of sulphur dioxide, and A. Ditte, hydrogen sulphide and sulphur. The rate of dissolution of magnesium in dil. acids has been investigated by N. Kajander, and he found that the wt. of metal dissolved in unit of time is, *ceteris paribus*, a simple function of the mol. wt. of the acid, of its conc., and of the nature (water, saline soln., etc.) of the medium in which the reaction is effected. Heat accelerates the reaction only because it diminishes the internal friction of the liquid. P. B. Ganguly and B. C. Banerji found that a rod of magnesium partly immersed in dil. acid is most attacked near the surface of the liquid. K. Seubert and A. Schmidt found **sulphur chloride**, S_2Cl_2 , gives sulphur when heated with magnesium.

According to C. Brückner, when an **alkali sulphite** is heated with magnesium, alkali sulphide and sulphate are formed, while the **heavy metal sulphites**, *e.g.* zinc

sulphite, furnish sulphur dioxide, and the metal oxide, sulphide, and sulphate. When the **alkali sulphates** are calcined with magnesium in a stream of nitrogen, the alkali polysulphide, thiosulphate, and sulphur are formed, but no sulphur dioxide is evolved; while the **alkaline earth sulphates**, and the **sulphates of magnesium, zinc, aluminium, and nickel** give sulphur dioxide and oxide; **cupric sulphate** also gives metallic copper; and the **sulphates of manganese and iron** give the higher metal oxide, thiosulphate, and sulphide as well as sulphur dioxide and sulphur. Some sulphates react giving sparks when they are triturated with magnesium. The products of the reaction in the cold are not the same as with heat; thus **nickel sulphate** gives nickel sulphide and magnesium oxide in the cold, and nickel sulphide, sulphur dioxide, and sulphur when heated. According to F. J. Faktor, when magnesium is calcined with **sodium thiosulphate**, the sulphide and sulphate are formed; and when magnesium is heated with a soln. of sodium thiosulphate the reactions are symbolized: $Mg + 2H_2O = Mg(OH)_2 + H_2$; $Na_2S_2O_3 + H_2 = H_2S + Na_2SO_3$; $Mg(OH)_2 + 2H_2S = Mg(SH)_2 + 2H_2O$. H. Mouraour also studied the action of magnesium on soln. of sodium thiosulphate. According to M. G. Levi, E. Migliorini, and G. Ercolini, magnesium rapidly dissolves in a soln. of **potassium persulphate**, with the evolution of gas; and the turbulent action of an aq. soln. of **ammonium persulphate** on magnesium, furnishes ammonia gas, etc.

F. W. Newmann⁶ studied the absorption of **nitrogen** by magnesium at the cathode of a vacuum tube. Magnesium is not attacked by nitrogen in the cold. H. Erdmann found liquid nitrogen extinguished the flame of burning magnesium. F. Briegleb and A. Geuther prepared magnesium nitride by heating the metal in a stream of nitrogen or **ammonia**. H. N. Warren added that there is very little action below a red heat, although the metal becomes less fusible and burns with violent decrepitations when ignited; at a dull red heat, the metal becomes yellow with a golden lustre; and at a full red heat it forms an orange-yellow powder of the nitride. According to T. L. Phipson, and G. A. Maack, aq. ammonia does not react with magnesium in the cold. Dry liquid ammonia, according to F. G. Cottrell, does act slowly on magnesium, forming a faint blue soln., which gradually decomposes into amide and hydrogen, in a manner analogous with the corresponding reaction between liquid ammonia and the alkali and alkaline earth metals. Liquid **acetylene** at ordinary temp. has no appreciable action on the metal. Electrical conductivity measurements show no signs of the formation of magnesium aminocarbide or aminoacetylide, but mixtures of liquid ammonia and acetylene readily act on magnesium, forming a crystalline compound, $MgC_2 \cdot C_2H_2 \cdot 5NH_3$, and some ethylene and ethane. The product is stable below 2°, but at this temp. it loses the eq. of $1.5NH_3$, and the residue is stable between 2° and 60°, when it loses ammonia and leaves behind a mixture of magnesium amide and nitride. According to C. A. L. de Bruyn, anhydrous **hydroxylamine** is without action on powdered magnesium. L. Kessler found that the flame of burning magnesium is not extinguished in **nitrous oxide** or in **nitric oxide**; and P. Sabatier and J. B. Senderens found that magnesium filings begin to react with **nitrogen peroxide** at a dull red heat. R. Weber found **nitrogen pentoxide** only exerts a slight action on the metal; and J. J. Sudborough, that **nitrosyl chloride** has no action on the metal either in the cold or at 100°. According to W. N. Hartley, aq. soln. of **nitrates** are reduced by magnesium to nitrites, and C. Kippenberger showed that with a dil. soln. of a nitrate, the first reduction product is a nitrite, then hydroxylamine, and finally ammonia. These primary reduction products can interact with one another to yield secondary products—nitrous and nitric oxides, nitrogen, etc. J. von Liebig stated that with cold **nitric acid**, nitric oxide is evolved, while C. Montemartini found that nitrous and nitric oxides, nitrogen, ammonia, and hydrogen are developed. The amount of ammonia produced in the reaction between magnesium and nitric acid increases with the concentration of the latter until 40 per cent. acid is reached, the quantity then decreases. Much hydrogen is formed; the mixture of this gas and nitric oxide liberated by 13 per cent. acid may be exploded by an electric spark.

J. J. Acworth and H. E. Armstrong obtained less nitric oxide and more nitrous oxide and nitrogen than is the case with cadmium or zinc. According to E. Divers, magnesium and nitric acid produce some hydroxylamine which is decomposed so rapidly as to escape detection unless some hydrochloric acid is also present. For some unknown reason sulphuric acid useful in the case of zinc is unsatisfactory with magnesium. According to P. T. Austen, magnesium burns with a white light in the vapour of nitric acid. According to W. Eidmann, many **nitrogenous substances**, when heated with magnesium, furnish magnesium nitride; and carbonitrogenous substances may give magnesium carbide as well.

J. Parkinson, P. T. Blunt, H. Schön, and O. Emmerling obtained magnesium phosphide by heating magnesium with **phosphorus**. A. Stock and B. Hoffmann obtained magnesium phosphide by heating the metal with **phosphorus nitride**, P_3N_5 ; K. Seubert and A. Schmidt obtained phosphorus by the action of magnesium on **phosphorus trichloride**; and B. Reinitzer and H. Goldschmidt found that magnesium reacts with **phosphoryl chloride**, $POCl_3$, at ordinary temp., forming phosphorus trichloride, magnesium chloride, and phosphate, as well as a red substance which they think is an oxide of phosphorus; the reaction is very vigorous at 100° . H. Mouraour found magnesium slowly attacks soln. of **disodium hydrophosphate**; and A. Duboin found that a mixture of a mol of normal **calcium phosphate** with eight gram-atoms of magnesium reacts vigorously when heated in an atm. of hydrogen, some phosphine being formed. J. Parkinson heated to redness a mixture of magnesium filings and **arsenic** in a stream of hydrogen, and obtained a hard brown mass, which rapidly disintegrates on exposure to air. J. Parkinson prepared a similar product with **antimony** and magnesium. A. Stock and W. Doht obtained a

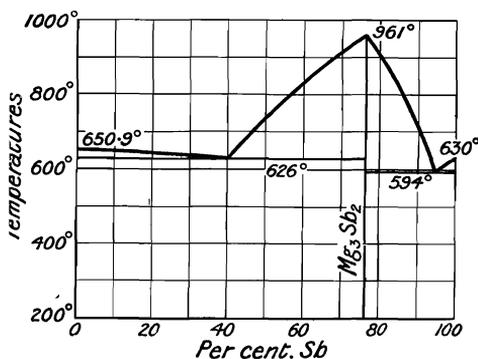


FIG. 4.—Freezing-point Curves of the Binary System Sb—Mg.

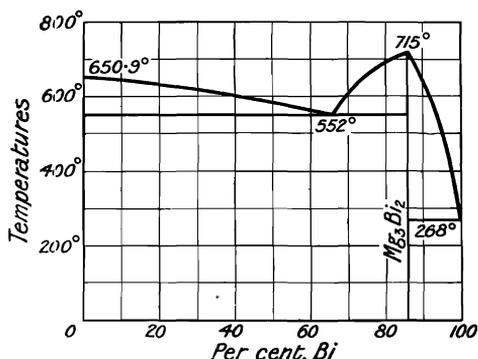


FIG. 5.—Freezing-point Curves of the Binary System Bi—Mg.

similar product. G. Grube obtained the f.p. curve shown in Fig. 4. There are two eutectics, with a maximum corresponding with **magnesium antimonide**, Mg_3Sb_2 , melting at 961° . Magnesium readily alloys with **bismuth**, and G. Grube similarly obtained **magnesium bismuthide**, Mg_3Bi_2 , melting at 715° , Fig. 5.

C. Winkler⁶ observed that a superficial layer of magnesium carbide is formed when magnesium is heated with **carbon**; and J. Parkinson observed that some carbide is likewise formed when magnesium is heated in a stream of **benzene** vapour, although **methane** and **coal gas** have very little action. C. O. V. Engler and E. Kneis have studied the action of **petroleum** on magnesium, and found no appreciable solvent action after four months' exposure in air; the impure oil may exert a solvent action. K. Seubert and A. Schmidt found **carbon tetrachloride** forms carbon when heated with magnesium. According to L. Kessler, when a spiral of burning magnesium ribbon is immersed in **carbon monoxide**, combustion ceases; but if the metal be heated in a stream of the gas, vivid combustion occurs, and a grey coating of carbide is formed on the metal. J. Parkinson noted the separation

of carbon when magnesium is heated in an atm. of carbon monoxide. C. Winkler, and H. Cretier also made observations on the reduction of carbon monoxide by heated magnesium. V. Meyer seems to have regarded this gas as neutral at an incipient white heat. J. Parkinson, and L. Kessler noted that **carbon dioxide** is reduced to carbon by red-hot magnesium. C. Winkler showed that if magnesium be moderately heated in a stream of carbon dioxide, the metal is slowly converted into carbide, and some carbon monoxide is formed; on raising the temp. to a full red heat, the metal inflames, forming magnesia and carbon. These reactions are more readily observed if the powdered metal is employed. When a mixture of magnesium and calcium carbonate is heated in a current of hydrogen, a violent explosion occurs, and magnesium carbide is formed, but no calcium. K. Brunner found that when magnesium powder is scattered over a flat dish containing solid carbon dioxide and a small amount of burning magnesium is dropped into this, the metal continues to burn, forming a grey cake, which, on treatment with water and hydrochloric acid, leaves a residue of black, flocculent carbon. S. Kappel, M. Ballo, and G. Giorgis have studied the action of water saturated with carbon dioxide on magnesium—some hydrogen is developed but no magnesium carbonate is precipitated—water alone, under the same conditions, is without action on the metal. J. von Liebig found magnesium is attacked by cold dil. **acetic acid**, and R. Lohnstein found that the solvent action of dil. acetic acid on magnesium is inhibited if potassium dichromate is added in sufficient quantity to the soln. The magnesium loses its power of dissolving spontaneously in the soln., but, if it is made the anode of an electrolytic cell, it dissolves readily. The conc. of the dichromate required to produce the passive condition increases with the conc. of the acetic acid. If soln. still takes place, the rate is greatly diminished by the dichromate. The passive condition may be destroyed by the addition of an alkali or magnesium salt of a strong acid, the rate of soln. of the active magnesium increasing with the conc. of the added salt. R. Lohnstein suggested that the phenomena are of catalytic nature. According to A. Cavazzi, the vapour of **carbon disulphide** converts red-hot magnesium into the sulphide. According to A. Rossel, magnesium reacts with incandescence when heated in air with **calcium carbide**: $2\text{CaC}_2 + 6\text{Mg} + 2\text{N}_2 + 5\text{O}_2 = 2\text{CaO} + 2\text{Mg}_3\text{N}_2 + 4\text{CO}_2$. L. Kahlenberg and H. Schlundt found that magnesium is not attacked by anhydrous liquid **hydrogen cyanide**, nor by a soln. of sulphur trioxide; on the other hand, the metal is attacked by a soln. of hydrochloric acid or fuming sulphuric acid in that liquid. W. Eidmann found that when magnesium is heated with the **cyanides** of the alkalis or alkaline earths, the metal carbide and magnesium nitride are formed; the less stable cyanides—*e.g.* those of zinc, cadmium, nickel, cobalt, lead, and copper—react with incandescence, forming the metal magnesium nitride and carbon; and the unstable cyanides—*e.g.* those of gold and mercury—first decompose into the metal and **cyanogen**, which latter reacts explosively with magnesium. A. Brochet and J. Petit found that magnesium is vigorously attacked in the cold by a soln. of **potassium cyanide**.

According to C. Winkler, **silicon** reacts with magnesium with feeble incandescence when the two elements are heated together. G. Rauter found that magnesium exerts very little action on **silicon tetrachloride**, when heated for 67 hrs. to 390°–400°, although some silicon is formed; while K. Seubert and A. Schmidt say that much silicon is formed. T. L. Phipson and J. Parkinson found **silica** is reduced by magnesium when heated by the flame of a spirit lamp; C. Winkler found the reduction of the silica is attended by incandescence, and in the cooler parts of the containing vessel, bluish-grey magnesium silicide is formed, and in the hotter parts, brown amorphous silicon is formed. If an excess of silica be employed, no silicide is formed. **Silicates** were found by C. Winkler to be reduced like silica itself when heated with magnesium. J. von Liebig noted that **glass** on which magnesium has been burnt, and D. P. Smith that glass on which the metal has been fused, shows a black stain which is not removed by acids. V. Meyer found **porcelain** is strongly attacked by magnesium at an incipient white heat. According to J. Parkinson, and C. Winkler,

titanium dioxide is reduced by magnesium at a red heat, and the mass becomes incandescent—some *magnesium titanate*, but no *magnesium titanide* is formed. According to C. Winkler, **magnesium titanate**, $MgTiO_3$, is not reduced by magnesium. E. A. Schneider found **titanium nitride**, Ti_3N_4 , reacts with magnesium like magnesium nitride, Mg_3N_2 , reacts with titanium. T. L. Phipson found that **zirconium dioxide** is reduced by magnesium at the temp. of an alcohol flame; C. Winkler showed that the reaction is not complete, and if it takes place in an atm. of hydrogen some magnesium hydride is formed; no *magnesium zirconide* was observed. According to C. Winkler, **cerium dioxide** is reduced to the sesquioxide or the metal according to the proportion of *magnesium ceride*; **thorium dioxide** is incompletely reduced with feeble incandescence; **germanium dioxide** is very vigorously reduced to metal; likewise **stannic oxide** and **lead dioxide** are vigorously and violently reduced to the respective metals.

According to H. Moissan, when magnesium is heated with **boron** in a neutral atm., magnesium boride, Mg_3B_2 , is formed; and with **boron sulphide**, boron and magnesium sulphide. K. Seubert and A. Schmidt say that boron is formed when magnesium is heated with **boron chloride**. T. L. Phipson, A. Geuther, H. N. Warren, A. Duboin, and L. Gattermann observed that **boron trioxide** is reduced by magnesium, forming boron, and C. Winkler obtained a mixture of boron and magnesium boride. H. Moissan has studied the reaction as a means of preparing boron. C. Winkler and L. Gattermann found fused **borax** is reduced like boron trioxide. J. Parkinson, and C. Winkler reduced **alumina** by magnesium; and the latter reduced **yttrium, lanthanum, gallium, indium, and thallium sesquioxides** in a similar way. J. Parkinson found **chromic oxide** is reduced by magnesium. W. R. Dunstan and J. R. Hill found that the immersion of the metal in one per cent. soln. of **potassium dichromate or chromate** furnishes **passive magnesium**, for the metal so treated and washed remained unchanged in distilled water for some hours under conditions where the untreated metal is oxidized all over. The passive metal is, however, also oxidized in about 24 hrs. A. Vyskocil also obtained passive magnesium. **Chromic acid** soln. act on magnesium tarnishing the surface. H. N. Warren found that **molybdenum oxide** reacts explosively with the element.

At a high temp. magnesium acts as a powerful reducing agent. H. N. Warren stated that magnesium does not reduce the alkali oxides and alkaline earths, but C. Winkler showed that this statement is wrong, for he found the **alkali hydroxides** and **alkali carbonates**, excepting caesium carbonate, to be readily reduced by magnesium when a mixture of the two is heated in a sealed tube or in a stream of hydrogen. The reaction is very energetic with lithium and sodium carbonates. A. Geuther, and T. L. Phipson observed the ready reduction of sodium carbonate; the latter found the reaction occurred at the temp. of an alcohol flame. C. Winkler thought that caesium carbonate was not reduced under these conditions, but the work of E. Graefe and M. Eckardt, N. N. Beketoff and A. Scherbatscheff, and of H. Erdmann and co-workers shows that caesium hydroxide or carbonate is readily reduced. **Cuprous oxide** and **silver oxide** are violently reduced by magnesium; silver oxide and **gold oxide** are reduced by heat without the aid of magnesium. The **alkaline earth oxides** are readily reduced by magnesium; **beryllium, zinc, cadmium, and mercury oxides** are reduced explosively when heated with magnesium, but **magnesium oxide** is not changed. F. E. Weston and H. R. Ellis found that magnesium reduces **aluminium oxide** when the mixture is ignited with a fuse.

Magnesium acts as a reducing agent on soln. of salts of the metals. The available evidence is sometimes contradictory. Magnesium has been said to precipitate the element from soln. of salts of copper, silver, gold, zinc, cadmium, mercury, thallium, selenium, tellurium, arsenic, antimony, bismuth, tin, lead, manganese, iron, cobalt, nickel, platinum, and palladium; to precipitate the oxide from soln. of salts of chromium, and uranium; to reduce but not precipitate soln. of salts of molybdenum, tungsten, and vanadium. This subject had been investigated by G. A. Maack,⁷

T. L. Phipson, Z. Roussin, R. Böttger, C. Scheibler, etc. A. Vyskocil found that the ordinary equation for the speed of heterogeneous reactions cannot be applied to the reaction between magnesium and soln. of the ammonium salts, or of neutral metallic salts, since the metal first decomposes the water, and if the soln. is nearly neutral, the speed of the reaction depends to a great extent on the oxidizing or reducing power of the attacking soln. This view confirms V. Kistiakowsky's observations on the magnesium electrode. The anions of neutral salts in soln. act catalytically on the decomposition of water by magnesium. **Platinized magnesium** is also a powerful reducing agent; thus, according to M. Ballo, it reduces nitrobenzene in alcoholic soln. quantitatively to aniline. J. I. Michailenko and P. G. Mushinsky showed that the water of crystallization of certain salts is acted on by magnesium with the evolution of hydrogen.

According to F. Wöhler, aq. soln. of ammonium chloride or carbonate dissolve magnesium with the evolution of hydrogen; S. Kern, and D. Tommasi also found the attack is vigorous with soln. of ammonium chloride, and L. Santi, and D. Vitali stated that the double salt, $Mg(NH_4)_2Cl_4$, is formed; and H. Mouraour found soln. of various **ammonium salts**—carbonate, chloride, oxalate, and sulphide—act vigorously on magnesium, but no action was observed with soln. of ammonium fluoride. H. Mouraour attributed the specific action of soln. of the ammonium salts to their solvent action on magnesium hydroxide. D. Vitali found the action of a soln. of **hydroxylamine hydrochloride** to be analogous to that of ammonium chloride.

According to G. A. Maack, and T. L. Phipson, cold aq. soln. of the **alkali hydroxides** do not act on magnesium, and a similar observation was made by L. Kahlenberg with *N*-soln. of sodium and potassium hydroxides. The action of soln. of various **alkali salts** has been studied. H. Mouraour found a soln. of sodium carbonate is likewise attacked by magnesium. According to M. Ballo and G. Giorgis, aq. soln. of the alkali hydrocarbonates dissolve the metal with the evolution of hydrogen. According to S. Kern, when a soln. of sodium chloride is treated with magnesium, sodium hydroxide is formed with the slow development of hydrogen. D. Tommasi, however, states that in the case of potassium chloride soln. the action is catalytic, for the potassium chloride remains unchanged, and magnesium hydroxide is formed. As indicated above, W. Hughes found that the rate of evolution of hydrogen depends on the conc. of the soln., and there is a maximum with a soln. containing 32 mols of water per mol of sodium chloride; and the existence of this maximum is taken to correspond with a specific effect of the solute on the solvent. D. Tommasi and H. Mouraour also reported that aq. soln. of **salts of the alkaline earths** are feebly attacked by magnesium with the evolution of hydrogen. D. Tommasi found that with soln. of the alkali chlorides—of potassium, sodium, and lithium

—magnesium furnishes hydrogen more rapidly than with water, and magnesium hydroxide is formed. H. Mouraour found soln. of sodium carbonate, acetate, and tetraborate react vigorously with magnesium, but soln. of sodium phosphate, nitrate, and thiosulphate, and potassium ferrocyanide react feebly. C. F. Roberts and L. Brown found that the hydrogen eq. of magnesium can be obtained with soln. of sodium, potassium, magnesium, barium, strontium, and calcium chlorides, but only very slowly with magnesium, and probably also potassium and sodium sulphates. The action is in general more rapid with the chlorides than with the sulphates; and the rate is dependent on the conc. of the soln., although no proportionality was observed. Fig. 6 illustrates the vol. increment of hydrogen per hour, with soln. containing

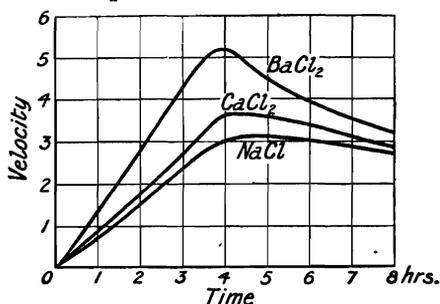


FIG. 6.—The Velocity of Attack on Magnesium by Solutions of Barium, Calcium, and Sodium Chlorides.

Fig. 6 illustrates the vol. increment of hydrogen per hour, with soln. containing

$\frac{1}{10}$ -mol. per litre of the salts named—temp. 18°–19°. The maximum velocity is more quickly attained with the more conc. soln., but the reaction is completed in about the same time. With equi-mol. soln. of the chlorides the rapidity of the reaction is completed in about the order: magnesium (fastest), barium, strontium, calcium, sodium, and potassium (slowest). H. Mouraour found that soln. of potassium sodium tartrate (Seignette's salt) and sodium nitrite are slowly attacked by magnesium, while a soln. of sodium acetate is rapidly attacked.

D. Tommasi obtained cuprous chloride, cupric oxychloride, and hydrogen, but no copper, by the action of magnesium on soln. of **cupric chloride**, and K. Seubert and A. Schmidt found neutral soln. of cupric chloride gave a large proportion of cuprous oxide; ammoniacal soln. gave cuprous oxide and copper; and acidic soln. gave only copper; D. Tommasi obtained cuprous hydroxide, copper, basic copper sulphate, magnesium sulphate, and hydrogen as a result of the action of magnesium on a soln. of **cupric sulphate**; D. Vitali obtained copper, a blue basic copper salt, and hydrogen when magnesium acts on a soln. of a copper salt—*vide* the metallic precipitation of copper. The precipitation, according to E. G. Bryant, is never quantitative. According to D. Tommasi, when a soln. of auric chloride is treated with magnesium, gold, magnesium hydroxide and chloride, and hydrogen are formed; K. Seubert found auric chloride, and silver chloride in the presence of water are reduced to the metal. F. J. Faktor obtained analogous results with **salts of silver and gold**, and D. Vitali, and A. Villiers and F. Borg stated the metals are quantitatively precipitated by magnesium from these salts.

F. J. Faktor found that when **beryllium salts** are treated with magnesium, the corresponding hydroxide is formed. Magnesium liberates hydrogen from soln. of **magnesium salts**. D. Tommasi studied the reaction with magnesium chloride; G. Lemoine with aq. soln. of magnesium nitrate, chloride, sulphate, and acetate, when basic salts are precipitated, and the amount of hydrogen evolved is nearly proportional to the amount of magnesium dissolved. H. Mouraour, G. Platner, and C. F. Roberts and L. Brown, C. Kippenberger, etc., have also studied the reaction. L. Kahlenberg found that soln. of magnesium nitrate when treated with magnesium yield nitrite and finally ammonia, which accounts for the small amount of hydrogen liberated by this salt as compared with other salts of magnesium. From soln. of magnesium acetate and iodide, magnesium also evolves hydrogen rapidly. A magnesium sulphate soln. was treated with a large excess of finely divided magnesium, but no reduction of the salt to sulphite took place. He also studied soln. of magnesium chloride in glycerol, and in alcohol. S. Kern obtained zinc hydroxide by treating soln. of zinc salts with magnesium. K. Seubert and A. Schmidt found that a soln. of zinc chloride or cadmium chloride, with magnesium, gives the metal and hydroxide with neutral and ammoniacal soln.; and the metal with acid soln.; while D. Tommasi found that a soln. of cadmium chloride furnishes cadmium, cadmium oxychloride, hydrogen, and magnesium chloride; F. J. Faktor also found **zinc and cadmium salts** give the corresponding hydroxides. With a soln. of zinc sulphate, D. Tommasi obtained zinc hydroxide, zinc, basic zinc sulphate, magnesium sulphate and hydrogen. According to H. N. Warren, zinc is precipitated by magnesium from soln. in acetic acid. According to D. Tommasi, **mercuric chloride** furnishes mercurous chloride, mercuric oxide, magnesium chloride and hydrogen. D. Vitali found hydrogen, mercuric and mercurous oxides, and mercuric oxychloride were formed with mercuric chloride soln. K. Seubert and A. Schmidt obtained with neutral and acid soln. of mercuric chloride, first mercuric chloride, and later, with neutral soln., mercury. S. Kern obtained with mercuric chloride a grey precipitate which rapidly reddened when heated. D. Vitali found that magnesium reacts with soln. of **mercuric cyanide**, forming hydrogen, mercury, hydrocyanic acid, and magnesium cyanide.

According to H. Mouraour, soln. of **sodium borate** (borax) and of **alum** are attacked by magnesium. According to S. Kern, aluminium salts are but slowly affected by magnesium. K. Seubert and A. Schmidt found that a neutral soln. of

aluminium chloride forms aluminium hydroxide, but there is no decomposition in acid soln. ; and **thallous chloride** forms thallium. D. Vitali also obtained aluminium hydroxide from soln. of aluminium salts. F. J. Faktor also found that soln. of **thallium salts** furnish thallium, and a soln. of thallium alum gives thallic hydroxide.

D. Tommasi found that when a soln. of **lead chloride** is treated with magnesium, lead, lead oxychloride, magnesium oxychloride, and hydrogen are formed. S. Kern found that pulverulent lead is rapidly precipitated from an aq. soln. of lead nitrate by magnesium ; K. Seubert and A. Schmidt found that soln. of lead chloride always give a precipitate of lead, while a neutral soln. of stannic chloride gives stannic hydroxide, and an acid soln., metallic tin. F. J. Faktor found soln. of **stannous and stannic salts** give the corresponding hydroxides.

D. Vitali found that when soln. of **arsenites** are treated with magnesium, arsenic, arsine, and hydrogen are produced ; and with **arsenates**, a precipitate of magnesium arsenate is formed. F. J. Faktor found soln. of **antimony salts** give black flocculent antimony, stibine, and hydrogen. Similar results were obtained by K. Seubert and A. Schmidt with soln. of arsenious and antimonious chlorides ; and acid soln. of **bismuth chloride** gave bismuth.

According to H. Mouraour, a soln. of **chrome alum** is attacked by magnesium. A soln. of **chromic chloride** was found by D. Tommasi to form chromic hydroxide, magnesium chloride and hydrogen, while K. Seubert and A. Schmidt obtained chromic hydroxide with neutral soln. of chromic chloride, and no decomposition with acid soln. According to F. J. Faktor, a soln. of **potassium dichromate** is converted magnesium to the chromate, while S. Kern stated that a soln. of potassium dichromate slowly forms magnesium chromate and potassium hydroxide. According to D. Tommasi, a soln. of **manganese sulphate** furnishes manganese hydroxide, magnesium sulphate, and hydrogen. K. Seubert and A. Schmidt found that a neutral soln. of **manganese chloride** gives manganous hydroxide, and no change occurs with an acid soln. S. Kern found manganous salts give brown manganous oxide when treated with magnesium. According to H. N. Warren, manganese is precipitated from acetic acid soln. by magnesium.

According to D. Vitali, a soln. of **ferric salt** gives hydrogen, ferrosferric oxide and metallic iron ; a soln. of a **cobalt salt** first gives a blue basic salt, and then black metallic cobalt ; and a soln. of a **nickel salt** is slowly coloured green owing to the formation of nickel hydroxide. According to D. Tommasi, a soln. of ferrous sulphate forms magnesium sulphate, hydrogen, and ferrous hydroxide when treated with magnesium ; and a soln. of ferric chloride gives, without reduction, ferric hydroxide, ferric oxychloride, magnesium chloride, and hydrogen ; he also found cobaltous chloride soln. give cobaltous hydroxide, magnesium chloride, and hydrogen. The action of magnesium on soln. of ferric sulphate has been studied by S. Sugden. S. Kern obtained ferric hydroxide from a soln. of ferric chloride. According to K. Seubert and A. Schmidt, neutral soln. of ferric chloride, cobaltous chloride, or nickelous chloride give the hydroxide, $M(OH)_2$; a similar result is obtained with cobaltous and nickelous chlorides in the presence of ammonia ; and acid soln. of ferric and cobaltous chlorides give the metal, but acid soln. of nickelous chloride remain unchanged. According to H. N. Warren, iron, cobalt, and nickel are precipitated by magnesium from acetic acid soln. of the corresponding salts. F. J. Faktor, and H. Mouraour found soln. of **potassium ferricyanide** are reduced to ferrocyanide.

K. Seubert and A. Schmidt, D. Vitali, F. J. Faktor, and A. Villiers and F. Borg found soln. of **platinum tetrachloride** give platinum quantitatively when treated with magnesium ; D. Tommasi reported the formation of magnesium hydroxide and hydrogen as well as platinum ; S. Kern stated that hydrogen, platinum, and platinum dioxide are formed when a soln. of platinum tetrachloride is treated with magnesium ; and with a soln. of a **palladium salt**, hydrogen, palladium monoxide, palladium, and palladium hydroxide are formed. A. W. Knapp showed that if magnesium powder be added to ten times its weight of water, and then to this

mixture is added such an amount of palladious chloride as contains $\frac{1}{100}$ th part of the weight of magnesium, a brisk evolution of hydrogen occurs.

As a rule, magnesium precipitates the metals from neutral aq. soln. of the salts, in some cases hydroxides or basic salts are precipitated and there is a development of hydrogen, particularly in the presence of ammonium salts. G. Platner, and E. Divers explain the evolution of hydrogen by assuming that the hydrolysis of the salt furnishes an acid which directly attacks the magnesium—*vide* the action of magnesium on cupric salts in 3. 21, 3. L. Kahlenberg gave a similar explanation for salts of the heavy metals, while H. Mouraour attributed the evolution of hydrogen to the secondary action of magnesium on water. A. Commaille, and R. M. Caven assume that a galvanic couple is formed by the metal precipitated on the magnesium, and this decomposes the water. G. Lemoine also attributed the action of magnesium on soln. of its own salts to hydrolysis, although, as L. Kahlenberg pointed out, the reaction of soln. of magnesium salts towards indicators may be perfectly neutral at the outset, but soon after the introduction of the magnesium, it becomes alkaline, and remains so. Consequently, he does not accept the free acid hypothesis with soln. of salts of the alkalis, alkaline earths, and magnesium; but he rather assumes that the solvent water is bound to the solute in variable proportions and that if the chemical affinity between the magnesium and the soln. (regarded as a combination of solute and solvent) is sufficient to overcome the cohesion of the magnesium, the latter is attacked, hydrogen is evolved, and the other products may remain in soln. or be further decomposed into a hydroxide or basic salt. If no precipitate forms, the speed of the reaction is not diminished by a decrease in the surface of the magnesium.

Reactions of analytical interest.—Magnesium salts are colourless; they do not give any distinctive flame reaction; but they have a characteristic influence on the absorption spectrum of purpurin, hæmatoxylin, etc.⁸ Soln. of magnesium salts do not give a precipitate with hydrochloric acid, nor with hydrogen sulphide. Neither **ammonium sulphide** nor **ammonium hydrosulphide** gives a precipitate with soln. of magnesium salts; but if the ammonium sulphide contains free ammonia, a precipitate may be formed. Aq. **ammonia** produces a precipitate of magnesium hydroxide provided ammonium salts be absent; about half the magnesium will be so precipitated, and the other half forms a soluble double salt, $(\text{NH}_4)_2\text{MgCl}_4$. According to F. Jackson,⁹ the sensitiveness of the test with aq. ammonia in the absence of ammonium salts is 1 : 32000. P. Harting gave a sensitiveness of 1 : 4000. Aq. ammonia in the presence of ammonium salts gives no precipitate because of the formation of this double salt. Several other salts of the bivalent metals behave similarly—*e.g.* salts of zinc, manganese, iron, cobalt, and nickel; the trivalent metals do not form these ammonium salts. In the absence of other ammonium salts, **ammonium carbonate** precipitates a basic carbonate, say, $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2$, but usually only after boiling or long standing; the composition of the precipitate, however, depends on the temp. and conc. of the soln.; the carbonates of the alkalis behave similarly. According to F. Jackson, the sensitiveness of the test with ammonium carbonate is 1 : 200; and with sodium carbonate, 1 : 4000. Magnesium salts give no precipitate with **barium carbonate** at ordinary temp., but with long-continued boiling, magnesium is completely precipitated from soln. of the sulphate, and partially precipitated from a soln. of the chloride or nitrate. A soln. of **barium hydroxide** likewise precipitates magnesium almost quantitatively as hydroxide, provided ammonium salts be absent; the hydroxides of the alkalis and alkaline earths behave similarly. No precipitation occurs with soln. of **hydrochloro-platinic acid**, with **sodium cobaltic nitrite**, with **hydrofluosilicic acid**, with **potassium chromate**, or with **sulphuric acid**. An **alkali phosphate** or **ammonium phosphate** is a characteristic reagent for magnesium; it produces in soln. containing ammonium chloride, and even free ammonium hydroxide, a white crystalline precipitate of ammonium magnesium phosphate, $\text{Mg}(\text{NH}_4)_4\text{PO}_4$; very dil. soln. give a precipitate only after long standing. When the precipitate is calcined, it

forms magnesium pyrophosphate, $Mg_2P_2O_7$, in which form the magnesium can be weighed. According to F. Jackson, the sensitiveness of the test with disodium hydrophosphate is 1 : 128000; and, according to P. Harting, with ammonium phosphate 1 : 200000. The **alkali arsenates** behave like the phosphates and give a precipitate of ammonium magnesium arsenate, $Mg(NH_4)AsO_4 \cdot 6H_2O$, which, on ignition forms magnesium pyroarsenate, $Mg_2As_2O_7$. If the soln. of magnesium salt be sufficiently dil., and a large proportion of ammonium chloride be present, no precipitation occurs with **ammonium oxalate**. A soln. of an **alkali acetate** gives no precipitate with magnesium salts. With **potassium ferrocyanide**, a cold dil. soln. of magnesium salts gives a white crystalline precipitate of potassium magnesium ferrocyanide after standing some time; conc. soln. give a precipitate immediately; if ammonium salts are present the triple salt ammonium potassium magnesium ferrocyanide is formed. According to F. G. Schlagdenhauffen,¹⁰ the presence of 0.02 per cent. of magnesium sulphate or chloride can be detected in salts of the alkaline earths by a soln. of so much iodine in a 2 per cent. soln. of sodium or potassium hydroxide that the liquid has a golden-yellow colour. A red coloration or a brownish-red precipitate is formed, which, according to T. Rettie, has no definite composition, and is probably a mixture of iodine with magnesium hydroxide. Lithium salts do not give the reaction. According to L. Grimbert, the original soln. is unstable, and not so sensitive as the soln. made by adding a few c.c. of a 10 per cent. soln. of potassium iodide to the liquid under examination, and then adding one or two drops of a soln. of sodium hypochlorite (*eau de Javal*). J. Bellier recommends using a one per cent. soln. of potassium iodide sat. with iodine; followed by a soln. of sodium hydroxide. According to L. Grimbert, the reaction is not so sensitive as the ammonium phosphate test, and the sensitiveness is 1 : 2000, while, according to J. Bellier, it is 1 : 20000.

The atomic weight of magnesium.—The hydrogen eq. of magnesium is about 12. J. J. Berzelius¹¹ assigned the formula MgO to the oxide. There was some discussion as to whether the formula was Mg_2O , MgO , MgO_2 , or Mg_2O_3 , with the corresponding at. wt. of the order of 12, 24, 48, or 36 respectively. The formula MgO was finally adopted because the corresponding at. wt. of magnesium is in harmony with J. H. van't Hoff's extension of Avogadro's rule; with Dulong and Petit's rule; with Mitscherlich's isomorphism rule; and with its position between zinc and beryllium in Mendeléeff's periodic table. T. Thomson discussed the at. wt. of magnesium in 1821.

The ratio $MgSO_4 : BaSO_4$.—J. J. Berzelius made the first at. wt. determination of magnesium in 1812, by weighing the SO_3 , in a given quantity of magnesium sulphate, as barium sulphate, and from the ratio $MgSO_4 : BaSO_4$ he computed an at. wt. 25.24, when oxygen 16 is taken as unit. J. L. Gay Lussac likewise used this method in 1819, and obtained 23.62; T. Scheerer, in 1846, 24.16, and in 1847, 24.20; V. A. Jacquelin, in 1851, 24.43; and A. Macdonnell, in 1852, 24.30.

The ratio $MgO : MgSO_4$.—J. J. Berzelius synthesized the sulphate, and from the ratio $MgO : MgSO_4$, obtained the at. wt. 24.20; and in 1826, 25.28; V. A. Jacquelin, in 1851, obtained 24.44; L. Svanberg and O. Nordenfeldt, in 1848, 24.71; J. F. Bahr, in 1852, 24.77; and J. C. G. de Marignac, in 1883, 24.372.

The ratio $MgSO_4 : MgO$.—V. A. Jacquelin, in 1851, calcined magnesium sulphate at a high temp. so as to convert it into the oxide, and from the ratio $MgSO_4 : MgO$, he computed an at. wt. 24.44; and J. C. G. de Marignac, in 1883, obtained 24.363. A. Macdonnell, in 1852, determined the ratio $MgSO_4 \cdot 7H_2O : MgO$ from which he calculated the at. wt. 24.30.

The ratio $MgC_2O_4 \cdot 2H_2O : MgO$, or $MgCO_3 : MgO$.—L. Svanberg and O. Nordenfeldt determined the ratio $MgC_2O_4 \cdot 2H_2O : MgO$, by calcining the oxalate, and hence computed the at. wt. 24.72. R. F. Marchand and T. Scheerer, in 1850, likewise calcined the carbonate, and from the ratio $MgCO_3 : MgO$, calculated the at. wt. 24.04; and, in 1858, T. Scheerer obtained the value 24.01.

The ratio $MgCl_2 : 2Ag$, or $MgCl_2 : 2AgCl$.—In 1859, J. B. A. Dumas determined

the chlorine in a soln. of magnesium chloride by titration with a standard soln. of silver nitrate, and from the ratio $MgCl_2 : 2Ag$ computed the at. wt. 24.63; and T. W. Richards and H. G. Parker, in 1896, 24.362. The last-named also converted the chlorine of the magnesium chloride into silver chloride, and from the ratio $MgCl_2 : 2AgCl$, computed the at. wt. 24.373.

The ratio $Mg : MgO$.—W. M. Burton and L. D. Vorce, in 1890, converted magnesium, distilled in vacuo, into the nitrate, and then calcined the nitrate to convert it into the oxide; from the ratio so obtained, they computed the at. wt. 24.29. T. W. Richards and E. F. Rogers showed that important errors are likely to accrue owing to the occlusion of gases by magnesium oxide obtained by the ignition of salts, etc.

F. W. Clarke's calculations averaged 24.398, and B. Brauner's 24.36. The best representative value for the at. wt. of magnesium, according to the International Table, 1922, is 24.32. The atomic number is 12. A. J. Dempster claimed to have resolved magnesium vapour into isotopes of at. wt. respectively 24, 25, and 26, and in the proportions 6 : 1 : 1.

REFERENCES.

- ¹ J. B. A. Dumas, *Compt. Rend.*, **90**, 1027, 1880; C. Winkler, *Ber.*, **24**, 1966, 1891; O. H. Basquin, *Proc. Amer. Acad.*, **37**, 166, 1901; G. D. Liveing and J. Dewar, *Proc. Roy. Soc.*, **27**, 495, 1878; **30**, 96, 1880; **32**, 198, 1881; W. N. Hartley, *ib.*, **79**, A, 244, 1907; A. Fowler, *Phil. Trans.*, **209**, A, 450, 1909; E. E. Brooks, *Astrophys. Journ.*, **29**, 177, 1909; *Nature*, **78**, 198, 1908; W. D. Bancroft and H. B. Weiser, *Journ. Phys. Chem.*, **18**, 213, 1914. Other references are indicated in connection with the spectrum of magnesium.
- ² A. A. B. Bussy, *Journ. Chim. Méd.*, **6**, 141, 1830; *Journ. Pharm. Chim.*, (1), **15**, 30, 1829; (1), **16**, 142, 1830; R. Bunsen, *Liebig's Ann.*, **82**, 137, 1852; E. Sonstadt, *Dingler's Journ.*, **169**, 444, 1863; *Journ. prakt. Chem.*, (1), **90**, 307, 1863; F. J. Rogers, *Amer. Journ. Science*, (3), **43**, 301, 1892; H. St. C. Deville and H. Caron, *Compt. Rend.*, **44**, 394, 1857; *Ann. Chim. Phys.*, (3), **67**, 340, 1863; J. Pinnow, *Chem. Ztg.*, **27**, 810, 1903; G. Babrowsky, *Ber.*, **36**, 2719, 1903; A. K. Christomanos, *ib.*, **36**, 2076, 1903; H. Kämmerer, *ib.*, **10**, 1684, 1877; M. Rosenfeld, *ib.*, **15**, 160, 1882; **26**, 59, 1893; F. Kessler, *ib.*, **2**, 369, 1869; J. W. Mallet, *Chem. News*, **38**, 39, 1878; P. L. Aslanoglou, *ib.*, **62**, 99, 1890; W. French, *ib.*, **80**, 254, 261, 1899; H. Leffmann, *ib.*, **42**, 118, 1880; A. Ditte, *Compt. Rend.*, **73**, 108, 1871; A. Duboin, *ib.*, **132**, 826, 1901; G. T. Moody, *Proc. Chem. Soc.*, **7**, 20, 1891; S. Kappel, *Arch. Pharm.*, (3), **24**, 897, 1886; C. Weltzien, *Liebig's Ann.*, **138**, 132, 1866; G. Giorgis, *Alli Accad. Lincei*, (4), **7**, 461, 1891; *Gazz. Chim. Ital.*, **21**, ii, 510, 1891; C. F. Roberts and L. Brown, *Journ. Amer. Chem. Soc.*, **25**, 801, 1903; D. Vitali, *L'Orosi*, **18**, 289, 1895; O. Ohmann, *Ber.*, **45**, 2973, 1912; W. Hughes, *Journ. Chem. Soc.*, **115**, 272, 1919; J. von Liebig, *Pogg. Ann.*, **19**, 137, 1830; W. Muthmann and K. Kraft, *Liebig's Ann.*, **325**, 261, 1902; H. T. Barnes and G. W. Scherer, *Journ. Phys. Chem.*, **12**, 155, 468, 1908; *Trans. Amer. Electrochem. Soc.*, **12**, 54, 1907; N. B. Pilling and R. E. Bedworth, *Chem. Trade Journ.*, **72**, 317, 1923.
- ³ H. Moissan, *Bull. Soc. Chim.*, (3), **5**, 880, 1891; J. von Liebig, *Pogg. Ann.*, **19**, 137, 1830; R. Bunsen, *Liebig's Ann.*, **82**, 137, 1852; K. Seubert and A. Schmidt, *ib.*, **267**, 218, 1892; J. A. Wanklyn and E. T. Chapman, *Journ. Chem. Soc.*, **19**, 141, 1866; R. Cowper, *ib.*, **43**, 153, 1883; H. Gautier and G. Charpy, *Compt. Rend.*, **113**, 597, 1891; A. D. White, *Journ. Soc. Chem. Ind.*, **22**, 132, 1903; W. S. Hendrixson, *Journ. Amer. Chem. Soc.*, **26**, 747, 1904; P. T. Austen, *Amer. Chem. Journ.*, **11**, 270, 1889; A. Ditte, *Ann. Chim. Phys.*, (6), **21**, 154, 1890; F. J. Faktor, *Pharm. Post*, **38**, 153, 1905; T. L. Phipson, *Proc. Roy. Soc.*, **13**, 217, 1864; D. Vitali, *L'Orosi*, **18**, 289, 1895; C. Kippenberger, *Chem. Ztg.*, **19**, 1269, 1895; S. Möller, *Arch. Pharm. Chem.*, **21**, 440, 1914.
- ⁴ J. von Liebig, *Pogg. Ann.*, **19**, 137, 1830; R. Bunsen, *Liebig's Ann.*, **82**, 137, 1852; K. Seubert and A. Schmidt, *ib.*, **267**, 218, 1892; T. L. Phipson, *Proc. Roy. Soc.*, **13**, 217, 1864; J. Parkinson, *Journ. Chem. Soc.*, **20**, 107, 1867; L. Kessler, *Ber.*, **2**, 369, 1869; J. Uhl, *ib.*, **23**, 2151, 1890; P. Schweitzer, *Amer. Chemist*, **1**, 296, 1871; M. G. Levi, E. Migliorini, and G. Ercolini, *Gazz. Chim. Ital.*, **38**, i, 583, 1908; A. Ditte, *Ann. Chim. Phys.*, (6), **19**, 98, 1891; C. Brückner, *Monatsh.*, **26**, 675, 1905; M. Billy, *Compt. Rend.*, **140**, 936, 1905; H. Mouraour, *ib.*, **130**, 140, 1900; F. G. Reichel, *Journ. prakt. Chem.*, (2), **12**, 55, 1875; W. Spring, *Bull. Acad. Belgique*, (3), **5**, 492, 1883; *Bull. Soc. Chim.*, (2), **39**, 641, 1883; *Chem. News*, **48**, 66, 1883; A. Orłowski, *Journ. Russ. Phys. Chem. Soc.*, **13**, 547, 1881; N. Kajander, *ib.*, **13**, 246, 1881; *Ber.*, **13**, 2387, 1880; F. J. Faktor, *Pharm. Post*, **38**, 219, 527, 1905; S. Möller, *Arch. Pharm. Chem.*, **21**, 440, 1914; P. B. Ganguly and B. C. Banerji, *Zeit. anorg. Chem.*, **124**, 140, 1922.
- ⁵ F. Briegleb and A. Geuther, *Liebig's Ann.*, **123**, 236, 1862; R. Bunsen, *ib.*, **82**, 137, 1852; *Liebig's Ann.*, **138**, 292, 1860; G. A. Maack, *Untersuchungen über das Verhalten des Magnesiums und Aluminiums zu den Salzlösungen verschiedener Metalle*, Göttingen, 1862; H. N. Warren,

Chem. News, 58. 297, 1888; W. N. Hartley, *ib.*, 14. 73, 1866; H. Erdmann, *Ber.*, 39. 1207, 1906; L. Kessler, *ib.*, 2. 369, 1869; A. Stock and B. Hoffmann, *Ber.*, 36. 314, 1903; B. Renitzer and H. Goldschmidt, *Sitzber. Akad. Wien*, 81. 820, 1880; W. Eidmann, *Journ. prakt. Chem.*, (2), 59. 1, 1899; C. A. L. de Bruyn, *Rec. Trav. Chim. Pays Bas*, 11. 18, 1892; F. G. Cottrell, *Journ. Phys. Chem.*, 18. 85, 1914; F. W. Newmann, *Proc. Phys. Soc.*, 33. 73, 1921; P. Sabatier and J. B. Senderens, *Compt. Rend.*, 115. 236, 1892; H. Mouraour, *ib.*, 130. 140, 1900; A. Duboin, *ib.*, 132. 826, 1901; T. L. Phipson, *Proc. Roy. Soc.*, 13. 217, 1864; R. Weber, *Pogg. Ann.*, 147. 113, 1872; J. von Liebig, *ib.*, 19. 137, 1830; C. Montemartini, *Gazz. Chim. Ital.*, 22. i, 426, 1892; P. T. Austen, *Amer. Chem. Journ.*, 11. 172, 1889; J. J. Acworth and H. E. Armstrong, *ib.*, 32. 54, 1877; J. J. Sudborough, *Journ. Chem. Soc.*, 59. 655, 1891; E. Divers, *ib.*, 43. 443, 1883; K. Seubert and A. Schmidt, *Liebig's Ann.*, 267. 218, 1892; C. Kippenberger, *Chem. Ztg.*, 19. 1269, 1895; J. Parkinson, *Journ. Chem. Soc.*, 20. 125, 309, 1867; P. T. Blunt, *ib.*, 18. 106, 1865; H. Schön, *Zeit. anal. Chem.*, 8. 53, 1869; O. Emmerling, *Ber.*, 12. 153, 1879; A. Stock and W. Doht, *ib.*, 35. 2273, 1902; G. Grube, *Zeit. anorg. Chem.*, 49. 83, 1906.

⁶ C. Winkler, *Ber.*, 23. 120, 772, 780, 873, 1890, 2642, 2664, 1890; L. Kessler, *ib.*, 2. 369, 1869; V. Meyer, *ib.*, 20. 497, 1887; M. Ballo, *ib.*, 15. 3003, 1882; K. Brunner, *ib.*, 38. 1432, 1905; L. Gattermann, *ib.*, 22. 195, 1889; J. Parkinson, *Journ. Chem. Soc.*, 20. 107, 1867; A. Cavazzi, *Mem. Akad. Bologna*, (4), 7. 27, 1887; C. Engler, *Tagebl. Vers. Naturforsch. Aertze Baden-Baden*, 192, 1879; C. O. V. Engler and E. Kneis, *Dingler's Journ.*, 263. 193, 1887; R. Lohnstein, *Zeit. Elektrochem.*, 13. 613, 1907; W. R. Dunstan and J. R. Hill, *Journ. Chem. Soc.*, 99. 1853, 1911; A. Vyskocil, *Chem. Listy*, 14. 121, 142, 166, 189, 1920; F. E. Weston and H. R. Ellis, *Trans. Faraday Soc.*, 4. 130, 166, 1909; A. Brochet and J. Petit, *Bull. Soc. Chim.*, (3), 31. 359, 1255, 1904; *Chem. News*, 91. 67, 1905; L. Kahlenberg and H. Schlundt, *Journ. Phys. Chem.*, 6. 447, 1903; W. Eidmann, *Journ. prakt. Chem.*, (2), 59. 1, 1899; J. von Liebig, *Pogg. Ann.*, 19. 137, 1830; H. Cretier, *Zeit. anal. Chem.*, 13. 2, 1874; S. Kappel, *Arch. Pharm.*, (3), 25. 448, 1887; G. Giorgis, *Atti Accad. Lincei*, 7. i, 461, 1891; *Gazz. Chim. Ital.*, 21. ii, 510, 1891; H. N. Warren, *Chem. News*, 60. 187, 1889; T. L. Phipson, *ib.*, 93. 119, 1906; *Proc. Roy. Soc.*, 13. 217, 1864; G. Rauter, *Liebig's Ann.*, 270. 236, 1892; H. Erdmann and P. Köthner, *ib.*, 294. 56, 1897; K. Seubert and A. Schmidt, *ib.*, 267. 218, 1892; A. Duboin, *Compt. Rend.*, 132. 826, 1901; A. Rossel, *ib.*, 121. 941, 1895; H. Moissan, *ib.*, 114. 392, 1892; 115. 203, 1892; *Ann. Chim. Phys.*, (7), 6. 296, 1896; A. Geuther, *Jenaische Zeit.*, 2. 209, 1865; E. A. Schneider, *Zeit. anorg. Chem.*, 8. 81, 1895; D. P. Smith, *ib.*, 56. 109, 1907; E. Graefe and M. Eckardt, *ib.*, 22. 158, 1899; N. N. Beketoff and A. Scherbatschew, *Bull. Acad. St. Petersburg*, (5), 1. 61, 1894; H. Erdmann and A. E. Menke, *Journ. Amer. Chem. Soc.*, 21. 259, 1899.

⁷ E. G. Bryant, *Chem. News*, 76. 30, 1897; H. N. Warren, *ib.*, 60. 187, 1889; S. Kern, *ib.*, 33. 112, 236, 1876; A. W. Knapp, *ib.*, 105. 253, 1912; D. Tommasi, *Bull. Soc. Chim.*, (3), 21. 885, 1899; K. Seubert and A. Schmidt, *Liebig's Ann.*, 267. 218, 1892; F. Wöhler, *ib.*, 101. 363, 1887; F. J. Faktor, *Pharm. Post*, 38. 175, 219, 527, 1905; G. Platner, *Elektrochem. Zeit.*, 4. 218, 1898; G. Lemoine, *Compt. Rend.*, 129. 291, 1899; H. Mouraour, *ib.*, 130. 140, 1900; A. Commaille, *ib.*, 63. 556, 1866; A. Villiers and F. Borg, *ib.*, 116. 1524, 1893; *Ber.*, 26. 728, 1893; M. Ballo, *Ber.*, 15. 3003, 1882; 16. 694, 1883; C. Scheibler, *ib.*, 2. 295, 1869; A. Vyskocil, *Chem. Listy*, 14. 121, 142, 166, 189, 1920; V. Kistiakowsky, *Zeit. phys. Chem.*, 70. 206, 1910; L. Kahlenberg, *Journ. Amer. Chem. Soc.*, 25. 380, 1903; C. F. Roberts and L. Brown, *ib.*, 25. 801, 1903; G. Giorgis, *Atti Accad. Lincei*, 7. i, 461, 1891; *Gazz. Chim. Ital.*, 21. ii, 510, 1891; D. Vitali, *L'Orosi*, 18. 289, 1895; L. Santi, *Boll. Chim. Farm.*, 43. 673, 1904; G. A. Maack, *Untersuchungen über das Verhalten des Magnesiums und Aluminiums zu den Salzlösungen verschiedener Metalle*, Göttingen, 1862; T. L. Phipson, *Proc. Roy. Soc.*, 13. 217, 1864; *Chem. News*, 93. 119, 1906; C. Kippenberger, *Chem. Ztg.*, 19. 269, 1895; Z. Roussin, *Journ. Pharm.*, (4), 3. 413, 1866; R. Böttger, *Jahresber. Ver. Frankfurt*, 87, 1869; 25, 1874; E. Divers, *Proc. Chem. Soc.*, 13. 57, 1897; R. M. Caven, *ib.*, 15. 232, 1899; F. Clowes and R. M. Caven, *ib.*, 13. 221, 1897; J. I. Michailenko and P. G. Mushinsky, *Journ. Russ. Phys. Chem. Soc.*, 44. 181, 1912; W. Hughes, *Journ. Chem. Soc.*, 115. 272, 1919; S. Sugden, *ib.*, 119. 233, 1921.

⁸ H. W. Vogel, *Zeit. anal. Chem.*, 5. 52, 1893; *Ber.*, 9. 1641, 1876; F. von Lepel, *ib.*, 9. 1849, 1876; 13. 763, 1880.

⁹ F. Jackson, *Journ. Amer. Chem. Soc.*, 25. 992, 1903; P. Harting, *Journ. prakt. Chem.*, (1), 22. 50, 1841.

¹⁰ F. G. Schlagdenhauffen, *Zeit. Oester. Apoth. Ver.*, 384, 1878; *Journ. Pharm. Chim.*, (4), 27. 375, 1878; T. Rettie, *Journ. Amer. Chem. Soc.*, 19. 333, 1897; J. Bellier, *Journ. Pharm. Chim.*, (6), 23. 378, 1906; L. Grimbert, *ib.*, (6), 23. 237, 1906.

¹¹ J. J. Berzelius, *Gilbert's Ann.*, 40. 256, 1812; *Journ. prakt. Chem.*, (1), 50. 392, 1850; *Schweigger's Journ.*, 31. 258, 1821; *Ann. Chim. Phys.*, (1), 14. 370, 1820; L. Svanberg and O. Nordenfeldt, *ib.*, (1), 45. 473, 1848; J. F. Bahr, *ib.*, (1), 56. 310, 1854; R. F. Marchand and T. Scheerer, *ib.*, (1), 50. 385, 1850; R. F. Marchand, *ib.*, (1), 56. 489, 1852; T. Scheerer, *Pogg. Ann.*, 69. 535, 1846; 70. 407, 1847; *Liebig's Ann.*, 110. 237, 1859; T. Thomson, *Ann. Phil.*, (2), 1. 1, 1821; F. W. Clarke, *A Recalculation of the Atomic Weights*, Washington, 212, 1910; V. A. Jacquelin, *Ann. Chim. Phys.*, (3), 32. 195, 1851; J. B. A. Dumas, *ib.*, (3), 55. 187, 1859; G. Longchamp, *ib.*, (2), 12. 255, 1819; J. L. Gay Lussac, *ib.*, (2), 13. 308, 1819; A. Macdonnell, *Proc. Roy. Irish Acad.*, 5. 303, 1852; *B. A. Rep.*, 36, 1852; J. C. G. de Marignac, *Arch. Sciences Genève*, (3), 10. 206, 1883; *Oeuvres complètes*, Genève, 2. 742, 1903; B. Brauner, *Abegg's Handbuch der anorganischen Chemie*, Leipzig, 2. ii, 80, 1905; W. M. Burton and L. D. Vorce, *Amer. Chem.*

Journ., 12. 219, 1890; T. W. Richards and E. F. Rogers, *ib.*, 15. 567, 1893; *Proc. Amer. Acad.*, 23. 200, 1893; *Chem. News*, 66. 240, 250, 1893; T. W. Richards and H. G. Parker, *ib.*, 75. 148, 158, 1899; 72. 183, 1897; *Proc. Amer. Acad.*, 32. 53, 1896; *Zeit. anorg. Chem.*, 13. 81, 1896; A. J. Dempster, *Science*, 52. 559, 1920; *Phys. Rev.*, (2), 18. 415, 1921; (2), 20. 631, 1922.

§ 6. Magnesium Oxides and Hydroxide

In 1866, E. Beetz¹ prepared what he regarded as **magnesium suboxide** as a black deposit on the positive pole during the electrolysis of a soln. of magnesium sulphate or sodium chloride with magnesium electrodes—hydrogen is given off at both electrodes. If the current is arrested, the black substance forms white flecks in the electrolyte. According to G. Bobarovsky, the best yield is obtained by working with a high current density, at a low temp., and for a short period with soln. of sodium or potassium chloride, or magnesium chloride or sulphate, and particularly with an alcoholic soln. of potassium acetate—the black product is not obtained with alkali hydroxides or ammonium salt soln. F. C. Frary and H. C. Berman obtained the suboxide by electrolyzing magnesium and potassium chlorides in a graphite crucible. They added that it is not formed when oxygen is completely excluded from the electrolyte, by melting the mixture in a stream of hydrogen chloride, and continuing the passage of the gas during electrolysis. The addition of a little magnesium oxide to the electrolyte results in the formation of the suboxide.

G. Gore found that if magnesium in contact with platinum be dipped in a soln. of glacial acetic acid in absolute alcohol, the black deposit appears in a few hours, and grows thicker for a few days. The product is formed more slowly if magnesium in contact with platinum, palladium, iron, gold, or silver, be dipped in water in the presence of carbon dioxide, coal gas, carbon tetrachloride, or ethylene tetrachloride, but not with carbon disulphide. The black product is indeed formed if the foreign metal is not employed. S. Kappel obtained a black substance by passing a stream of air over magnesium in contact with ammonia. A. K. Christomanos also obtained a black deposit when a cold substance was introduced into the flame of burning magnesium.

The black deposit, said G. Bobarovsky, appears to be homogeneous under the microscope; and his analyses range from Mg_3O_5 to Mg_3O_2 . G. Gore's product became white when heated. E. Beetz found that the suboxide decomposes water with the evolution of hydrogen, and the formation of a white precipitate—possibly magnesium hydroxide. According to F. C. Frary and H. C. Berman, the hydrogen is contaminated with 5 per cent. of nitrogen. E. Beetz found the black substance dissolves in acids with the evolution of hydrogen and the formation of a salt of ordinary bivalent magnesium. With aq. soln. of magnesium sulphate it forms basic magnesium sulphate, and it is soluble in aq. ammonium chloride. According to F. C. Frary and H. C. Berman, the black substance is without action on a soln. of anhydrous nickel chloride in absolute alcohol, whilst metallic magnesium rapidly precipitates nickel.

Magnesium oxide, MgO .—This oxide has also been called *magnesia*, *calcined magnesia*, *burnt magnesite*, *Talkerde*, *Bittererde*, *magnesia usta*, *magnesia calcinata*, *magnésie*, etc. It was discovered by A. Scacchi² at Monte Somma, Vesuvius, as a mineral, contaminated with more or less ferrous oxide, and called *periclase*— $\pi\epsilon\rho\iota$, about; $\kappa\lambda\acute{o}\sigma\iota\varsigma$, fracture—in allusion to the cleavage. The mineral has also been found at Teulada (Sardinia), Leon (Spain), Predazzo (Tyrol), Nordmarken (Norway) and Langban (Sweden), Pulpit Rock (Tasmania), etc. Analyses have been reported by A. Damour, H. St. C. Deville, E. Heydecke, and others.

Magnesium oxide is a product of the oxidation of the metal. The oxide is also produced in the amorphous or crystalline form by the calcination of many of the salts of magnesium—*e.g.* the carbonate, sulphate, nitrate, etc. It is also made commercially for the manufacture of magnesia bricks by the calcination of magnesite

in kilns of various kinds—*vide* lime. W. C. Riddell and C. N. Schuette described a shift kiln for making caustic calcined magnesite. O. Schumann³ also made it by the calcination of magnesium sulphide in a current of steam. Magnesium oxide is made by heating the chloride in a stream of moist air, or flue gas: $2\text{MgCl}_2 + 2\text{H}_2\text{O} = 4\text{HCl} + 2\text{MgO}$. This process has been studied by T. J. Pelouze, E. Solvay, C. Heinzerling and J. Schmidt, and by the Salzbergwerk Neu-Stassfurt; F. Konther made magnesia by heating magnesium chloride with calcium chloride when hydrogen chloride is formed, and the magnesium salt is transformed into the oxide, the remaining calcium chloride can be removed by leaching with water. H. P. Bassett converted the chloride into oxide by heating it with steam at about 480° – 650° , and removing any chlorine compounds by washing.

The extraction of magnesia from sea-water has been discussed by T. Schlösing. Processes for the recovery of magnesia from magnesium chloride soln., kainite or carnallite lye, etc. have been patented by M. Schliephacke and H. Riemann, and Ramdohr, Blumenthal u. Co., Alkaliwerke Westeregeln, A. Feldmann, G. Rosenthal, R. Heinz, M. von Maltzan, A. Rümpler, A. Vogt, etc. A. Rümpler devised a process for the recovery of magnesia from beet sugar residues; and C. J. Johanson, from mineral water residues. E. W. von Siemens and J. G. Halske patented a process for the recovery of magnesia from ferruginous magnesian minerals and silicates by calcination in a stream of sulphur dioxide and air, whereby the magnesium alone forms soluble sulphate. H. Holland, G. Mojon, and E. Priwoznik have discussed the extraction of magnesia from serpentine rocks.

G. d'Adelswärd patented a process for the separation of magnesia from dolomite involving the soln. of the carbonate in hydrochloric acid, and its subsequent precipitation with calcium hydroxide. J. B. M. P. Clousson treated dolomite with an aq. soln. of magnesium chloride: $\text{CaCl}_2 + \text{MgCl}_2 + \text{CaO.MgO} = 2\text{CaCl}_2 + 2\text{MgO}$. A small quantity of sugar or molasses greatly accelerates the decomposition. A compound of sugar and lime is produced, from which, by the action of magnesium chloride, calcium chloride, magnesia, and sugar are formed. The last again acts on more of the calcined dolomite, with the formation of the soluble sugar-lime, and so on. From the liquid finally obtained the sugar is removed as the insoluble tribasic sugar-lime compound by heating. C. Bernard and L. Ehrmann, and C. Scheibler proposed to extract lime from calcined dolomite by means of a soln. of sugar. The solubility of lime in this menstruum is high, and of magnesia, low. O. Henry slaked the calcined dolomite with water, and treated it with half the amount of pyroligneous acid or hydrochloric acid necessary to dissolve the whole. The lime was thus removed by "elective affinity," and the washed residue consisted of magnesia. T. Twynam also digested raw dolomite with pyroligneous acid, and found that the magnesia is first taken up, and then precipitated; the calcium acetate soln. was decanted off. R. T. Stull found that by treating calcined dolomite with just sufficient sulphuric acid to combine with the contained lime, the magnesia content could be raised from 42 to 75 per cent. R. D. Pike said that the lime is reduced by agitating the calcined mineral in a closed vessel at 300° – 600° in presence of a gas containing carbon dioxide and water vapour, and afterwards leaching with water.

According to G. Lemoine, by digesting dolomite with water charged with carbon dioxide, the magnesium carbonate dissolves more rapidly than the calcium carbonate. When the soln. is heated, the magnesium carbonate is precipitated, and the carbon dioxide which is evolved can be used over again; G. Moressée also found that when calcined dolomite is powdered and suspended in water at 10° , through which carbon dioxide, at 5–6 atm. press., is passed, only the magnesium oxide is dissolved. The extraction of magnesite from dolomite by the fractional soln. with carbonic acid has been also investigated by F. Findeisen, and H. L. Pattinson. C. Kippenberger based a technical process for the decalcification of dolomite, and the preparation of magnesium carbonate from magnesite, bitter spar, and from kainite or carnallite liquors, upon the fact that alkali hydrocarbonate soln. do not dissolve ferric hydroxide or calcium carbonate. The mineral is powdered, dissolved in commercial hydrochloric acid, and the iron oxidized by warming gently with a

little nitric acid. The soln. is then precipitated with sodium carbonate in slight excess, the filtered precipitate shaken with a sufficiently strong soln. of alkali bicarbonate, and the soln. filtered after the lapse of 20 minutes, and set aside to crystallize. The mother liquor can be used again and again for the extraction.

A cheap process for the **decalcification of dolomite** would make the large deposits of dolomite available for the manufacture of magnesia firebricks. Processes involving the use of chemicals would probably make the cost rather too high for the recovered magnesia to compete with imported magnesite. Physical methods of separation based on (i) the difference in the sp. gr. of the lime and magnesia when calcined at a high temp. ; and (ii) the greater inertness of magnesia when the calcined mass is treated with water, do not give a good separation, although F. Findeisen recommended such a process in 1860, and H. Auzies and A. Segoffin have patented a process for the decalcification of dolomite by slaking and levigating calcined dolomite in a series of tanks. The magnesium hydroxide being lighter than the calcium hydroxide is carried further by the water. They said that the deposit in the tank is nearly pure magnesium hydroxide. The method was examined by J. W. Mellor. L. H. Duschak found the best calcination temp. is 900° – 950° , and the water used for leaching should be free from carbon dioxide. If the dolomite has been calcined at a higher temp., and especially if "dead burnt," the extraction is very incomplete, and is not improved by fine grinding owing to the formation of an insoluble compound. R. T. Stull treated calcined dolomite with running water, and raised the magnesia content from 42 to 65 per cent. ; boiling the calcined dolomite with water, and running off the magnesium hydroxide by flotation raised the magnesia content from 42 to 65–75 per cent. H. G. Schurecht and D. Eyoub, and T. Simon also made some observations on this subject. W. Esch said that calcium oxide is leached from hot calcined dolomite by a soln. of calcium chloride ; and R. A. W. Black, by a soln. of carbon dioxide in water made alkaline with calcium hydrocarbonate.

J. J. Ebelmen obtained crystals of periclase by melting together lime and magnesium borate in a porcelain oven ; A. Daubrée, by decomposing magnesium chloride by lime at a red heat ; J. B. A. Dumas, by melting magnesium chloride ; H. Debray, by melting a mixture of magnesium and potassium sulphates ; H. St. C. Deville, by acting on red-hot magnesia with a slow current of hydrogen chloride ; A. Cossa, by strongly heating a mixture of magnesium sulphate and sodium chloride ; F. Fouqué and A. Michel-Levy, by acting on red-hot magnesium chloride with steam ; T. Hiortdahl, by melting magnesium chloride with silica and zirconia ; A de Schulten, by slowly cooling a molten mixture of potassium hydroxide and magnesia ; A. le Royer, A. Brun, and M. Collet, E. Sommerfeldt, F. Heussler, and H. Moissan, by heating magnesite in an electric arc furnace ; M. Houdard, by heating a mixture of magnesia with five times its weight of magnesium sulphide in a carbon crucible in an electric arc furnace ; and G. Brügelmann, by calcining the nitrate or hydroxide, not the carbonate, in a covered platinum crucible. J. Meunier prepared crystals by dissolving magnesia in hydrochloric acid, and after evaporating the soln. heating it until hydrogen chloride ceases to be evolved. When the product is heated to redness, the trace of hydrogen chloride which remains acts as a mineralizer, and "brilliant octahedrons and tetrahedrons of periclase deposit on the walls of the crucible and cover." R. Otto and J. H. Kloos found crystals of periclase in a kiln lined with magnesia blocks, and used for preparing chlorine from magnesium chloride. Periclase is also found in magnesia bricks which have been used as linings in high temp. furnaces.

H. Struve⁴ found *magnesia usta* contained traces of ammonium nitrate, but no peroxide ; and H. Rose found that the product obtained from *magnesia alba* containing chlorine, still retained chlorine. In general magnesia prepared by the calcination of magnesite will retain the non-volatile impurities of the original. T. W. Richards and E. F. Rogers found that magnesium oxide prepared by calcina-

tion is far more prone to occlude gases during ignition than is the case with zinc, copper, cadmium, or nickel oxide. The amount varied from 0.5 to 1.9 c.c. of gas per 10 grms. of magnesium oxide, and the gas contained oxygen, nitrogen, and carbon dioxide—in one case respectively in the proportions 38.9, 58.9, and 2.2 per cent. According to J. Meunier, magnesia may be freed from calcium by igniting at a red heat and subsequently, after cooling, extracting with successive portions of a 10 per cent. soln. of sucrose, until the last extract does not give a turbidity with ammonium oxalate. The residue is then washed and dried. If further purification is desired, this material is dissolved in hydrochloric acid and the soln. evaporated to dryness. The residue is gradually heated to 800°–900° in a covered crucible, and magnesia is obtained in its crystalline form as periclase on the lid and sides of the crucible and on the surface of the amorphous magnesia in the crucible.

V. Kohlschütter and J. L. Tüscher⁵ prepared **colloidal** magnesium oxide dispersed in a gaseous medium by making the metal one electrode of an electric arc, and oxidizing the vapour.

The physical properties of magnesium oxide.—V. Kohlschütter and J. L. Tüscher⁶ obtained highly dispersed magnesia, without a solvent, by volatilizing the metal in an electric arc, and suddenly cooling the vapour by a current of air. The precipitation of the fume was effected by a high-tension electric field. The **crystals** of magnesium oxide, and periclase, belong to the cubic system. F. Rinne believes that there is a hexagonal modification of magnesium oxide. According to W. P. Davey and E. O. Hoffman, E. Schiebold, W. Gerlach and O. Pauli, A. W. Hull, R. W. G. Wyckoff and J. A. Hedvall, **X-radiograms** of crystals of magnesia exhibit a simple cubic lattice of the sodium chloride type with sides 4.220 ± 0.02 Å. W. L. Bragg gives for the distance between the neighbouring atom centres as 2.11 Å. J. A. Hedvall examined the X-ray spectra of magnesia prepared in different ways, and found no change in the structure to be produced by heating. According to A. Scacchi, the **specific gravity** of the mineral (natural crystals) is 3.75; A. Damour gave 3.674; A. Cossa, 3.642 at 12°; H. M. Goodwin and R. D. Mailey, 3.674 (20°); and A. Sjögren, 3.90. For the artificial crystals, J. J. Ebelmen gave 3.636; A. de Schulten, 3.566; E. Mallard, 3.50; R. Otto and J. H. Kloos, 3.555 to 3.571; M. Houdard, 3.579 at 0°; and E. Madelung and R. Fuchs, 3.466–3.476 (0°). The sp. gr. of the amorphous, white, voluminous powder was given by C. J. B. Karsten as 3.2; by J. B. Richter as 3.07; by R. Kirwan as 2.3; and by G. Brügelmann as 3.42; H. Beckurts found the sp. gr. of *magnesia usta levis*, obtained by calcining light magnesia alba, to be 2.74; that of *magnesia usta*, obtained by calcining heavy magnesium carbonate, to be 3.057; and that obtained from neutral magnesium carbonate, to be 3.69. The sp. gr. of amorphous magnesia depends upon the temp. of calcination, thus, A. Ditte found:

	350° (1 hr.)	440° (1 hr.)	c. 560° (1 hr.)	c. 1200° (12 hrs.)
Sp. gr. at 0° . . .	3.1932	3.2014	3.2482	3.5692
Sp. gr. at 100° . . .	3.0971	3.1263	3.1909	3.5131

H. Rose showed that the sp. gr. of amorphous magnesia was raised to 3.647 near that of the natural mineral after calcination in a porcelain oven—temp. near 1600°. H. Moissan further found that when magnesia is heated for 2 hrs. in a blast, with retort carbon as fuel, the sp. gr. at 20° was 3.577; when heated 2 hrs. in the electric arc, 3.587; and when heated in an electric crucible furnace, 3.654. H. M. Goodwin and R. D. Mailey gave 3.493 for the sp. gr. of fused magnesia at 20°. In some cases—G. Brügelmann, and K. Arndt—the sp. gr. of amorphous magnesia is stated to be greater than that of the crystalline or fused material—there is always a possibility that minute air blebs entangled in the fused material will spoil the observations. J. W. Mellor suggested the possibility of estimating the proportion of α -magnesia (low sp. gr. form) and β -magnesia (high sp. gr. form) in a given sample of burnt magnesite from the observed sp. gr., and the following data give an idea of the

rate of conversion from the presumably amorphous to the presumably crystalline variety. After a two hours' calcination between 1300° and 1350°,

Number of calcinations	1	2	3	4	5	6
Sp. gr.	3.16	3.32	3.46	3.54	3.59	3.60
Per cent. converted	—	26	54	70	78	80

V. Tadokoro found the sp. gr. of magnesia brick at different temp. to be

	20°	100°	200°	400°	600°	800°	1000°
Sp. gr.	2.295	2.291	2.285	2.266	2.247	2.231	2.213

The **hardness** of periclase is approximately 6 on Mohs' scale; the artificial crystals prepared by R. Otto and J. H. Kloos had a hardness between that of felspar and of quartz; and J. J. Ebelmen's crystals a hardness of 4. A. Reis and L. Zimmermann have discussed this subject. E. Madelung and R. Fuchs gave $0.70-0.80 \times 10^{-6}$ megabars per sq. cm. for the **compressibility** of artificial magnesia.

According to L. B. Guyton de Morveau,⁷ magnesia fuses with difficulty in a fire fed with oxygen, and its surface has after cooling the appearance of a porcelain glaze. In 1802, R. Hare fused magnesia in the oxyhydrogen blowpipe flame, and in 1819 E. D. Clarke also found that magnesia is converted by the oxyhydrogen blowpipe flame into a kind of opaque glass, which scratches glass like the diamond. H. Davy also fused magnesia under the influence of a powerful voltaic current. H. Moissan fused magnesia in an electric arc furnace whose temp. was estimated to be 3000°. K. Arndt gives 2500° for the **melting point** of purified magnesia, and he said that magnesia cannot be melted in the oxyhydrogen flame unless it be contaminated with silica, iron oxide, etc. H. M. Goodwin and R. D. Mailey found that fragments of pre-fused oxide did not fuse or soften below 1890°; but above 1940°, the grains always fused together, and it was considered that 1910° may be taken as the approximate m.p. of the fused oxide—this temp. appears rather low, indicating that the oxide was not of a high degree of purity. W. Hempel found Veitsch magnesite fused at 1825°-1830°; and magnesia at 2250°; A. Lampen found that fused magnesia had a m.p. of 2000°; and a magnesia brick with a high percentage of iron at 1900° had its edges rounded, and was quite fused at 2000°. C. W. Kanolt gave $2800 \pm 13^\circ$ for the m.p. of magnesia; and O. Ruff, 2500°; and O. Ruff and P. Schmidt, 2800° in an atm. of nitrogen. H. Caron stated that magnesium oxide cannot be fused in a wind furnace at a white heat, but in the oxy-coal-gas flame, it melts, and partially volatilizes. E. Tiede and E. Birnbräuer could not melt magnesia, but said that volatilization begins at about 2000°. A. A. Read did not detect any change when magnesium oxide is heated to the m.p. of platinum. C. Despretz claimed that by the simultaneous action of a current from 185 Bunsen's cells, the burning glass, and a hydrogen flame, he was able to volatilize magnesia; and P. Lebeau has stated that magnesia boils vigorously when heated seven minutes by a current of 110 volts and 700 amps., and that the volatilization of the oxide is much faster in the presence of three or four times its weight of sugar charcoal—possibly owing to the intermediary formation of magnesium or magnesium carbide, for R. E. Slade has shown that magnesia can react with carbon at a temp. below the m.p. of the oxide. O. Ruff and P. Schmidt measured the **vapour pressure** of magnesia. According to O. Ruff and O. Goecke, the **sublimation temperature** at one atm. press. is about 2000°, and W. R. Mott estimated the **boiling point** to be 3600°; O. Ruff and P. Schmidt found 2800°-2850° in an atm. of an indifferent gas at 760 mm. E. Tiede and E. Birnbräuer found that magnesia dissociates readily at 1900° in a vacuum furnace producing a deposit of magnesium. E. W. Washburn computed the latent **heat of fusion** to be 30,000 cal. per mol, or 700 (± 15 per cent.) cal. per gram.

H. V. Regnault found the **specific heat** of artificial magnesium oxide to be 0.24394 between 24° and 100°; and A. S. Russell found 0.1006 between -79.3° and -190.8°; 0.1933 between 0° and -79°; and 0.2385 between 1.4° and 48.6°. H. von Wartenberg and G. Witzel found the mol. ht. of magnesium oxide at 2780°

to be 11.6 cal. Observations were also made by W. Steger, and E. Heyn and co-workers. V. Tadokoro found the mean sp. ht. of a magnesia brick to be

Sp. ht.	218°	303°	382°	480°	579°	687°	796°	894°
	0.223	0.238	0.254	0.263	0.266	0.265	0.264	0.263

It is not clear if the decrease at the more elevated temp. is due to errors of experiment. Measurements of the sp. ht. at a low temp. were made by A. Magnus. H. M. Goodwin and R. D. Mailey found the linear **coefficient of thermal expansion** of fused magnesia at θ° between 120° and 270° , to be $\alpha=0.00001140+0.000000092(\theta-120)$, a value not much greater than that for a quartz crystal cut parallel to its optical axis, and nearly equal to that of platinum. H. Fizeau found $\alpha=0.00001043$ for the coeff. of expansion of periclase, and for the increase per degree rise of temp. $da/d\theta=0.000000267$. J. W. Mellor found $\alpha=0.0000126$ for magnesite bricks between 15° and 1350° ; H. J. Hodsman and J. W. Cobb obtained 0.00001274 for the coeff. of expansion of a magnesia brick between 15° and 1000° . B. Bogitch measured the expansion of magnesia bricks. V. Tadokoro found the mean coeff. of expansion of a magnesia brick to be

Coeff. exp.	20°	100°	200°	400°	600°	800°	1000°
	0.04000	0.04063	0.04131	0.04142	0.04126	0.04125	0.04128

R. S. Hutton and J. R. Beard found that fused magnesia, powdered to pass a sieve with 600 meshes per sq. cm., had a **thermal conductivity** between 20° and 100° $k=0.00047$ cal. per sq. cm. degree difference of temp., per second; against $k=0.00029$ for lime; and $k=0.00028$ for firebrick. He also found for a magnesia firebrick 0.00050 ; for calcined Greek magnesite, 0.00045 ; for calcined Styrian magnesite, 0.00034 ; and for lightly calcined magnesite, 0.00016 . S. Wologdine found 0.0065 and 0.0055 for two magnesite bricks with respectively 41 and 35.1 per cent. porosity. B. Dudley obtained 0.0343 for the mean conductivity of a magnesia brick over the range from 445° to 830° . C. Dougill, H. J. Hodsman, and J. W. Cobb found the conductivity of a magnesite firebrick fell from $K=0.017$ at 380° to 0.0132 at 700° to 0.00000091 at 1370° . V. Tadokoro found the thermal conductivity of a magnesia brick to be

Conductivity $\times 10^8$	200°	300°	400°	500°	600°	700°	800°	900°
	6.57	5.47	4.91	4.71	4.39	4.14	3.85	3.73

The **heat of formation** of magnesium oxide, according to J. Thomsen, is (Mg, O), 145.86 Cals.; H. von Wartenberg gave 143.9 Cals. According to the former, the heat of formation of magnesium hydroxide is (Mg, O, H₂O), 148.96 Cals., and (Mg, O₂, H₂), 217.32 Cals.; M. Berthelot gave respectively 148.8 and 217.8 Cals.; and for (MgO, H₂O), he gave 5.4 Cals. M. Berthelot also measured the heat of precipitation of magnesium hydroxide by adding a soln. of ammonia or sodium hydroxide to a soln. of a magnesium salt. J. Johnston gives for the free energy of the change hydroxide to oxide, 3600 cal. at 25° . According to A. Ditte, the **heat of the solution**, in sulphuric acid, of magnesia calcined at different temp. is very different:

Temp. calcination	350°	440°	c. 560°	c. 1200°
A. Ditte	832.8	920.8	961.7	1004.6 cal.
J. C. G. de Marignac	—	874	875	867 cal.

J. C. G. de Marignac examined what he called *l'influence prétendue* of calcination on the heat of soln., and his data are indicated along with those of A. Ditte.

E. Mallard⁸ gave for the **index of refraction** of artificial crystals 1.7307 for Li-light, 1.7364 for Na-light, and 1.74133 for Tl-light; S. Sommerfeldt, 1.7298 for red light, 1.7350 for Na-light, and 1.7460 for blue light; A. Le Royer, A. Brun, and L. W. Collet gave 1.700 for red light, and 1.717 for green light. According to D. Brewster, H. Caron, and C. M. T. du Motay and C. R. M. de Maréchal, at a high temp. magnesia has a very high emissive power for light; the light is not very different from that of burning magnesium. F. Henning and W. Heuse studied the

reflecting power of magnesia. J. Drummond tried magnesia in place of lime for the lime-light, but found the intensity of its illumination to be less than half that of lime. H. E. Ives and co-workers studied the illuminating power and emissivity of mantles made of magnesia and heated by Bunsen's flame. The results compare favourably with those of thoria. W. Crookes, and H. Jackson found magnesia has a marked reddish **fluorescence** in the cathode rays, and L. de Boisbaudran found the fluorescence is a bright red if the magnesia has about one per cent. of chromium. P. Bary found that magnesia does not phosphoresce when exposed either to the **X-rays** or to **Becquerel's rays**. E. L. Nichols and D. T. Wilber found that magnesium oxide, like calcium oxide, exhibits **flame luminescence**. E. L. Nichols studied the brightness of the luminescence, and found that when heated to 1000° in the oxyhydrogen flame magnesia appears blue. W. W. Coblentz found a transparent region in the **ultra-red transmission spectrum** at 5μ , preceded and followed by almost complete opacity. The bands at 3.3μ and 3.8μ are virtually the same as those of calcite. The **ultra-red reflection spectrum**, like that of calcite, has maxima at 6.5μ and 6.8μ . E. L. Nichols found the **colour temperature** of incandescent magnesia is 5000°, while the actual temp. is not over 2000°.

According to F. Beijerinck,⁹ periclase is a non-conductor of electricity at ordinary temp. H. M. Goodwin and R. D. Mailey found the specific **electrical conductivity** of small cylinders of fused magnesia at different temp. in mhos :

	700°	800°	900°	1000°	1050°	1100°	1150°	1500°
Sp. conductivity $\times 10^6$	—	0.01	0.10	0.20	0.34	1.00	2.60	85.0

The results are plotted with those of porcelain in Fig. 7. Fused magnesia is thus

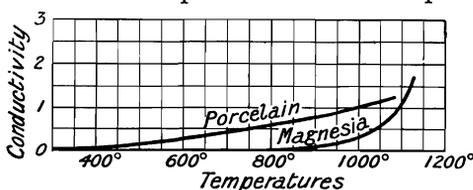


Fig. 7.—Specific Conductivity of Porcelain and Fused Magnesia.

a much better insulator than porcelain at temp. below 1100°, and above that temp., its conductivity exceeds that of porcelain. A. A. Somerville found that a column of the oxide 1 cm. diam. and 10 cms. long has an electrical resistance of 10^7 ohms at 545°. According to F. Horton, the effect of temp. on the electrical resistance (ohms) and the

electrical conductivity (mhos) of magnesia is

	471°	630°	828°	1055°	1191°	1204°	1341°
Ohms	35×10^6	8×10^5	88000	12450	4900	12900	29×10^4
Mhos	3.69×10^{-9}	1.61×10^{-7}	1.46×10^{-6}	1.04×10^{-5}	2.63×10^{-5}	1.00×10^{-5}	4.45×10^{-7}

The electrical conductivity of magnesium oxide thus increases rapidly with the temp. up to 1200°–1250° and then decreases. If the temp. is kept constant above 1200°, the conductivity also decreases with the time. The phenomenon is probably due to a change of the oxide into a less conducting form of greater density. There is evidence of a slight electrolysis during the passage of the current. F. Kohlrausch and F. Rose found the specific conductivity of a sat. soln. of magnesium hydroxide at 18° to be 83×10^{-6} mhos; and F. Kohlrausch, 69×10^{-6} to 94×10^{-6} mhos. S. Glixelli measured the **electro-osmosis** of magnesium oxide. S. Meyer gives for the **magnetic susceptibility** -0.008×10^{-6} units per mol, or -0.055×10^{-6} units per gram. E. Thomson¹⁰ has studied the orientation of fine particles of magnesium oxide in the magnetic field.

The chemical properties of magnesium oxide.—As indicated above, T. W. Richards and E. F. Rogers¹¹ found magnesium oxide prepared by the ignition of the nitrate or carbonate always contained occluded gas; the gas mainly consisting of oxygen and nitrogen, with a smaller proportion of carbon dioxide. J. A. Hedvall and N. von Zweigbergh have studied the action of **barium dioxide**

on magnesia. According to H. Davy, magnesia absorbs **chlorine** at a red heat, and forms magnesium chloride with the evolution of oxygen. V. H. Veley found that while dry **hydrogen chloride** has no action on magnesia at ordinary temp., a reaction occurs at about 40°. A. J. Balard stated that calcined magnesia is not decomposed by **bromine**. L. Meyer observed that when magnesia is heated in a stream of **carbon tetrachloride**, magnesium chloride, carbon dioxide and monoxide, and carbonyl chloride are formed. P. N. Raikow found **carbon dioxide** converts magnesium hydroxide into an acid carbonate. C. J. B. Karsten found that molten **sodium chloride** is not decomposed by magnesia. According to R. E. Hughes, dry **hydrogen sulphide** has not an appreciable action on dried magnesia between 15° and 40°, but in presence of moisture, the gas is absorbed; O. Schumann noted the formation of magnesium sulphide when hydrogen sulphide is passed over heated magnesia. E. Frémy observed that red-hot magnesia is converted into the sulphide by the vapour of **carbon disulphide**. K. Birnbaum and C. Wittich found that **sulphur dioxide** is absorbed by magnesia at 360°, but so slowly that three months are needed for the completion of the reaction. W. T. Smith and R. B. Parkhurst studied the absorption of sulphur dioxide by milk of magnesia. V. Lenher found magnesia dissolves in a soln. of **selenium oxychloride**. When magnesia is heated in a stream of **phosphorus pentachloride**, A. Daubrée noted the formation of crystals of normal magnesium phosphate. M. Berthelot and G. André found magnesia drives ammonia with difficulty from, even boiling, soln. of **ammonium salts**—thus ammonium magnesium phosphate is but very slowly decomposed when boiled with magnesium hydroxide suspended in water. The reduction of magnesia by **carbon** has been discussed in connection with the preparation of magnesium. E. Tiede and E. Birnbraüer said that magnesia is not reduced. O. P. Watts found magnesium oxide is more effectively reduced by certain **carbides** than by carbon alone. The carbides of iron, nickel, and chromium are very active, but those of copper and tin have scarcely any action on the reduction of magnesium oxide. W. G. Palmer found magnesia admixed with cupric oxide to act catalytically on the dehydrogenation of ethyl alcohol. **Siloxicon** and **carborundum** accelerate the reduction. H. Davy studied the action of the **alkali metals** on heated magnesia—*vide* magnesium. F. E. Weston and H. R. Ellis found that magnesia is reduced by **calcium**, but nitride is simultaneously formed. According to H. N. Morse and J. White, when a mixture of magnesia and **magnesium** is heated to redness in an evacuated tube, the magnesium oxide is transported to the cooler part of the tube. The phenomenon is not due to the volatility of the oxide, but is thought to be due to the free metal attracting the oxygen and causing a dissociation of the oxide, which reforms in the cooler part of the tube where the temp. is lower—*vide* zinc and cadmium oxides. C. Matignon argues that every system of liquid or solid bodies which is capable of giving rise to a system furnishing volatile substances, will undergo reaction in that sense at a convenient temp., and the reduction of magnesia by **aluminium**: $2\text{Al} + 3\text{MgO} = 3\text{Mg} + \text{Al}_2\text{O}_3$, is possible because magnesium is volatile at a comparatively low temp. F. E. Weston and H. R. Ellis stated that magnesia is not reduced by aluminium. R. Fink found that when magnesium hydroxide is added to soln. of manganese, iron, or nickel sulphate, basic salts of these metals are precipitated. S. Meunier found that molten potassium hydroxide dissolves half its weight of magnesia, and the molten mixture absorbs oxygen from the air. L. B. Guyton de Morveau heated mixtures of magnesia with **baryta** and with **lime**, but obtained no special results. E. S. Shepherd and co-workers found that the components of fused mixtures of lime and magnesia crystallize out side by side; they furnish a simple eutectic mixture with no evidence of combination; J. B. Ferguson and H. E. Merwin estimated a eutectic at about 2300° and about 32 per cent. MgO. According to J. J. Berzelius, when moistened with **cobalt nitrate**, and strongly ignited before the blowpipe, it takes a fine rose colour; and J. A. Hedvall noted the formation of mixed crystals of calcium and magnesium oxides,

P. Butini, H. Davy, etc., noted the inertness towards **water** of magnesia calcined at a high temp., and H. Rose stated that magnesia prepared by calcining *magnesia alba* does not become warm when mixed with water, while magnesia prepared by calcining trihydrated magnesium carbonate to 300°, becomes hot when mixed with water. The properties of magnesia calcined at high and at low temp. are therefore in marked contrast. As shown by A. Ditte, and W. C. Anderson,¹² the low temp. and low sp. gr. form readily absorbs gases, and moisture; it is readily and quickly dissolved by mineral acids; and it reacts quickly with water. The high temp., high sp. gr. form of magnesia is very resistant to these influences, and it remains practically unacted upon by water, even after the lapse of a considerable time. H. M. Goodwin and R. D. Mailey have stated that fused magnesium oxide possesses in a remarkable degree the ability to withstand the action of many **neutral salts** at high temp., and is therefore well adapted for use as vessels and apparatus for containing such salts when subjected to high temp. Silver, sodium, and potassium nitrates; sodium and potassium chlorides, bromides, and sulphates; zinc chloride; and barium nitrate showed no action on a polished sample of fused oxide when the latter was heated for an hour or more in the fused salt. Barium chloride had a very slight action; while **sodium carbonate, potassium carbonate, potassium hydroxide, and cryolite** attacked the fused oxide energetically. Dil. **nitric, hydrochloric, or sulphuric acid** slowly attacks the fused oxide in the cold; the conc. acids are less active than the dil. acids.

In addition to the manufacture from calcined magnesite of refractory firebricks for basic steel furnaces, the Königlichen Porzellan-manufaktur, Berlin, make various chemical apparatus—tubes, dishes, crucibles, etc.—from fused magnesia. According to K. Arndt, they can be heated in the blast flame without cracking, but, according to E. Wedekind, care is necessary on cooling. J. W. Mellor and F. Austin noted that fused magnesia does not crack like fused quartz does during its devitrification. E. Wedekind says fused magnesia undergoes no shrinkage or electrolysis when heated in the electric furnace at 1750°. In 1806, J. L. Proust mentioned the use of magnesia as a refractory in furnace building; and the use of magnesia in making pottery.

H. St. C. Deville, H. Schwarz, and F. Knapp noted that magnesium oxide prepared by heating magnesium chloride or nitrate to redness has **hydraulic properties** in that when mixed with a limited quantity of water, it sets rigid like portland cement, and the product is hard enough to scratch marble. On the other hand, magnesia, prepared by calcination for 12 hrs. at a white heat, no longer sets with water, or, if it does, the setting is very slow. A. Ditte also made observations: Magnesia prepared by calcining the nitrate at 350°, when fashioned into rods and spheres with water, remains soft and friable when under water 8 months; that calcined at 440°, hardens under water and in 2 months is like polished marble; that calcined at 560°, also is very hard after standing 2 months under water; while that calcined at 1200° does not harden under water. According to W. C. Anderson, magnesium oxide prepared by gently heating the native carbonate reacts quickly with water, and, when in presence of a limited amount of water, sets to a firm mass. The product obtained by heating similarly the artificial carbonates does not set, although it also appears to slake rapidly with water, but if these carbonates be treated with nitric acid and the resulting nitrate ignited gently, the oxide left will set similarly to that obtained from the native carbonate by heat.

Magnesia gradually absorbs moisture and carbon dioxide from the atm. E. de M. Campbell¹³ has measured the **rate of hydration** of magnesium oxide burned at different temp., and selections from his measurements are shown graphically and diagrammatically in Fig. 8. The hydration of magnesium oxide burned between 600° and 800° is practically complete in three days; and a change in the constitution of magnesium oxide sets in between 1000° and 1100°, resulting in a marked decrease in the rate of hydration, and this change becomes more and more marked with rise of burning temp., until, at 1450°, or nearly the temp. employed in burning portland cement, the magnesium oxide combines with

only 61.4 per cent. of the water required for complete hydration. C. Edwards and A. Rigby have measured the rates of hydration of dolomite calcined at different temp., and then exposed to atm. of different degrees of humidity, from which it appears that the lime hydrates faster than the magnesia, and that the higher the temp. of calcination up to about 1150°, the faster the rate of hydration; beyond that temp., the higher the temp. of calcination, the slower the rate of hydration. The subject has also been studied by A. M. Sen, and N. Parravano and C. Mazzetti. The latter found that H. le Chatelier's statement that magnesium oxide undergoes a transformation at about 1600°, and E. de M. Campbell's that it changes at about 1100°, are incorrect. The change occurs at 800°, but very slowly. The presence of impurities in the magnesite modify the transformation—e.g. iron oxides accelerate the change. J. W. Mellor showed that there is no definite transformation temp., but that the change proceeds more quickly the higher the temp. of calcination, and each variety of native magnesite has its own specific rate of transformation. The change is possibly a conversion from amorphous to crystalline periclase.

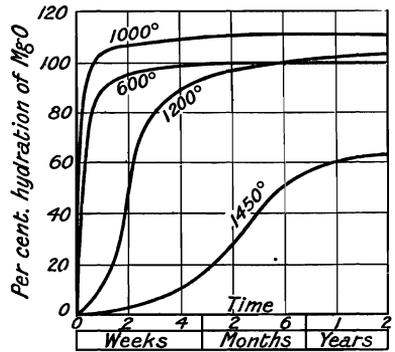


FIG. 8.—Rates of Hydration of Magnesium Oxide Calcined at different Temperatures.

The various determinations of the **solubility** of magnesium oxide or rather hydroxide in *water* are discordant. Reducing the data by the different observers to milligrams of magnesium hydroxide, $\text{Mg}(\text{OH})_2$, per litre, J. Dalton¹⁴ gave 62.5 in cold water; R. Kirwan, 126.5 in cold water; O. Henry, 172.4 at 15°; A. Fyfe, 194.5 at ordinary temp., and 27.8 at 100°; R. Fresenius, 27.8 in either cold or boiling water; A. Bineau, 5 to 10 in cold water; F. Kohlrausch and F. Rose, 9 at 18°; A. Dupré and M. Bialas, 8 at 18°; and G. C. Whipple and A. Mayer, 12 at 22°. The wide variations in the results are due to the magnitude of the sources of error in contrast with the magnitude of the constant being measured. These errors are: (i) The solvent action of carbon dioxide dissolved by the water from the air; (ii) the action of water on the glass containing vessels whereby bases are dissolved, and when the solubility is estimated from the alkalinity of the soln., the dissolved alkali introduces a large error; (iii) the presence of such impurities as lime in the magnesia would introduce a large error when lime plus magnesia is regarded as magnesia; and (iv) the uncertainty involved in the assumption that equilibrium is attained since the rates of dissolution of magnesia, prepared in different ways, are very different. The best representative value of the modern determinations of the solubility of magnesia in water is 10 mgrms. of magnesium hydroxide per litre of water at 20°. W. C. Anderson showed that a given oxide, calcined at different temp., dissolves in water at different rates, the rate of soln. being diminished as the temp. of preparation is increased; on the other hand, the extent of this diminution is not the same for oxides obtained from different sources. It is greatest in the case of the oxide obtained from heavy carbonate, less marked in the product from crystal carbonate, and scarcely appreciable in that from light carbonate. The aq. soln. of magnesia is not caustic, but it has an alkaline reaction, changing red litmus blue, etc.

According to H. Precht, a litre of a 2*N*-soln. of *potassium hydroxide* dissolves 16.13 mgrms. of magnesium hydroxide. R. Warrington showed that the solubility of magnesium hydroxide is augmented by *ammonium salts*, even in the presence of free ammonia. From experiments on the equilibrium: $\text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl} \rightleftharpoons \text{MgCl}_2 + 2\text{NH}_4\text{OH}$, at 10°, J. M. Lovén calculated that the solubility of magnesium hydroxide is 3.5×10^{-4} mols per litre; and at 29°, W. Herz and G. Muhs calculated

2.3×10^{-4} mols per litre. Like J. M. Lovén, F. P. Treadwell concludes that the non-precipitation of magnesium hydroxide by ammonia in the presence of ammonium salts is not due to the formation of a complex salt, but solely to the retardation of the dissociation of the ammonium hydroxide by the ammonium chloride according to the law of mass action. W. Herz and G. Muhs give for the solubility of magnesia in ammonium salt soln. at 29° , when the conc. are expressed in grams per litre,

Ammonium salt	NH ₄ Cl					NH ₄ NO ₃	
	4.13	5.67	9.21	13.39	20.86	6.00	14.69
Magnesium hydroxide	1.43	1.86	2.00	3.15	4.55	1.45	2.43

When warm soln. of ammonium salts are heated with magnesia, ammonia is evolved. R. Warington found *sodium and potassium salts* act similarly in their solvent action on magnesia, but to a less degree. C. J. B. Karsten stated that magnesium hydroxide is insoluble in conc. aq. soln. of many salts—*e.g.* sodium chloride, sulphate or nitrate, barium nitrate and chloride, and potassium nitrate. O. Henry reported that the presence of *calcium hydroxide, calcium sulphate, or potassium sulphate* does not interfere with the solvent action of water on magnesia. In general, however, F. K. Cameron and J. M. Bell say that *the solubility of magnesia in water is augmented by various salts, including magnesium salts, but is depressed by the alkali hydroxides.* E. Maigret found the presence of the free base, sodium hydroxide, lowers the solubility of magnesia in a soln. of sodium chloride. Expressing conc. in grams per litre,

Sodium chloride	0.8 gm. NaOH			4.0 grms. NaOH		
	125	140	160	125	140	160 grms.
Magnesium hydroxide	0.07	0.045	nil	0.03	nil	nil

G. Fleury found the solubility of magnesia in water is increased when *glucose* is present; although C. Bernard and L. Ehrmann ignored this in using sugar soln. to remove lime from magnesia. C. Neuberger and B. Rewald¹⁵ found that magnesia slowly dissolves when shaken for a long time with *methyl alcohol*, forming a typical **magnesia alcocol** which contains in a litre an amount of magnesia corresponding with 4.5 per cent. Mg₂P₂O₇, *i.e.* 1.63 per cent. MgO.

Magnesium hydroxide, Mg(OH)₂.—The mineral *brucite* was discovered in 1814 by A. Bruce¹⁶ at Hoboken (New Jersey); it was called *talc-hydrate* by C. C. von Leonhard; *magnésie hydratée* by R. J. Haiüy, and F. S. Beudant applied the term *brucite* in 1824. The mineral is found with magnesite and dolomite in serpentine as a result of the decomposition of magnesian silicates. J. Pierce, and T. Nuttall described a fibrous or amiantoidal form of magnesia which was designated *nematolite* or *nematolite*—from *νήμα*, a fibre. J. D. Whitney, and C. F. Rammelsberg proved its chemical identity with *brucite*. Magnesium hydroxide is formed during the hydration of magnesium oxide. G. O. Rees¹⁷ stated that magnesia is converted into the hydroxide by moistening it with water, and drying the mass on a water-bath. Colloidal and a readily soluble form of the hydroxide is produced by the action of water or steam at 150° on magnesia. The **colloidal magnesium hydroxide** is readily obtained by adding an excess of potassium or sodium hydroxide to a soln. of a magnesium salt. As remarked by P. Grouvelle,¹⁸ and R. F. Marchand and T. Scheerer, it is difficult to wash the precipitate free from alkalies. H. E. Patten found that magnesium hydroxide does not carry into precipitation with it either chlorine or sulphur trioxide; and at 20° , more than the theoretical amount of potassium hydroxide is required for complete precipitation. The washed and dried hydroxide is a white powder, or, when dried at 100° , is a translucent, coherent, soft brittle mass—presumably in the colloidal state. A. de Schulten prepared crystallized magnesium hydroxide as follows:

12 grms. of magnesium chloride, MgCl₂, 6H₂O, 340 grms. of potassium hydroxide, and 60 c.c. of water, are heated at 212° – 220° until the magnesium hydroxide completely dissolves. If the proportion of potash is larger, a lower temp. is sufficient. The liquid is allowed to

cool, and the solid residue treated with water to remove the alkali. The magnesium hydroxide is left undissolved in the form of small, distinct crystals of sp. gr. 2.36 at 15°; these dissolve easily in acids and in warm conc. soln. of ammonium chloride. If soda is used instead of potash, the magnesium hydroxide does not dissolve, but the precipitate rapidly becomes crystalline.

G. Friedel also made crystals of the hydroxide by the action of soda lye on magnesia at 400°, and he considers that this explains the formation of crystals of brucite in boiler deposits, observed by G. A. Kenngott, A. Weisbach, and O. Luedecke.

According to F. Hessenberg,¹⁹ the crystals of brucite are trigonal, with $a : c = 1 : 1.52078$, and $\alpha = 81^\circ 12'$. R. Hermann described some crystals of magnesium hydroxide from Texas, Pa., as monoclinic, and called the mineral *texalite*, which would make magnesium hydroxide dimorphous, but this is not yet established because the crystals behave optically like brucite. G. Aminoff calculated from the **X-radiograms** that the elementary parallelepiped has $a = 3.13$ A., and $c = 4.75$ A. The **specific gravity** of artificial crystals was found by A. de Schulten to be 2.36 at 15°. For brucite, R. Hermann gave 2.36; W. Beck, 2.376; A. A. Lösch, 2.388; F. R. Mallet, 2.454 at 15°; M. F. Heddle, 2.336–2.37; L. Peruzzi, 2.385 at 17°; and V. von Zepharovich, 2.39. The **hardness** is 2 on Mohs' scale. O. Mügge has studied the **percussion figures** of brucite.

According to J. M. van Bemmelen,²⁰ the hydroxide passes into the oxide at a temp. below a red heat; it does not lose its combined water in a dry atm. at 350°, but it does so between 350° and dull redness. The hydroxide dried over sulphuric acid without heating, absorbs about 1.6 mols of water when exposed to moist air, but it loses this property if previously heated to 200°, owing to its conversion from the colloidal to the crystalline state. Magnesia obtained at a dull red heat, again takes up $1\frac{1}{2}$ mols of water and one mol of this is retained as water of constitution, $Mg(OH)_2$; if the magnesia has been obtained by ignition at a still higher temp., it is only partially converted into hydroxide in a moist atm., and if calcined 20 hrs. at this temp., it no longer takes up water of constitution. J. Johnston found the **dissociation pressure** of magnesium hydroxide to be :

	35°	53°	74°	100°	147°	c. 160°
Vap. press.	9.2	31.5	92	234	526	760 mm.

At 25°, the press. is 2.3×10^{-3} atm., and the dissociation temp. is approximately 160°.

A. des Cloizeaux²¹ found brucite had a strong positive **double refraction**. The plate-like crystals of brucite resemble those of gypsum and talc in softness, foliated structure, cleavage and lustre, but gypsum is biaxial, and talc has negative double refraction. M. Bauer gave for the **index of refraction** with red light for the ordinary ray $\omega = 1.559$, and for the extraordinary ray $\epsilon = 1.5795$. L. Peruzzi found $\omega = 1.562$, and $\epsilon = 1.5827$. M. Bauer, R. Brauns, and H. Rosenbusch have studied the modification in the optical properties of the crystals by strain. U. Panichi found that no change in the optical properties occurred when the crystals were cooled to -190° . W. W. Coblentz,²² and J. Königsberger studied the **infra-red absorption spectrum** of brucite and noted that gypsum shows an absorption spectrum which is a composite of the bands of water and of anhydrite, while that of brucite is different, thus distinguishing between the water of crystallization of gypsum from the water of constitution of brucite. There is a large band near 2.5μ which with higher dispersion is resolved into three bands with maxima at 2.5μ , 2.7μ , and 3μ ; beyond this region there are no marked bands, while beyond 12μ there is complete opacity. There are depressions in the transmission curve for 5μ , 7μ , 7.7μ , 8.2μ , 9.7μ , and 10.8μ ; but as a whole the curve is conspicuous for the absence of sharp absorption bands.

F. Beijerinck²³ found that the **electrical conductivity** of brucite is nil. W. Hankel found that the crystals exhibit **pyroelectricity**, for, on cooling, the two ends of the principal axis and the adjacent surfaces are electrically negative, while

the corners of the base and the neighbouring surfaces are electrically positive. J. C. Bose studied the absorption of electrical waves by nematicite.

Magnesium peroxide.—C. Weltzien's experiment²⁴ on the action of hydrogen peroxide on magnesium has already been indicated. R. Haas treated a soln. of a magnesium salt, containing 3 per cent. hydrogen peroxide, with aq. ammonia, and obtained a precipitate which contained some active oxygen, and appeared to have the characteristics of a peroxide. R. Wagnitz patented a preparation made by mixing 50 parts of magnesium hydroxide or hydrocarbonate, moistened with about 5 parts of water, with 10 to 12 parts of sodium peroxide; other modes of mixing were also employed. Undue heating of the mixture should be avoided. F. J. Homeyer also added sodium or barium peroxide to the soln. of a magnesium salt and obtained a product estimated to contain 30 per cent. magnesium dioxide, MgO_2 . A. Krause also patented analogous mixtures. O. Ruff and E. Geisel attempted to prepare pure magnesium peroxide by the addition of pure sodium hydroxide to magnesium sulphate soln. in the presence of hydrogen peroxide. Even when a large excess of the latter is used, the precipitate in the moist state has the ratio $MgO : O = 1 : 0.67$. Drying the precipitate reduces the proportion of peroxide oxygen, and a product is obtained which has the composition $MgO.MgO_2$, aq. The dried product readily loses oxygen at 25° or 37° , and at atm. press., but even after 22 days the ratio $MgO : O$ was $1 : 0.39$, and the ratio appears to remain constant at $1 : 0.35$, corresponding roughly with the formula $MgO_2, 3MgO$, aq. The decomposition is more rapid in the presence of water.

E. Merck agitated dried magnesium oxide with anhydrous hydrogen peroxide; the anhydrous solid is easily separated from the water formed in the reaction, and does not require washing. A repetition of the treatment furnishes a peroxide of high degree of purity. F. Hinz used an electrolytic process for preparing magnesium peroxide. The anode compartment of an electrolytic cell is supplied with an aq. (about 20 per cent.) soln. of magnesium or zinc chloride, whilst the cathode compartment contains magnesium or zinc chloride soln. to which hydrogen peroxide has been added; the anode is of platinum or carbon, and the cathode platinum. An e.m.f. of 6 or 7 volts is used in preparing magnesium peroxide, and 2.5 to 3 volts for zinc peroxide. Any free acid formed in the cathode compartment is neutralized by the addition of magnesium or zinc oxide or hydroxide. The reaction presumably progresses $Mg + H_2O_2 + 2H_2O \rightarrow H_2 + Mg(OH)_4$.

The peroxides of the alkaline earths, zinc, and magnesium have attracted some attention on account of their chemical and physiological properties and their use as antiseptics. Magnesium peroxide is a white powder which may be magnesium hydroperoxide, $Mg(OH)_4$; and it usually contains some magnesium hydroxide, and water. R. von Foregger and H. Philipp say "preparations containing certain amounts of available oxygen are more stable than other preparations containing more or less than these." Thus, a product containing 9.2 per cent. of available oxygen seems to be stable, whilst if a product contains less than this it gradually loses its available oxygen, till it reaches 8 per cent. available oxygen, when it again remains stable; and stable products occur containing 6.85 to 6.9 per cent., and also 4.3 per cent. oxygen. The less available oxygen the product contains the more stable it is under atm. conditions. The ordinary product contains about 8 per cent. oxygen and has a sp. gr. of 0.615. Magnesium peroxide has the solubility of 1 part in 14,550 parts of water at $20^\circ C$. Suspended in water it loses its available oxygen quicker than zinc peroxide, and slower than calcium or strontium peroxides, but it loses its available oxygen quicker in moist atm. than the other peroxides, as it is apparently more subject to the influence of carbon dioxide. In a dry atm. it is, however, comparatively stable, and can be heated to $160^\circ C$. without any loss. It reacts like these other peroxides with acids and certain organic matters.

REFERENCES.

- ¹ E. Beetz, *Pogg. Ann.*, **127**, 45, 1866; G. Bobarovsky, *Zeit. Elektrochem.*, **11**, 465, 1905; *Ber.*, **36**, 2719, 1903; A. K. Christomanos, *ib.*, **36**, 2076, 1903; G. Gore, *Chem. News*, **50**, 157, 1884; S. Kappel, *Arch. Pharm.*, (3), **24**, 897, 1886; F. C. Frary and H. C. Berman, *Trans. Amer. Electrochem. Soc.*, **27**, 209, 1915.
- ² A. Scacchi, *Journ. prakt. Chem.*, (1), **28**, 486, 1843; *Memorie mineralogiche e geologiche*, Napoli, 22, 1841; *Neues Jahrb. Min.*, 261, 1853; ii, 137, 1882; A. Cossa, *Atti Accad. Lincei*, **3**, 1, 1876; O. Lenecek, *Tschermak's Mitt.*, **12**, 433, 448, 455, 1891; L. Peruzzi, *Rend. Accad. Lincei*, (5), **14**, ii, 83, 1905; O. Schumann, *Liebig's Ann.*, **187**, 286, 1877; C. F. A. Tenne and S. Calderon, *Mineralfundstätten der iberischen Halbinsel*, Berlin, 85, 1902; A. Sjögren, *Ofver. Akad. Förh. Stockholm*, 479, 1887; *Geol. För. Förh.*, **9**, 527, 1887; H. Sjögren, *ib.*, **17**, 288, 1895; **20**, 25, 1898; W. F. Petterd, *Catalogue of the Minerals of Tasmania*, Hobart, 1910; H. St. C. Deville, *Compt. Rend.*, **53**, 199, 1861; A. Damour, *Ann. Mines*, (4), **3**, 381, 1843; *Bull. Géol. Soc.*, **6**, 311, 1849; E. Heydecke, *Ber.*, **24**, 1480, 1891; G. Brügelmann, *Zeit. anal. Chem.*, **29**, 126, 1890; *Wied. Ann.*, **2**, 466, 1877; **4**, 277, 1878; *Zeit. anorg. Chem.*, **9**, 415, 1895; R. Otto and J. H. Kloos, *Ber.*, **24**, 1480, 1891; A. Daubrée, *L'Inst.*, **22**, 241, 1854; *Compt. Rend.*, **39**, 135, 1854; H. Debray, *ib.*, **52**, 985, 1861; M. Houdard, *ib.*, **144**, 1349, 1907; H. St. C. Deville, *ib.*, **53**, 199, 1861; J. J. Ebelmen, *ib.*, **33**, 525, 1851; *Ann. Mines*, (5), **4**, 185, 1851; *Ann. Chim. Phys.*, (3), **33**, 34, 1851; J. B. A. Dumas, *ib.*, (3), **55**, 189, 1859; H. Moissan, *Bull. Soc. Chim.*, (3), **9**, 955, 1893; *Compt. Rend.*, **52**, 985, 1861; E. Mallard, *Bull. Soc. Min.*, **16**, 19, 1893; A. de Schulten, *ib.*, **21**, 87, 1898; A. le Royer, A. Brun, and M. Collet, *Arch. Sciences Genève*, **18**, 409, 1904; E. Sommerfeldt, *Centr. Min.*, **213**, 1907; F. Fouqué and A. Michel-Lévy, *Synthèse des minéraux et des roches*, Paris, **382**, 1882; L. Bourgeois, *La synthèse minéralogique*, Paris, 1884; T. Hiortdahl, *Liebig's Ann.*, **137**, 236, 1866; J. Meunier, *Bull. Soc. Chim.*, (4), **25**, 560, 1919.
- ³ Salzbergwerk Neu-Stassfurt, *German Pat.*, *D.R.P.P.* 36673, 1885; 47043, 1888; 48552, 1889; 54830, 1890; F. Konther, *ib.*, 41351, 1887; M. Schliephacke and H. Riemann, *ib.*, 43922, 1888; A. Feldmann, *ib.*, 41717, 44100, 1887; Ramdohr, Blumenthal u. Co., *ib.*, 11580, 1879; 11746, 1880; A. Rümpler, *ib.*, 8777, 9144, 1879; G. Rosenthal, *ib.*, 31357, 1884; Alkaliwerke Westeregeln, *ib.*, 50596, 1889; R. Heinz, *ib.*, 186738, 1907; M. Maltzan, *ib.*, 37333, 1886; A. Vogt, *ib.*, 35668, 1885; Glenck, Kornmann u. Co., *ib.*, 135834, 1899; E. W. von Siemens and J. G. Halske, *ib.*, 130298, 1901; J. B. M. P. Closson, *ib.*, 11456, 1879; 15342, 1881; G. d'Adelswärd, *ib.*, 11321, 1880; C. Scheibler, *ib.*, 14936, 16575, 1881; P. de Wilde, *ib.*, 50155, 1889; C. Heinzerling and J. Schmidt, *ib.*, 41996, 1887; G. Lemoine, *Bull. Soc. d'Enc.*, (2), **20**, 362, 1873; H. P. Basset, *U.S. Pat. No.* 1405388, 1922; H. Moissan, *Ann. Chim. Phys.*, (7), **4**, 136, 1895; F. Heussler, *Zeit. anorg. Chem.*, **11**, 298, 1906; O. Schumann, *Liebig's Ann.*, **187**, 286, 1877; F. Mohr, *Repert. Pharm.*, **1**, 53, 1852; O. Henry, *Ann. Chim. Phys.*, (2), **6**, 86, 1817; J. B. A. Dumas, *ib.*, (3), **55**, 189, 1859; E. Priwoznik, *Dingler's Journ.*, **260**, 335, 1886; H. Holland, *Phil. Trans.*, **106**, 294, 1816; C. J. Johanson, *Zeit. Mineralwasser. Fabr.*, **4**, 161, 1887; C. Kippenberger, *Zeit. anorg. Chem.*, **6**, 183, 1894; R. T. Stull, *Journ. Franklin Inst.*, **190**, 739, 1920; D. Eyoub, *Eng. Min. Journ.*, **112**, 619, 1921; T. Twynam, *Brit. Pat. Nos.* 1019, 1880; 4397, 1882; E. Solvay, *ib.*, **171**, 1877; H. Auzies and A. Segoffin, *ib.*, **1425**, 1907; J. W. Mellor, *Trans. Cer. Soc.*, **17**, 119, 1913; T. J. Pelouze, *Compt. Rend.*, **52**, 1267, 1861; J. J. Ebelmen, *ib.*, **33**, 525, 1851; C. Bernard and L. Ehrmann, *ib.*, **33**, 1239, 1876; G. Eschellmann, *Chem. Ind.*, **12**, **2**, 25, 51, 1889; G. Moressée, *Ann. Soc. Géol. Belg.*, **37**, 151, 1910; F. Findeisen, *Polyt. Notizblatt*, **81**, 1860; *Wagner's Jahrb.*, **25**, 5, 1860; H. L. Pattinson, *Chem. News*, **8**, 128, 1863; *Brit. Pat. No.* 9102, 1841; G. Mojon, *Mem. Ist. Ligure*, **1**, ii, 67, 1806; L. H. Duschak, *Chem. Met. Eng.*, **23**, 628, 1920; A. Daubrée, *L'Inst.*, **22**, 211, 1854; *Compt. Rend.*, **39**, 135, 1854; H. Debray, *ib.*, **52**, 985, 1861; H. St. C. Deville, *ib.*, **53**, 199, 1861; M. Houdard, *ib.*, **144**, 1349, 1907; A. Cossa, *Atti Accad. Lincei*, **3**, 1, 1876; F. Fouqué and A. Michel-Lévy, *Synthèse des minéraux et des roches*, Paris, **382**, 1882; T. Hiortdahl, *Liebig's Ann.*, **137**, 236, 1866; A. de Schulten, *Bull. Soc. Min.*, **21**, 87, 1898; A. le Royer, A. Brun, and M. Collet, *Arch. Sciences Genève*, **18**, 409, 1904; E. Sommerfeldt, *Centr. Min.*, **213**, 1907; G. Brügelmann, *Zeit. anal. Chem.*, **29**, 126, 1890; J. Meunier, *Bull. Soc. Chim.*, (4), **25**, 560, 1919; R. Otto and J. H. Kloos, *Ber.*, **24**, 1480, 1891; H. G. Schurecht, *Journ. Amer. Cer. Soc.*, **4**, 558, 1921; W. Esch, *German Pat.*, *D.R.P.* 338888, 1917; R. D. Pike, *Canadian Pat. No.* 217635, 1922; T. Schlösing, *Bull. Soc. Chim.*, (2), **44**, 360, 1885; *Compt. Rend.*, **101**, 131, 1885; R. A. W. Black, *U.S. Pat. No.* 1436230, 1921; C. E. Oliver, *ib.*, 1436520, 1922; T. Simon, *Brit. Pat. No.* 176785, 1922; W. C. Riddell and C. N. Schuette, *Eng. Min. Press*, **114**, 981, 1922.
- ⁴ H. Struve, *Zeit. anal. Chem.*, **11**, 22, 1872; H. Rose, *Pogg. Ann.*, **86**, 283, 1852; T. W. Richards and E. F. Rogers, *Proc. Amer. Acad.*, **23**, 200, 1893; *Amer. Chem. Journ.*, **15**, 567, 1893; *Chem. News*, **68**, 240, 250, 1893; J. Meunier, *Bull. Soc. Chim.*, (4), **25**, 560, 1919.
- ⁵ V. Kohlschütter and J. L. Tüscher, *Zeit. Elektrochem.*, **27**, 225, 1921.
- ⁶ F. Rinne, *Zeit. deut. geol. Ges.*, **43**, 231, 1891; A. Scacchi, *Memorie mineralogiche e geologiche*, Napoli, 1841; *Journ. prakt. Chem.*, (1), **28**, 486, 1843; V. Kohlschütter and J. L. Tüscher, *Zeit. Elektrochem.*, **27**, 225, 1921; W. P. Davey, *Phys. Rev.*, (2), **17**, 402, 1921; W. P. Davey and E. O. Hoffman, *ib.*, (2), **15**, 333, 1920; E. Schiebold, *Min. Soc. Göttingen*, **4**, 1921; W. Gerlach and O. Pauli, *Zeit. Physik*, **7**, 116, 1921; A. W. Hull, *Journ. Amer. Chem. Soc.*, **41**, 1169, 1919;

Journ. Franklin Inst., **188**, 131, 1919; W. L. Bragg, *Phil. Mag.*, (6), **40**, 174, 1920; J. A. Hedvall, *Zeit. anorg. Chem.*, **120**, 327, 1922; W. Gerlach, *Phys. Zeit.*, **22**, 557, 1921; *Zeit. Physik*, **9**, 184, 1922; V. Tadokoro, *Science Rep. Tohoku Univ.*, **10**, 339, 1921; R. W. G. Wyckoff, *Amer. Journ. Science*, (5), **1**, 138, 1921; E. Madelung and R. Fuchs, *Ann. Physik*, (4), **65**, 289, 1921; A. Damour, *Ann. Mines*, (4), **3**, 381, 1843; J. J. Ebelmen, *ib.*, (5), **4**, 185, 1851; *Compt. Rend.*, **33**, 525, 1851; *Ann. Chim. Phys.*, (3), **33**, 34, 1851; H. Moissan, *ib.*, (7), **4**, 136, 1895; *Bull. Soc. Chim.*, (3), **11**, 1020, 1895; *Le four électrique*, Paris, **35**, 1897; *Compt. Rend.*, **118**, 506, 1894; A. Ditte, *ib.*, **73**, 111, 191, 270, 1871; M. Houdard, *ib.*, **144**, 1349, 1907; A. Cossa, *Atti Accad. Lincei*, **3**, 1, 1876; A. Reis and L. Zimmermann, *Zeit. phys. Chem.*, **102**, 298, 1922; R. Otto and J. H. Kloos, *Ber.*, **24**, 1480, 1891; G. Brügelmann, *ib.*, **13**, 1741, 1880; H. Beckurts, *Arch. Pharm.*, (3), **18**, 429, 1881; (3), **19**, 13, 1881; A. de Schulten, *Bull. Soc. Min.*, **21**, 87, 1898; E. Mallard, *ib.*, **16**, 19, 1893; H. Rose, *Pogg. Ann.*, **74**, 437, 1847; K. Arndt, *Chem. Ztg.*, **30**, 211, 1906; C. J. B. Karsten, *Schweigger's Journ.*, **65**, 394, 1832; R. Kirwan, *Elements of Mineralogy*, London, **6**, 1784; *Phil. Trans.*, **71**, 7, 1781; **72**, 179, 1782; **73**, 15, 1783; J. W. Mellor, *Trans. Cer. Soc.*, **16**, 85, 1917; A. Sjögren, *Oefvers. Akad. Förh. Stockholm*, 479, 1887; *Geol. För. Förh. Stockholm*, **9**, 527, 1887; F. Heussler, *Zeit. anorg. Chem.*, **11**, 298, 1906; H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, (1), **23**, 1, 1906; J. B. Richter, *Crelle's Ann.*, **ii**, 17, 1795; F. Cornu, *Centr. Min.*, **305**, 1908; A. Scott, *Trans. Cer. Soc.*, **17**, 475, 1918; *Trans. Geol. Soc. Glasgow*, **16**, 393, 1918; K. A. Redlich in C. Doelter, *Handbuch der Mineralchemie*, Dresden, **1**, 243, 1915.

⁷ L. B. Guyton de Morveau, *Journ. Phys.*, **19**, 310, 382, 1782; E. D. Clarke, *The Gas Blow-pipe*, London, 1819; *Ann. Phil.*, **17**, 421, 1821; R. Hare, *Memoir of the Supply and Application of the Blowpipe*, Philadelphia, 1802; H. Davy, *Phil. Trans.*, **98**, 1, 333, 1808; J. W. Mellor, *Trans. Cer. Soc.*, **16**, 270, 1917; H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, (1), **23**, 1, 1906; K. Arndt, *Chem. Ztg.*, **30**, 211, 1906; C. Despretz, *Compt. Rend.*, **28**, 755, 1849; P. Lebeau, *ib.*, **144**, 799, 1907; H. Caron, *ib.*, **66**, 850, 1868; H. Moissan, *ib.*, **115**, 1034, 1892; *Bull. Soc. Chim.*, (3), **9**, 955, 1893; C. W. Kanolt, *Journ. Washington Acad.*, **3**, 315, 1913; *Bur. Standards Reprint*, **212**, 19, 1913; H. V. Regnault, *Ann. Chim. Phys.*, (3), **1**, 129, 1841; O. Ruff, *Zeit. anorg. Chem.*, **82**, 373, 1913; O. Ruff and P. Schmidt, *ib.*, **117**, 172, 1921; E. Tiede and E. Birnbräuer, *ib.*, **87**, 129, 1914; R. E. Slade, *Journ. Chem. Soc.*, **93**, 327, 1907; A. A. Read, *ib.*, **65**, 313, 1894; E. W. Washburn, *Trans. Amer. Cer. Soc.*, **19**, 1, 1917; R. S. Hutton and J. R. Beard, *Trans. Faraday Soc.*, **1**, 266, 1905; S. Wologdine, *Bull. Soc. Enc.*, **110**, 821, 1908; *Rev. Mét.*, **6**, 767, 1909; A. L. Queneau, *Met. Chem. Eng.*, **7**, 383, 433, 1909; C. Dougill, H. J. Hodsmann, and J. W. Cobb, *Journ. Soc. Chem. Ind.*, **34**, 465, 1915; J. Thomsen, *Journ. prakt. Chem.*, (2), **16**, 97, 1877; B. Dudley, *Trans. Amer. Electrochem. Soc.*, **27**, 285, 1915; W. R. Mott, *ib.*, **37**, 665, 1920; H. J. Hodsmann and J. W. Cobb, *Trans. Soc. Glass Tech.*, **3**, 201, 1919; H. Fizeau, *Compt. Rend.*, **64**, 314, 1867; **66**, 1005, 1072, 1868; **68**, 1125, 1869; M. Berthelot, *ib.*, **103**, 844, 966, 1886; A. Ditte, *ib.*, **72**, 858, 1871; **73**, 191, 1871; O. Ruff and O. Goecke, *Zeit. angew. Chem.*, **24**, 1459, 1911; A. S. Russell, *Phys. Zeit.*, **13**, 59, 1912; H. von Wartenberg, *Zeit. Elektrochem.*, **15**, 866, 1909; H. von Wartenberg and G. Witzel, *ib.*, **25**, 209, 1919; V. Tadokoro, *Science Rep. Tohoku Univ.*, **10**, 339, 1921; A. Magnus, *Phys. Zeit.*, **14**, 5, 1913; J. Johnston, *Journ. Amer. Chem. Soc.*, **30**, 1357, 1908; W. Hempel, *Chem. Ztg.*, **27**, 564, 1903; *Ber. Internat. Congress App. Chem. Berlin*, **1**, 715, 725, 1903; A. Lampen, *Journ. Amer. Chem. Soc.*, **28**, 846, 1906; J. C. G. de Marignac, *Arch. Bibl. Univ.*, **42**, 209, 1871; B. Bogitch, *Compt. Rend.*, **173**, 1358, 1921; W. Steger, *Silicat Zeit.*, **2**, 51, 1914; E. Heyn, O. Bauer and E. Wetzel, *Mitt. Mat. Prüf.*, **33**, 83, 1914.

⁸ F. Horton, *Phil. Mag.*, (6), **11**, 505, 1906; H. E. Ives, E. F. Kingsbury, and E. Karrer, *Journ. Franklin Inst.*, **186**, 401, 1918; T. Drummond, *Edin. Journ. Science*, **5**, 319, 1826; D. Brewster, *ib.*, **3**, 343, 1820; F. Henning and W. Heuse, *Zeit. Physik*, **10**, 111, 1922; H. Caron, *Compt. Rend.*, **66**, 850, 1868; L. de Boisbaudran, *ib.*, **103**, 1107, 1886; P. Bary, *ib.*, **130**, 776, 1900; C. M. T. du Motay and C. R. M. de Maréchal, *Bull. Soc. Chim.*, (2), **10**, 318, 1868; H. Jackson, *Journ. Chem. Soc.*, **65**, 734, 1894; W. Crookes, *Proc. Roy. Soc.*, **32**, 206, 1881; E. Mallard, *Bull. Soc. Min.*, **16**, 19, 1893; E. Sommerfeldt, *Centr. Min.*, **213**, 1907; A. Le Royer, A. Brun, and L. W. Collet, *Arch. Sciences Genève*, (4), **18**, 409, 1904; E. L. Nichols and D. T. Wilber, *Phys. Rev.*, (2), **17**, 269, 707, 1921; E. L. Nichols, *Trans. Amer. Eng. Soc.*, **16**, 331, 1921; W. W. Coblenz, *Investigations of Infra-red Spectra*, Washington, **3**, 79, 1906; **4**, 80, 1906.

⁹ H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, (1), **23**, 1, 1906; F. Horton, *Phil. Mag.*, (6), **11**, 505, 1906; F. Kohlrausch and F. Rose, *Wied. Ann.*, **50**, 127, 1893; F. Kohlrausch, *Zeit. phys. Chem.*, **44**, 197, 1903; S. Meyer, *Wied. Ann.*, **69**, 236, 1899; A. A. Somerville, *Met. Chem. Eng.*, **10**, 422, 1912; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**, 448, 1897; S. Glixelli, *Anz. Akad. Cracow*, **102**, 1917.

¹⁰ E. Thomson, *Nature*, **107**, 520, 619, 1921; O. J. Lodge, *ib.*, **107**, 553, 1921; R. W. Gray, *ib.*, **107**, 619, 1921; J. B. Speakman, *ib.*, **107**, 619, 1921.

¹¹ H. Davy, *Phil. Trans.*, **100**, 1, 1811; V. H. Velej, *Proc. Chem. Soc.*, **10**, 240, 1894; *Chem. News*, **71**, 34, 1894; H. N. Morse and J. White, *ib.*, **63**, 279, 1897; *Amer. Chem. Journ.*, **13**, 128, 1891; L. Meyer, *Ber.*, **20**, 681, 1887; K. Birnbaum and C. Wittich, *ib.*, **13**, 651, 1880; A. J. Balard, *Ann. Chim. Phys.*, (2), **32**, 337, 1826; M. Berthelot and G. André, *ib.*, (6), **11**, 294, 1887; *Bull. Soc. Chim.*, (2), **47**, 835, 1887; O. Schumann, *Liebigs Ann.*, **187**, 286, 1877; R. E. Hughes, *Phil. Mag.*, (5), **33**, 471, 1892; E. Frémy, *Ann. Chim. Phys.*, (3), **38**, 324, 1853; C. J. B. Karsten, *Lehrbuch der Salinenkunde*, Berlin, **2**, 50, 280, 1847; C. Matignon, *Compt. Rend.*, **156**, 1536, 1913; S. Meunier, *ib.*, **60**, 557, 1805; F. E. Weston and H. R. Ellis, *Trans.*

Faraday Soc., 4. 130, 166, 1899; E. Tiede and E. Birnbräuer, *Zeit. anorg. Chem.*, 87. 129, 1914; W. T. Smith and R. B. Parkhurst, *Journ. Amer. Chem. Soc.*, 44. 1918, 1922; A. Daubrée, *Ann. Mines*, (4), 19. 684, 1851; L. B. Guyton de Morveau, *Journ. Phys.*, 19. 310, 382, 1782; J. J. Berzelius, *Om Blasrörets Användande i Kemien och Mineralogien*, Stockholm, 1820; J. A. Hedvall, *Ueber Reaktionsprodukte von Kobaltoxyden mit anderen Metalloxyden bei hohen Temperaturen*, Upsala, 1915; P. N. Raikow, *Chem. Ztg.*, 31. 55, 1907; R. Fink, *Ber.*, 20. 2106, 1887; O. P. Watts, *Journ. Amer. Electrochem. Soc.*, 11. 279, 1907; T. W. Richards and E. F. Rogers, *Proc. Amer. Acad.*, 28. 200, 1893; *Chem. News*, 68. 240, 250, 1893; *Amer. Chem. Journ.*, 15. 567, 1893; P. Butini, *Nouvelles observations et recherches analytiques sur la magnésie du sel d'Epsom, suivies de réflexions sur l'union chimique des corps*, Genève, 1781; E. S. Shepherd, G. A. Rankin, and F. E. Wright, *Amer. Journ. Science*, (4), 28. 293, 1909; J. B. Ferguson and H. E. Merwin, *ib.* (4), 48. 81, 1919; J. A. Hedvall and N. von Zweigbergh, *Zeit. anorg. Chem.*, 108. 119, 1919; V. Lenher, *Journ. Amer. Chem. Soc.*, 43. 29, 1921; W. G. Palmer, *Proc. Roy. Soc.*, 101. A, 175, 1922.

¹² H. M. Goodwin and R. D. Mailey, *Phys. Rev.*, (1), 23. 1, 1906; E. Wedekind, *Zeit. angew. Chem.*, 18. 1369, 1905; *Chem. Ztg.*, 33. 329, 1909; K. Arndt, *ib.*, 30. 211, 1906; J. W. Mellor and F. Austin, *Journ. Soc. Chem. Ind.*, 26. 380, 1907; W. C. Anderson, *Journ. Chem. Soc.*, 87. 257, 1905; H. Rose, *Pogg. Ann.*, 86. 283, 1852; H. St. C. Deville, *Compt. Rend.*, 61. 975, 1865; A. Ditte, *ib.*, 73. 111, 191, 270, 1871; F. Knapp, *Dingler's Journ.*, 202. 513, 1872; H. Schwarz, *ib.*, 186. 25, 1867; H. Davy, *Elements of Chemical Philosophy*, London, 1820; J. L. Proust, *Ann. Chim. Phys.*, (1), 57. 196, 1806; *Nicholson's Journ.*, 15. 224, 1806.

¹³ E. de M. Campbell, *Journ. Ind. Eng. Chem.*, 1. 665, 1909; N. Parravano and C. Mazzetti, *Atti Accad. Lincei*, (5), 30. i, 63, 1921; J. W. Mellor, *Trans. Cer. Soc.*, 16. 85, 1917; C. Edwards and A. Rigby, *ib.*, 17. 116, 1918; A. M. Sen, *Rep. Mysore Dept. Mines*, 15. 158, 1916; H. le Chatelier, *Compt. Rend.*, 102. 1243, 1883.

¹⁴ J. Dalton, *New System of Chemical Philosophy*, Manchester, 1808; R. Kirwan, *Elements of Mineralogy*, London, 6. 1784; O. Henry, *Journ. Pharm.*, (1), 13. 1, 1827; G. Fleury, *ib.*, (4), 28. 400, 1878; A. Fyfe, *Edin. Phil. Journ.*, 5. 305, 1821; R. Fresenius, *Liebig's Ann.*, 59. 117, 1847; A. Bineau, *Compt. Rend.*, 41. 510, 1855; C. Bernard and L. Ehrmann, *ib.*, 83. 1239, 1876; F. Köhlerausch and F. Rose, *Zeit. phys. Chem.*, 12. 241, 1893; A. Dupré and M. Bialas, *Zeit. angew. Chem.*, 16. 54, 1903; G. C. Whipple and A. Mayer, *Journ. Infectious Diseases, Suppl.*, 2. 151, 1906; E. Maigret, *Bull. Soc. Chim.*, (3), 33. 631, 1905; R. Warington, *Journ. Chem. Soc.*, 18. 27, 1865; W. C. Anderson, *ib.*, 87. 257, 1905; J. M. Lovón, *Zeit. anorg. Chem.*, 11. 404, 1896; F. P. Treadwell, *ib.*, 37. 326, 1903; W. Herz and G. Muhs, *ib.*, 38. 138, 1904; H. Precht, *Zeit. anal. Chem.*, 18. 439, 1879; F. K. Cameron and J. M. Bell, *The Action of Water and Aqueous Solutions upon Soil Carbonates*, Washington, 1907; C. J. B. Karsten, *Lehrbuch der Salinenkunde*, Berlin, 1847.

¹⁵ C. Neuberg and B. Rewald, *Biochem. Zeit.*, 9. 547, 1908; *Zeit. Koll.*, 2. 354, 1908.

¹⁶ A. Bruce, *Amer. Min. Journ.*, 1. 26, 1814; C. C. von Leonhard, *Handbuch der Oryktognosie*, Heidelberg, 537, 1821; R. J. Haüy, *Traité de minéralogie*, Paris, 68, 1822; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, 487, 1824; J. Pierce, *Amer. Journ. Science*, (1), 1. 54, 1818; T. Nuttall, *ib.*, (1), 4. 18, 1821; J. D. Whitney, *Boston Journ. Nat. Hist.*, 6. 36, 1848; C. F. Rammsberg, *Pogg. Ann.*, 80. 284, 1850.

¹⁷ Salzbergwerk Neu-Stassfurt, *German Pat.*, D.R.P. 53574, 1890; G. O. Rees, *Phil. Mag.*, (3), 10. 454, 1837.

¹⁸ P. Grouvelle, *Ann. Chim. Phys.*, (2), 17. 354, 1821; R. F. Marchand and T. Scheerer, *Journ. prakt. Chem.*, (1), 50. 385, 1850; H. E. Patten, *Journ. Amer. Chem. Soc.*, 25. 186, 1903; A. de Schulten, *Compt. Rend.*, 101. 72, 1885; G. Friedel, *Bull. Soc. Min.*, 14. 74, 1891; G. A. Kennigott, *Uebersicht der Resultate mineralogischer Forschungen*, Wien, 120, 1865; A. Weisbach, *Neues Jahrb. Min.*, ii, 119, 1883; O. Luedecke, *Zeit. Kryst.*, 7. 502, 1883.

¹⁹ F. Hessenberg, *Mineralogische Notizen*, Frankfurt, 8. 45, 1868; J. B. Dana, *Amer. Journ. Science*, (2), 17. 83, 1854; G. J. Brush, *ib.*, (2), 82. 94, 1861; G. Rose, *Zeit. deut. geol. Ges.*, 12. 178, 1860; G. Aminoff, *Zeit. Kryst.*, 56. 506, 1921; *Geol. För. Förh.*, 41. 407, 1919; R. Hermann, *Bull. Soc. Nat. Moscou*, 575, 1860; *Journ. prakt. Chem.*, (1), 82. 368, 1861; F. R. Mallet, *Min. Mag.*, 11. 211, 1897; M. F. Hedde, *ib.*, 2. 27, 1878; A. A. Lösch, *Geol. För. Förh. Stockholm*, 7. 733, 1885; *Proc. Russ. Min. Soc.*, 20. 318, 1885; W. Beck, *ib.*, 87. 1862; *Neues Jahrb. Min.*, 468. 1 863; O. Mügge, *ib.*, i, 57, 1884; i, 110, 1898; L. Peruzzi, *Rend. Accad. Lincei*, (ii), 14. 83, 1905; V. von Zepharovich, *Mineralogisches Lexicon, für das Kaiserthum Oesterreich*, Wien, 2. 73, 1873; A. de Schulten, *Compt. Rend.*, 101. 72, 1885.

²⁰ J. M. van Bemmelen, *Journ. prakt. Chem.*, (2), 26. 237, 1882; *Zeit. anorg. Chem.*, 18. 98, 1898; J. Johnston, *Journ. Amer. Chem. Soc.*, 30. 1357, 1908; *Zeit. phys. Chem.*, 62. 330, 1908.

²¹ A. des Cloizeaux, *Ann. Mines*, (5), 11. 301, 1857; M. Bauer, *Sitzber. Akad. Berlin*, 958, 1881; *Neues Jahrb. Min. B.B.*, 2. 64, 1883; L. Peruzzi, *Rend. Accad. Lincei*, (5), 14. ii, 83, 1905; U. Panichi, *ib.*, 4. 389, 1902; *Zeit. Kryst.*, 40. 89, 1904; R. Brauns, *Die optischen Anomalien der Krystalle*, Leipzig, 1891; C. Doelter, *Neues Jahrb. Min.*, ii, 221, 1884; H. Rosenbusch, *Mikroskopische Physiographie der Mineralien und Gesteine*, Stuttgart, 1. 337, 1885.

²² W. W. Coblenz, *Phys. Rev.*, (1), 20. 252, 1905; (1), 22. 1, 1906; *Investigations of the Infra-red Spectrum*, Washington, 3. 43, 1906; J. Königsberger, *Wied. Ann.*, 61. 703, 1897.

²³ F. Beijerinck, *Neues Jahrb. Min. E.B.*, 11. 455, 463, 1897; W. Hankel, *Abhandl. Sächs. Ges. Wiss. Leipzig*, 12, 1878; *Wied. Ann.*, 6. 53, 1879; J. C. Bose, *Nature*, 57. 353, 1898.

²⁴ C. Weltzien, *Liebig's Ann.*, **138**, 132, 1866; R. Haas, *Ber.*, **17**, 2254, 1884; O. Ruff and E. Geisel, *ib.*, **37**, 3683, 1904; F. J. Homeyer, *Apoth. Ztg.*, **17**, 697, 1902; A. Krause, *German Pat.*, *D.R.P.P.* 168271, 179781, 1901; F. Hinz, *ib.*, 151129, 1902; E. Merck, *ib.*, 171372, 1903; R. Wagnitz, *ib.*, 107231, 1899; *Brit. Pat. No.* 11534, 1899; R. von Foregger and H. Philipp, *Journ. Soc. Chem. Ind.*, **25**, 298, 461, 1906.

§ 7. Magnesium Fluoride

The mineral *sellaïte* is a native magnesium fluoride, MgF_2 , which G. Strüver¹ found at Moutiers in France. It forms colourless or white tetragonal crystals of sp. gr. 2·9·3·2; and hardness 5–6. A. and E. Scacchi found some crystals in the lava of the Vesuvian eruption of 1872 which they called *belonesite* or *belonite*, and which were shown by F. Zambonini to be identical with G. Strüver's sellaïte.

J. L. Gay Lussac and L. J. Thénard² dissolved magnesium oxide in hydrofluoric acid. J. J. Berzelius prepared magnesium fluoride by treating magnesium carbonate with hydrofluoric acid, or by precipitation from a soln. of magnesium sulphate by potassium fluoride. F. Röder obtained it by melting together 5 parts of magnesium chloride, 4 parts each of sodium fluoride and chloride; on cooling, long needle-like crystals of magnesium fluoride are obtained. H. Moissan made magnesium fluoride by burning the powdered metal in fluorine gas—the combustion proceeds *avec beaucoup d'éclat*; A. Feldmann heated magnesium chloride with calcium fluoride, and digested the product with water acidulated with hydrochloric acid. The product obtained by dissolving the oxide or carbonate in hydrofluoric acid, or by passing gaseous hydrogen fluoride over magnesium oxide, is an amorphous powder which is not converted into crystals either by heating it with dil. hydrochloric acid to 250°, or by the evaporation of its soln. in nitric acid; but, according to A. Cossa, it may be crystallized by cooling the fused fluoride, or by melting it with alkali chlorides—these crystals resemble sellaïte. According to A. Sella, the crystals are tetragonal with the axial ratio $a : c = 1 : 0\cdot6596$.

The sp. gr. of artificial crystals of magnesium fluoride, determined by A. Cossa,³ is 2·857 (12°), and for the natural crystals the sp. gr. vary from G. Strüver's 2·962 to 3·153 (16°); H. G. F. Schröder gives 2·472 as the sp. gr. of the precipitated and calcined powder. The hardness of sellaïte is about the same as apatite, 6. Magnesium fluoride, said E. Beck, has the m.p. 1396°, and it forms a eutectic with 48 per cent. of calcium fluoride, melting at 945°. This eutectic appears to form mixed crystals with up to 17 per cent. of barium fluoride. There is a ternary eutectic with 15 per cent. magnesium fluoride, 15 per cent. calcium fluoride, and 70 per cent. barium fluoride, which melts at 790°; and by adding magnesium oxide, the ternary eutectic is lowered to 764°. According to A. Guntz, the heat of formation ($Mg, F_{2(gas)}$) = 67·4 Cals.; and the thermal values of the reactions $MgSO_4 + 2KF = MgF_{2(solid)} + K_2SO_{4(soln)}$, -0·87 Cal. at 10° when an eq. of the salts are present in two litres of water; $MgO_{ppd.} + 2HF_{soln.} = MgF_{2ppd.} + H_2O + 15\cdot2$ Cals. with an eq. of the acid in two litres of water; and $Mg(OH)_{2ppd.} + 2HF_{gas} = MgF_2 + 2H_2O_{solid} + 28\cdot4$ Cals.; E. Petersen gives $Mg(OH)_{2aq.} + 2HF_{aq.} = 30\cdot12$ Cals. Sellaïte has a feeble refracting power; the double refraction is positive. E. Mallard, A. Sella, and F. Zambonini found for sodium light indices of refraction between $\omega = 1\cdot3775$ and 1·379; and $\epsilon = 1\cdot3889$ and 1·3897. Warm crystals of sellaïte show a faint violet luminescence with cleavage, a property which is lost by calcination; A. Cossa also found that the natural or artificial crystals give a violet fluorescence when heated after exposure to the arc light. S. Datta studied the three groups of spectral bands of magnesium fluoride.

According to F. Kohlrausch, a litre of water at 18° dissolves 0·076 gm. of MgF_2 by the conductivity method—the specific conductivity of the sat. soln. being 0·000224 at 18°—but the salt is rather more soluble in ammoniacal soln. Magnesium fluoride in many of its properties recalls those of calcium fluoride. J. L. Gay

Lussac and L. J. Thénard found magnesium fluoride is but slightly soluble in acids ; and J. J. Berzelius, that it is insoluble in hydrofluoric acid. A. Cossa showed that it is decomposed by conc. sulphuric acid less easily than calcium fluoride ; and decomposed by fusion with alkali carbonates more easily than calcium fluoride. L. E. Rivot found it to be insoluble in soln. of ammonium or magnesium salts. The amorphous form, however, is more readily attacked than the crystalline variety. H. Schulze said that magnesium fluoride is not decomposed when calcined in oxygen ; A. Tissier, that it is not decomposed by calcium oxide ; A. Cossa, that it forms fusible compounds with the sulphates of the alkaline earths, and that when calcined with beryllium or aluminium sulphate it forms the respective fluoride. W. Weldon once recommended the use of magnesium fluoride in the manufacture of soda ash ; and it has also been tried as an opacifying agent in the manufacture of glass.

A. Tissier,⁴ and M. Netto prepared cubic crystals of **sodium magnesium fluoride**, NaF.MgF_2 , by boiling magnesium hydroxide with an aq. soln. of sodium fluoride : $3\text{NaF} + \text{Mg(OH)}_2 = 2\text{NaOH} + \text{NaF.MgF}_2$. A. Geuther found crystals of the same product in the slag obtained in the preparation of magnesium silicide by fusing magnesium with sodium fluosilicate and chloride. The compound is decomposed by conc. sulphuric acid, and by milk of lime : $\text{Ca(OH)}_2 + 2\text{NaF.MgF}_2 = 2\text{NaOH} + \text{CaF}_2 + 2\text{MgF}_2$. M. Netto also made 2NaF.MgF_2 by fusing hexahydrated magnesium chloride or sulphate with sodium fluoride and chloride.

A. Duboin prepared quadratic prisms of **potassium magnesium fluoride**, KF.MgF_2 by extracting with water the slowly cooled cake obtained by fusing a mixture of an excess of potassium fluoride and magnesium oxide at a red heat. The magnesium slowly dissolves in the fused fluoride. The sp. gr. of the insoluble crystals is 2.8 (0°) ; they are decomposed by sulphuric and hydrochloric acids. If a large proportion of magnesium oxide be used, a hard transparent mass of 2KF.MgF_2 is formed of sp. gr. 2.7 (0°). It is completely decomposed by hydrochloric and sulphuric acids, and slightly decomposed by the prolonged action of boiling water.

REFERENCES.

¹ G. Strüver, *Atti Accad. Torino*, 4. 35, 1868 ; E. Mallard, *Bull. Soc. Min.*, 11. 302, 1888 ; A. Lacroix, *ib.*, 30. 247, 1907 ; A. and E. Scacchi, *Rend. Accad. Napoli*, 281, 1883 ; *Atti Accad. Napoli*, 5. 1, 1886 ; F. Zambonini, *Rend. Accad. Lincei*, 18. 305, 1899.

² J. L. Gay Lussac and L. J. Thénard, *Recherches physico-chimiques*, Paris, 1811 ; S. Datta, *Proc. Roy. Soc.*, 99. A, 436, 1921 ; J. J. Berzelius, *Pogg. Ann.*, 1. 22, 1824 ; H. Moissan, *Ann. Chim. Phys.*, (6), 12. 524, 1887 ; (6), 24. 245, 1891 ; F. Röder, *Ueber krystallizirte wasserfreie Fluorverbindungen*, Göttingen, 1862 ; A. Cossa, *Mem. Accad. Lincei*, 1. 33, 1877 ; *Atti Accad. Torino*, 12. 60, 409, 1876 ; *Gazz. Chim. Ital.*, 7. 212, 1877 ; A. Sella, *Atti Accad. Lincei*, 4. 454, 1888 ; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873 ; A. Feldmann, *Brit. Pat. No.* 15295, 1887.

³ F. Kohlrausch, *Zeit. phys. Chem.*, 16. 55, 1895 ; 44. 197, 1903 ; 50. 355, 1905 ; E. Petersen, *ib.*, 4. 384, 1889 ; H. Schulze, *Journ. prakt. Chem.*, (2), 21. 407, 1880 ; G. Strüver, *Atti Accad. Torino*, 4. 35, 1868 ; A. Sella, *Atti Accad. Lincei*, 4. 454, 1888 ; J. J. Berzelius, *Pogg. Ann.*, 1. 22, 1824 ; J. L. Gay Lussac and L. J. Thénard, *Recherches physico-chimiques*, Paris, 1811 ; A. Cossa, *Zeit. Kryst.*, 1. 207, 1877 ; *Gazz. Chim. Ital.*, 7. 212, 1877 ; L. E. Rivot, *Docimasie*, Paris, 1. 199, 1861 ; A. Tissier, *Compt. Rend.*, 56. 848, 1863 ; A. Guntz, *Ann. Chim. Phys.*, (6), 3. 39, 1884 ; E. Beck, *Metallurgie*, 5. 504, 1908 ; E. Mallard, *Bull. Soc. Min.*, 11. 302, 1888 ; W. Weldon, *Brit. Pat. Nos.* 967, 968, 1881 ; A. R. Péchiney and W. Weldon, *ib.*, 9305, 11035, 1884 ; 14653, 14654, 1887 ; F. Zambonini, *Mineralogia Vesuviana*, Napoli, 44, 1910 ; A. Lacroix, *Mineralogie de la France et de ses colonies*, Paris, 2. 796, 1896 ; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873 ; G. Strüver, *Neues Jahrb. Min.*, 370, 1869 ; S. Datta, *Proc. Roy. Soc.*, 99. A, 436, 1921.

⁴ A. Tissier, *Compt. Rend.*, 56. 848, 1863 ; A. Duboin, *ib.*, 120. 678, 1895 ; M. Netto, *Zeit. angew. Chem.*, 4. 45, 1890 ; A. Geuther, *Jenaische Zeit. Med. Naturwiss.*, 2. 208, 1865.

§ 8. Magnesium Chloride

Magnesium chloride is widely scattered in nature; it occurs in many mineral waters and in sea-water. The water of the Mediterranean is said to contain a rather larger proportion than the Atlantic Ocean, and *le sel*, which is extracted from the salt gardens of the Mediterranean, has a more bitter taste than *le sel* obtained from those which are concentrated from the waters of the Atlantic. In 1825, T. Monticelli and N. Covelli¹ found *magnesia muriata* in the fumaroles and volcanic vents of Vesuvius; in 1832, L. Pilla noted its occurrence along with sodium chloride in the crater crusts; and A. Scacchi found it in the eruptions in 1855 and 1872, and he proposed the name *chloromagnesite*, and assigned to it the formula $MgCl_2 \cdot xH_2O$. F. Zambonini considers the magnesium chloride in these deposits is united as a double salt with the alkali chloride. The mineral *bischofite*, hexahydrated magnesium chloride, $MgCl_2 \cdot 6H_2O$, found in the Stassfurt deposits, was named by C. Ochsenius in honour of G. Bischof. It occurs in the carnallite, kieserite, and salt clay regions, and it is supposed to be a secondary constituent formed by the action of water on carnallite. Magnesium chloride also occurs as *carnallite*, $MgCl_2 \cdot KCl \cdot 6H_2O$, or $KMgCl_3 \cdot 6H_2O$; and as *tachyhydrite*, *tachhydrite*, or *tachydrite*, $MgCl_2 \cdot CaCl_2 \cdot 12H_2O$, or $(Ca, Mg)Cl_2 \cdot 6H_2O$, in the Stassfurt deposits.

J. L. Gay Lussac and L. J. Thénard² made anhydrous magnesium chloride by leading chlorine gas over red-hot magnesium oxide. The oxygen simultaneously evolved was attributed to the decomposition of chlorine which they called oxy-muriatic acid—according to R. Weber, the reaction proceeds without incandescence, and requires a much higher temp. than is needed for the analogous reaction with lime or baryta. P. S. Curie also made the chloride by passing hydrogen chloride over magnesium sulphide. A. A. B. Bussy and J. J. Berzelius made it by passing chlorine over a red-hot mixture of magnesia and carbon in a porcelain tube—the magnesium chloride collected at the bottom of the tube without sublimation. The De Nordske Saltverker has a modification of this process for working on a large scale. J. von Liebig, R. Bunsen, and J. A. Wanklyn and E. T. Chapman obtained the anhydrous chloride by burning the metal in chlorine gas. According to R. Cowper, if the gas is quite dry magnesium is not attacked by chlorine. J. W. Döbereiner and R. Bunsen obtained the anhydrous chloride by calcining dry ammonium magnesium chloride.

R. Bunsen added sufficient ammonium chloride to a soln. of magnesium carbonate in hydrochloric acid, to prevent the precipitation of magnesium hydroxide when aqua ammonia is added until the soln. is slightly alkaline. Any silica, etc., which separates is filtered off, and the clear liquid is neutralized with hydrochloric acid and evaporated to dryness. The double ammonium and magnesium chloride so obtained is melted at about 460° in a Hessian crucible, in the bottom of which is placed a smaller platinum dish. When the ammonium chloride is all expelled, the magnesium chloride collects in the platinum dish.

According to H. St. C. Deville and H. Caron, and E. Sonstadt, the magnesium chloride so prepared frequently contains nitrogen, and, according to J. B. A. Dumas, magnesium oxide. In a modification of the process, a mixture of magnesium oxide and ammonium chloride is heated, and more ammonium chloride added from time to time. M. M. T. K. Kaisha, and I. Namari and Y. Hiraoka added ammonium chloride and the oxide, hydroxide, carbonate, or oxychloride of magnesium to a fused halide of a more electropositive metal. The product was considered suitable for electrolysis for magnesium.

W. Heap and E. Newbery made anhydrous magnesium chloride by treating the oxide or a salt with a weak acid—carbonate or oxalate—with carbonyl chloride at 500°–600°. A mixture of carbon monoxide and chlorine passed over animal charcoal will serve the same purpose. H. J. Bull used carbon tetrachloride or carbonyl chloride with magnesia, or magnesite; if dolomite is used, a mixture of calcium and magnesium chlorides is obtained which may be used in electrolysis.

V. M. Goldschmidt chlorinated magnesia in the presence of sulphur or sulphur chlorides free from oxygen, and at 200°-500° found that the reaction went according to the equation: $2\text{MgO} + 2\text{Cl}_2 + \text{S} = \text{SO}_2 + 2\text{MgCl}_2$.

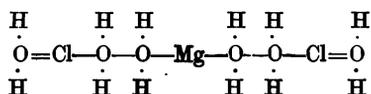
T. W. Richards and H. G. Parker heated the dried ammonium magnesium chloride in a stream of dry hydrogen chloride and obtained magnesium chloride of a high degree of purity. The magnesium chloride soln. used in the preparation of the double salt was purified in the following manner:

About 500 grms. of magnesium chloride were sat. with hydrogen sulphide, a small amount of ammonia was added, and the whole was allowed to stand in a warm place for several days. To the supernatant liquid after decantation a small quantity of very pure ammonium oxalate was added. The magnesium chloride thus almost wholly freed from calcium was again decanted; and after more ammonium oxalate had been added, the whole was allowed to stand, and the clear liquid was yet once more decanted. The soln. was then evaporated to dryness, and the resulting cake dried in an oven and ignited in a platinum dish. The mixture of magnesium oxide and oxychloride thus formed was washed with the aid of a filter pump for about sixty hours. At the end of this time, although the wash water contained no sodium, the insoluble precipitate was not free from that metal. The precipitate was therefore dissolved in hydrochloric acid, previously distilled in platinum for the purpose, and the soln. was filtered. In order to eliminate the sodium, a portion of the magnesium was precipitated by passing into the soln. a current of ammonia gas. The precipitate formed by this very wasteful process was washed for several days, at the end of which time it was found to be free from any appreciable traces of sodium and potassium, when tested with the spectrocope. The precipitate was then dissolved in hydrochloric acid.

In the laboratory a soln. of magnesium chloride is made by dissolving magnesium oxide or carbonate in hydrochloric acid. It can also be made by a process analogous to that employed by A. J. Balard for separating Glauber's salt from sea-water, namely, by cooling a conc. soln. of magnesium sulphate and sodium chloride whereby sodium sulphate crystallizes out, and magnesium chloride remains in soln. According to L. Michels, the hydrated salt is made from the mother liquor remaining after extracting potassium chloride from the Stassfurt salts; this is evaporated until its sp. gr. is about 1.375, and then allowed to cool and crystallize. The syrupy yellowish-brown mother liquid contains bromides. The crystals, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, are melted (about 400°), and they are at the same time partially dehydrated and partly oxidized to an oxychloride. The mixture forms some of the magnesium chloride of commerce. Magnesium chloride could be obtained as a by-product in one of W. Weldon's processes for chlorine; and in E. Solvay's ammonio-soda process if magnesium oxide be used to decompose the ammonium chloride. K. S. Boynton and co-workers discuss the recovery of magnesium chloride from sea-water, where it is obtained as a by-product in the extraction of salt. H. H. Dow and E. O. Barstow proposed to remove calcium chloride from magnesium chloride brine by precipitation as calcium sulphate. C. Clerc and A. Nihoul added calcined dolomite in powder to a soln. of magnesium chloride, and found magnesia to be precipitated and calcium chloride to pass into soln.

The hydrated salt cannot be dehydrated without a loss of hydrogen chloride by simple heating. According to R. Brandes, the loss of hydrogen chloride begins at 106°, and, according to H. Grimshaw, at 117° or even lower temp. H. Hof detected the formation of hydrogen chloride at 157° when soln. of magnesium chloride are evaporated under conditions where the superheating of any part of the soln. is prevented. F. P. Dunnington and F. W. Smither say that all but one mol of the water of crystallization can be expelled at 98° without decomposition, and that the principal loss of hydrogen chloride occurs during the expulsion of the residual water. E. Solvay has patented a process in which an approximation is made by heating the hexahydrated salt to 120° until 80 per cent. of the water is expelled; the residue is then much more resistant, and it can be heated to a higher temp. without much loss as hydrogen chloride; or the hexahydrated salt can be heated until about 50 per cent. of the water is expelled, and the molten salt then broken into small fragments and heated between 300° and 400° in a stream of dry air. In the

Salzbergwerk Neu-Stassfurt's process, it is claimed that the hexahydrated salt can be dehydrated without much loss of hydrogen chloride by heating it to about 175° in vacuo. E. Sonstadt and W. Hempel recommended dehydrating the hexahydrated salt in a stream of dry hydrogen chloride. H. J. Bull used a stream of carbon tetrachloride or carbonyl chloride at 500°–600°. H. H. Dow has described a process for dehydrating this salt. If magnesium oxide is once formed, J. B. A. Dumas found it to be difficult to chlorinate subsequently the oxide. F. A. Gooch and F. M. McClenahan say that the passage of hydrogen chloride has no influence on the speed of dehydration of the first third of the water which occurs at 100°, but that it retards the dehydration between 100° and 130°; and accelerates it above 130°. The hydrolytic dissociation of this salt is not very marked below 200° in air or in hydrogen chloride. F. A. Gooch and F. M. McClenahan found that one-third of the combined water can be expelled from the hexahydrated chloride easily without hydrolysis, but the remaining two-thirds can be driven off only when accompanied by hydrogen chloride, and they explain this by assuming that two-thirds of the combined water is more intimately associated in the mol. complex than the remaining third. They illustrate this graphically :



Compare this with the behaviour of hydrated barium and aluminium chlorides.

J. L. Gay Lussac and L. J. Thénard³ described anhydrous magnesium chloride as forming a white transparent mass of large lustrous **crystals** with a sharp bitter taste. L. Playfair and J. P. Joule found the sp. gr. to be 2.177. H. St. C. Deville and H. Caron say that the salt may be distilled in a current of hydrogen, forming a distillate resembling butter, which forms a mass of crystalline plates on cooling. E. E. Somermeier found the heat of dissolution of a gram-atom of magnesium in $\text{HCl}+19.15\text{H}_2\text{O}$ to be 111.40 Cals. The **melting point** is 708°, according to T. Carnelley, and the f.p. 711°, according to O. Menge. J. Thomsen gives the **heat of formation**, (Mg, Cl_2), 151.01 Cals.; ($\text{Mg}, \text{Cl}_2, \text{aq.}$), 186.93 Cals.; ($\text{MgCl}_2, \text{aq.}$), 35.92 Cals.; ($\text{Mg}, \text{Cl}_2, 6\text{aq.}$), 133.98 Cals.; ($\text{MgCl}_2, 6\text{aq.}$), 32.97 Cals.; $\text{Mg}(\text{OH})_{2\text{aq.}}+2\text{HCl}_{\text{aq.}}=27.69$ Cals. G. F. Hüttig gave 2.325 at 25°/4°, for the **specific gravity** of anhydrous magnesium chloride, 2.316 for that of the unmelted and porous salt; and, assuming the sp. gr. is 2.320, W. Biltz gives the mol. vol. 41.05. The **heat of solution** of $\text{MgCl}_2.6\text{H}_2\text{O}$ in 400 mols. of water is 2.95 Cals., and P. Sabatier gives the ht. of soln. of $\text{MgCl}_2.6\text{H}_2\text{O}$ at 19.6° as 6.4 Cals. M. Berthelot and L. Ilosvay de N. Ilosva give for the heat of soln. of magnesium chloride, MgCl_2 at θ° , $35480+0.0000796(\theta-15^\circ)$; and for $\text{MgCl}_2.6\text{H}_2\text{O}$, $2800+0.000025(\theta-15^\circ)$. R. Görgey found for sodium light the **indices of refraction** $\alpha=1.495$; $\beta=1.507$; and $\gamma=1.58$. W. Hampe says that the molten salt is a good conductor of electricity.

According to H. Schulze,⁴ magnesium chloride forms magnesium oxide when calcined in oxygen. The reaction has been discussed in connection with the preparation of chlorine, or of hydrogen chloride. F. Haber and F. Fleischmann represent the equilibrium constant K_p of the reaction: $2\text{MgCl}_2+\text{O}_2\rightleftharpoons 2\text{MgO}+2\text{Cl}_2$, by the expression $\log_{10} K_p=-1950T^{-1}-1.87 \log_{10} T+7.01$, where K_p is equal to $p/p_0^{\frac{3}{2}}$, where p denotes the partial press. of the chlorine, and p_0 that of the oxygen. According to W. Moldenhauer, the following are the values of K_p and the corresponding percentage amounts of oxygen and chlorine by volume calculated from the conc. of oxygen $C_0=100-C$, where C is the conc. of the chlorine; hence $K_p=C/(100-C)^{\frac{3}{2}}$:

	50°	150°	250°	350°	450°	550°	650°	750°
K_p	0.03	0.4	1.9	5.3	10.6	17.4	25.3	35.9
Chlorine	0.3	4.0	17.6	40.8	63.5	79.3	88.0	93.3
Oxygen	99.7	96.0	82.4	59.2	36.5	20.7	12.0	6.7

The equilibrium at the lower temp. is attained very slowly; the values below 350° are computed by extrapolation in the formula; the equilibrium curve is shown in Fig. 9, the dotted curve shows the results obtained after 10 hrs. heating and illustrates the tardiness with which equilibrium is attained at the lower temp. The heats of formation of magnesium chloride is 151 Cals., and of magnesium oxide, 143·3; consequently the thermal value of the reaction: $MgCl_2 + O = MgO + Cl_2$

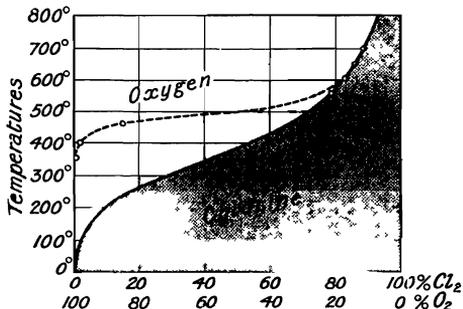


FIG. 9.—Equilibrium Conditions in $2MgCl_2 + O_2 = 2MgO + 2Cl_2$.

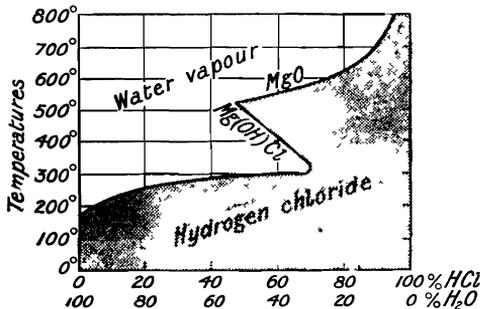


FIG. 10.—Equilibrium Conditions in the Reaction: $MgCl_2 + H_2O$.

—7·7 Cals. at constant press. The value computed from J. H. van't Hoff's equation between 550° and 650° is:

$$\log \frac{K_1}{K_2} = \frac{Q}{2} \left(\frac{1}{T_1} - \frac{1}{T_2} \right); \text{ or } \log \frac{25\cdot3}{17\cdot4} = \frac{Q}{2} \left(\frac{1}{923} - \frac{1}{823} \right)$$

or $Q = -5600$ cal. at about 600°, and at room temp., about —7400 cal. J. W. Döbereiner also showed that magnesium chloride is decomposed when heated with potassium chlorate; and by water vapour.

The action of steam on magnesium chloride has been studied by W. Moldenhauer. The composition of the solid residue at different temp. when magnesium chloride is heated with steam is:

		250°	300°	350°	400°	600°
MgCl ₂	.	78·2	72·9	77·7	64·3	44·8
MgO	.	5·1	17·6	15·0	24·3	54·4
H ₂ O	.	16·7	9·5	7·3	11·6	0·8

The composition of the gases in percentages of volume:

	183°	213°	250°	300°	350°	400°	500°	600°	700°
HCl	0·8	7·9	21·0	66·5	69·4	62·15	50·2	75·1	90·2
H ₂ O	99·2	92·1	79·0	33·5	30·3	37·85	49·8	24·9	9·8

The results are plotted in Fig. 10. W. Moldenhauer attributes the phenomena to changes in the composition, the solid phase being such that the amount of hydrogen chloride in the reaction between steam and magnesium chloride steadily increases up to a maximum between 300° and 350°; between 350° and 505°, magnesium hydroxychloride, Mg(OH)Cl, is formed by a reaction which decreases the proportion of hydrogen chloride in the system; the equilibrium reaction is then represented, $MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$; between 500° and 510°, the hydroxychloride, Mg(OH)Cl, decomposes; and above this temp., the equilibrium reaction is: $MgCl_2 + H_2O \rightleftharpoons 2HCl + MgO$. The curve between 200° and 350° is uncertain because of the long time required to attain equilibrium. The equilibrium constant K in the reaction: $MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$, when $K = [HCl]/[H_2O]$, where the bracketed terms represent concentrations, is $K = 1\cdot64$ at 400°, and $K = 1\cdot01$ at 500°, so that from J. H. van't Hoff's equation, the heat of the reaction between these temp. is 5100 cal. Similarly, the equilibrium constant K' in the reaction $MgCl_2 + H_2O$

$=\text{MgO}+2\text{HCl}$, when $K=[\text{HCl}]^2/[\text{H}_2\text{O}]$ is $K=226.5$ at 600° , and $K=830.2$ at 700° ; and the computed heat of the reaction is -22000 cal. on the imperfect assumption that the sp. ht. of the reacting substances are independent of temp. From the thermochemical data, $\text{MgCl}_2+\text{H}_2\text{O}=\text{MgO}+2\text{HCl}$, $-151000-57000+143300+44000=-20700$ cal. The reaction involving the formation of the intermediate $\text{Mg}(\text{OH})\text{Cl}$ is exothermal, the other reaction at the higher temp. being endothermal.

The **solubility** of magnesium chloride expressed in grams of MgCl_2 per 100 grms. of soln. between 0° and 100° , where the solid phase is $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, is

	0°	10°	20°	40°	60°	80°	100°
MgCl_2	34.5	34.9	35.3	36.5	37.9	39.8	42.2

The solubility curve covering the range between 50° and 200° is illustrated in Fig. 11. The solubility with ice as the solid phase falls from 11.1 per cent. at -10° to the eutectic B with the solubility 20.6 per cent. at -33.6° ; when the solid phase is a mixture of ice and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$; the solubility with $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ as the solid phase then rises to 31.6 per cent. at -16.8° , C , where the solid phase is a mixture of $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ and $\alpha\text{-MgCl}_2 \cdot 8\text{H}_2\text{O}$; at -17.4° , H , solubility 32.3 per cent. the solid phases are $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ and $\beta\text{-MgCl}_2 \cdot 8\text{H}_2\text{O}$; at -19.4° , K , solubility 33.3 per cent., the solid phases are $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; at -9.6° , J , solubility 34.9 per cent., the solid phases are $\beta\text{-MgCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; at -3.4° , I , solubility 34.4 per cent., the solid phases are $\alpha\text{-MgCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and the last-named salt is the solid phase from -3.4° to 116.7° , F , when the solubility is 46.2 per cent., and the solid phases are $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$.

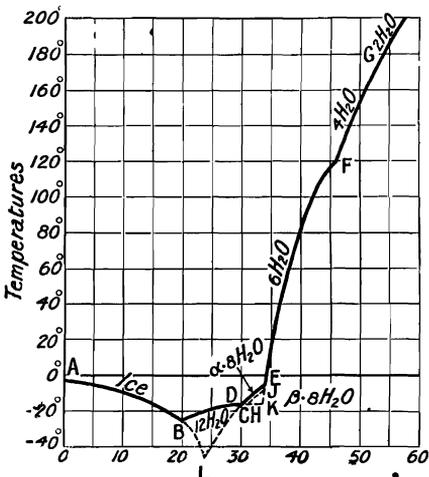


FIG. 11.—Solubility Curves of Magnesium Chloride.

At 152.6° , the solubility is 49.1 per cent., and the solid phase is $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$; at 181.5° , G , solubility 55.8 per cent., the solid phases are $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. At 186° the solubility is 56.1 per cent., and the solid phase is $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. The maximum in the curve at -16.4° , D , represents the m.p. of $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$. The system at H , J , K , is not stable and represent undercooled soln.

There are at least six different hydrates of magnesium chloride, indicated in Fig. 11. J. H. van't Hoff and W. Meyerhoffer⁵ found that **dodecahydrated magnesium chloride**, $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, is formed when a soln. with more than 12 and less than 20 mols of water *per* mol of MgCl_2 , is cooled to -30° or -35° ; or by adding a piece of solid carbon dioxide to an under-cooled soln. $\text{MgCl}_2+12\text{H}_2\text{O}$ at -20° . A. Bogorodsky cooled a soln. of $\text{MgCl}_2+10\text{H}_2\text{O}$ at -20° , and added a little of a soln. $\text{MgCl}_2+12\text{H}_2\text{O}$ cooled below -20° . This salt melts at -16.7° to a clear liquid. The crystals are lighter than the mother liquid, says A. Bogorodsky, and it is not usual for an increase in volume to be observed in the formation of a hydrate. J. H. van't Hoff and W. Meyerhoffer prepared **octohydrated magnesium chloride**, $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$, by allowing a sat. soln. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to stand in contact with the solid phase between -15° and -20° ; or by cooling a soln. of $\text{MgCl}_2+10\text{H}_2\text{O}$ to -20° , and removing the mass from the freezing mixture, the dodecahydrated salt disappears and the octahydrated salt remains as a coarse crystalline powder which when mixed with the original soln., and cooled to -10° or -12° , forms thick crystalline plates, which decompose at -3.4° ; A. Bogorodsky says -9.8° . The

range of its existence extends from -16.7° to -3.4° . **Hexahydrated magnesium chloride**, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, crystallizes from aq. soln. between -3.4° and 116.67° . According to J. C. G. de Marignac, it forms prismatic monoclinic crystals with axial ratios $a : b : c = 1.348 : 1 : 0.818$ and $\beta = 96^\circ 39'$. E. Filhol gives the sp. gr. 1.558 at ordinary temp., and for bischofite, C. Ochsenius gives 1.65; at -188° , J. Dewar found a sp. gr. 1.6039, and he computes the mean coeff. of thermal expansion between 17° and -188° to be 0.0001072. J. H. van't Hoff and H. M. Dawson have examined the lowering of the f.p. of this salt in the presence of ammonium and alkali chlorides; with potassium sulphate there is a raising of the f.p. owing to the formation of kieserite; hexahydrated magnesium bromide forms mixed crystals with hexahydrated magnesium chloride. The crystals deliquesce in air, and W. Müller-Erzbach found the vap. press. to be from 0.012 to 0.016 of that of pure water. P. Bary states that the crystals are phosphorescent when exposed to Röntgen's or Becquerel's rays. H. Davy noted that when this salt is dehydrated, it loses hydrogen chloride, forming magnesium oxide along with the chloride. According to R. Brandes, the crystals begin to lose hydrogen chloride at 106° , they partially melt at 112° , and completely melt at 119° . C. Przibylla gives 116° — 118° for the m.p. of bischofite. The phenomena attending the dehydration of this salt have been previously discussed. H. Lescœur prepared **tetrahydrated magnesium chloride**, $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$, by passing hydrogen chloride into a soln. of magnesium chloride; P. Sabatier, and W. Müller-Erzbach, by exposing the hexahydrated salt to a dry atm.; J. H. van't Hoff and W. Meyerhoffer, by drying the hexahydrated salt at 100° to a constant weight; or by melting the hexahydrated salt at 130° in a current of air; when the composition approximates to $\text{MgCl}_2 + 5\text{H}_2\text{O}$, cooling slowly to 117° ; warming to 150° and pouring off the mother liquid. A. Ditte made **dihydrated magnesium chloride**, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, by saturating with hydrogen chloride a water-cooled soln. of magnesium chloride; and by adding anhydrous magnesium chloride to conc. hydrochloric acid without allowing the temp. to rise. J. H. van't Hoff and W. Meyerhoffer made the dihydrated salt by passing dry hydrogen chloride over the tetrahydrated salt at 140° . The crystalline plates are very deliquescent, and, according to W. Müller-Erzbach, have 0.0013th of the vap. press. of water. W. Moldenhauer made **monohydrated magnesium chloride**, $\text{MgCl}_2 \cdot \text{H}_2\text{O}$, by passing hydrogen chloride over the hexahydrated-salt for 4–6 hrs. at 135° until there is no further loss in weight; the same result was obtained by 12–14 hrs. heating at 110° .

The **specific gravity** of aq. soln. of magnesium chloride has been determined by D. I. Mendeleeff,⁶ R. Engel, P. Kremers, H. Schiff, A. C. Oudemans, and G. T. Gerlach at 15° , and by O. Pulvermacher, H. T. Barnes and A. P. Scott, at 0° and 20° . According to G. T. Gerlach, at 15° ,

Per cent. MgCl_2 .	1	5	10	15	20	25	30	35
Sp. gr.	1.0084	1.0412	1.0859	1.1311	1.1780	1.2273	1.2794	1.3340

W. Biltz gave 2.325 at $25^\circ/4^\circ$ for the sp. gr. of fused magnesium chloride, and 2.316 for the unfused porous salt. According to G. J. W. Bremer, an empirical relation between the sp. gr. D and the percentage composition p is $D = 1 + 0.0091729p + 0.00005507p^2$; and the sp. gr. D at the temp. θ° , is $D = D_0(1 - a\theta - b\theta^2)$, where D represents the sp. gr. at 0° , and a and b constants, the former of which is greater in value and the latter smaller in value the more conc. the soln. The expansion curves of the different soln. intersect at approximately 60° . According to N. A. Tschernay, unit volume of a soln. $\text{MgCl}_2 + 50\text{H}_2\text{O}$ at θ° becomes $v = 1 + 0.0001394\theta + 0.00002892\theta^2$, and for $\text{MgCl}_2 + 100\text{H}_2\text{O}$, $v = 1 + 0.0000688\theta + 0.00003922\theta^2$. J. Wagner's values for the **viscosities** of $\frac{1}{2}N$ -, $\frac{1}{4}N$ -, $\frac{1}{8}N$ -, and N -soln. of magnesium chloride are respectively 1.026, 1.0445, 1.0940, and 1.2015—water unity. O. Pulvermacher also made some measurements. F. E. Bartell and O. E. Madison studied the **osmosis** of soln. of magnesium chloride through animal membranes; and F. E. Bartell and L. B. Sims, through collodion. F. E. Bartell and D. C. Carpenter also measured the rate of osmosis.

According to J. C. G. de Marignac,⁷ the **specific heat** at 22·52° of a soln. of one mol of magnesium chloride in n mols of water is :

n	.	.	15	25	50	100	200H ₂ O
Sp. ht.	.	.	0·6824	0·7716	0·8665	0·9235	0·9594
Mol. ht.	.	.	249·4	421·0	862	1750	3545

G. Jäger found the **heat conductivities** of 11, 14·5, 22, and 29 per cent. soln. of magnesium chloride are respectively 94·9, 91·7, 89·0, and 85·4 (water=100). According to W. Müller-Erbach, the **vapour pressure** of a sat. soln. of magnesium chloride is about 0·27th that of water. S. Skinner has measured the **boiling points** of aq. and alcoholic soln. of magnesium chloride ; and E. M. Baker and V. H. Waite found that U. Dühring's rule applies to the boiling of aq. soln. of magnesium chloride. H. C. Jones and F. H. Getman, and J. H. van't Hoff measured the **freezing points** of the soln.

The refraction and dispersion of soln. of magnesium chloride have been investigated by P. Barbier and L. Roux.⁸ For the difference between the **refractive index** of the soln., μ , and that of water, μ_0 , for soln. with $\frac{1}{2}$ MgCl₂ per v litres, D. Dijken found when $v=1$, $\mu-\mu_0=0\cdot011957$; and when $v=128$, $\mu-\mu_0=0\cdot0001013$. O. Pulvermacher measured the refractive index of soln. of magnesium chloride. The **electrical conductivity** has been measured by S. Arrhenius,⁹ P. Walden, and others. H. C. Jones and co-workers found for the mol. conductivity, μ , and the percentage **degree of ionization**, α , of soln. of magnesium chloride with a mol of the salt in v litres of water :

v	.	.	.	4	8	32	128	512	2048	4096
μ_0	.	.	.	80·2	87·6	99·9	110·3	115·7	120·3	123·5
μ_{65}	.	.	.	280·6	303·8	364·8	401·6	433·1	465·6	—
α_0	.	.	.	64·9	70·9	80·9	89·2	93·7	97·3	100·0
α_{65}	.	.	.	60·3	65·3	78·4	86·3	93·0	100·0	—

The temp. coeff. of the conductivity were also computed by H. C. Jones and A. P. West ; and the degree of ionization, by G. Kümmell, and K. Drücker. S. Arrhenius computed the **heat of ionization** in a 0·1 eq. soln. at 35° to be -651 cal. Data for the **transport numbers** of the ions have been measured by W. Hittorf, W. Bein, A. Chassy, and B. D. Steele ; and S. von Lasczynsky and S. von Gorsky worked with soln. of magnesium chloride in pyridine. F. E. Bartell and D. C. Carpenter measured the **difference of potential** of water and soln. of magnesium chloride separated by a permeable membrane. S. Meyer gave $-0\cdot420 \times 10^{-6}$ units per gm. or $-0\cdot044 \times 10^{-6}$ units per mol for the **magnetic susceptibility** of anhydrous magnesium chloride, and for the hexahydrated salt, $-0\cdot347 \times 10^{-6}$ units per gm. or $-0\cdot092 \times 10^{-6}$ units per mol.

According to F. Margueritte,¹⁰ gaseous *hydrogen chloride* does not precipitate magnesium chloride from its aq. soln., but R. Engel, and A. Ditte showed that this statement is erroneous ; the solubility of magnesium chloride is considerably diminished by hydrogen chloride. Expressing the concentrations in grams per 100 c.c. of soln., R. Engel found at 0°,

Per cent. HCl	.	0	1·49	3·46	6·20	10·39	5·31	21·42	27·71
Per cent. MgCl ₂	.	47·42	45·48	42·86	39·30	33·83	28·64	22·03	15·20

and a soln. sat. with hydrogen chloride dissolves 6·5 per cent. of magnesium chloride. The solubility of magnesium chloride in the presence of other salts has been investigated by R. Löwenherz¹¹ and by J. H. van't Hoff and co-workers in connection with their studies on the Stassfurt deposits.

Alcohol of sp. gr. 0·90 and 0·871 dissolves respectively 20 and 50 parts of magnesium chloride per 100 c.c. of solvent. S. E. Simon¹² found that heat is evolved when anhydrous magnesium chloride is allowed to act on dry methyl or ethyl alcohol, and on cooling the soln. with a freezing mixture compounds with alcohol

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of crystallization separate in deliquescent crystals—*e.g.* **magnesium chloride hexamethyl-alcoholate**, $\text{MgCl}_2 \cdot 6\text{CH}_3\text{OH}$; and **magnesium chloride hexa-ethyl-alcoholate**, $\text{MgCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$. L. Kahlenberg and F. C. Kraushoff find the very low solubility of magnesium chloride in anhydrous *pyridine* and its greater solubility in pyridine with 3 or 4 per cent. of water resembles that of calcium and strontium chlorides in the same menstruum.

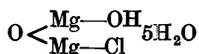
According to W. S. Clark,¹³ magnesium chloride volatilizes when heated in a stream of *ammonia*, leaving a residue of magnesium oxide; the sublimate is **magnesium tetrammino-chloride**, $\text{MgCl}_2 \cdot 4\text{NH}_3$, which on exposure decomposes rapidly with the loss of ammonia, but which can be sublimed in an atm. of ammonia. **Magnesium hexammino-chloride**, $\text{MgCl}_2 \cdot 6\text{NH}_3$, analogous with calcium hexammino-chloride, was made by F. Ephraim; according to C. Matignon, the heat of dissociation into **magnesium diammino-chloride**, $\text{MgCl}_2 \cdot 2\text{NH}_3$, and ammonia at 142° is 13.07 Cals. According to W. Biltz and G. F. Hüttig, the dissociation press. of the hexammines could not be determined because of the formation of mixed crystals or solid soln. of two amines. G. Spacu and R. Ripan obtained a colourless crystalline powder of **magnesium pentammino-aquachloride**, $[\text{Mg}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_2$, by passing ammonia into an alcoholic soln. of magnesium chloride at ordinary temp. W. Biltz and G. F. Hüttig found that the heat of formation and absolute temp. at which the dissociation press. of magnesium diammino-chloride is 100 mm. are respectively 17.9 Cals. and 495° ; similarly for **magnesium ammino-chloride**, $\text{Mg}(\text{NH}_3)\text{Cl}_2$, 20.8 Cals. and 573° ; G. N. Antonoff made the double compound of magnesium chloride with hydroxylamine, **magnesium hydroxylamine chloride**, $\text{MgCl}_2 \cdot 2\text{NH}_2\text{OH} \cdot 2\text{H}_2\text{O}$. H. Niggemann found that when a mixture of air and ammonia was passed into a soln. of 50 grms. of hexahydrated magnesium chloride in 50 c.c. of water at 90° , a precipitate of magnesium hydroxide appeared in about 15 mins. The soln. still contained 40.5 grms. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ when sat. with ammonia. A mixture of ammonia and carbon dioxide gave an immediate precipitation of magnesium carbonate. G. Spacu made complex salts of magnesium chloride with pyridine and triethylene diammine.

The ready hydrolysis of magnesium chloride soln., as in the case of soln. of beryllium chloride, has led to the production of a number of basic chlorides or **magnesium oxychlorides**. The arguments for the individuality of these products have been based on chemical analyses and are not therefore satisfactory in the light of our present knowledge.¹⁴ The crystalline precipitate, deposited by ammoniacal soln. of magnesium chloride, after washing with water gave G. E. Davis numbers in agreement with $5\text{MgO} \cdot \text{MgCl}_2 \cdot 13\text{H}_2\text{O}$; G. Krause obtained a product $10\text{MgO} \cdot \text{MgCl}_2 \cdot 18\text{H}_2\text{O}$; and C. Bender, $5\text{MgO} \cdot \text{MgCl}_2 \cdot x\text{H}_2\text{O}$, and $9\text{MgCl}_2 \cdot x\text{H}_2\text{O}$. G. André found that needle-like crystals of a product $\text{MgO} \cdot \text{MgCl}_2 \cdot 16\text{H}_2\text{O}$ separate when a boiling soln. of 400 grms. of hexahydrated magnesium chloride and 20 grms. of magnesium oxide in 500 grms. of water is filtered, and allowed to stand 24 hrs. When the crystals are dried in vacuo, they have the composition $\text{MgO} \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$. The crystals are decomposed by water and alcohol. The product $\text{MgO} \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$ can be resymbolized $\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2$, or $\text{Mg}(\text{OH})\text{Cl}$, thus recalling W. Moldenhauer's intermediate product in the action of steam on magnesium chloride between 350° and 500° . The product $\text{MgO} \cdot \text{MgCl}_2$ prepared by calcining to 300° an intimate mixture of eq. proportions of magnesium oxide and ammonium magnesium chloride, can also be symbolized $\text{Cl}-\text{Mg}-\text{O}-\text{Mg}-\text{Cl}$. G. André calculates the heats of formation ($\text{MgO} \cdot \text{MgCl}_2$) to be 7.72 Cals.; ($\text{MgO} \cdot \text{MgCl}_2 + 6\text{H}_2\text{O}_{\text{solid}}$), 1.68 Cals.; ($\text{MgO} \cdot \text{MgCl}_2 + 16\text{H}_2\text{O}$), 1.58 Cals.; and ($\text{MgCl}_2 + \text{Mg}(\text{OH})_2 + 6\text{H}_2\text{O}_{\text{liquid}}$), 13.7 Cals. A mol. of the product $\text{MgO} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ dissolves at 9° in dil. hydrochloric acid containing two mols. of HCl, with the evolution of 18 Cals.; and under the same conditions, $\text{MgO} \cdot \text{MgCl}_2 \cdot 16\text{H}_2\text{O}$ develops 11 Cals. Since the magnesium oxychlorides are decomposed by washing preparatory to the analysis, and if not washed, they will be contaminated with mother liquid, W. O. Robinson and W. H. Waggaman attempted to determine the composition of the basic chlorides, and the ranges of

conc. of the soln. over which they can exist, by studying *the solubility of magnesium hydroxide in solutions of magnesium chloride* of different conc. The percentage amounts of magnesium oxide present in soln. of magnesium chloride at 25°, are as follows :

Per cent. MgCl .	2.36	6.79	13.14	22.04	28.34	30.04	34.22
MgO .	0.00008	0.00048	0.00115	0.00245	0.00230	0.00250	0.0030

The detailed results show that at 25°, up to a conc. of about 10 grms. MgCl₂ per 100 c.c. of soln., the solid is an indefinite solid soln. of magnesium oxide and chloride, and water, and from that conc. up to a sat. soln. of magnesium chloride, the solid phase is a basic magnesium chloride 2MgO.HCl.5H₂O, that is, 3MgO.MgCl₂.11H₂O, or still differently expressed :

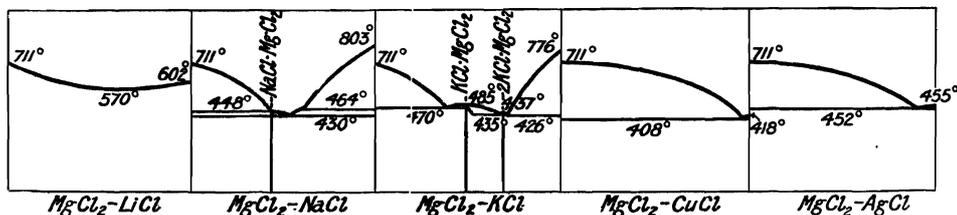


The so-called *Sorel's magnesia cement* was described by E. Sorel¹⁵ in 1867, and it is made by mixing calcined magnesia with an aq. soln. of magnesium chloride of sp. gr. 1.16 to 1.26. A mixture of finely powdered, dry, calcined magnesite and dry magnesium chloride—which can be preserved in sealed tin vessels—furnishes the same result when mixed with water. The two substances apparently unite with the development of heat, forming what is presumably a magnesium oxychloride, and A. Krieger, E. Luhmann, and L. Preussner have shown that the resulting cement is a mass of minute interlacing crystals. It is supposed that the magnesium chloride and oxide react in soln., forming a supersat. soln. of oxychloride from which crystals are deposited as in the setting of plaster of Paris. Various formulæ have been assigned to the oxychloride. Taking the mol. ratio MgCl₂ : MgO : H₂O, C. Bender gave 1 : 5 : 17 ; G. E. Davis, 1 : 5 : 13 ; and G. Krause 1 : 10 : 14 when dried at 110° and 1 : 10 : 18 when air-dried. The cement is used for cementing glass and metal, and for making artificial stones, etc.—*e.g.* the so-called *xyolith* is a mixture of sawdust, cement, and water. Several methods of preparing the mixture have been patented—*e.g.* by O. Kraner, F. M. Lyte and J. G. Tatters, etc. F. M. Lyte and J. G. Tatters heated to 300° an intimate mixture of ammonium magnesium chloride, NH₄Cl.MgCl₂, with one-fifth of its weight of magnesium oxide ; the residue contained a little less magnesium oxide than corresponded with the formula MgO.MgCl₂. A great many modifications have been patented with calcium or barium compounds as accessory constituents, and with starch, gelatinous silica, etc., admixed with the soln. of magnesium chloride. Prolonged treatment of the cement with boiling water dissolves magnesium chloride leaving behind hard magnesium oxide. M. Y. Seaton and co-workers have discussed the action of free lime on the cement.

In 1789, A. F. de Fourcroy¹⁶ showed that ammonium magnesium chloride could be crystallized from a mixed soln. of the component salts ; and K. von Hauer purified the salt by crystallization. The analyses corresponded with the formula for **hexahydrated ammonium magnesium chloride**, NH₄Cl.MgCl₂.6H₂O, or *hexahydrated ammonium trichloro-magnesiate*, NH₄MgCl₃.6H₂O ; also called *ammonium carnallite*. C. H. Pfaff obtained crystals of the same salt by evaporating the filtrate from the precipitate obtained by treating a soln. of magnesium chloride with an excess of ammonia ; and O. Hautz, by similarly treating the liquid remaining after shaking magnesium oxide with a cold aq. soln. of ammonium chloride. J. C. G. de Marignac found that the double pyramidal rhombic crystals have the axial ratios *a* : *b* : *c* = 1.0295 : 1.07220. Potassium and ammonium carnallites form solid soln. with one another. C. H. D. Bödeker's value for the sp. gr. is 1.456. O. Hautz found the salt loses 10.9 per cent. of water at 100°, and 31.15 per cent. (4H₂O) at 135°. The crystals are deliquescent and melt when heated, losing first water, and then ammonium chloride ; finally, magnesium chloride alone remains. The salt is sparingly soluble in water ; and the electrical conductivity of aq. soln. has been investigated by H. C. Jones and N. Knight. M. Berthelot and G. André reported a crystalline salt, 2NH₄Cl.5MgCl₂.33H₂O ; and G. Linck, 2NH₄Cl.3MgCl₂.20H₂O.

C. Sandonnini¹⁷ found that lithium and magnesium chlorides form solid soln. in all proportions, and that these are stable at low temp. The f.p. curve, Fig. 12, shows a minimum with about 40 molar per cent. MgCl₂, at 570°. O. Menge obtained the results shown in Fig. 13, for the f.p. curve of the binary mixtures indicated. A

mixture of sodium and magnesium chlorides has a eutectic at 430° and 55 per cent. of NaCl, and two breaks, one corresponding with sodium magnesium trichloride, $\text{NaCl}\cdot\text{MgCl}_2$, and the other with a compound of uncertain composition. K. Scholich also obtained the two compounds $\text{NaCl}\cdot\text{MgCl}_2$ and $2\text{NaCl}\cdot\text{MgCl}_2$. There is some doubt about the existence of the hydrated sodium magnesium trichloride, $\text{NaCl}\cdot\text{MgCl}_2\cdot x\text{H}_2\text{O}$. A. B. Poggiale, and A. de Schulten mention this salt, but C. J. B. Karsten, A. J. Balard, and J. N. von Fuchs were unable to dissolve sodium chloride in a soln. of magnesium chloride; and they found that on cooling a boiling sat. soln. of the two salts, crystals of sodium chloride alone separated out. C. Schröder obtained only mixtures of the component salts by passing hydrogen chloride into soln. of magnesium chloride with sodium or potassium chloride.



FIGS. 12 TO 16.—Freezing-point Curves of Binary Systems of Magnesium Chloride with Lithium, Sodium, Potassium, Cuprous, and Silver Chlorides.

O. Menge found the f.p. curve of mixtures of magnesium and potassium chlorides has two maxima, Fig. 14, at 485° and 437° corresponding respectively with the m.p. of potassium magnesium trichloride, $\text{KCl}\cdot\text{MgCl}_2$, and potassium magnesium tetrachloride, $2\text{KCl}\cdot\text{MgCl}_2$. The existence of these compounds was confirmed by a microscopic examination of the products. J. Valentin obtained only $\text{MgCl}_2\cdot\text{KCl}$ on the f.p. curve, and K. Scholich could confirm only the same compound; he studied the ternary system MgCl_2 - KCl - NaCl . The solubility of magnesium chloride in soln. of potassium chloride was measured by H. Precht and B. Wittjen, J. H. van't Hoff and W. Meyerhoffer, W. Feit and C. Przibylla, and W. B. Lee and A. C. Egerton. W. B. Lee and A. C. Egerton studied the ternary system KCl - MgCl_2 - H_2O at 25° . Hexahydrated **potassium magnesium trichloride**, $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, or hexahydrated *potassium trichloro-magnesiote*, $\text{KMgCl}_3\cdot 6\text{H}_2\text{O}$, occurs in the Stassfurt and other salt deposits. H. Rose¹⁸ identified the mineral in the Stassfurt deposits with the double salt which J. von Liebig had found to be deposited from the mother liquors of the brines from the Salzhausem during a winter's cold, and which A. Marcet had previously obtained from the mother liquors in the evaporation of sea-water. In order to indicate that the double salt occurs as a mineral species, H. Rose named it **carnallite**, in honour of R. von Carnall. C. F. Rammelsberg thought that the double salt deposited from mixed soln. of the component salts belonged to the hexagonal system, but J. C. G. de Marignac, and A. des Cloizeaux showed that the artificial, and A. des Cloizeaux, F. Hesseberg, and C. Busz that the natural, crystals belong to the rhombic system, and have axial ratios $a : b : c = 0.59304 : 1 : 0.69758$. F. Bischof's value for the sp. gr. of natural carnallite is 1.615; E. Reichardt's, 1.60; and C. Przibylla's, as a mean of eleven determinations at 19.4° (water at 4° unity), with the weighings reduced to those in vacuo, 1.6018. H. H. Kunze studied the sp. gr. and the m.p. of mixtures of carnallite and potassium chloride. J. H. van't Hoff and W. Meyerhoffer found the m.p. in a sealed tube to be 265° . The double refraction is strong and positive; and C. Busz found the indices of refraction in sodium light to be $\alpha = 1.46658$; $\beta = 1.47529$; $\gamma = 1.49371$. According to F. Beijerinck, carnallite is a non-conductor of electricity. F. Rüdorff examined the diffusion of soln. of carnallite; and H. H. Kunze, H. C. Jones and N. Knight their electrical conductivity.

J. von Liebig¹⁹ noticed that the crystals of carnallite deliquesce and then

decompose on exposure to air leaving a residue of potassium chloride, and magnesium chloride in soln.; and A. Marcet, that alcohol extracts magnesium chloride leaving behind potassium chloride. Carnallite is thus partly decomposed in contact with a little water; at 25° about 85 per cent. is decomposed in agreement with the symbols: $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + 7 \cdot 8\text{H}_2\text{O} = 0 \cdot 84\text{KCl} + (\text{MgCl}_2, 0 \cdot 16\text{KCl}, 13 \cdot 8\text{H}_2\text{O})$, where the bracketed term represents the composition of the soln. At temp. below -21°, carnallite cannot exist in contact with its soln., for it forms potassium chloride and dodecahydrated magnesium chloride; at that temp. there is a reversible reaction $\text{KCl} + \text{MgCl}_2 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + 6\text{H}_2\text{O}$; the upper temp. limit for carnallite is 167·5°. This limiting temp. is reduced to 152·5° if magnesium chloride be present. The solubility curve *AB* of mixtures of $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ and KCl , is shown diagram-

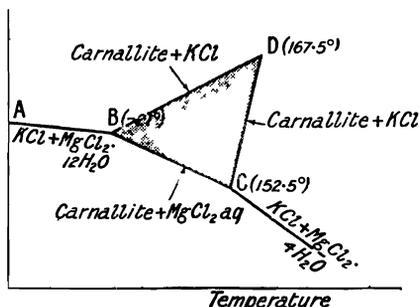


FIG. 17.—Diagrammatic Representation of the Region of Existence of Carnallite.

mat-ically in Fig. 17; it extends from the eutectic temp. up to *B*, -21°, the temp. at which carnallite is formed, when two solubility curves *BC* and *BD* appear—the one curve, *BC*, represents sat. soln. of carnallite in the presence of hydrated magnesium chloride—the particular hydrate depending on the temp.; the other curve, *BD*, sat. soln. of carnallite in the presence of potassium chloride. The curve *BC* ends at *C*, 152·5°, the upper limiting temp. for the existence of carnallite in the presence of magnesium chloride—at this temp., $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$; while the curve *BD* ends at *D*, 167·5°, where the sat. soln. has magnesium chloride and water in the same proportion as carnallite. The curve *DC* represents sat. soln. of carnallite and potassium chloride with less and less water than is represented by the formula of carnallite. These three curves enclose a region *BCD* within which carnallite can exist in contact with the soln. indicated. The equilibrium conditions of potassium and magnesium chloride are more precisely indicated by the diagram in connection with the chapter on the Stassfurt deposits (*vide* potassium).

W. Feit and K. Kubierschky,²⁰ and H. Erdmann, crystallized *rubidium carnallite*, or **rubidium magnesium chloride**, $\text{RbCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, from a mixed conc. soln. of the constituent salts, and measured the mutual solubility of rubidium and magnesium chlorides. Unlike carnallite, rubidium carnallite is decomposed neither by cold nor by hot water. H. L. Wells and G. F. Campbell also prepared colourless rectangular plates or flat prisms of *cæsium carnallite*, or **cæsium magnesium chloride**, $\text{CsCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, by crystallization from soln. of its component salts. Double salts of a different composition were not obtained by varying the proportions of the component salts. O. Menge found that magnesium chloride forms a simple eutectiferous series with cuprous or silver chloride, Figs. 15 and 16, and from E. Chauvenet, P. Job, and G. Urbain's examination of the thermal effects attending the admixture of soln., they inferred that the double salts **cupric trimagnesium decachloride**, $2\text{CuCl}_2 \cdot 3\text{MgCl}_2$, and **cupric dimagnesium decachloride**, $3\text{CuCl}_2 \cdot 2\text{MgCl}_2$, exist in soln.

According to O. Menge, mixtures of calcium and magnesium chlorides furnish a simple V-eutectic at 621° and 42·8 per cent. of calcium chloride. Solid soln. appear at the calcium chloride end of the series. C. Sandonini²¹ observed no solid soln. with mixtures of strontium and magnesium chlorides, but there is a eutectic at 535°, and 50 molar per cent. of strontium chloride. With mixtures of magnesium and barium chlorides, there is a eutectic at 556° and 36 molar per cent. of barium chloride; and with greater proportions of the latter salt, there is an arrest in the cooling curve at 590°, and at the eutectic, 556°; only the upper arrest occurs with more barium chloride, and when still more is added the upper arrest is lowered

down to that of the eutectic. This phenomenon is taken to indicate the production of a compound of barium and magnesium chlorides which decomposes on fusion.

In 1856, C. F. Rammelsberg found a mineral in the Stassfurt salts whose analysis corresponded with **calcium dimagnesium chloride**, $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, or $\text{Ca}(\text{MgCl}_3)_2 \cdot 12\text{H}_2\text{O}$, and he named it *tachhydrite*, and afterwards (1860) abbreviated it to tachydrite—from $\tau\alpha\chi\upsilon\varsigma$, rapid; $\upsilon\delta\omega\upsilon\varsigma$, water—in reference to its great hygroscopicity. The relation of tachydrite to carnallite is evident by doubling the formula of the latter; thus, carnallite, $\text{K}_2(\text{MgCl}_3)_2 \cdot 12\text{H}_2\text{O}$; tachydrite, $\text{Ca}(\text{MgCl}_3)_2 \cdot 12\text{H}_2\text{O}$, where the two univalent atoms of potassium replace the bivalent atom of calcium. A. de Schulten made artificial crystals of this salt by concentrating a mixed aq. soln. of 200 grms. of anhydrous calcium chloride and 150 grms. of hexahydrated magnesium chloride on a water-bath until the liquid crystallized on cooling. A. des Cloizeaux showed that the crystals are rhombohedral (hexagonal); and, according to P. Groth, they have the axial ratio $a : c = 1 : 1.900$. F. Bischof's value for the sp. gr. is 1.671; E. Erdmann's, 1.867; and J. H. van't Hoff's value is 1.6655, the mean of 1.6634 and 1.6683. R. Görgey, and H. E. Boeke give the hardness 1 to 2—that of gypsum. A. des Cloizeaux says the double refraction is negative, and the mean refractive index, according to R. Görgey, is 1.52. The salt is soluble in water—100 parts of water at 18.75° dissolve 160.3 parts of the salt. J. H. van't Hoff found the mol. ht. of soln. to be 23.55 Cals., and in the formation of a gram of tachydrite 33.82 Cals. are absorbed. F. Bischof found the temp. rises from 18.75° to 26.5° when 20 parts of tachydrite are dissolved in 80 of water.

The conditions of equilibrium have been largely determined by J. H. van't Hoff and his co-workers.²² Below 22° a soln. of tachydrite decomposes into its component salts, so A. de Schulten's soln. furnishes tachydrite, provided the temp. is over 22° . At this temp. there is the balanced reaction: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} + 2(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}) = \text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O} + 6\text{H}_2\text{O}$. The temp. of formation is raised 0.017° per atm.

increase of press. At temp. exceeding 168° tachydrite partially melts and decomposes. The conditions of equilibrium are represented graphically by J. H. van't Hoff's diagram, Fig. 18. The curve CA is the sat. curve of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; C is at 16.7° ; A , the formation temp. of tachydrite, is at 21.95° . The curve AN is the sat. curve of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and tachydrite; the curve ends at N , the transformation temp. of $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$. The curve AB likewise represents the sat. curve of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and tachydrite; and BM , of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ and tachydrite; B , 25° is the transformation temp. of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ into $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$. The curve BG is the sat. curve of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$; the curve HI is the sat. curve of magnesium chloride alone— $H = 16.7^\circ$, $I = 32^\circ$; the curve KG and GL represents the sat. curve of calcium chloride alone and at G , 29.44° , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ passes into $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$. The region $MBAN$ is sat. with tachydrite; $LGBM$, with $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$; $HCANI$, with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; and $KCABG$, with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Lines represent soln. sat. by the salts indicated by the adjoining regions; and points represent soln. sat. by the salts of the adjacent regions. The

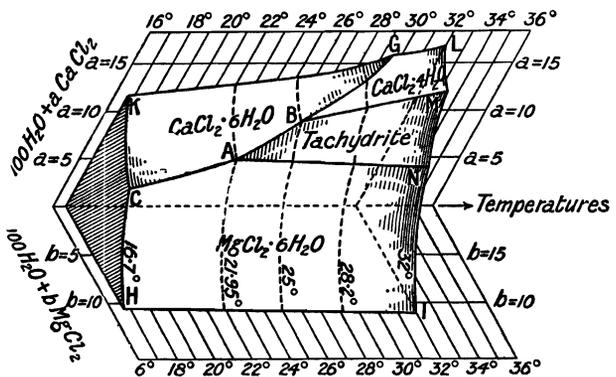


FIG. 18.—Equilibrium Curves for the System $\text{CaCl}_2\text{—MgCl}_2\text{—H}_2\text{O}$, after J. H. van't Hoff.

temp., 116.67° , of the transformation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ into $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ is not much affected by the presence of tachydrite, but the temp. of the transformation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ into $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ is lowered by the presence of tachydrite from 29.2° to 25° . The ternary system $\text{MgCl}_2\text{—CaCl}_2\text{—H}_2\text{O}$ at 25° was studied by W. B. Lee and A. C. Egerton. J. Valentin obtained potassium barium tetrachloride, $2\text{KCl} \cdot \text{BaCl}_2$, on the f.p. curve; and studied the ternary system $\text{BaCl}_2\text{—KCl—MgCl}_2$.

REFERENCES.

- ¹ T. Monticelli and N. Covelli, *Prodromo della mineralogia Vesuviana*, Napoli, 1825; L. Pilla, *Lo Spettatore del Vesuviana*, Napoli, 1835; A. Scacchi, *Memoria sullo incendio Vesuviano nel mese di maggio*, Napoli, 182, 1855; *Atti Acad. Napoli*, 6, 43, 1875; F. Zambonini, *Mineralogia Vesuviana*, Leipzig, 1910; C. Ochsensius, *Die Bildung der Steinsalzlager*, Halle, 1877.
- ² J. L. Gay Lussac and L. J. Thénard, *Recherches physico-chimiques*, Paris, 2, 143, 1811; R. Weber, *Pogg. Ann.*, 112, 619, 1861; A. A. B. Bussy, *ib.*, 18, 140, 1830; *Journ. Chim. Méd.*, 6, 142, 1830; R. Bunsen, *Liebigs Ann.*, 82, 137, 1852; H. St. C. Deville and H. Caron, *Compt. Rend.*, 44, 394, 1857; *Ann. Chim. Phys.*, (3), 67, 340, 1863; E. Sonstadt, *Chem. News*, 7, 294, 1863; 8, 4, 1863; J. J. Berzelius, *Schweigger's Journ.*, 31, 258, 1821; J. W. Döbereiner, *ib.*, 28, 90, 1820; L. Michels, *Zeit. Ver. deut. Ing.*, 19, 320, 1868; E. Solvay, *German Pat.*, D.R.P. 51084, 1889; Salzbergwerk Neu-Stassfurt, *ib.*, 161662, 1903; R. Brandes, *Brandes' Archiv.*, 12, 195, 1837; H. Grimshaw, *Journ. Soc. Chim. Ind.*, 9, 472, 1890; K. S. Boynton, V. Langford, and J. F. G. Hicks, *Journ. Ind. Eng. Chem.*, 14, 146, 1922; C. Clerc and A. Nihoul, *Brit. Pat. No. 173502*, 1921; H. H. Dow and E. O. Barstow, *U.S. Pat. No. 1336425*, 1920; W. Heap and E. Newbery, *Brit. Pat. No. 130626*, 1918; H. J. Bull, *ib.*, 149670, 1920; H. Hof, *Chem. Ztg.*, 39, 470, 1915; J. B. A. Dumas, *Ann. Chim. Phys.*, (3), 55, 187, 1859; A. J. Balard, *Compt. Rend.*, 19, 699, 1844; V. M. Goldschmidt, *Brit. Pat. No. 161165*, 1921; H. H. Dow, *U.S. Pat. No. 1389546*, 1921; M. M. T. K. Kaisha, *Brit. Pat. No. 163304*, 1921; I. Namari and Y. Hiraoka, *Japan Pat. No. 37118*, 1920; F. P. Dunnington and F. W. Smither, *Amer. Chem. Journ.*, 19, 227, 1897; W. Hempel, *Ber.*, 21, 897, 1888; F. A. Gooch and F. M. McClenahan, *Amer. Journ. Science*, (4), 17, 365, 1904; J. A. Wanklyn and E. T. Chapman, *Journ. Chem. Soc.*, 19, 141, 1866; R. Cowper, *ib.*, 43, 153, 1883; T. W. Richards and H. G. Parker, *Proc. Amer. Acad.*, 32, 53, 1896; *Chem. News*, 75, 148, 158, 172, 183, 1897; P. S. Curie, *ib.*, 28, 307, 1873; De Nordske Saltverker, *Brit. Pat. No. 181375*, 1922; J. von Liebig, *Pogg. Ann.*, 19, 137, 1830.
- ³ L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, 2, 401, 1845; R. Görgey, *Tschermak's Mitt.*, (2), 29, 200, 1910; J. L. Gay Lussac and L. J. Thénard, *Recherches physico-chimiques*, Paris, 2, 143, 1911; T. Carnelley, *Journ. Chem. Soc.*, 33, 273, 1878; O. Menge, *Zeit. anorg. Chem.*, 72, 162, 1911; J. Thomsen, *Journ. prakt. Chem.*, (2), 11, 233, 402, 1875; (2), 12, 85, 271, 1875; (2), 16, 117, 1877; P. Sabatier, *Bull. Soc. Chim.*, (3), 1, 88, 1889; W. Hampe, *Chem. Ztg.*, 11, 816, 846, 904, 934, 1109, 1158, 1549, 1887; M. Berthelot and L. Ilosvay de N. Ilosvay, *Ann. Chim. Phys.*, (5), 29, 309, 1883; F. E. Bartell and L. B. Sims, *Journ. Amer. Chem. Soc.*, 44, 289, 1922; E. E. Somermeier, *Phys. Rev.*, (2), 1, 141, 1913; G. F. Hüttig, *Zeit. anorg. Chem.*, 115, 251, 1921; W. Biltz, *ib.*, 115, 241, 1921; H. St. C. Deville and H. Caron, *Compt. Rend.*, 44, 394, 1857.
- ⁴ H. Schulze, *Journ. prakt. Chem.*, (2), 21, 407, 1880; J. H. van't Hoff, *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen*, Leipzig, 1912; F. Haber and F. Fleischmann, *Zeit. anorg. Chem.*, 51, 336, 1907; W. Moldenhauer, *ib.*, 51, 369, 1907; F. Haber, *ib.*, 52, 127, 1907; K. von Falckenstein, *Zeit. Elektrochem.*, 12, 763, 1906; J. W. Döbereiner, *Arch. Pharm.*, (2), 13, 155, 1838; H. Kunheim, *Ueber Einwirkung des Wasserdampfes auf Chlormetalle bei hoher Temperatur*, Göttingen, 1861.
- ⁵ R. Engel, *Bull. Soc. Chim.*, (2), 47, 318, 1887; R. Lowenherz, *Zeit. phys. Chem.*, 13, 459, 1894; J. H. van't Hoff and H. M. Dawson, *ib.*, 22, 598, 1897; J. H. van't Hoff and W. Meyerhoffer, *ib.*, 27, 74, 1898; *Sitzber. Akad. Berlin*, 73, 1897; J. F. Casaseca, *Compt. Rend.*, 37, 350, 1853; A. Bogorodsky, *Journ. Russian Phys. Chem. Soc.*, 30, 735, 1898; *Bull. Soc. Chim.*, (3), 22, 918, 1899; J. C. G. de Marignac, *Ann. Mines*, (5), 9, 3, 1856; C. Ochsensius, *Bull. Soc. Min.*, 1, 128, 1899; E. Filhol, *Ann. Chim. Phys.*, (3), 21, 415, 1822; H. Lescœur, *ib.*, (7), 2, 78, 1894; A. Ditte, *ib.*, (5), 22, 560, 1881; J. Dewar, *Chem. News*, 91, 216, 1905; F. A. Gooch and F. M. McClenahan, *Amer. Journ. Science*, (4), 17, 365, 1904; H. Hof, *Chem. Ztg.*, 39, 470, 1915; R. Brandes, *Brandes' Archiv.*, 12, 195, 1837; W. Müller-Erbach, *Wied. Ann.*, 27, 626, 1886; P. Bary, *Compt. Rend.*, 130, 776, 1900; H. Davy, *Phil. Trans.*, 101, 1, 1811; P. Sabatier, *Bull. Soc. Chim.*, (3), 11, 546, 1895; W. Moldenhauer, *Zeit. anorg. Chem.*, 51, 369, 1906; C. Przibylla, *Centr. Min.*, 238, 1904.
- ⁶ G. T. Gerlach, *Zeit. anal. Chem.*, 8, 281, 1896; A. C. Oudemans, *ib.*, 7, 419, 1868; H. T. Barnes and A. P. Scott, *Journ. Phys. Chem.*, 2, 536, 1898; G. J. W. Bremer, *Arch. Néerl.*, (2), 6, 455, 1902; *Rec. Trav. Chim. Pays-Bas*, 21, 59, 1902; D. I. Mendeléeff, *Journ. Russian Phys. Chem. Soc.*, 15, 184, 1884; N. A. Tschernay, *ib.*, 20, 486, 1888; 21, 126, 1890; P. Kremers, *Pogg. Ann.*, 104, 33, 1858; 105, 368, 1858; J. Wagner, *Zeit. phys. Chem.*, 5, 31, 1890; H. Schiff,

Liebig's *Ann.*, **108**, 326, 1859; **110**, 72, 1859; R. Engel, *Bull. Soc. Chim.*, (2), **47**, 318, 1887; J. H. Pollok, *Proc. Roy. Soc. Edin.*, **13**, 626, 1886; O. Pulvermacher, *Zeit. anorg. Chem.*, **113**, 142, 1920; F. E. Bartell and O. E. Madison, *Journ. Phys. Chem.*, **24**, 593, 1920; F. E. Bartell and L. B. Sims, *Journ. Amer. Chem. Soc.*, **44**, 289, 1922; G. J. W. Bremer, *Zeit. phys. Chem.*, **3**, 136, 1889; W. Biltz, *Zeit. anorg. Chem.*, **115**, 241, 1921; F. E. Bartell and D. C. Carpenter, *Journ. Phys. Chem.*, **27**, 101, 1923.

⁷ J. C. G. de Marignac, *Ann. Chim. Phys.*, (5), **8**, 410, 1876; G. Jäger, *Sitzber. Akad. Wien*, **99**, 245, 1890; W. Müller-Erzbach, *Wied. Ann.*, **27**, 623, 1886; H. C. Jones, *Amer. Chem. Journ.*, **23**, 89, 1900; J. H. van't Hoff and W. Meyerhoffer, *Sitzber. Akad. Berlin*, **140**, 1897; H. C. Jones and F. H. Getman, *Zeit. phys. Chem.*, **49**, 385, 1904; S. Skinner, *Journ. Chem. Soc.*, **61**, 339, 1892; E. M. Baker and V. H. Waite, *Chem. Met. Eng.*, **25**, 1137, 1921; U. Dührung, *Ber.*, **27**, 3028, 1894, and this work **1**, 9, 4.

⁸ P. Barbier and L. Roux, *Compt. Rend.*, **110**, 457, 527, 1890; *Bull. Soc. Chim.*, (3), **3**, 255, 419, 424, 1890; (3), **4**, 9, 614, 620, 1890; D. Dijken, *Zeit. phys. Chem.*, **24**, 81, 1897; O. Pulvermacher, *Zeit. anorg. Chem.*, **113**, 141, 1920.

⁹ S. Arrhenius, *Recherches sur la conductibilité galvanique des électrolytes*, Stockholm, 1883; *Zeit. phys. Chem.*, **9**, 339, 1892; H. C. Jones and A. P. West, *Amer. Chem. Journ.*, **34**, 357, 1905; H. C. Jones, *ib.*, **35**, 445, 1906; H. C. Jones and H. P. Basset, *ib.*, **33**, 534, 1905; H. C. Jones and J. N. Pearce, *ib.*, **38**, 696, 1907; G. Kümmell, *Zeit. Elektrochem.*, **11**, 94, 1905; S. von Laszczyński and S. von Gorsky, *ib.*, **4**, 290, 1897; W. Hittorf, *Pogg. Ann.*, **106**, 337, 513, 1859; W. Bien, *Zeit. phys. Chem.*, **27**, 1, 1898; A. Chassy, *Ann. Chim. Phys.*, (6), **21**, 241, 1890; B. D. Steele, *Phil. Trans.*, **198**, A, 105, 1902; *Journ. Chem. Soc.*, **79**, 414, 1902; K. Drücker, *Zeit. Elektrochem.*, **11**, 211, 1905; P. Walden, *Zeit. phys. Chem.*, **1**, 529, 1887; S. Meyer, *Wied. Ann.*, **69**, 236, 1899; H. C. Jones, *The Electrical Conductivity, Dissociation, and Temperature Coefficients of Conductivity of Aqueous Solutions of a Number of Salts and Organic Acids*, Washington, 1912; F. E. Bartell and D. C. Carpenter, *Journ. Phys. Chem.*, **27**, 101, 1923.

¹⁰ F. Margueritte, *Comp. Rend.*, **43**, 50, 1856; R. Engel, *ib.*, **104**, 433, 506, 1887; *Bull. Soc. Chim.*, (2), **47**, 497, 1887; A. Ditte, *Ann. Chim. Phys.*, (5), **22**, 561, 1881.

¹¹ C. J. B. Karsten, *Lehrbuch der Salinenkunde*, Berlin, 1846-7; H. Droeze, *Ber.*, **10**, 337, 1877; R. Löwenherz, *Zeit. phys. Chem.*, **13**, 479, 1894; J. H. van't Hoff, *Zur Bildung der ozeanischen Salzablagerungen*, Braunschweig, 1905-9; *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen insbesondere der Stassfurter Salzlagers*, Leipzig, 1912.

¹² S. E. Simon, *Journ. prakt. Chem.*, (2), **20**, 371, 1879; L. Kahlenberg and F. C. Kraushoff, *Journ. Amer. Chem. Soc.*, **30**, 1104, 1908.

¹³ W. S. Clark, *Liebig's Ann.*, **78**, 369, 1851; H. Niggemann, *Ges. Abhand. Kenntnis Kohle*, **1**, 289, 1917; W. Biltz and G. F. Hüttig, *Zeit. anorg. Chem.*, **119**, 115, 1921; F. Ephraim, *Ber.*, **45**, 1322, 1912; F. Isambert, *Compt. Rend.*, **66**, 1259, 1868; C. Matignon, *ib.*, **128**, 103, 1899; G. N. Antonoff, *Journ. Russ. Phys. Chem. Soc.*, **37**, 478, 1905; G. Spacu, *Bul. Soc. Stiinte Cluj*, **1**, 247, 1922; G. Spacu and R. Ripan, *ib.*, **1**, 267, 1922.

¹⁴ G. André, *Ann. Chim. Phys.*, (6), **3**, 79, 1884; G. E. Davis, *Chem. News*, **25**, 258, 1872; G. Krause, *Liebig's Ann.*, **165**, 38, 1873; C. Bender, *ib.*, **159**, 341, 1871; F. M. Lyte and J. G. Tatters, *Brit. Pat. No.* 11545, 1890; O. Kraner, *ib.*, 29654, 1890; M. Sorel, *Compt. Rend.*, **65**, 102, 1867; E. Luhmann, *Chem. Ztg.*, **25**, 345, 1901; A. Krieger, *ib.*, **34**, 246, 1910; L. Preussner, *Tonind. Ztg.*, **25**, 2115, 1902; W. O. Robinson and W. H. Waggaman, *Journ. Phys. Chem.*, **13**, 673, 1909; W. Moldenhauer, *Zeit. anorg. Chem.*, **51**, 369, 1906.

¹⁵ A. Krieger, *Chem. Ztg.*, **34**, 246, 1910; E. Luhmann, *ib.*, **25**, 345, 1901; E. Sorel, *Compt. Rend.*, **65**, 102, 1867; C. Bender, *Liebig's Ann.*, **159**, 341, 1871; G. Krause, *ib.*, **165**, 38, 1873; G. E. Davis, *Chem. News*, **25**, 258, 1872; O. Kraner, *German Pat.*, D.R.P. 143933, 1902; F. M. Lyte and J. G. Tatters, *ib.*, 56454, 1890; *Brit. Pat. No.* 11545, 1890; L. Preussner, *Tonind. Ztg.*, **25**, 2115, 1901; M. Y. Seaton, C. R. Hill, and L. C. Stewart, *Met. Chem. Eng.*, **25**, 270, 1921.

¹⁶ A. F. de Fourcroy, *Ann. Chim. Phys.*, (1), **2**, 278, 1789; M. Berthelot and G. André, *ib.*, (6), **11**, 306, 1887; K. von Hauer, *Journ. prakt. Chem.*, (1), **63**, 434, 1854; O. Hautz, *Liebig's Ann.*, **66**, 280, 1847; J. C. G. de Marignac, *Ann. Mines*, (5), **12**, 1, 1857; H. C. Jones and N. Knight, *Amer. Chem. Journ.*, **22**, 110, 1899; G. Linck, *Proc. Amer. Assoc.*, **235**, 1850; C. H. D. Bödeker, *Die Beziehungen zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen*, Leipzig, 1860; C. H. Pfaff, *Schweigger's Journ.*, **21**, 74, 1817.

¹⁷ C. Sandonini, *Atti Accad. Lincei*, (5), **22**, 1, 629, 1913; O. Menge, *Zeit. anorg. Chem.*, **72**, 162, 1911; K. Scholich, *Neues Jahrb. Min. B.B.*, **43**, 251, 1920; A. B. Poggiale, *Compt. Rend.*, **20**, 1180, 1845; A. de Schulten, *Bull. Soc. Chim.*, (3), **27**, 169, 1897; C. Schröder, *Liebig's Ann.*, **123**, 265, 1862; A. J. Balard, *Journ. prakt. Chem.*, (1), **35**, 331, 1845; H. Reinsch, *Neues Jahrb. Pharm.*, **18**, 306, 1862; C. J. B. Karsten, *Lehrbuch der Salinenkunde*, Berlin, **2**, 296, 1847; J. N. von Fuchs, *Kastner's Arch.*, **7**, 407, 1826; J. Valentin, *Compt. Rend.*, **175**, 1061, 1922; H. Precht and B. Wittjen, *Ber.*, **14**, 1667, 1881; W. Feit and C. Przibylla, *Zeit. Kalb.*, **3**, 393, 1909; W. B. Lee and A. C. Egerton, *Journ. Chem. Soc.*, **123**, 706, 1923; A. Marcet, *Phil. Trans.*, **112**, 448, 1822; J. H. van't Hoff and W. Meyerhoffer, *Zeit. phys. Chem.*, **30**, 64, 1899.

¹⁸ H. Rose, *Pogg. Ann.*, **98**, 161, 1856; C. F. Rammelsberg, *ib.*, **94**, 508, 1855; J. von Liebig, *Liebig's Ann.*, **33**, 5, 1840; J. C. G. de Marignac, *Ann. Mines*, (5), **12**, 1, 1857; A. des Cloizeaux, *ib.*, (6), **6**, 37, 1864; *Nouvelles recherches sur les propriétés optiques des cristaux*, Paris, 1867; H. H. Kunze, *Ueber schmelzflüssigen Karnallit*, Berlin, 1912; F. Hessenberg, *Minerologische Notizen*, Frankfurt, **7**, 14, 1866; C. Busz, *Neues Jahrb. Min.*, **1**, 192, 1907; F. Bischof, *Berg.*

Hütt. Ztg., **24**, 276, 1865; E. Reichardt, *Neues Jahrb. Min.*, 326, 1866; C. Busz, *ib.*, i, 192, 1907; F. Beijerinck, *Neues Jahrb. Min. B.B.*, **11**, 462, 1897; C. Przibylla, *Centr. Min.*, 236, 1904; J. H. van't Hoff and W. Meyerhoffer, *Sitzber. Akad. Berlin*, 487, 1897; *Zeit. phys. Chem.*, **30**, 84, 1899; F. Rüdorff, *Ber.*, **20**, 3044, 1888; H. C. Jones and N. Knight, *Amer. Chem. Journ.*, **22**, 110, 1899; A. Marcet, *Phil. Trans.*, **112**, 448, 1822.

¹⁹ J. von Liebig, *Liebig's Ann.*, **43**, 5, 1840; J. H. van't Hoff and W. Meyerhoffer, *Sitzber. Akad. Berlin*, 487, 1897; *Zeit. phys. Chem.*, **30**, 64, 1899; R. Löwenharz, *ib.*, **13**, 479, 1894; A. Marcet, *Phil. Trans.*, **112**, 448, 1822.

²⁰ W. Feit and K. Kubierschky, *Chem. Ztg.*, **16**, 335, 1892; H. Erdmann, *Arch. Pharm.*, **232**, 22, 1894; H. L. Wells and G. F. Campbell, *Amer. Journ. Science*, (4), **46**, 431, 1893; O. Menge, *Zeit. anorg. Chem.*, **72**, 162, 1911; E. Chauvenet, P. Job, and G. Urbain, *Compt. Rend.*, **171**, 855, 1920.

²¹ C. F. Rammelsberg, *Pogg. Ann.*, **98**, 261, 1856; *Handbuch der Mineralchemie*, Berlin, 1860; A. de Schulten, *Compt. Rend.*, **111**, 929, 1890; P. Groth, *Chemische Krystallographie*, Leipzig, **2**, 408, 1908; C. Sandonnini, *Atti Accad. Lincei*, (5), **21**, ii, 634, 1912; A. des Cloizeaux, *Nouvelles recherches sur les propriétés optiques des cristaux*, Paris, 1867; R. Görggey, *Tschermak's Mitt.*, (2), **29**, 198, 1909; F. Bischof, *Berg. Hütt. Ztg.*, **24**, 276, 1865; E. Erdmann, *Deutschlands Kalibergbau*, Berlin, **22**, 1907; H. E. Boeke, *Uebersicht der Mineralogie des Kalisalzlagertätten*, Berlin, **25**, 1909; J. H. van't Hoff, *Zeit. phys. Chem.*, **39**, 53, 1902; F. Bischof, *Die Steinsalzwerke bei Stassfurt*, Halle, 1864; J. Valentin, *Compt. Rend.*, **175**, 1061, 1922; A. de Schulten, *ib.*, **111**, 929, 1890.

²² J. H. van't Hoff and F. B. Kenrick, *Sitzber. Akad. Berlin*, 508, 1897; J. H. van't Hoff and H. M. Dawson, *ib.*, 557, 1889; J. H. van't Hoff and L. Lichtenstein, *ib.*, 232, 1905; J. H. van't Hoff and J. d'Ans, *ib.*, 913, 1905; J. H. van't Hoff, *Zeit. anorg. Chem.*, **47**, 244, 1905; *Untersuchungen über die Bildungsverhältnisse der ozeanischer Salzablagerungen insbesondere des Stassfurter Salzlagert*, Leipzig, 1912; W. B. Lee and A. C. Egerton, *Journ. Chem. Soc.*, **123**, 706, 1923; A. de Schulten, *Compt. Rend.*, **111**, 929, 1890.

§ 9. Magnesium Bromide

Magnesium bromide occurs in soln. in sea-water and brine springs. It has been reported in the Stassfurt salts, and A. J. Balard¹ extracted magnesium bromide from sea-water in 1826, and from kelp salts. The waters of the Dead Sea are particularly rich in magnesium bromide.

Bromine water slowly attacks magnesium with the evolution of hydrogen, but, according to J. A. Wanklyn and E. T. Chapman, dry liquid bromine had no perceptible action on magnesium after a year's contact. Magnesium burns in bromine vapour forming magnesium bromide, but, says R. Bunsen, the combustion is not so vigorous as in chlorine. O. Lerch conducted bromine vapour over magnesium at a red heat, when the mass became incandescent; and if any metal remained unattacked it floated as small spheres on the surface of the specifically heavier bromide. H. Gautier and G. Charpy also made magnesium bromide by direct combination of the elements. C. Löwig, and G. S. Sérullas say that a part of the magnesium bromide is carried forward by the stream of bromine vapour mixed with carbon monoxide. C. F. Rammelsberg neutralized hydrobromic acid with magnesium oxide; F. Klein neutralized the acid liquid obtained from bromine water and phosphorus by *magnesia alba*; and O. Lerch treated magnesium and water with liquid bromine. The evaporation of the resulting soln. furnishes crystals of hexahydrated magnesium bromide, $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$. If the aq. soln. of magnesium bromide be mixed with ammonium bromide, and then evaporated to dryness, the resulting ammonium magnesium bromide gives anhydrous magnesium bromide when heated until the ammonium bromide is all expelled; otherwise, some hydrogen bromide escapes during the dehydration. O. Lerch also heated a mixture of the crystalline salt with ammonium bromide so as to prevent hydrolytic dissociation.

Anhydrous magnesium bromide, said G. S. Sérullas,² is a white crystalline non-volatile substance whose **crystals**, according to O. Lerch, resemble those of magnesium chloride. G. F. Hüttig gave 3.722 at 25°/4° for the **specific gravity** of anhydrous magnesium bromide, and W. Biltz, the mol. vol. as 49.48; and for the sp. gr., 3.72 at 25°/4°. The **melting point**, according to T. Carnelley, is 695°. W. Hampe found the molten mass to be a good conductor of electricity. M. Berthelot's value for the **heat of formation** is (Mg, Br₂) 140 Cals. nearly; and N. N. Beketoff's,

121.7 Cals. ; J. Thomsen's value for (Mg, Br₂, aq.) is 160.5 Cals. ; and N. N. Beketoff's value for (MgBr₂, aq.) 43.3 Cals.

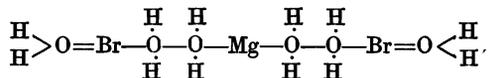
According to O. Lerch, magnesium bromide is not decomposed when heated to its m.p. provided air be excluded, but if oxygen be present, bromine is evolved and magnesium oxide is formed. When the solid or a conc. soln. is treated with conc. sulphuric acid, bromine is evolved, and, added C. Löwig, if a dil. soln. be distilled with sulphuric acid, hydrobromic acid is formed. O. Lerch said that anhydrous magnesium bromide deliquesces in air more rapidly than magnesium bromide, and that it dissolves in water with a hissing noise.

The **solubility** determinations of magnesium bromide have been made by B. N. Menshutkin,³ A. Étard, F. Mylius and R. Funk, and I. Panfiloff. A. Étard's results are considered to be too high, and where his data cross with those of F. Mylius and R. Funk, there is a difference of 7 to 8 per cent. The data of the latter agree with those of B. N. Menshutkin, whose results, expressed in grams of MgBr₂ per 100 grms. of soln., are as follows :

	-10°	0°	20°	40°	60°	80°	100°	120°	140°	160°
MgBr ₂ . . .	47.2	47.9	49.1	50.4	51.8	53.2	54.6	56.0	58.0	62.0

The solid phase over this range of temperature is **hexahydrated magnesium bromide**, MgBr₂.6H₂O, so that at ordinary temp. this salt crystallizes from aq. soln. The solubility of this salt is thus greater than that of the corresponding hexahydrated chloride. The equilibrium diagram has not yet been worked out. I. Panfiloff believes that at -12° there is a transition temp. below which decahydrated magnesium bromide, MgBr₂.10H₂O, is formed ; and he obtained crystals in thin plates by cooling 45-47.8 per cent. soln. of MgBr₂ to -18°, and drying them below 0° by press. between filter-paper. The crystals of the decahydrated salt melt between 11.5° and 12.5° with partial decomposition : MgBr₂.10H₂O ⇌ MgBr₂.6H₂O + 4H₂O.

Hexahydrated magnesium bromide forms transparent prisms and needles which, according to J. H. van't Hoff and H. M. Dawson, and H. E. Boeke, are isomorphous with those of the corresponding chloride ; the two salts form mixed crystals with one another. I. Panfiloff gives the **melting point** of hexahydrated magnesium bromide as 152° ; B. N. Menshutkin, 164° ; and F. Mylius and R. Funk, 165°. P. Bary found the salt to be fluorescent when exposed to Röntgen's or Becquerel's rays. H. Lesœur thought that his measurements of the vap. press. of the hexahydrate at different temp. corresponded with the formation of monohydrated *magnesium bromide*, MgBr₂.H₂O, but no other evidence is yet forthcoming of the existence of this salt. According to A. J. Balard, the crystals of hexahydrated magnesium bromide deliquesce in air, and when heated decompose into hydrogen bromide and magnesium oxide. J. L. Kreider showed, however, that approximately two of the six mols of the water may be removed from the hexahydrate between 70° and 160°, without any appreciable loss of hydrogen bromide ; any further loss of water, when the salt is heated in air, is attended by a loss of hydrogen bromide—an atm. of hydrogen bromide inhibits the loss of hydrogen bromide by the salt. J. L. Kreider accordingly argued that in the molecule of hexahydrated magnesium bromide two of the six mols of water are differently placed from the other four ; and he suggests the graphic formula :



There is yet no evidence of the formation of a tetrahydrated salt.

According to F. Mylius and R. Funk,⁴ a soln. sat. at 18° contains 103.4 grms. of MgBr₂ per 100 grms. of water—i.e. 50.8 per cent. of MgBr₂, or MgBr₂ + 9.9H₂O—and the **specific gravity** is 1.655 (18°). For the sp. gr. of aq. soln. of magnesium bromide at 19.5°, G. T. Gerlach calculated from P. Kremers' data :

Per cent. MgBr ₂ . . .	5	10	15	20	30	40	50
Sp. gr.	1.043	1.087	1.137	1.191	1.310	1.451	1.625

D. I. Mendeléeff also made observations on this subject. K. Jauch found the sp. ht. of soln. containing m eq. of magnesium bromide per litre, at 18° , to be

m	0.5	1.0	2.0	3.0	4.0
Sp. ht.	0.9441	0.8941	0.8068	0.7333	0.6688

H. C. Jones and F. H. Getman have investigated the **lowering of the freezing points** of soln.; while H. C. Jones and H. P. Basset have investigated the formation of hydrates in soln. from the lowering of the f.p., and the **electrical conductivities**. P. Walden measured the **equivalent conductivities** of aq. soln. H. C. Jones and co-workers found the mol conductivity, μ , and the percentage **degree of ionization**, α , of a soln. containing a mol of the salt in v litres, to be

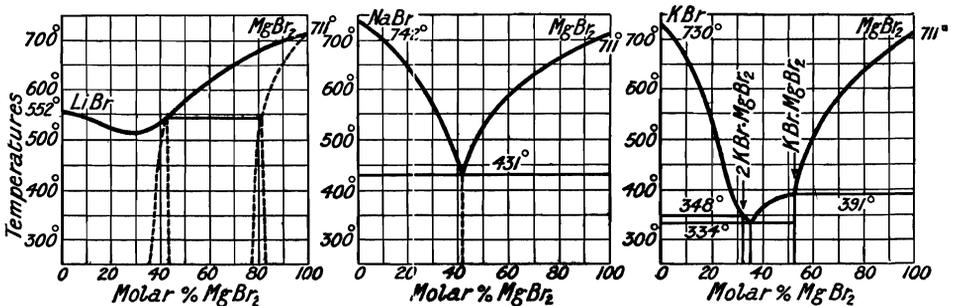
v	2	8	32	128	512	2048
μ_{0°	76.34	93.73	104.56	113.52	118.93	127.28
μ_{65°	—	324.4	367.7	412.8	445.5	471.3
α_{0°	59.3	71.6	79.9	86.8	90.9	97.3
α_{65°	—	68.8	78.0	87.6	94.5	100.0

They also measured the temp. coeff. of the conductivities. S. Meyer gave -0.449×10^{-6} units per grm. or -0.083 unit per mol for the **magnetic susceptibility** of anhydrous magnesium bromide.

Magnesium bromide is hydrolyzed by water in a manner analogous to magnesium chloride, and similar remarks apply to the formation of basic salts, or **magnesium oxybromides**. E. Tassilly,⁵ boiled a soln. of 145 grms. of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ in 300 c.c. of water, and added 5 grms. of magnesium oxide, prepared at a low temp., in small quantities at a time. The mixture was finally heated to about 150° , and filtered hot. In a few days, the soln., protected from the air, deposited needle-like crystals of $3\text{MgO} \cdot \text{MgBr}_2 \cdot 12\text{H}_2\text{O}$, which when heated to 120° in a stream of air, freed from carbon dioxide, gave crystals of $3\text{MgO} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$. This oxybromide is decomposed by water and alcohol.

W. Biltz and G. F. Hüttig,⁶ and G. Spacu and R. Ripan prepared **magnesium hexamminobromide**, $\text{Mg}(\text{NH}_3)_6\text{Br}_2$; and they found the heat of formation and the temp. at which the dissociation press. is 100 mm. to be respectively 20.1 Cals., and 559° for **magnesium diamminobromide**, $\text{Mg}(\text{NH}_3)_2\text{Br}_2$, and 21.7 Cals., and 606° for **magnesium amminobromide**, $\text{Mg}(\text{NH}_3)\text{Br}_2$. A. de Schulten prepared rhombic prisms of **ammonium magnesium bromide**, $\text{NH}_4\text{Br} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, or hexahydrated **ammonium tribromomagnesiante**, $\text{NH}_4\text{MgBr}_3 \cdot 6\text{H}_2\text{O}$, or **ammonium bromocarnallite** isomorphous with the corresponding potassium salt, $\text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, by evaporating an aq. soln. of 30 grms. of ammonium bromide, and 250 grms. of hexahydrated magnesium bromide over sulphuric acid. The rhombic (pseudo-tetragonal) crystals have the axial ratio $a : b = 1 : 1.0255$, and sp. gr. 1.989. The same crystals were made by O. Lerch. G. Kellner studied the binary systems of magnesium bromide with lithium, sodium, and potassium bromides. The products are isomorphous with the corresponding chlorides. No case of dimorphism was observed. The results are summarized in Figs. 19 to 21. Lithium bromide forms solid soln. of limited conc. Sodium and magnesium bromides form a simple eutectiferous series with the eutectic at 431° . Potassium and magnesium bromides form double salts—potassium magnesium tetrabromide, $2\text{KBr} \cdot \text{MgBr}_2$, and potassium magnesium tribromide, $\text{KBr} \cdot \text{MgBr}_2$, which decompose respectively at 348° and 391° , and there is a eutectic between them at 334° . Solid soln. are not formed. A. de Schulten made crystals of **hexahydrated potassium magnesium tribromide**, or **potassium tribromo-magnesiante**, $\text{KMgBr}_3 \cdot 6\text{H}_2\text{O}$, by a method similar to that employed for the ammonium salt. W. Feit first made the same salt by mixing a soln. of 12 grms. of magnesium bromide, sat. at ordinary temp. with a boiling sat. soln. of one grm. of potassium bromide. On cooling, crystals of the last-named salt separated out, but which on standing were transformed into the salt in question. On account of the analogy between this salt and carnallite, it has been called *bromocarnallite*. According to A. de Schulten, it forms transparent prisms belonging to the rhombic (pseudo-tetragonal)

system with axial ratio $a : b = 1 : 1.0255$; the sp. gr. is 2.134 (15°). The crystals of $2\text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, reported by C. Löwig, could not be made by A. de Schulten, O. Lerch, or W. Feit; they are thought to be a mixture of $\text{KBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ with some potassium bromide. H. E. Boeke has constructed the equilibrium diagram of potassium and magnesium chlorides and bromides in water at 25° . The mixed crystals of carnallite and bromocarnallite appear in three different modifications: (i) those with from 0 to 12.2 mol per cent. are rhombic pseudo-hexagonal, resembling carnallite; (ii) those with from 12.2 to 85 mols per cent. have the tetragonal form; and (iii) those with 85 to 100 mols per cent. are rhombic pseudo-tetragonal. H. L. Wells and G. F. Campbell made crystals of **caesium magnesium**



FIGS. 19 TO 21.—Freezing-point Curves of Binary Mixtures of Magnesium Bromide with Lithium, Sodium, and Potassium Bromides.

bromide, $\text{CsBr} \cdot \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, by a process similar to that used for the corresponding chloride; the general properties of the two salts were similar.

According to B. N. Menschutkin,⁷ magnesium bromide forms compounds $\text{MgBr}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ with methyl alcohol; $\text{MgBr}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ with ethyl alcohol; $\text{MgBr}_2 \cdot 6\text{C}_3\text{H}_7\text{OH}$ with propyl alcohol; $\text{MgBr}_2 \cdot 6(\text{CH}_3)_2\text{CH} \cdot \text{CH}_2\text{OH}$ with isobutyl alcohol; and $\text{MgBr}_2 \cdot 4(\text{CH}_3)_2\text{CHOH}$ in isopropyl alcohol. Similarly, with ether it forms $\text{MgBr}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$. He also made hexa-compounds with formic and acetic acids; and obtained compounds of magnesium bromide with aniline— $\text{MgBr}_2 \cdot 6\text{C}_6\text{H}_5\text{NH}_2$; $\text{MgBr}_2 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$; and $\text{MgBr}_2 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ or $\text{MgBr}_2 \cdot \text{C}_6\text{H}_5\text{NH}_2$. Magnesium bromide also forms compounds with phenyl hydrazine, etc. The solubility of these salts in the corresponding solvent was also investigated, and in general, the higher the alcohol in the series the smaller the solubility of the corresponding alcoholate.

REFERENCES.

- ¹ R. Bunsen, *Liebig's Ann.*, **82**, 137, 1852; F. Klein, *ib.*, **128**, 238, 1863; C. Löwig, *Das Brom, und seine chemischen Verbindungen*, Heidelberg, 1829; O. Lerch, *Journ. prakt. Chem.*, (2), **28**, 338, 1883; G. S. Sérullas, *Journ. Chim. Méd.*, **8**, 4, 1832; *Ann. Chim. Phys.*, (2), **43**, 87, 1831; A. J. Balard, *ib.*, (2), **32**, 337, 1826; C. F. Rammelsberg, *Pogg. Ann.*, **55**, 239, 1842; H. Gautier and G. Charpy, *Compt. Rend.*, **113**, 597, 1891; J. A. Wanklyn and E. T. Chapman, *Journ. Chem. Soc.*, **19**, 141, 1866; A. J. Balard, *Ann. Chim. Phys.*, (2), **32**, 337, 1826.
- ² T. Carnelley, *Journ. Chem. Soc.*, **33**, 273, 1878; W. Hampe, *Chem. Ztg.*, **11**, 316, 846, 904, 934, 1109, 1158, 1549, 1887; J. Thomsen, *Journ. prakt. Chem.*, (2), **16**, 97, 1877; H. Schulze, *ib.*, (2), **21**, 407, 1880; O. Lerch, *ib.*, (2), **28**, 338, 1883; M. Berthelot, *Ann. Chim. Phys.*, (5), **15**, 185, 1878; (2), **16**, 97, 1877; N. N. Beketoff, *Bull. Acad. St. Petersburg*, (2), **34**, 291, 1891; C. Löwig, *Das Brom, und seine chemischen Verbindungen*, Heidelberg, 1829; G. F. Hüttig, *Zeit. anorg. Chem.*, **115**, 251, 1921; W. Biltz, *ib.*, **115**, 241, 1921; G. S. Sérullas, *Journ. Chim. Méd.*, **8**, 4, 1832.
- ³ B. N. Menschutkin, *Zeit. anorg. Chem.*, **52**, 152, 1907; K. Jauch, *Zeit. Physik*, **4**, 441, 1920; J. H. van't Hoff and H. M. Dawson, *Zeit. phys. Chem.*, **22**, 598, 1897; J. L. Kreider, *Amer. Journ. Science*, (4), **20**, 97, 1905; F. Mylius and R. Funk, *Ber.*, **1718**, 1897; P. Bary, *Compt. Rend.*, **130**, 776, 1900; A. Étard, *Ann. Chim. Phys.*, (7), **2**, 541, 1894; A. J. Balard, *ib.*, (2), **32**, 337, 1826; I. Panfiloff, *Journ. Russ. Phys. Chem. Soc.*, **26**, 234, 1894; H. E. Boeke,

Sitzber. Akad. Berlin, 439, 1908; H. Lescœur, *Ann. Chim. Phys.*, (7), 4, 215, 1895; *Recherches sur la dissociation des hydrates salins et des composés analogues*, Lille, 1888.

⁴ F. Mylius and R. Funk, *Ber.*, 30, 1718, 1897; D. I. Mendeléeff, *Journ. Russ. Phys. Chem. Soc.*, 14, 184, 1884; K. Jauch, *Zeit. Physik*, 4, 441, 1921; P. Kremers, *Pogg. Ann.*, 108, 118, 1859; G. T. Gerlach, *Zeit. anal. Chem.*, 8, 285, 1869; H. C. Jones and H. P. Basset, *ib.*, 33, 534, 1905; H. C. Jones and F. H. Getman, *Zeit. phys. Chem.*, 49, 385, 1904; P. Walden, *ib.*, 1, 529, 1887; S. Meyer, *Wied. Ann.*, 69, 236, 1899; H. C. Jones, *The Electrical Conductivity, Dissociation, and Temperature Coefficients of Conductivity of Aqueous Solutions of a Number of Salts and Organic Acids*, Washington, 1912.

⁵ E. Tassilly, *Compt. Rend.*, 125, 605, 1897; *Ann. Chim. Phys.*, (7), 17, 69, 1899; *Bull. Soc. Chim.*, (3), 17, 964, 1897.

⁶ A. de Schulten, *Bull. Soc. Chim.*, (3), 17, 167, 1897; O. Lerch, *Journ. prakt. Chem.*, (2), 28, 338, 351, 1883; W. Feit, *ib.*, (2), 39, 373, 1889; C. Löwig, *Repert. Pharm.*, 29, 261, 1829; H. L. Wells and G. F. Campbell, *Amer. Journ. Science*, (4), 46, 431, 1893; F. Ephraim, *Ber.*, 45, 1322, 1912; W. Biltz and G. F. Hüttig, *Zeit. anorg. Chem.*, 119, 115, 1921; H. E. Boeke, *Zeit. Kryst.*, 45, 352, 1908; *Neues Jahrb. Min.*, i, 16, 1910; G. Kellner, *Zeit. anorg. Chem.*, 99, 137, 1917; *Die binären Systeme aus den Bromiden der Alkali- und Erdalkalimetalle*, Berlin, 1917; G. Spacu and R. Ripan, *Bul. Soc. Stiinta Cluj*, 1, 267, 1922.

⁷ B. N. Menschutkin, *Zeit. anorg. Chem.*, 49, 208, 1906; 52, 9, 152, 1906; *Bull. Polyt. Inst. St. Petersburg*, 3, 12, 29, 1905; 5, 293, 1906.

§ 10. Magnesium Iodide

Small traces of magnesium iodide have been reported in sea-water and in certain saline waters. For example, some mineral springs in Java contain magnesium iodide eq. to 0.012 grm. per litre, and iodine can be obtained from the water by the copper sulphate process. According to R. Bunsen,¹ magnesium burns vigorously in iodine vapour, forming anhydrous magnesium iodide, MgI_2 , but, according to T. L. Phipson, iodine may be distilled from magnesium without appreciable action; O. Lerch also found that magnesium does not react with iodine unless the metal is melted, and he recommends melting the metal in a vertical tube of hard glass, sealed at one end; when solid iodine is dropped on the molten metal, a vigorous reaction occurs with incandescence. Air should be excluded as much as possible or some magnesium oxide will be formed—globules of the unchanged magnesium float on the surface of the heavier iodide. F. Bodroux noted the action of iodine on magnesium in the presence of water; when water is dropped on a mixture of magnesium filings and iodine, the reaction is quite brilliant, and suited for a lecture experiment. O. Lerch made magnesium iodide by heating anhydrous magnesium chloride with ammonium iodide, when ammonium chloride volatilizes, and molten magnesium iodide remains; he obtained a similar result by heating ammonium magnesium iodide with an excess of ammonium iodide, first driving off the water at a relatively low temp. and afterwards subliming the ammonium iodide at a higher temp.

G. F. Hüttig gave 4.244 at $25^\circ/4^\circ$ for the **specific gravity** of anhydrous magnesium iodide, and W. Biltz gave 65.36 for the mol. vol. and 4.244 to 4.268 for the sp. gr. at $25^\circ/4^\circ$. According to O. Lerch, the **melting point** of anhydrous magnesium iodide lies above that of the corresponding bromide, as does magnesium bromide above the corresponding chloride. The crystals are snow white, but they are usually coloured by iodine, because, says O. Lerch, the anhydrous iodide is decomposed at ordinary temp. by atm. oxygen; and M. Berthelot converted the iodide completely into oxide by heating it in oxygen. The anhydrous iodide dissolves in water with a hissing noise, and O. Lerch found the salt is also soluble in alcohol, ether, and methyl iodide; and W. Eidmann says the hydrated salt is soluble in acetone. B. N. Menschutkin obtained a series of compounds of magnesium iodide with methyl and ethyl alcohols, ether, the alkyl esters, and acetic acid— $MgI_2 \cdot 6CH_3OH$; $MgI_2 \cdot 6C_2H_5OH$; $MgI_2 \cdot 2(C_2H_5)_2O$; etc.—analogous to those obtained with magnesium bromide. He also measured the solubilities of these compounds in the corresponding menstrua.

F. Faktor, and J. A. Wanklyn and E. T. Chapman noted that aq., alcoholic, and ethereal soln. of iodine act slowly on magnesium. According to I. Panfiloff,

if hydriodic acid be sat. with freshly precipitated magnesium hydroxide, at ordinary temp., crystals of the octohydrate are formed. O. Lerch found that if the soln. obtained by the joint action of iodine, water, and magnesium be decanted from the basic iodide, and slowly evaporated over sulphuric acid, the liquid becomes brown and furnishes crystals of octohydrated magnesium iodide, $MgI_2 \cdot 8H_2O$. This salt melts at 41° , according to I. Panfiloff; 45° , F. Mylius and R. Funk; 43.5° , B. N. Menshutkin. It effloresces over sulphuric acid, and deliquesces in air. B. N. Menshutkin showed that hexahydrated magnesium iodide, $MgI_2 \cdot 6H_2O$, is the stable form between 44° and upwards of 200° , and his data for the solubility of magnesium iodide in grms. of MgI_2 per 100 grms. of soln. are:

MgI_2	0°	20°	40°	43°	50°	90°	140°	160°	200°
Solid phase	$MgI_2 \cdot 8H_2O$			\rightleftharpoons	$MgI_2 \cdot 6H_2O$				
	50.0	53.4	57.8	59.4	61.6	62.1	62.5	63.0	64.1

The m.p. of the octohydrated salt is between 43° and 43.5° ; the hexahydrated salt does not melt in a sealed tube at 180° – 190° , but the walls of the tube begin to get a brown film; and above 200° – 210° , the salt decomposes. Consequently, the anhydrous iodide is not made by the dehydration of the hydrated salt. A comparison of the solubility curves of the three hexahydrated salts— $MgCl_2 \cdot 6H_2O$; $MgBr_2 \cdot 6H_2O$; and $MgI_2 \cdot 6H_2O$ —shows that in passing from the chloride to the iodide, as is frequently the case with the metal halides, the solubility increases. If an aq. soln. of a mol of MgI_2 in 10 mols of water be cooled to 8° , colourless six-sided crystalline plates of decahydrated magnesium iodide, $MgI_2 \cdot 10H_2O$, are formed which, after drying between filter paper at -4° to -5° , melt at 23° .

According to F. Mylius and R. Funk, a soln. sat. at 18° has a sp. gr. 1.909, and contains 59.7 per cent. of MgI_2 or 148 grms. of MgI_2 per 100 grms. of water. According to G. T. Gerlach, P. Kremers' data give for the sp. gr. of soln. at 19.5° :

Per cent. MgI_2	5	10	20	30	40	50	60
Sp. gr.	1.043	1.088	1.194	1.32	1.474	1.668	1.915

According to A. Heydweiller, the eq. electrical conductivity with 4, 0.5, and 0.05 gram-eq. per litre at 18° rises from 41.0 to 75.7, and to 94.6 respectively. Data for the **transport numbers** of the ions of magnesium iodide were obtained by W. Hittorf.

F. Ephraim,² and W. Biltz and G. F. Hüttig prepared **magnesium hexammino-iodide**, $Mg(NH_3)_6I_2$; and W. Biltz and G. F. Hüttig found that with **magnesium diammino-iodide**, $Mg(NH_3)_2I_2$, the heat of formation is 22.7 Cals.; and at 636° , the dissociation press. is 100 mm. O. Lerch, and A. de Schulten evaporated a soln. of 15 grms. of ammonium iodide and 125 grms. of hexahydrated magnesium iodide in vacuo over sulphuric acid, and obtained hygroscopic prismatic crystals of **ammonium magnesium iodide**, $NH_4I \cdot MgI_2 \cdot 6H_2O$. G. Spacu made complex salts of magnesium iodide with triethylenediammine and diethylenediammine. The corresponding **potassium magnesium iodide**, $KI \cdot MgI_2 \cdot 6H_2O$, was similar, and was prepared in a similar manner. The sp. gr. of the former was 2.346 (15°) and of the latter 2.547 (15°). The potassium salt has been called *iodocarnallite*, and the ammonium salt *iodo-ammonium carnallite*. H. E. Boeke found that carnallite does not form mixed crystals with iodocarnallite. **Magnesium iodo-chloride**, $MgCl_2 \cdot 2ICl_3 \cdot 8H_2O$, was made by E. Filhol by triturating conc. hydrochloric acid with magnesium iodate, and by saturating an aq. soln. of magnesium iodide with chlorine, or mixing iodine trichloride with magnesium chloride; and R. F. Weinland and F. Schlegelmilch, by the action of chlorine on a mixture of iodine and magnesium chloride in water. It forms yellow deliquescent needle-like crystals which resemble the potassium analogue: $KICl_4$ or $KCl \cdot ICl_3$. C. K. Tinkler obtained some evidence of the existence of *magnesium polyiodide* from the identity of the absorption spectra of soln. of magnesium iodide and iodine with the spectra of analogous soln. of cadmium, sodium, potassium, barium, zinc, and aluminium.

REFERENCES.

- ¹ R. Bunsen, *Liebig's Ann.*, **82**, 137, 1852; T. L. Phipson, *Proc. Roy. Soc.*, **13**, 217, 1864; *Chem. News*, **93**, 119, 1906; F. Faktor, *Pharm. Post*, **38**, 153, 1906; F. Bodroux, *Bull. Soc. Chim.*, (3), **27**, 349, 1902; W. Hittorf, *Pogg. Ann.*, **106**, 337, 513, 1859; G. F. Hüttig, *Zeit. anorg. Chem.*, **115**, 251, 1921; W. Biltz, *ib.*, **115**, 241, 1921; F. Mylius and R. Funk, *Ber.*, **30**, 1718, 1897; J. A. Wanklyn and E. T. Chapman, *Journ. Chem. Soc.*, **19**, 141, 1866; O. Lerch, *Journ. prakt. Chem.*, (2), **28**, 342, 1883; J. Thomsen, *ib.*, (2), **16**, 97, 1877; I. Panfiloff, *Journ. Russian Phys. Chem. Soc.*, **26**, 234, 1894; B. N. Menshutkin, *ib.*, **37**, 1166, 1906; *Zeit. anorg. Chem.*, **52**, 156, 1906; M. Berthelot, *Ann. Chim. Phys.*, (5), **15**, 185, 1878; (5), **16**, 442, 1878; N. N. Beketoff, *Bull. Akad. St. Petersburg*, (2), **34**, 291, 1891; W. Eidmann, *Ein Beitrag zur Erkenntnis des Verhaltens chemischer Verbindungen in nichtwässrigen Lösungen*, Giessen, 1899; A. Heydweiller, *Ann. Physik*, (4), **30**, 873, 1909; (4), **37**, 739, 1912; P. Kremers, *Pogg. Ann.*, **111**, 62, 1860; G. F. Gerlach, *Zeit. anal. Chem.*, **8**, 285, 1869; B. N. Menshutkin, *Zeit. anorg. Chem.*, **49**, 208, 1906; **52**, 9, 152, 1906; *Bull. Polyt. Inst. St. Petersburg*, **3**, 12, 29, 1905.
- ² A. de Schulten, *Bull. Soc. Chim.*, (3), **23**, 158, 1900; O. Lerch, *Journ. prakt. Chem.*, (2), **28**, 353, 1883; E. Filhol, *Journ. Pharm. Chim.*, **25**, 442, 1839; R. F. Weinland and F. Schlegelmilch, *Zeit. anorg. Chem.*, **30**, 141, 1902; W. Biltz and G. F. Hüttig, *ib.*, **119**, 115, 1921; F. Ephraim, *Ber.*, **45**, 1322, 1912; H. E. Boeke, *Zeit. Kryst.*, **45**, 352, 1908; *Neues Jahrb. Min.*, i, 16, 1910; C. K. Tinkler, *Journ. Chem. Soc.*, **91**, 996, 1907; G. Spacu, *Bul. Soc. Stiinte Cluj*, **1**, 247, 1922.

§ 11. Magnesium Sulphides

L. Kessler¹ made **magnesium sulphide**, MgS , by the action of hydrogen sulphide on red-hot magnesia, by heating a mixture of magnesium and sulphur, and by plunging burning magnesium in a jar of dry hydrogen sulphide; but F. G. Reichel found that magnesium does not readily combine with molten sulphur, although a little is formed if the sulphur be heated with carbon, or if the two elements be heated in a stream of hydrogen or hydrogen sulphide, and A. Mourlot also obtained the sulphide by heating a mixture of sulphur and magnesium filings in hydrogen; F. G. Reichel, and J. Parkinson, by passing the vapour of sulphur mixed with hydrogen over the red-hot metal. E. Tiede could not get magnesium sulphide prepared by this process free from magnesium by the sublimation of the metal in vacuo; but a highly purified product was obtained by boiling for 3 hrs. in a reflux condenser 10 grms. of the crude sulphide with 100 c.c. of ether freshly distilled from sodium, 10 grms. of ethyl iodide, and a fragment of iodine. Moisture must be excluded. The residue was washed with ether, and dried in a vacuum desiccator on a water-bath. E. Tiede and F. Richter made the anhydrous sulphide by heating the oxide in a current of nitrogen laden with the vapour of carbon disulphide. O. Schumann found very little magnesium sulphide is produced by passing hydrogen sulphide over red-hot magnesium oxide, but A. Mourlot observed a slow transformation by heating the oxide or sulphate at about 1200° in a stream of hydrogen sulphide. E. Tiede had no success by heating anhydrous magnesium sulphate for an hour at 1200° in a stream of hydrogen sulphide, although at 450° water and sulphur were formed. F. Briegleb and A. Geuther obtained the sulphide by the action of the same gas on magnesium nitride. E. Frémy prepared the sulphide mixed with a little polysulphide by passing the vapour of carbon disulphide over red-hot magnesium oxide, and F. G. Reichel found that some carbonyl sulphide is formed at the same time: $MgO + CS_2 = MgS + COS$, and if the vapour of carbon disulphide is mixed with carbon dioxide, some **magnesium oxysulphide**, $MgO.MgS$, is formed. According to A. Mourlot, the amorphous sulphide obtained by these methods is converted into the crystalline state by heating it for a few minutes in an electric arc-furnace; and he also obtained crystalline magnesium sulphide by heating a mixture of magnesium chloride and stannous sulphide in the electric arc-furnace. Magnesium sulphide is not obtained by heating the sulphate with carbon, hydrogen, hydrogen sulphide, ammonium sulphide or carbon monoxide. P. Berthier obtained but a small conversion of magnesium sulphate to sulphide by heating the sulphate with carbon, and A. Mourlot said that the conversion is incomplete in the electric arc-furnace.

The colour of the amorphous magnesium sulphide so far prepared varies from pale red to reddish-brown. E. Tiede's sample was reddish-white and amorphous. A. Mourlot stated that the **crystals** belonged to the cubic system. According to W. L. Bragg, the **X-radiogram** corresponds with a simple cubic lattice with the neighbouring atoms 2.54 Å. apart. S. Holgersson gave 5.078 ± 0.012 Å. The crystalline sulphide has a **specific gravity** 2.79–2.85 at 15°, while the amorphous sulphide has a sp. gr. 2.2 at 15°. P. Sabatier's value for the **heat of formation** ($\text{Mg, S}_{\text{solid}}$) = 79.6 Cals., and the heat of the reaction: ($\text{MgS, HCl}_{\text{dil. aq.}}$) = 21.80 Cals. at 13°. E. Tiede prepared a sample free from spectroscopic traces of alkaline earths, and from organic solvents, and when exposed for a few seconds to daylight or arc-light, it became faintly luminous. Less purified samples were more **phosphorescent**. Pure magnesium sulphide, say E. Tiede and F. Richter, is not phosphorescent, but it becomes so by suitable additions of manganese, bismuth, or antimony; the optimum amounts per gram of sulphide are 0.001–0.002 gm. of manganese chloride or sulphate; 0.0024 gm. of basic bismuth nitrate; or 0.0013 gm. of potassium antimonyl tartrate. E. Tiede and A. Schleede discussed the preparation and properties of phosphorescent magnesium sulphide. Magnesium sulphide is more sensitive to the rays of long wave-length. No excitation was observed with **X-rays, radium rays, or ultra-violet light**; but in the **cathode rays**, it gives a lively blue and red fluorescence, with a feeble after-glow.

The amorphous sulphide prepared by F. G. Reichel, and J. Parkinson developed hydrogen sulphide when exposed to moist **air**, and in contact with cold **water**, magnesium hydrosulphide, $\text{Mg}(\text{SH})_2$, is formed. According to E. Frémy, water dissolves magnesium sulphide very sparingly, and on standing hydrogen sulphide is evolved and magnesium hydroxide is precipitated; the action is rapid with warm water. According to A. Mourlot, water does not attack the crystalline sulphide in the cold, but when heated, magnesium oxide and hydrogen sulphide are formed. O. Schumann found that in superheated steam, magnesium sulphide is decomposed, furnishing hydrogen sulphide, sulphur, sulphur dioxide, and magnesium oxide. Magnesium sulphide is not changed by heating it in **hydrogen, coal gas, or carbon monoxide**, but if any polysulphide is present, the excess of sulphur was found by F. G. Reichel to be withdrawn.

According to A. Mourlot, **chlorine** reacts with crystalline magnesium sulphide at 300°, and the mass becomes incandescent with the formation of sulphur chloride and magnesium chloride; **bromine and iodine** act at dull redness in a similar way without incandescence. The crystalline sulphide is decomposed in the cold by **hydrogen fluoride and hydrogen chloride**; if warm, the mass becomes red hot. The **metalloid chlorides** react with the suitably heated crystalline sulphide, forming the corresponding oxide—the reaction is quite vigorous with **phosphorus trichloride** or with **arsenic trichloride**—**chromyl chloride** behaves similarly. The action of **oxygen** on the warm crystalline sulphide is quite vigorous and sulphur dioxide is formed; **oxidizing agents** also react vigorously with crystalline magnesium sulphide—even **phosphorus pentoxide** is reduced to phosphorus sulphide. F. G. Reichel found that when the vapour of **sulphur** mixed with hydrogen or hydrogen sulphide is passed over amorphous magnesium sulphide, no polysulphide is formed, nor does **carbon disulphide** unite with the sulphide. A. Mourlot found dil. or conc. **sulphuric acid** reacts with crystalline magnesium sulphide with the evolution of hydrogen sulphide; and with cold conc. **nitric acid**, sulphur is separated. The crystalline sulphide is not reduced by **phosphorus** at 1000°, and at a red heat, **boron** and **silicon** have no action. The crystalline sulphide is not reduced by **carbon** when heated for 15 mins. in the electric-arc furnace, no carbide is formed, and no volatilization is perceptible. H. C. Geelmuyden found that **calcium carbide** reduces magnesium sulphide in the electric-arc furnace, and the metal is volatilized. Crystalline magnesium sulphide is reduced by **sodium** without incandescence; but **iron** does not reduce it at a dull red heat. F. G. Reichel also found that if the amorphous sulphide is heated with iron or with **copper**, the

corresponding sulphide is formed, but he did not succeed in isolating magnesium. T. Petitjean has also studied these reactions.

V. Calcagni found 100 c.c. of a cold sat. soln. of magnesium hydroxide dissolved 0.014 grms of sulphur so that the relation is $Mg : S = 1 : 2$. The soln. responds to the reactions for sulphides, polysulphides, thiosulphates, and sulphites. According to F. G. Reichel, if magnesium sulphide be warmed with water and sulphur, not to the b.p., a dark yellow liquid is produced which presumably contains magnesium polysulphide. This liquid decomposes when exposed to the air, and gives off hydrogen sulphide, forming sulphur, magnesium hydroxide, and a trace of magnesium thiosulphate. The liquid is slowly decomposed when boiled, but more slowly than magnesium sulphide. The sulphides of antimony and arsenic dissolve in the liquid, but not so with the sulphide of mercury. J. Stingl and T. Morawsky prepared magnesium trisulphide, Mg_4S_3 , by the action of magnesium chloride on calcium polysulphide.

F. G. Reichel found that with cold water, amorphous magnesium sulphide furnishes magnesium hydrosulphide, $Mg(SH)_2$, thus: $2MgS + 2H_2O = Mg(OH)_2 + Mg(SH)_2$. According to J. J. Berzelius, and T. J. Pelouze finely divided magnesium hydroxide suspended in water is slowly but abundantly dissolved when hydrogen sulphide is passed through the liquid, and a soln. of magnesium hydrosulphide is formed. A. Béchamp, and L. Naudin and F. de Montholon, used magnesium carbonate; and E. Divers and T. Shimidzu prepared a soln. by suspending one part of freshly calcined magnesia in not less than ten parts of water. A stream of hydrogen sulphide is passed through the liquid, and the magnesia slowly passes into soln., although much gas passes away unabsorbed. If much more magnesia be added to the water, the resulting soln. of magnesium sulphide is not so conc. as if the proportion of magnesia be less. The soln. can be preserved unchanged by corking the flask and sealing the cork with wax or paraffin to exclude air; when exposed to air, an alkaline liquid is formed which contains magnesium acid carbonate as well as magnesium hydroxide. Magnesium hydrosulphide mixed with an alkali salt is obtained by mixing a soln. of a magnesium salt with an alkali hydrosulphide or barium hydrosulphide. F. Gerhard prepared a similar soln. by mixing magnesium sulphate with sodium sulphide or calcium sulphide; J. Thomsen, and A. Béchamp worked with a soln. of barium hydrosulphide.

J. J. Berzelius, and A. Béchamp, found that the soln. decomposes when an attempt is made to conc. it by evaporation in vacuo or in an atm. of hydrogen; F. G. Reichel found some thiosulphate is formed. Similarly, when the soln. of magnesium hydrosulphide is mixed with a conc. soln. of potassium hydrosulphide, or when a conc. aq. soln. of magnesium chloride is mixed with a conc. soln. of potassium hydrosulphide, hydrogen sulphide is given off. The soln. is also decomposed on boiling. According to E. Divers and T. Shimidzu, when the impurities have settled, the soln. is nearly colourless, and the slight yellow coloration is due to polysulphide formed by the action of ferric oxide in the magnesia, or of air. The polysulphide is decomposed by hydrogen sulphide and sulphur when the products are magnesium hydrosulphide and sulphur; and it is but slightly decomposed by boiling the liquid when the products are magnesium hydroxide, sulphur, and hydrogen sulphide. At 12° , a soln. of magnesium hydrosulphide with 16.31 per cent. of $Mg(SH)_2$ has a sp. gr. 1.118; the aq. soln., at 60° , develops a steady stream of hydrogen sulphide, and magnesium hydroxide is precipitated, and the evolution of gas can be maintained for a considerable time longer by raising the temp. to 90° – 100° . This is recommended by them as a source of arsenic-free hydrogen sulphide. The aq. soln. oxidizes on exposure to air, forming thiosulphate and polysulphide. "If the soln. be left at rest, oxidation is much impeded by the formation of a firm colourless transparent amorphous film on the surface of the liquid, consisting apparently of magnesium hydroxide, but possibly of *magnesium hydroxyhydrosulphide*, $Mg(OH)SH$. The soln. does not readily, if at all, absorb carbon dioxide from the atm. in the early stages of its decomposition." Magnesium hydrosulphide is readily decomposed by an acid giving off hydrogen sulphide. A soln. of magnesium hydrosulphide dissolves antimonious or mercuric sulphide, forming

thiosalts. J. Thomsen found for the heat of formation, $(\text{Mg}, 2\text{S}, \text{H}_2)\text{aq.} = 114.88$ Cals., and $(\text{MgO}_{\text{aq.}}, 2\text{H}_2\text{S}_{\text{aq.}}) = 15.68$ Cals.

REFERENCES.

¹ E. Tiede, *Zeit. Elektrochem.*, **28**, 20, 1922; E. Tiede and A. Schleede, *Ann. Physik*, (4), **67**, 573, 1922; *Ber.*, **49**, 1745, 1916; E. Tiede and F. Richter, *ib.*, **55**, B, 69, 1922; W. L. Bragg, *Phil. Mag.*, (6), **40**, 174, 1920; F. G. Reichel, *Journ. prakt. Chem.*, (2), **12**, 55, 1875; J. Stingl and T. Morawsky, *ib.*, (2), **20**, 81, 1879; J. Thomsen, *ib.*, (2), **19**, 1, 1878; *Pogg. Ann.*, **140**, 526, 1870; J. J. Berzelius, *ib.*, **6**, 442, 1826; J. Parkinson, *Journ. Chem. Soc.*, **20**, 127, 1867; E. Divers and T. Shimidzu, *ib.*, **45**, 699, 1884; L. Naudin and F. de Montholon, *Compt. Rend.*, **83**, 58, 1876; A. Mourlot, *ib.*, **127**, 180, 1899; *Ann. Chim. Phys.*, (7), **17**, 527, 1899; P. Berthier, *ib.*, (2), **22**, 236, 1823; T. J. Pelouze, *ib.*, (4), **7**, 172, 1866; A. Béchamp, *ib.*, (4), **16**, 245, 1868; E. Frémy, *ib.*, (3), **38**, 324, 1853; P. Sabatier, *ib.*, (5), **22**, 5, 1881; *Compt. Rend.*, **90**, 819, 1880; H. C. Geelmuyden, *ib.*, **130**, 1026, 1900; *Bull. Soc. Chim.*, (3), **23**, 635, 1900; T. Petitjean, *Dingler's Journ.*, **148**, 371, 1858; O. Schumann, *Liebig's Ann.*, **187**, 306, 1877; F. Briegleb and A. Geuther, *ib.*, **123**, 236, 1862; F. Gerhard, *Rep. Anal. Chem.*, **5**, 214, 1885; *Arch. Pharm.*, (3), **33**, 384, 1885; L. Kessler, *Ber.*, **2**, 369, 1869; V. Calcagni, *Gazz. Chim. Ital.*, **50**, ii, 331, 1920; S. Holgersson, *Zeit. anorg. Chem.*, **126**, 183, 1923.

§ 12. Magnesium Sulphates

Magnesium sulphate occurs in nature in rhombic crystals of *kieserite* or *reichardtite*, which is the monohydrated sulphate, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. The mineral may be massive, compact, or granular. Early analyses were made by C. F. Rammelsberg, M. Siewert, B. Leopold, L. N. Vauquelin, and E. Reichardt.¹ It occurs in the Stassfurt salt-mines in beds 9–12 ft. thick with alternating layers of sodium chloride; and it is often mixed with carnallite and gypsum. Magnesium sulphate also occurs in rhombic crystals as *Epsom salts*, or *epsomite*, which is the heptahydrated sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Heptahydrated magnesium sulphate has received many other names: *Seidlitz salt*, *sal amarum*, *sal anglicum*, *sal catharticum*, *Seidschütz salt*, *bitter salts*, etc. The mineral appears as a delicate fibrous scum or efflorescence on walls, and rocks; and in the galleries of mines and caves; it has been reported in gypsum mines, limestone caves, and on dolomites, serpentines, etc. W. H. Emory² reported it in the Californian plains, east of San Diego. Magnesium sulphate is also found in many mineral waters and springs, and in the bittern of sea-water. Analyses have been made by J. Bouis, A. Dufrenoy, F. Stromeyer and J. F. L. Hausmann, etc. It also occurs combined with calcium, sodium, and potassium sulphates as complex or double salts (*q.v.*).

Crude salts are mined, and shipped as a commercial grade, or the salts may be refined by crystallization. Magnesium sulphate obtained by crystallization from aq. soln. is usually in the form of epsomite, *i.e.* the heptahydrate; and it is conveniently made by dissolving the oxide, hydroxide, or carbonate in sulphuric acid, and evaporating the soln. to crystallization. The purified carbonate or hydroxide can be obtained from the purified chloride, *q.v.* It is doubtful if crystals of the anhydrous sulphate have been made. According to T. Graham,³ anhydrous magnesium sulphate, MgSO_4 , is obtained by heating the hydrated salt "to an incipient red heat for a considerable time." Incipient red heat is certainly over 500° . Hence, from G. H. Bailey's observations some oxide is probably formed as well. C. Schmidt made the anhydrous sulphate by warming the heptahydrate to 200° . H. G. F. Schröder found all the water is expelled from the hydrated salt in vacuo at 180° .

Magnesium sulphate has been obtained by evaporation from mineral waters and salt springs; or as a by-product from the mother liquid remaining after the evaporation of sea-water in making sea-salt. F. Michels⁴ prepared it from the kieserite remaining after the extraction of potassium chloride from the Stassfurt Abraumsalzen. E. F. Anthon obtained it as a by-product in the preparation of carbon dioxide by the action of sulphuric acid on magnesite. J. H. Swindells treated dolomite with sulphuric acid, but found much

acid was expended in converting the calcium carbonate into sulphate; and F. Findeisen proposed to remove the lime by washing calcined dolomite with water—*vide* the decalcification of dolomite. The impurities in commercial magnesium sulphate have been discussed by W. L. Kölreuter,⁵ J. S. F. Pagenstecher, and by E. Biltz, and E. Merok.

The hydrates of magnesium sulphate.—Hydrates of magnesium sulphate, $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$, have been reported, with $n=1, 1\frac{1}{2}, 2, 4, 5, 6, 7,$ and 12. The hexa- and hepta-hydrates have each two different crystalline forms. The mineral *kieserite* occurring in the Stassfurt salt-beds, Hallstadt, etc., and named after M. Kieser, of Jena, is the native form of **monohydrated magnesium sulphate**, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. This is a light grey, fine-grained mass which has been analysed by C. F. Rammelsberg,⁶ E. Reichardt, J. Bräuning, etc. According to H. Grüneberg, the grains are often cemented together with sodium chloride, which can be removed by washing. L. Playfair and J. P. Joule made the monohydrate by heating the heptahydrate to $130^\circ\text{--}140^\circ$. According to J. H. van't Hoff, W. Meyerhoffer, and N. Smith, it is formed by heating the heptahydrate to 132° ; its temp. of formation from the hexahydrate is between 67° and 68° , so that the intermediate hydrates can be formed only by slowing down the speed of the transformation. Well-formed crystals are not common; but it does occur as octahedral crystals. According to G. Tschermak, the crystals do not lose their water at 100° , and when heated to a higher temp., they fly to pieces without melting. G. Clemm found that the crystals dissolve unchanged in cold water, and that the solubility does not exceed that of gypsum. The solubility curve is indicated in connection with Fig. 22. When kept in moist air, E. Reichardt found that the crystals become opaque, take up a mol of water, and set like a cement; while F. Bischof said that under water, the crystals likewise set to a cement-like mass which dissolves in warm water as the heptahydrate. According to H. Grüneberg, when the crystals are calcined—presumably the anhydrous salt is formed—the powdered mass readily dissolves in hot water. T. Graham showed that the odd mol of water is not expelled from the monohydrate at $210^\circ\text{--}238^\circ$, and he applied the term *water of constitution* or *water of halhydration* to this mol of water to distinguish it from the water of crystallization. S. U. Pickering said that the gist of this theory is that the so-called constitutional water is not *water* at all, but hydrogen and oxygen, forming part of the salt nucleus itself; crystallized magnesium sulphate is not the heptahydrate of $\text{SO}_2(\text{MgO}_2)$ but the hexahydrate of $\text{SO}(\text{MgO}_2)(\text{HO})_2$, that this latter salt (improperly regarded as a monohydrate, $\text{SO}_2(\text{MgO}_2) \cdot \text{H}_2\text{O}$, is an “atomic” compound decomposable by heat into $\text{SO}_2(\text{MgO}_2) + \text{H}_2\text{O}$, just as monosodium phosphate, $\text{PO}(\text{NaO})(\text{HO})_2$, is decomposed by the same agent into a totally different salt, $\text{PO}_2(\text{NaO})$ and H_2O . He further argued that we have no grounds for supposing that the various water mols. in a hydrated salt are not all combined in a similar manner, and do not all occupy exactly the same position with regard to the salt nucleus; that, in short, a hydrated salt is not a symmetrical substance. At the same time, it must be admitted that we have no positive evidence to show that it is symmetrical. E. Erlenmeyer represented the formula of magnesium sulphate with a molecule of T. Graham's water of halhydration, by HO.Mg.HSO_4 .

Analyses by C. F. Rammelsberg, and by E. Reichardt point to the possible existence of a hydrate intermediate between the mono- and di-hydrates; N. A. E. Millon also obtained a hydrate which he regarded as $\text{MgSO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, by heating a higher hydrate to $110^\circ\text{--}115^\circ$ while the monohydrate is formed at 140° to 180° ; J. H. van't Hoff and H. M. Dawson showed that the composition more probably corresponds with **pentatetritahydrated magnesium sulphate**, $\text{MgSO}_4 \cdot 1\frac{1}{4}\text{H}_2\text{O}$, and that it is best obtained by keeping the soln. used for the preparation of the tetrahydrate, or by evaporating that soln., at a rather higher temp. than is employed for the last-named salt. These temp. are above the transition temp. for the change $\text{MgSO}_4 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 1\frac{1}{4}\text{H}_2\text{O}$, which is nearly 20° , but at 20° the evaporation must be very slow to produce the pentatetritahydrate. This salt crystallizes more readily than the dihydrate from which it is readily obtained,

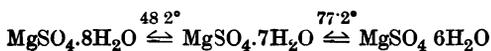
in the presence of magnesium chloride, by evaporation at 65°. The crystals of this hydrate are quite different from those of kieserite.

L. Playfair prepared **dihydrated magnesium sulphate**, $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$, by boiling the finely powdered heptahydrate with absolute alcohol, and also by heating the heptahydrate to 100°. Observations by N. A. E. Millon pointed to the existence of a dihydrated magnesium sulphate. J. H. van't Hoff and H. M. Dawson found that this salt is not obtained by keeping at 25° the soln. containing magnesium chloride from which the tetrahydrate is produced, but is formed by evaporating the soln. at a higher temp. when a white, badly crystallizing mass is formed along with the crystals of the tetrahydrate. The transition temp. $\text{MgSO}_4 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ is approximately 25°, and the change, at this temp., can be observed under the microscope. J. B. Hannay obtained evidence of the formation of this compound from the dehydration curve of the higher hydrates; and J. Thomsen from the heats of hydration.

According to J. H. van't Hoff and T. Estreicher-Rozbiersky, when a soln. of magnesium sulphate and chloride is evaporated over sulphuric acid at 25°, crystals of the hepta- and hexa-hydrates first separate, then follow crystals of **pentahydrated magnesium sulphate**, $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$, and later still, six-sided plates of **tetrahydrated magnesium sulphate**, $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, appear. The crystals of the two last-named salts are unstable. L. Playfair, and T. E. Thorpe and J. I. Watts claimed to have made the pentahydrate by drying the heptahydrate over sulphuric acid until it ceased to lose weight. J. H. van't Hoff, W. Meyerhoffer, and N. Smith found the transition temp. $\text{MgSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, to be 77.5°; and nearly the same temp. for $\text{MgSO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 5\text{H}_2\text{O}$.

W. Haidinger, and H. Löwel obtained monoclinic crystals of **α -hexahydrated magnesium sulphate**, $\alpha\text{-MgSO}_4 \cdot 6\text{H}_2\text{O}$ resembling those of borax, by evaporating an aq. soln. of magnesium sulphate until a skin is formed, and then keeping the soln. for a long time at 25° to 30°. J. C. G. de Marignac recommended draining the crystals, and drying them at 100°. According to E. Mitscherlich, the crystals of the heptahydrate at 52° rapidly lose one-seventh of their water, and form an aggregate of small prisms. H. Löwel observed that when a soln., prepared by dissolving 200 to 225 parts of the heptahydrate in 100 parts of water, is allowed to stand for some time in a closed vessel, monoclinic crystals of the hexahydrate, or hexagonal crystals of the heptahydrate, may be formed; if the temp. is between 14° and 21°, the crystals form slowly and appear as long prisms; if the temp. be lower than this, the crystals form rapidly and appear as small needles. According to L. de Boisbaudran, tetragonal pyramidal crystals of **β -hexahydrated magnesium sulphate**, $\beta\text{-MgSO}_4 \cdot 6\text{H}_2\text{O}$, are produced by seeding a conc. soln. of magnesium sulphate with tetragonal crystals of nickel cupric sulphate or zinc cupric sulphate. The crystals are unstable and readily pass into the α -form. E. Wiedemann found that at about 50°, the heptahydrate passes into a labile or β -hexahydrate; J. K. van der Heide placed the temp at 48.2°, and later, 47.2°. In the presence of potassium sulphate, E. Wiedemann found that the labile β -hexahydrate passed into the stable α -form at 90°; or, according to J. K. van der Heide, at 88.5°.

The crystallization of an aq. soln. of magnesium sulphate below 25° furnishes the ordinary or rhombic crystals of **α -heptahydrated magnesium sulphate**, $\alpha\text{-MgSO}_4 \cdot 7\text{H}_2\text{O}$. This salt is represented in nature by the mineral *epsomite*. According to H. Löwel, a second form: **β -heptahydrated magnesium sulphate**, $\beta\text{-MgSO}_4 \cdot 7\text{H}_2\text{O}$, appears in monoclinic crystals when a supersaturated aq. soln. of 200 to 225 grms. of heptahydrated magnesium sulphate is kept between 14° and 21° for some time; and L. de Boisbaudran obtained the β -heptahydrate by seeding a rather more dil. soln. with a crystal of cupric or ferrous sulphate. E. Jänecke found the heptahydrate is in equilibrium with the hexahydrate at 51°. S. Takegami obtained **octohydrated magnesium sulphate**, $\text{MgSO}_4 \cdot 8\text{H}_2\text{O}$, and he gave for the transition points:



J. Fritzsche prepared crystals of **dodecahydrated magnesium sulphate**, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, by freezing a sat. soln. of magnesium sulphate below 0° , and slowly thawing out the ice at 0° . The crystals are opaque when prepared on a small scale, but transparent if prepared on a large scale. Above 0° , they give off water and are converted into opaque crystals of the heptahydrate, without changing their form.

The solubility of magnesium sulphate.—Some idea of the relationship between most of the different hydrates of magnesium sulphate can be gathered from the solubility curve, Fig. 22. Early determinations were made by J. L. Gay Lussac,⁷ E. Tobler, E. Diacon, G. J. Mulder, C. von Hauer, and A. Gérardin. The first named represented his results at θ° , by the solubility curve $S=25.76+0.47816\theta$, but A. Étard showed that between 0° and 123° $S=20.5+0.2276\theta$ gives better results, and between 123° and 190° , $S=48.5-0.4403\theta$. The best representative values, compiled by R. Kremann for the stable binary system $\text{MgSO}_4\text{—H}_2\text{O}$, are illustrated by the continuous curve *ABCDELM*, Fig. 22. The ice-line, *AB*, by F. Rüdorff, and L. C. de Coppet, corresponds with a percentage solubility, according to L. C. de Coppet, of 13.9 per cent. MgSO_4 at -2.9° , and, according to J. H. van't Hoff, W. Meyerhoffer, and N. Smith, with a eutectic at -3.9° and 19 per cent. MgSO_4 , *B*. The solubility curve *BC* refers to systems with the dodecahydrate, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, at 1.8° and 21.1 per cent. MgSO_4 . At the transition point *C*, 1.8° , both the dodeca- and the rhombic hepta-hydrates are in equilibrium. The solubility curve *CD* refers to systems with the rhombic heptahydrate as solid phase; at the transition point *D*, by J. K. van der Heide, 48° and 33 per cent. MgSO_4 , both the rhombic heptahydrate and the hexahydrate are in equilibrium as solid phases. J. K. van der Heide gave $48^\circ\text{—}48.5^\circ$ for the transition point of the hepta- to the hexahydrate; and C. D. Carpenter and E. R. Jette gave 48.4° . The curve *DE* represents the solubility of hexahydrated magnesium sulphate where *E*, according to J. H. van't Hoff, W. Meyerhoffer, and N. Smith, represents the transition point—at 68° and 37 per cent. of magnesium sulphate—between the hexa- and mono-hydrates. The solubility curve *ELM* refers to the monohydrate. The percentage solubilities at the intermediate points are :

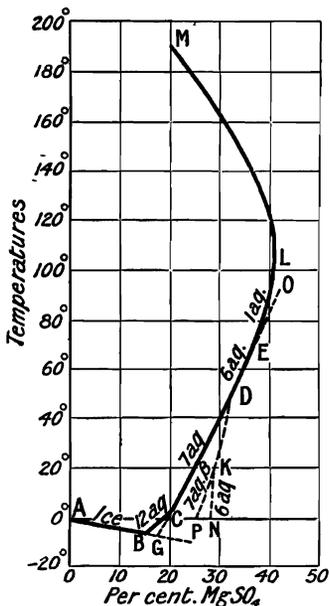


FIG. 22.—Solubility Curves of Magnesium Sulphate.

MgSO_4	.	.	10°	20°	30°	40°	50°	60°	80°	99.4°	164°	188°
			23.6	26.2	29.0	31.3	33.5	35.5	38.6	40.6	29.3	20.3
			$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$				$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$		$\text{MgSO}_4 \cdot \text{H}_2\text{O}$			

where *CD* is compiled from data by H. Löwel, E. E. Basch, and G. J. Mulder; for *DE*, from G. J. Mulder; for *EL*, from A. Geiger; and for *LM*, from A. Étard. Metastable systems are represented by the continuation of the ice-line *BG* to -8.4° , a compound, according to L. C. de Coppet, with 23.6 per cent. of magnesium sulphate, and *G*, according to F. Guthrie, with the eutectic between rhombic heptahydrate and ice, at -5.0° , and 19 per cent. MgSO_4 . The curve *CG* by H. Löwel represents the rhombic heptahydrate which has 20.6 per cent. MgSO_4 at 0° . The dotted curve *PK* by H. Löwel represents the solubility of the hexagonal heptahydrate with solubilities at 0° , 10° , and 20° of 25.8, 27.9, and 30.0 per cent. MgSO_4 .

respectively. The dotted curves *NK*, *KD*, and *EO*, by G. J. Mulder, represent the percentage solubilities of the hexahydrate :

	0°	10°	20°	30°	70°	80°	90°	100°
MgSO ₄ .6H ₂ O . . .	29.0	29.7	30.8	31.2	37.3	39.1	40.8	42.5

By cooling a hot soln. of conc. *sulphuric acid* sat. with anhydrous magnesium sulphate, H. Schiff obtained a syrupy liquid which furnished six-sided plates of **magnesium hydrotetrasulphate**, MgSO₄.3H₂SO₄; and C. Schultz obtained crystals of **magnesium hydrodisulphate**, MgSO₄.H₂SO₄, or Mg(HSO₄)₂, under similar conditions. J. Kendall and A. W. Davidson found the solubility of normal magnesium sulphate in sulphuric acid does not exceed 1.4 molar per cent. even on boiling. The sat. temp. of soln., with the solid phase MgSO₄.3H₂SO₄, were :

Per cent. MgSO ₄ . . .	0.18	0.32	0.62	0.77	1.07	1.18	1.37
Sat. temp.	25.7°	44.2°	66.0°	72.3°	82.8°	86.7°	91.7°

The salt was not completely dissolved with 1.53 per cent. MgSO₄. H. Haushofer found the crystals are hexagonal plates too deliquescent to be satisfactorily measured crystallographically. G. Tammann found the salt to be completely decomposed when the soln. is diluted. C. Schultz also found that boiling conc. sulphuric acid dissolves about 2 per cent. of anhydrous magnesium sulphate, and the cooling soln. deposits crystals of **magnesium hexahydrotetrasulphate**, Mg(HSO₄)₂.2H₂SO₄, or MgH₆(SO₄)₄, which K. Haushofer believed to belong to the monoclinic system.

J. B. Richter stated that magnesium sulphate dissolves much more rapidly and abundantly in dil. *hydrochloric acid* than in water, and a clear syrupy liquid is formed. According to F. Margueritte, no precipitation occurs when hydrogen chloride is passed into an aq. soln. of magnesium sulphate; and, according to R. Schiff, no acid salt is formed. According to R. J. Kane, magnesium sulphate is not decomposed by hydrochloric acid, for it can be crystallized unchanged from its soln. in this acid. S. Setschenoff studied the absorption of *carbon dioxide* by soln. of magnesium sulphate. O. Aschan found 100 grms. of 95 per cent. *formic acid*, at 19°, dissolve 0.34 gm. of MgSO₄. According to C. Hensgen, anhydrous magnesium sulphate is but very sparingly soluble in conc. hydrochloric acid, and the hydrated salt dissolves therein only because its water of crystallization dilutes the acid. Hence it appears that, in the action of hydrogen chloride on the hydrated salt, the gas is at first absorbed by the water of crystallization, forming a liquid in which the anhydrous salt is soluble, but as the hydrochloric acid thus formed becomes more conc. the anhydrous sulphate is gradually deposited.

According to C. J. B. Karsten, a conc. soln. of *sodium chloride* dissolves heptahydrated magnesium sulphate without separating the former salt, but conversely, if sodium chloride be dissolved in a conc. soln. of magnesium sulphate, the last-named salt separates out. The crystallization of a soln. of the two salts re-deposits both salts in crystals without alteration, but T. F. von Grotthus found that if the residue be pulverized and boiled in alcohol, a little magnesium chloride is dissolved; consequently, as stated by C. J. B. Karsten, the products are: magnesium chloride and sodium sulphate as well as the original salts. C. W. Scheele showed that above 0°, there is very little change, but below that temp. decahydrated sodium sulphate crystallizes out and magnesium chloride remains in soln. According to J. J. Berzelius, if a soln. of 2 parts of heptahydrated magnesium sulphate and one part of sodium chloride be dissolved in 4.5 parts of water; evaporated a little; and then cooled to -3°, decahydrated sodium sulphate is precipitated and magnesium chloride remains in soln. If the mixture be gently warmed the original salts are reproduced, but above 50°, added H. Rose, the soln. deposits anhydrous sodium sulphate. C. J. B. Karsten stated that an aq. soln. of magnesium sulphate is decomposed by double affinity when mixed with *ammonium chloride*, *potassium chloride*, or *potassium nitrate*, and the alkali sulphate so produced unites with the undecomposed magnesium salt to form a double sulphate. F. Pfaff found a sat.

soln. contains 13.09 parts of *sodium sulphate* and 15.31 parts of *magnesium sulphate* per 100 parts of water at 0°; and E. Diacon further found that 100 grms. of water dissolve at

	17.9°	24.1°	30°	33°	36°	40°
Na ₂ SO ₄ . . .	16.70	25.70	29.73	27.82	26.29	24.01
MgSO ₄ . . .	30.41	31.01	28.92	24.87	26.59	30.89

C. J. B. Karsten and others have also discussed this subject in connection with the double salts of *magnesium sulphate* with *sodium* or *potassium sulphate*. C. J. B. Karsten found *heptahydrated magnesium sulphate* dissolves rapidly and without precipitation in a conc. soln. of *potassium nitrate*, but when *potassium nitrate* is slowly dissolved in a conc. soln. of *magnesium sulphate*, *potassium sulphate* is precipitated. The *heptahydrate* dissolves in a conc. soln. of *sodium nitrate* without precipitation, but only a little *sodium nitrate* can be dissolved in a conc. soln. of the *heptahydrate* without the soln. becoming turbid owing to the separation of *magnesium sulphate*. H. Precht and B. Wittgen, C. J. B. Karsten, G. J. Mulder, E. Tobler, H. Schiff, and H. Schwarz made observations on the solubility of *magnesium sulphate* in soln. of *potassium sulphate*. H. S. van Klooster measured the percentage solubility (grams of salt in 100 grms. of sat. soln.) of *magnesium sulphate* in aq. soln. of *potassium sulphate*, and found:

MgSO ₄ . . .	26.76	26.57	26.39	16.36	13.26	12.68	10.69	4.00	0
K ₂ SO ₄ . . .	0	2.34	4.02	8.43	10.34	10.70	10.84	11.03	10.77
Solid phases . . .	MgSO ₄ .7H ₂ O			MgSO ₄ .K ₂ SO ₄ .6H ₂ O			K ₂ SO ₄		

According to C. J. B. Karsten, an aq. soln. of *magnesium sulphate* dissolves some **calcium hydroxide** from which *calcium sulphate* and *magnesium hydroxide* separate when the soln. is dil., and a *basic magnesium sulphate* if the soln. is conc. According to H. Grüneberg, a mixture of 2 mols of *kieserite*, and one of *calcium hydroxide* made into a slip with water, sets to a hardness with the evolution of heat; if the mixture be calcined and powdered, and again mixed with water, a marble-like mass is formed. C. J. B. Karsten found a soln. of *magnesium sulphate* dissolves a little **calcium sulphate**, while J. H. Dröse found that a conc. soln. of *magnesium sulphate* dissolves no *calcium sulphate*, and *gypsum* is precipitated from its aq. soln. by adding some *heptahydrated magnesium sulphate*; according to R. Fassbender, the precipitate contains 15 per cent. of *magnesium sulphate* and has a crystalline form different from *gypsum*. T. S. Hunt and F. Hoppe-Seyler have studied the action of **calcium carbonate** on soln. of *magnesium sulphate*.

According to H. Schiff, aq. soln. containing 10, 20, and 40 per cent. of *ethyl alcohol* dissolve respectively 64.7, 27.1, and 1.65 per cent. of *heptahydrated magnesium sulphate* at 10°. At higher temp., said A. Gérardin, the solubility increases proportionally with the temp. C. A. L. de Bruyn found that 100 grms. of absolute *ethyl alcohol*, at 3°, dissolved 13 grms. of the *heptahydrate*, and 100 grms. of absolute *methyl alcohol*, at 18°, dissolved 1.18 grms. of anhydrous *magnesium sulphate*, 41 grms. of the *heptahydrate* at 17°, and 29 grms. of the *heptahydrate* at 3° to 4°; while 100 grms. of 93 per cent. *methyl alcohol* dissolved 9.7 grms. of the *heptahydrate* at 17°, and 100 grms. of 50 per cent. *methyl alcohol* dissolved 4.1 grms. of the *heptahydrate* at 3° to 4°. According to W. Eidmann, *magnesium sulphate* is insoluble in *acetone*, and J. F. Snell found that with *acetone* and *water*, the soln. separates into layers with certain concentrations. J. Timmermans studied the ternary system *phenol*, *magnesium sulphate*, and *water*. A. Köhler found 100 grms. of a sat. soln. at 31.25° contained 46.52 grms. of *sugar* and 14 grms. of *magnesium sulphate*; 100 grms. of *water* dissolve 119.6 grms. of *sugar* and 36 grms. of *magnesium sulphate*.

The physical properties of magnesium sulphate.—The crystals of *monohydrated magnesium sulphate* were found by G. Tschermak⁸ to be *monoclinic pyramids* with axial ratios $a : b : c = 0.9147 : 1 : 1.7455$, and $\beta = 91^\circ 7'$. G. Wyrzouboff found the crystals of the *tetrahydrate* to be *monoclinic prisms*, with $a : b : c$

$=0.450:1:?$, and $\beta=90^\circ 11'$; while the pentahydrate forms triclinic pinacoids, with $a:b:c=0.6021:1:0.5605$, and $\alpha=81^\circ 30'$, $\beta=109^\circ 0'$, and $\gamma=104^\circ 55'$. L. de Boisbaudran found the crystals of $\beta\text{-MgSO}_4\cdot 6\text{H}_2\text{O}$ to be tetragonal pyramids; and those of $\alpha\text{-MgSO}_4\cdot 6\text{H}_2\text{O}$ were found by J. C. G. de Marignac to be monoclinic prisms with axial ratios $a:b:c=1.4039:1:1.6683$, and $\beta=98^\circ 34'$. J. C. G. de Marignac regarded the crystals of $\beta\text{-MgSO}_4\cdot 7\text{H}_2\text{O}$ as trigonal, but H. Kopp supposed them to be monoclinic prisms, and B. Gossner recalculated the measurements and obtained the axial ratios $a:b:c=1.220:1:1.582$, and $\beta=104^\circ 24'$. From H. J. Brooke's measurements it follows that $\alpha\text{-MgSO}_4\cdot 7\text{H}_2\text{O}$, or epsomite, forms rhombic crystals with axial ratios $a:b:c=0.9901:1:0.5709$. H. Grandinger made observations on this subject. E. Blasius, and J. Grailich have studied the **corrosion figures** of epsomite. The latter salt is the ordinary form of magnesium sulphate; it readily forms supersaturated soln., and, according to J. M. Thomson, the seeding of such soln. with crystals of zinc, nickel, iron (ous), or cobalt sulphate causes crystallization, but this is not the case when the soln. is seeded with crystals of sodium chloride, thiosulphate, or with potassium magnesium sulphate.

The reported numbers for the **specific gravity** of anhydrous magnesium sulphate, MgSO_4 , range from C. J. F. Karsten's 2.6066 ; E. Filhol's 2.628 ; C. Pape's 2.675 (16°); L. Playfair and J. P. Joule's 2.706 ; T. E. Thorpe and J. I. Watts' 2.709 at 15° ; to O. Pettersson's 2.770 at 13.8° and 2.795 at 14° . H. G. F. Schröder gave 2.829 , and if prepared by dehydrating the ordinary salt without fusion, 2.480 . The sp. gr. of monohydrated magnesium sulphate, $\text{MgSO}_4\cdot\text{H}_2\text{O}$, in the form of kieserite was given by F. Bischof as 2.517 ; and G. Tschermak gave 2.569 . For the artificial salt H. G. F. Schröder gave 2.385 ; L. Playfair and J. P. Joule, 2.478 ; C. Pape, 2.281 at 16° ; O. Pettersson, 2.339 at 14° ; and T. E. Thorpe and J. I. Watts, 2.445 at 15° . For the sp. gr. of dihydrated magnesium sulphate, $\text{MgSO}_4\cdot 2\text{H}_2\text{O}$, L. Playfair and J. P. Joule gave 2.279 ; and T. E. Thorpe and J. I. Watts, 2.373 at 15° . For the sp. gr. of pentahydrated magnesium sulphate, $\text{MgSO}_4\cdot 5\text{H}_2\text{O}$, L. Playfair and J. P. Joule gave 1.869 ; G. Wyrouboff, 1.718 ; and T. E. Thorpe and J. I. Watts, 1.869 at 15° . Similarly, for monoclinic hexahydrated magnesium sulphate, $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$, L. Playfair and J. P. Joule gave 1.751 , and T. E. Thorpe and J. I. Watts, 1.734 at 15° . According to C. R. Schulze, the sp. gr. of the two modifications of the hexahydrate are respectively 1.8981 and 1.6151 . J. W. Retgers gave 1.691 at 16° for the sp. gr. of labile monoclinic heptahydrated magnesium sulphate. A large number of determinations of the sp. gr. of rhombic heptahydrated magnesium sulphate have been made, and the results range from J. D. Forbes' 1.636 at 15.5° to E. Filhol's 1.571 . Other determinations were made by J. H. Hassenfratz, 1.6603 ; H. Kopp, 1.674 ; L. Playfair and J. P. Joule, 1.6829 at 4° ; H. Schiff, 1.685 ; H. J. Buignet, 1.675 ; S. Holker, 1.665 at 15.5° ; C. Pape, 1.701 at 16° ; O. Pettersson, 1.688 ; H. G. F. Schröder, 1.678 ; W. C. Smith, 1.632 ; J. W. Retgers, 1.678 at 16° ; and T. E. Thorpe and J. I. Watts, 1.678 at 15° . G. Krause gave 1.61 to 1.71 for the sp. gr. of reichardite, and 2 to 3 for its **hardness**; the hardness of kieserite is 3. The **specific volumes** of magnesium sulphate and its hydrates, determined by T. E. Thorpe and J. I. Watts, are:

Hydrate	0	1	$1\frac{1}{2}$	2	4	5	6	7
Mol. wt.	120	138	—	156	—	210	228	246
Sp. vol.	44.8	55.6	—	67.0	—	112.4	130.8	146.6

The mol. vol. of the dissolved magnesium sulphate, calculated from the sp. gr. of the aq. soln., is zero in $0.3N$ -soln., and increases with a rising positive value as the conc. is augmented. L. de Boisbaudran,¹⁰ and J. H. Pollok found a contraction occurs when the heptahydrate crystallizes from a supersaturated soln. According to R. Broom, if a soln. of 30.5 grms. of anhydrous magnesium sulphate in 100 c.c. of water be mixed with an equal volume of water, a percentage contraction 0.677 occurs. E. F. Anthon, A. Michel and L. Krafft, W. W. J. Nicol, H. Schiff, and A. C. Oudemans have measured the 'sp. gr. of soln. sat. at different temp.

G. T. Gerlach measured the sp. gr. of aq. soln. of magnesium sulphate at 15°, and making a selection from these values,

Per cent. MgSO ₄	1	2	5	10	15	20	25
Sp. gr.	1.01031	1.02062	1.05154	1.10529	1.16222	1.22212	1.28478

H. T. Barnes and A. P. Scott also measured the sp. gr. of soln. with 2.01 to 26.25 per cent. of MgSO₄ at 18.2°; and J. G. McGregor over the range 0.191 to 1.132 per cent. of MgSO₄ at 19.5°. The latter represented his results at 20° by the formula $S=S_t+0.0106324w$, where w denotes the percentage composition, and S_t the sp. gr. of water; at 23°, the constant is 0.0098176. F. Kohlrausch and W. Hallwachs, O. Pulvermacher, and several others have made more or less subsidiary determinations—*e.g.*, H. C. Jones and F. H. Getman, D. Dijken, J. Forchheimer, O. Schönrock, W. Ostwald, J. Kannonikoff, C. A. Valson, J. Thomsen, S. Charpy, P. Barbier and L. Roux, E. Forster, H. Hager, P. de Heen, A. Sprung, R. J. Holland, H. Sentsis, O. Knöfler, etc.

The **viscosity** of aq. soln. of magnesium sulphate has been measured by S. Arrhenius, O. Pulvermacher, W. W. J. Nicol, and J. Wagner. The latter found at 25° for N -, $\frac{1}{2}N$ -, $\frac{1}{4}N$ -, and $\frac{1}{8}N$ -soln., the respective viscosities 1.3673, 1.1639, 1.0784, and 1.0320, when water is unity. H. Sentsis, A. Battelli and A. Stefanini, and W. Grabowsky have measured the **surface tension** of soln. of magnesium sulphate. The latter found for the surface tension σ and the capillary constant a^2

Per cent. MgSO ₄	10°			30°		
	a^2 sq. mm.	10.63	18.83	21.35	10.63	18.83
σ dynes per cm.	13.94	13.21	13.05	13.45	12.79	12.45
	76.2	78.4	79.3	73.0	75.5	79.2

P. G. Tait found the **compressibility** of 16.06, 10.51, and 6.23 per cent. aq. soln. of magnesium sulphate to be $\beta \times 10^6 = 29.6, 33.5, \text{ and } 36.5$ respectively. W. Watson also measured this constant. T. Graham experimented on the diffusion of magnesium sulphate in aq. soln. J. D. R. Scheffer measured the **diffusion coefficient**, k , of magnesium sulphate and at 5.5°, found that for soln. with 0.54 and 2.18 mols per litre, k is 0.32 and 0.28 respectively, and at 10° for soln. with 0.40 and 3.23 mols per litre, k is 0.34 and 0.27 respectively; similarly, J. Schuhmeister found that k is 0.28 for a soln. with 1.7 mols per litre at 10°. W. Stiles found that the rate of diffusion in 0.5 per cent. agar-agar is nearly the same as in water; and in 10 per cent. gelatine, the rate is decreased nearly 25 per cent.

S. de Lannoy measured the thermal expansion of soln. of magnesium sulphate, and he found that with 3.796 per cent. of heptahydrated magnesium sulphate, for a temp. θ , between 0° and 40°, $v=v_0(1-0.0_5\theta+0.0_6585\theta^2)$; and between 40° and 75°, $v=v_0(1+0.0_4591\theta+0.0_5397\theta^2)$; for soln. with 9.915 per cent. of the heptahydrate, between 0° and 40°, $v=v_0(1+0.0_4708\theta+0.0_5431\theta^2)$, and between 40° and 85°, $v=v_0(1+0.0_31037\theta+0.0_53453\theta^2)$; for soln. with 19.688 per cent. of the heptahydrate, between 0° and 40°, $v=v_0(1+0.0_3139\theta+0.0_5335\theta^2)$, and between 40° and 82°, $v=v_0(1+0.0_3162\theta+0.0_52775\theta^2)$; while for soln. with 24.437 per cent. of the heptahydrate, between 0° and 82°, $v=v_0(1+0.0_32079\theta+0.0_5224\theta^2)$. E. Wiedemann found the thermal expansion up to 50° to be quite regular, when the vol. abruptly increases, owing to the elimination of water by the salt: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$, and then expands quite regularly up to 93°; between 93° and 100° there is a marked contraction, and this is subsequently followed by a regular expansion.

According to G. H. Bailey,¹¹ when magnesium sulphate moistened with sulphuric acid is heated to 360°, all the free sulphuric acid is expelled and the weight remains constant up to 450°. R. Reidenbach found the weight of anhydrous magnesium sulphate remains constant from 650° to 700°, but dissociation begins at 750°, and is completed at 850°. G. H. Bailey added that when the sulphate is ignited for the oxide, a trace of sulphuric acid is retained very tenaciously even after a prolonged

ignition. C. Daubeny found that the sulphate lost about a quarter of its contained sulphur trioxide when heated for 3 hrs. at a bright red heat; and he stated that if heated for a still longer time, the cold product gives a residue insoluble in water, and which gives off some hydrogen sulphide when treated with acids. J. B. J. D. Boussingault stated that when small quantities are heated in the blast-flame, all the sulphur trioxide can be expelled. H. le Chatelier stated that the decomposition of the sulphate begins at 1160°. A. S. Ginsberg gave 1120° for the **melting point** (f.p.) of molten magnesium sulphate, and R. Nacken, 1124°. The latter stated that the salt is considerably decomposed at its m.p. According to G. J. Mulder, heptahydrated magnesium sulphate, in dry air for 45 days, loses 8·3 to 9·1 per cent. of water, and its composition remains constant; and, according to T. Graham, if kept at 22° in vacuo, or at 100° in air, rather more water than is required for the dihydrate remains, at about 130° the monohydrate is formed, and the latter loses all its combined water at a higher temp.—*vide* preparation of the anhydrous sulphate. According to G. J. Mulder, the per cent. water which is lost after heating to:

	40°	60°	82°	101°	119°	172°	201°
Water lost . . .	8·7	33·2	34·7	34·7	40·5	40·8	41·5
Mol. eq.	H ₂ O	3·5H ₂ O	—	5H ₂ O	—	—	6H ₂ O

The theoretical loss for the whole of the water in the heptahydrate is 51·2 per cent. H. G. F. Schröder found dehydration was complete in vacuo at 180°; and V. A. Jacquelin found that the salt which has lost 12·4 per cent. of water in vacuo, regains all the lost water on exposure to air. J. B. Hannay found the dehydration curve of the heptahydrate at 100° has breaks indicating the formation of the dihydrate and of *trihydrated magnesium sulphate*, but there is no other evidence in favour of the individuality of the trihydrate. See the individual hydrates for their temp. of formation.

According to C. Pape,¹² the **specific heat** of solid anhydrous magnesium sulphate is 0·225 between 25° and 100°; and, according to H. Kopp, the sp. ht. of heptahydrated magnesium sulphate is 0·3615 between 20° and 42°; C. Pape gave 0·407 for the heptahydrate between 15° and 28°; and 0·265 for the monohydrate between 25° and 100°. J. C. G. de Marignac found that the sp. ht. of aq. soln. of magnesium sulphate containing *n* mols of water per mol of MgSO₄, are 0·8690, 0·9230, and 0·9550, when *n*=50, 100, and 200 at 22·52°. G. Tammann measured the sp. ht. of dil. soln.; and other determinations have been made by K. Bindel, S. Pagliani, J. Thomsen, and H. Teudt. G. Jäger found the **thermal conductivity** of a 22 per cent. soln. of magnesium sulphate to be 97·5 when that of water is 100.

E. Cohen,¹³ and P. C. F. Frowein have measured the **vapour pressure** of heptahydrated magnesium sulphate; the former's results above 30·75°, and the latter's results below that temp., are:

	14·95°	25·75°	30·75°	40·04°	41·42°	43·40°	47·45°
Vap. press. . . .	4·93	12·29	18·34	37·90	41·89	43·37	64·31 mm.

P. C. F. Frowein obtained 18·35 mm. for the vap. press. of hexahydrated magnesium chloride at 30·75°. This number is probably low, since E. Cohen obtained 18·96 mm. and H. Bolte 18·92 mm. The vap. press., *p*, obtained by H. W. Foote and S. R. Scholes; and *p'* by H. Bolte, are, at 25°,

	0-1H ₂ O	1-4H ₂ O	4-5H ₂ O	5-6H ₂ O	6-7H ₂ O
<i>p</i> mm.	1·0	4·9	8·8	9·8	11·5
<i>p'</i> mm.	—	4·6	7·9	10·1	12·0

For the 6-7 hydrate, P. C. F. Frowein gave 11·5 mm.; H. Lescœur, 11·7 mm.; E. Cohen, 12·0 mm.; W. C. Schumb, 12·50 mm.; and G. Wiedemann, 18·0 mm. at 25°. A. W. C. Menzies showed that there are initial disturbances in the observed results due to the redistribution of absorbed air by the salt and apparatus. H. Lescœur found the vap. press. of a sat. soln. of magnesium

sulphate at 20° to be 5.75 mm. G. Tamman found that with soln. containing 10.43, 25.33, and 50.74 grms. of $MgSO_4$ in 100 grms. of water, the vap. press. at 100° was lowered respectively 10.8, 26.4, and 82.7 mm.; and with soln. containing 6.33, 26.10, and 48.71 grms. of $Mg(HSO_4)_2$ in 100 grms. of water, the vap. press. at 100° was lowered 10.3, 57.0, and 136.1 mm. respectively. Measurements were also made by C. D. Carpenter and E. R. Jette. According to H. C. Jones and F. H. Getman,¹⁴ the molecular **freezing point** lowering has a minimum with 0.48*N*-soln. This has been also studied by T. G. Bedford, H. Hausrath, F. M. Raoult, L. Kahlenberg, E. H. Loomis, S. Arrhenius, and A. A. Noyes and F. G. Falk. From these observations:

Grms. $MgSO_4$ per 100 grms. H_2O	0.00141	0.02867	0.699	2.534	9.768	18.343
Lowering of f.p.	0.000433°	0.007382°	0.154°	0.469°	1.629°	3.471°
Mol. lowering of f.p.	3.70°	3.16°	2.65°	2.23°	2.01°	2.08°

The **boiling point** of a sat. soln. is 105°, according to T. Griffiths, and G. J. Mulder, 108.4°; G. T. Gerlach found soln. with 8.8, 39.5 and 75 grms. of $MgSO_4$ in 100 grms. of water boiled respectively at 100.5°, 103°, and 108°. L. Kahlenberg found the raising of the b.p. of soln. with 2.733, 7.236, 43.47, and 72.28 grms. $MgSO_4$ per 100 grms. of water was respectively 0.097°, 0.281°, 1.455°, and 3.630°, and the mol. raising of the b.p. respectively 0.43°, 0.47°, 0.403°, and 0.605°.

According to J. Thomsen,¹⁵ the **heat of formation** is ($Mg, O, SO_3, aq.$)=180.18 Cals.; and (Mg, O_2, SO_2)=232.31 Cals. M. Berthelot gave ($Mg, S, 2O_2$)=309.0 Cals., and he also found for ($Mg(OH)_2$ precipitated; $H_2SO_{4(aq.)}$)=31.2 Cals. J. Thomsen's values for the **heat of hydration** with the 1st, 2nd, 3rd, . . . and the 7th mols of water are:

1st	2nd	3rd	4th	5th	6th	7th
6.98	2.25	3.60	3.21	2.23	2.11	3.70 Cals.

F. Rüdorff found the temp. fell from 19.1° to 3.1° on mixing 85 parts of the heptahydrate with 100 parts of water. T. Graham concluded from his observations on the heat disengaged in the combination of dehydrated magnesium sulphate with water that "of the whole heat evolved in the complete hydration of magnesium sulphate, as nearly as possible one-fourth is due to the combination of the first mol. of water." S. U. Pickering's values for the **heat of solution** in 420 mols of water per mol $MgSO_4$, at 22.2°, are 20.765 Cals. for the anhydrous salt, 12.131 Cals. for the monohydrate, and -3.86 to -3.915 Cals. for the heptahydrate. J. Thomsen found for the heat of soln. in 400 mols of water per mol of the sulphate:

nH_2O	0	1	2	3	4	5	6	7
Cals.	20.28	13.30	11.05	7.45	4.24	2.01	-0.10	-3.80

M. Berthelot and L. Ilosvay de N. Ilosva represent the heat of soln. of the anhydrous sulphate in water at θ° by $20000 + 0.00007(\theta - 15)$. C. M. van Deventer and H. J. van de Stadt give -4.1 Cals. for the integral heat of soln.

According to G. Tschermak,¹⁶ the monohydrated sulphate has a positive **double refraction**; so also, according to G. Wyruboff, has the tetrahydrate, while the pentahydrate and the hexahydrate have a negative double refraction; and, according to A. des Cloizeaux, the rhombic heptahydrate has also a negative double refraction. The **indices of refraction** of crystals of heptahydrated magnesium sulphate for the *D*-line have been determined by F. Kohlrausch, H. Dufet, and A. Fock, while H. Töpsöe and C. Christiansen found:

		μ_c	μ_B	μ_γ
<i>F</i> -line	.	1.4374	1.4607	1.4657
<i>D</i> -line	.	1.4325	1.4554	1.4608
<i>C</i> -line	.	1.4305	1.4530	1.4583

C. Borel also made determinations over the range $\lambda=226$ to $\lambda=718$. The index of refraction of soln. of magnesium sulphate has been measured by W. Hallwachs,

O. Pulvermacher, B. Wagner, J. Dinkhauser, and D. Dijken. The sp. refractive power of the solid salt (calculated from measurements on soln.) was found by E. Forster to be 0.2102 at 24°. P. Barbier and L. Roux measured the dispersion of soln., and D. Dijken; the mol. refraction and dispersion. According to J. Forchheimer, the **magnetic rotatory power**, or the specific electromagnetic **rotation of the plane of polarization** of 0.934*N*-, 1.86*N*-, and 2.73*N*-soln. is 0.306, 0.313, and 0.305 respectively, and the mol. electromagnetic rotation of the plane of polarization, 2.04, 2.02, and 2.03 respectively. This constant is therefore independent of conc. O. Schönrock gave 0.2978 for the specific rotation and 1.986 for the mol. rotation. L. Longchambon found the rotatory power of heptahydrated magnesium sulphate is 19° 15' for both axes. According to P. Bary, anhydrous magnesium sulphate does not fluoresce on exposure to **X-rays** or to **Becquerel's rays**.

The **electrical conductivity** of molten magnesium sulphate and of mixtures with potassium sulphate has been measured by A. Benrath and K. Drekopf¹⁷; the electrical conductivity of aq. soln. of magnesium sulphate has been measured by W. C. D. Whetham, E. Klein, etc. P. Walden found the conductivity, λ , for an eq. of the salt in v litres to be :

v	.	.	.	32	64	128	256	512	1024
λ	.	.	.	73.0	83.0	92.6	101.8	110.1	116.9

H. C. Jones also measured the mol. conductivity, μ , and calculated the percentage **degree of ionization** α , and the **temperature coefficient**, k , of the mol. conductivity between 0° and 10°; he found at 0° :

v	.	.	.	2	8	16	32	128	512	1024	2048
μ	.	.	.	32.12	45.70	50.95	59.57	71.17	95.57	102.7	111.1
α	.	.	.	28.9	41.1	45.9	53.6	64.1	86.0	92.4	100.0
k	.	.	.	1.10	1.52	1.71	2.01	2.42	3.27	3.57	3.74

Analogous results were obtained at 10°, 25°, 35°, 50°, and 65°. J. Kendall and co-workers measured the conductivity of soln. in anhydrous sulphuric acid. G. N. Lewis and G. A. Linhart measured the **degree of ionization** of dil. soln. of magnesium sulphate; and G. N. Lewis and M. Randall, the activity coeff. of the ions. The **transport numbers** of the ions have been studied by W. Hittorf, A. Chassy, B. D. Steele, W. Bein, K. Hopfgartner, R. B. Denison, and O. Masson. C. Heim found no sudden change in the electrical conductivity on passing from a state of supersaturation to a state of ordinary soln. According to C. Borel,¹⁸ the **dielectric constants** k_1 , k_2 , and k_3 of epsomite are respectively 8.28, 6.05, and 5.26; A. de Gramont studied the **pyroelectricity** of epsomite. J. Grailich and V. von Lang found that the crystals are feebly diamagnetic. The **magnetic susceptibility** of anhydrous magnesium sulphate at 18° and 19° was found by G. Quincke, and S. Meyer to be -0.36×10^{-6} units; C. K. Studley gave -0.46×10^{-6} , and G. Meslin, -0.62×10^{-6} ; for the heptahydrated salt, S. Meyer gave -0.36×10^{-6} . P. Pascal gave 1357×10^{-7} units for the mol coeff. of magnetization.

The chemical properties of magnesium sulphate.—J. B. Richter¹⁹ first noted the evolution of heat which occurs when magnesium sulphate, after ignition, is mixed with **water**; and H. von Blücher noticed that the ignited salt gradually absorbed the eq. of 7H₂O from the air. When the sulphate is heated in a current of steam, G. Clemm noted that the sulphur trioxide can be all driven off. C. W. Scheele found "vitrified magnesia" is but little affected by **hydrofluoric acid**. C. Hensgen found that **hydrogen chloride** begins to act on magnesium sulphate at a temp. approaching redness, and the reaction is not completed at this temp. in 3 hrs. A. B. Prescott found that when a gram of magnesium sulphate is evaporated to dryness with 4.035 grms. of hydrochloric acid containing 1.251 grms. of HCl, 0.003 gm. of magnesium chloride is formed. C. J. B. Karsten stated that magnesium sulphate melts when heated with **sodium chloride**, and this the more readily the greater the proportion of the latter salt; and G. Clemm noted that when a mixture of the two salts is heated in a current of steam, hydrogen chloride

is evolved. V. Merz and W. Weith found that when melted in air with **potassium iodide**, iodine is set free. J. Zawadsky and co-workers obtained **magnesia** by the reduction of magnesium sulphate with **hydrogen sulphide**. According to J. L. Gay Lussac, when a mixture of anhydrous magnesium sulphate and **carbon** is heated to redness, a mixture of one vol. of carbon dioxide and two vols. of sulphur dioxide is obtained, some sulphur is liberated but no magnesium sulphide is formed; but P. Berthier obtained a trace of the sulphide when the reaction occurs at a white heat. E. Kunheim obtained similar results. E. H. Riesenfeld has studied the reduction, and found that there are concurrent reactions: $2\text{MgSO}_4 + \text{C} = 2\text{MgO} + 2\text{SO}_2 + \text{CO}_2$, and $\text{MgSO}_4 + \text{C} = \text{MgO} + \text{SO}_2 + \text{CO}$. According to K. Stammer, **carbon monoxide** has no action on red-hot magnesium sulphate; but, according to F. G. Reichel, magnesium oxide, carbonyl sulphide, and carbon dioxide are formed; while O. Boudouard obtained **magnesia**, and carbon and sulphur dioxides; J. Zawadsky and co-workers obtained in addition free sulphur; and, according to E. Jacquemin, in the presence of steam, carbon dioxide and hydrogen sulphide are formed. A recently prepared mixture of hydrated magnesium sulphate and **sodium hydrocarbonate** was found by L. A. Planche to dissolve in water without turbidity, but a similar mixture, after keeping some months, deposits magnesium carbonate. According to A. d'Heureuse, when a mixture of magnesium sulphate and **iron** is heated to redness, a little sulphur dioxide is evolved, and a mixture of magnesium and iron oxides with a little iron sulphide is formed; when **zinc** replaces the iron, a fulmination occurs. When a mixture of 33 grms. of heptahydrated magnesium sulphate, 5.5 to 9 grms. of **sodium hydroxide**, and 100 c.c. of water is heated between 195° and 205° for 31-55 hrs., two-thirds of the magnesium separates as hydroxide, and the remainder forms doubly refracting acicular crystals of **magnesium hydroxy-sulphate**, $6\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, which are sparingly soluble in cold and hot water, but readily soluble in hydrochloric acid.

Magnesium sulphate is used in tanning leather, in sizing and loading cotton textiles; in weighting silk, paper, and leather; in dyeing; in enamelling industries; in fireproofing; in making paints and soaps; in the manufacture of mineral waters; and medicinally.

REFERENCES.

¹ C. F. Rammelsberg, *Pogg. Ann.*, **98**, 262, 1856; M. Siewert, *Zeit. Ges. Naturw.*, **17**, 49, 1860; B. Leopold, *ib.*, **17**, 51, 1860; E. Reichardt, *Neues Jahrb. Min.*, **343**, 1866; L. N. Vauquelin, *Journ. Mines*, **9**, 30, 1799.

² W. H. Emory, *Amer. Journ. Science*, (2), **6**, 389, 1848; W. Hüttner, *Chem. Ztg.*, **46**, 197, 1922; J. L. Proust, *Anales Hist. Nat. Madrid*, **1**, 137, 1799; F. Stromeyer, *Pogg. Ann.*, **31**, 137, 1834; F. Stromeyer and J. F. L. Hausmann, *Schweigger's Journ.*, **69**, 255, 1833; J. Bouis, *Rev. Scient. Ind.*, **14**, 300, 1843; A. Dufrenoy, *Traité de minéralogie*, Paris, **2**, 333, 1844; E. Priwoznik, *Dingler's Journ.*, **260**, 335, 1886; R. B. Ladoo, *Rep. U.S. Bur. Mines*, **2333**, 1922; *Chem. Age*, **7**, 203, 1922.

³ T. Graham, *Phil. Mag.*, (3), **6**, 422, 1835; H. G. F. Schröder, *Ber.*, **4**, 471, 1871; G. H. Bailey, *Journ. Chem. Soc.*, **51**, 676, 1887; C. Schmidt, *Pharm. Centr.*, **1**, 664, 1859.

⁴ H. Holland, *On the manufacture of the sulphate of magnesia at Monte della Guardia*, Genoa, 1816; F. Michels, *Zeit. Ver. deut. Ing.*, **12**, 320, 1868; F. F. Anthon, *Journ. prakt. Chem.*, (1), **9**, 1, 1836; J. H. Swindells, *Dingler's Journ.*, **185**, 219, 1867; F. Findeisen, *Polyt. Notizbl.*, **81**, 1860; M. Freydiere and M. Dubreul, *French Pat. No.* 94553, 1872.

⁵ W. L. Kölreuter, *Mag. Pharm.*, **8**, 181, 1824; *Grosh. Bad. Staats- und Regierungsblatt*, **89**, 1821; J. S. F. Pagenstecher, *Schweizer. Ges. Ver.*, **97**, 1826; *Pommer. Zeit.*, **5**, 232, 1840; E. Merck, *Prüfung der chemischen Reagenzien auf Reinheit*, Darmstadt, **237**, 1912; E. Biltz, *Arch. Pharm.*, (3), **4**, 46, 1874.

⁶ J. H. van't Hoff, W. Meyerhoffer, and N. Smith, *Sitzber. Akad. Berlin*, **1034**, 1901; J. H. van't Hoff and T. Estreicher-Rozbiersky, *ib.*, **487**, 1898; J. H. van't Hoff and H. M. Dawson, *ib.*, **340**, 1899; C. F. Rammelsberg, *Pogg. Ann.*, **98**, 253, 1856; *Arch. Pharm.*, (2), **127**, 58, 1866; E. Reichardt, *ib.*, (2), **103**, 346, 1860; (2), **109**, 299, 1862; *Neues Jahrb. Min.*, **343**, 1866; F. Bischof, *Berg. Hütt. Ztg.*, **24**, 268, 1865; *Die Steinsalzwerke bei Stassfurt*, Halle, 1864; T. E. Thorpe and J. I. Watts, *Journ. Chem. Soc.*, **37**, 102, 1880; L. Playfair, *Journ. Chem. Soc.*, **16**, 274, 1863; M. Siewert, *Zeit. ges. Naturw.*, **17**, 49, 1860; B. Leopold, *ib.*, **17**, 51, 1860; J. Bräuning, *ib.*, **20**, 33, 1862; E. Jänecke, *Kalk*, **10**, 371, 1916; **11**, 10, 21, 1917; J. K. van der

Heide, *Zeit. phys. Chem.*, 12. 418, 1893; E. Wiedemann, *Wied. Ann.*, 17. 571, 1882; S. Takegami, *Journ. Chem. Soc. Japan*, 42. 441, 1921; *Mem. Coll. Science Kyoto*, 5. 191, 1921; F. Erlenmeyer, *Ber.*, 2. 289, 1869; G. Tschermak, *Sitzber. Akad. Wien*, 53. 317, 1866; J. Thomsen, *Journ. prakt. Chem.*, (2), 18. 16, 1878; J. Fritzsche, *Pogg. Ann.*, 42. 577, 1842; H. Grüneberg, *Dingler's Journ.*, 189. 238, 1868; G. Clemm, *Bull. Soc. Chim.*, (2), 1. 297, 1864; S. U. Pickering, *ib.*, 49. 406, 1886; J. B. Hannay, *ib.*, 32. 388, 1877; N. A. E. Millon, *Ann. Chim. Phys.*, (3), 13. 134, 1845; H. Löwel, *ib.*, (3), 43. 405, 1855; L. de Boisbaudran, *ib.*, (4), 18. 260, 1869; J. C. G. de Marignac, *Ann. Mines*, (5), 12. 50, 1857; E. Mitscherlich, *Gesammelte Schriften*, Berlin, 311, 1896; W. Haidinger, *Pogg. Ann.*, 6. 191, 1826; L. Playfair and J. P. Joule, *Journ. Chem. Soc.*, 1. 138, 1849; *Mem. Chem. Soc.*, 2. 401, 1845; T. Graham, *ib.*, 1. 82, 106, 1849; *Trans. Roy. Soc. Edin.*, 13. 297, 1836; *Phil. Mag.*, (4), 6. 422, 1853; *Phil. Trans.*, 127. 47, 1837; E. Wiedemann, *Wied. Ann.*, 17. 571, 1882.

⁷ C. Schultz, *Pogg. Ann.*, 133. 147, 1868; *Ueber die wasserhaltigen und die wasserfreien sauren Salze der Schwefelsäure*, Göttingen, 26, 1868; G. Tammann, *Mém. Acad. St. Petersburg*, (7), 35. 1, 1888; J. L. Gay Lussac, *Ann. Chim. Phys.*, (2), 11. 311, 1819; L. de Boisbaudran, *ib.*, (4), 18. 260, 1869; L. C. de Coppet, *ib.*, (4), 25. 532, 1872; A. Gérardin, *ib.*, (4), 5. 145, 1865; H. Löwel, *ib.*, (3), 43. 405, 1855; A. Étard, *ib.*, (7), 2. 54, 1894; *Compt. Rend.*, 106. 206, 740, 1888; F. Margueritte, *ib.*, 43. 50, 1856; R. J. Kane, *Phil. Mag.*, 8. 353, 1836; *Ann. Chim. Phys.*, (2), 72. 337, 1839; J. C. G. de Marignac, *Ann. Mines*, (5), 12. 50, 1857; C. J. B. Karsten, *Philosophie der Chemie*, Berlin, 93. 101, 1843; *Lehrbuch der Salinenkunde*, Berlin, 2. 311, 1847; R. Diacon, *Mém. Acad. Montpellier*, 6. 45, 1864; *Recherches sur la solubilité des mélanges salins*, Montpellier, 1864; G. J. Mulder, *Bijdragen tot de geschiedenis van het scheikundig gebonden water*, Rotterdam, 51, 1864; C. von Hauer, *Sitzber. Akad. Wien*, 53. 221, 1866; H. Schwarz, *Dingler's Journ.*, 198. 159, 1870; K. Haushofer, *Sitzber. Akad. München*, 15. 403, 1885; *Mikroskopische Reaktionen*, Braunschweig, 94, 1885; S. Setschenoff, *Ber.*, 6. 1461, 1873; H. Grüneberg, *ib.*, 5. 340, 1872; R. Fassbender, *ib.*, 9. 1358, 1876; J. H. Dröze, *ib.*, 10. 340, 1877; H. Precht and B. Wittgen, *ib.*, 15. 1666, 1882; T. S. Hunt, *Amer. Journ. Science*, (2), 26. 109, 1858; (2), 28. 170, 365, 1859; F. Hoppe-Seyler, *Zeit. deut. geol. Ges.*, 27. 495, 1875; F. Pfaff, *Liebig's Ann.*, 99. 224, 1856; E. Tobler, *ib.*, 95. 193, 1855; H. Schiff, *ib.*, 106. 115, 1858; 118. 365, 1861; J. H. van't Hoff, W. Meyerhoffer, and N. Smith, *Sitzber. Akad. Berlin*, 1035, 1901; J. H. van't Hoff and H. M. Dawson, *ib.*, 340, 1899; J. Kendall and A. W. Davidson, *Journ. Amer. Chem. Soc.*, 43. 979, 1921; F. Rüdorff, *Pogg. Ann.*, 145. 612, 1872; H. Rose, *ib.*, 35. 180, 1835; W. Haidinger, *ib.*, 6. 191, 1826; F. Guthrie, *Phil. Mag.*, (5), 1. 366, 1876; E. E. Basch, *Die künstliche Darstellung und die Bildungsverhältnisse des Polyhalit*, Berlin, 17, 1901; A. Geiger, *Die künstliche Darstellung und die Bildungsverhältnisse des Krugits*, Berlin, 22, 1904; R. Kremann, *Landolt-Börnstein's Physikalisch-chemische Tabellen*, Berlin, 481, 1912; J. Timmermans, *Bull. Soc. Chim. Belg.*, 20. 305, 1906; C. Hensgen, *Ber.*, 10. 259, 1877; J. B. Richter, *Anfangsgründe der Stöchiometrie*, Breslau, 2. 245, 1794; J. F. Snell, *Journ. Phys. Chem.*, 2. 457, 1899; W. Eidmann, *Ein Beitrag zur Erkenntnis des Verhaltens chemischer Verbindungen in nichtwässrigen Lösungen*, Giessen, 1899; O. Aschan, *Chem. Ztg.*, 37. 1117, 1913; T. F. von Groth, *Scherer's Nord. Blatt. Chem.*, 235, 1817; E. Wiedemann, *Wied. Ann.*, 17. 571, 1882; C. W. Scheele, *Nova Acta Acad. Stockholm*, 1, 1785; H. S. van Klooster, *Journ. Phys. Chem.*, 23. 513, 1917; J. K. van der Heide, *Zeit. phys. Chem.*, 12. 418, 1893; C. A. L. de Bruyn, *ib.*, 10. 782, 1892; *Rec. Trav. Chim. Pays-Bas*, 11. 112, 1892; *Ber.*, 26. 268, 1893; A. Köhler, *Zeit. Ver. Zuckerind.*, 47. 447, 1897; C. D. Carpenter and E. R. Jette, *Journ. Amer. Chem. Soc.*, 45. 578, 1923.

⁸ G. Tschermak, *Sitzber. Akad. Wien*, 53. 317, 1866; J. Grailich, *ib.*, 27. 22, 1857; G. Wyrouboff, *Bull. Soc. Min.*, 12. 75, 371, 1889; L. de Boisbaudran, *Ann. Chim. Phys.*, (4), 18. 260, 1869; J. C. G. de Marignac, *Ann. Mines*, (5), 12. 50, 1857; H. Kopp, *Liebig's Ann.*, 125. 369, 1863; B. Gossner in P. Groth, *Chemische Krystallographie*, Leipzig, 2. 422, 1908; H. J. Brooke, *Ann. Phil.*, 22. 40, 1823; H. Grandinger, *Centr. Min.*, 49, 1917; J. M. Thomson, *Journ. Chem. Soc.*, 35. 196, 1879; E. Blasius, *Zeit. Kryst.*, 10. 227, 1885.

⁹ L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, 2. 401, 1845; *Journ. Chem. Soc.*, 1. 138, 1849; L. Playfair, *ib.*, 16. 274, 1863; T. E. Thorpe and J. I. Watts, *ib.*, 37. 102, 1880; C. J. B. Karsten, *Schweigger's Journ.*, 65. 394, 1832; E. Filhol, *Ann. Chim. Phys.*, (3), 21. 415, 1847; J. H. Hassenfratz, *ib.*, (1), 28. 3, 1798; C. Pape, *Pogg. Ann.*, 120. 367, 1863; C. R. Schulze, *ib.*, 31. 229, 1887; O. Pettersson, *Nova Acta Upsala*, 9. 4, 1873; 10. 7, 1876; J. W. Retgers, *Zeit. phys. Chem.*, 3. 497, 1889; H. G. F. Schröder, *Journ. prakt. Chem.*, (2), 19. 266, 1879; *Dichtigkeitsmessungen*, Heidelberg, 1873; F. Bischof, *Berg. Hutt. Ztg.*, 24. 268, 1865; *Die Steinsalzwerke bei Stassfurt*, Halle, 1864; G. Wyrouboff, *Bull. Soc. Min.*, 12. 371, 1889; G. Tschermak, *Sitzber. Akad. Wien*, 53. 317, 1866; H. J. Buignet, *Journ. Pharm. Chem.*, (3), 40. 161, 337, 1861; H. Schiff, *Liebig's Ann.*, 107. 64, 1858; H. Kopp, *ib.*, 36. 1, 1840; J. D. Forbes, *Phil. Mag.*, (3), 32. 135, 1848; S. Holker, *ib.*, (3), 27. 213, 1845; W. C. Smith, *Amer. Journ. Pharm.*, 53. 148, 1882; G. Krause, *Arch. Pharm.*, (3), 6. 41, 1875.

¹⁰ G. T. Gerlach, *Zeit. anal. Chem.*, 8. 287, 1869; *Specifiche Gewichte der gebräuchlichsten Salzlösungen*, Freiburg, 1859; A. C. Oudemans, *ib.*, 7. 419, 1868; H. T. Barnes and A. P. Scott, *Journ. Phys. Chem.*, 2. 536, 1898; J. G. McGregor, *Chem. News*, 55. 3, 1887; 62. 223, 232, 1890; S. de Lannoy, *Zeit. phys. Chem.*, 18. 443, 1895; S. Arrhenius, *ib.*, 1. 285, 1887; F. Kohlrausch and W. Hallwachs, *Gött. Nachr.*, 350, 1893; F. Kohlrausch, *Wied. Ann.*, 56. 185, 1895; *Zeit. phys. Chem.*, 5. 31, 1890; J. Wagner, *Wied. Ann.*, 18. 259, 1883; E. Wiedemann, *ib.*, 17. 561, 1882; 26. 161, 1885; W. Hallwachs, *ib.*, 53. 1, 1894; L. de Boisbaudran, *Compt. Rend.*,

121. 539, 1895; J. H. Pollok, *Proc. Roy. Soc. Edin.*, 13. 626, 1886; R. Broom, *ib.*, 13. 172, 1886; H. Schiff, *Liebig's Ann.*, 113. 186, 1860; W. W. J. Nicol, *Phil. Mag.*, (5), 16. 121, 1883; E. F. Anthon, *Journ. prakt. Chem.*, (1), 9. 3, 1836; A. Michel and L. Krafft, *Ann. Chim. Phys.*, (3), 41. 482, 1854; C. J. B. Karsten, *Philosophie der Chemie*, Berlin, 1843; *Lehrbuch der Salinenkunde*, Berlin, 1847; W. Watson, *Proc. Roy. Soc. Edin.*, 23. 282, 1913; W. Stiles, *Biochem. Journ.*, 15. 629, 1921; A. Battelli and A. Stefanini, *Atti Accad. Lincei (Rend.)*, (5), 16. i, 11, 1907; W. W. J. Nicol, *Journ. Chem. Soc.*, 51. 389, 1887; P. G. Tait, *Proc. Roy. Soc. Edin.*, 20. 63, 141, 1895; W. Grabowsky, *Beiträge zur Feststellung der wahren Oberflächenspannung wässeriger Chloridlösungen (zwischen 10° und 30° C.) und zu ihrer physikalisch-chemischen Verwertung*, Gräfenhainichen, 1904; J. D. R. Scheffer, *Ber.*, 15. 788, 1882; 16. 1903, 1883; *Zeit. phys. Chem.*, 2. 390, 1888; J. Schuhmeister, *Sitzber. Akad. Wien*, 79. 603, 1879; H. Sentsis, *Tension superficielle de l'eau et des solutions salines*, Paris, 1897; T. Graham, *Phil. Trans.*, 140. 1, 805, 1850; 141. 483, 1851; *Phil. Mag.*, (3), 37. 181, 341, 1850; *Journ. Chem. Soc.*, 3. 60, 1851; H. C. Jones and F. H. Getman, *Zeit. phys. Chem.*, 49. 390, 1904; D. Dijken, *ib.*, 24. 81, 1897; J. Forchheimer, *ib.*, 34. 20, 1900; O. Schönrock, *ib.*, 11. 781, 1893; W. Ostwald, *Journ. prakt. Chem.*, (2), 18. 328, 1878; J. Kannonkoff, *ib.*, (2), 31. 321, 1885; E. Forster, *Mitt. Nat. Bern*, 3, 1878; *Untersuchungen über die Beziehungen die zwischen dem spezifischen Brechungsvermögen und der Concentration der Salzlösungen bestehen*, Bern, 1878; J. Thomsen, *Pogg. Ann.*, 142. 337, 1871; A. Sprung, *ib.*, 159. 1, 1876; C. A. Valson, *Compt. Rend.*, 74. 103, 1872; S. Charpy, *Ann. Chim. Phys.*, (6), 29. 5, 1893; *Recherches sur les solutions salines*, Paris, 1892; P. Barbier and L. Roux, *Bull. Soc. Chim.*, (3), 3. 424, 1890; H. Hager, *Manuale pharmaceuticum adjumenta varia*, Leipzig, 1876; P. de Heen, *Physique comparée*, Paris, 1888; R. J. Holland, *Wied. Ann.*, 50. 350, 1893; O. Knöfler, *ib.*, 38. 136, 1889; O. Pulvermacher, *Zeit. anorg. Chem.*, 113. 142, 1920.

¹¹ G. H. Bailey, *Journ. Chem. Soc.*, 51. 676, 1887; J. B. Hannay, *ib.*, 32. 388, 1877; C. Daubeny, *Edin. Phil. Journ.*, 7. 111, 1822; J. B. J. D. Boussingault, *Ann. Chim. Phys.*, (4), 12. 419, 1867; H. le Chatelier, *Bull. Soc. Chim.*, (2), 47. 300, 1887; A. S. Ginsberg, *Zeit. anorg. Chem.*, 59. 346, 1908; 61. 122, 1909; R. Nacken, *Gött. Nachr.*, 602, 1907; G. J. Mulder, *Bijdragen tot de geschiedenis van het scheikundig gebonden water*, Rotterdam, 53, 1864; H. G. F. Schröder, *Ber.*, 4. 471, 1871; V. A. Jacquelin, *Ann. Chim. Phys.*, (3), 82. 201, 1851; T. Graham, *Trans. Roy. Soc. Edin.*, 18. 297, 1836; *Phil. Mag.*, (3), 6. 327, 417, 1835; (3), 20. 539, 1842; *Mem. Chem. Soc.*, 1. 83, 1843; R. Reidenbach, *Ueber die quantitative Bestimmung des Magnesiums als Magnesiumpyrophosphat*, Kusel, 1910.

¹² J. C. G. de Marignac, *Arch. Sciences Genève*, 55. 113, 1876; *Ann. Chim. Phys.*, (5), 8. 410, 1876; G. Tammann, *Zeit. phys. Chem.*, 18. 625, 1895; G. Jäger, *Sitzber. Akad. Wien*, 99. 245, 1890; C. Pape, *Pogg. Ann.*, 120. 337, 1863; H. Kopp, *Liebig's Ann. Suppl.*, 3. 289, 1865; *Phil. Trans.*, 155. 71, 1865; K. Bindel, *Wied. Ann.*, 40. 370, 1890; S. Pagliani, *Atti Accad. Torino*, 16. 595, 1881; J. Thomsen, *Pogg. Ann.*, 142. 337, 1871; H. Teudt, *Sitzber. Phys. Med. Soc. Erlangen*, 31. 131, 1900; *Ueber die Aenderung der spezifischen Wärmen wässriger Salzlösungen mit der Temperatur*, Erlangen, 1900.

¹³ E. Cohen, *Arch. Néerl.*, (2), 5. 295, 1901; P. C. F. Frowein, *Zeit. phys. Chem.*, 1. 13, 1887; E. Cohen, *ib.*, 36. 517, 1901; H. Bolte, *ib.*, 80. 338, 1912; A. W. C. Menzies, *Journ. Amer. Chem. Soc.*, 42. 1951, 1920; W. C. Schumb, *ib.*, 45. 342, 1923; H. W. Foote and S. R. Scholes, *ib.*, 33. 1309, 1911; W. Müller-Erzbach, *Ber.*, 17. 1417, 1884; *Wied. Ann.*, 23. 607, 1884; C. R. Schulze, *ib.*, 31. 204, 1887; G. Wiedemann, *Pogg. Ann. Jubelbd.*, 474, 1874; H. Lescoeur, *Compt. Rend.*, 103. 1260, 1886; G. Tammann, *Mém. Acad. St. Petersburg*, (7), 35. 1, 1887; C. D. Carpenter and E. R. Jette, *Journ. Amer. Chem. Soc.*, 45. 578, 1923.

¹⁴ H. C. Jones and F. H. Getman, *Hydrates in Aqueous Solution*, Washington, D.C., 69, 1907; *Zeit. phys. Chem.*, 49. 385, 1904; S. Arrhenius, *ib.*, 2. 461, 1888; F. M. Raoult, *ib.*, 2. 489, 1888; E. H. Loomis, *Wied. Ann.*, 51. 500, 1894; G. J. Mulder, *Bijdragen tot de geschiedenis van het scheikundig gebonden water*, Rotterdam, 1864; T. Griffiths, *Journ. Science*, 18. 90, 1825; L. Kahlenberg, *Journ. phys. Chem.*, 5. 353, 1901; A. A. Noyes and F. G. Falk, *Journ. Amer. Chem. Soc.*, 32. 1011, 1910; T. G. Bedford, *Proc. Roy. Soc.*, 83. A, 459, 1910; H. Hausrath, *Ann. Physik*, (4), 9. 545, 1902; G. T. Gerlach, *Zeit. anal. Chem.*, 26. 413, 1887.

¹⁵ J. Thomsen, *Journ. prakt. Chem.*, (2), 11. 233, 402, 1875; (2), 12. 85, 271, 1875; (2), 18. 1, 1878; (2), 17. 165, 1878; (2), 18. 1, 1878; S. U. Pickering, *Journ. Chem. Soc.*, 47. 100, 1885; 49. 260, 1886; M. Berthelot, *Ann. Bur. Longitudes*, 395, 1877; C. M. van Deventer and H. J. van de Stadt, *Zeit. phys. Chem.*, 9. 43, 1892; F. Rüdorff, *Ber.*, 2. 68, 1869; T. Graham, *Phil. Mag.*, (3), 22. 329, 1843; (3), 24. 401, 1844; *Mem. Chem. Soc.*, 1. 106, 1843; 2. 51, 1845; M. Berthelot and L. Ilosvay de N. Ilosva, *Ann. Chim. Phys.*, (5), 29. 305, 1883.

¹⁶ L. Longchambon, *Compt. Rend.*, 172. 1187, 1921; G. Tschermak, *Sitzber. Akad. Wien*, 53. 317, 1866; A. des Cloizeaux, *Ann. Mines*, (5), 14. 375, 1858; H. C. Pocklington, *Nature*, 73. 270, 1906; O. Schönrock, *Zeit. phys. Chem.*, 11. 753, 1893; F. Kohlrausch, *Wied. Ann.*, 4. 28, 1878; H. Dufet, *Bull. Soc. Min.*, 3. 188, 1880; A. Fock, *Zeit. Kryst.*, 4. 583, 1880; C. Borel, *Arch. Sciences Genève*, (3), 34. 151, 1895; *Compt. Rend.*, 120. 1406, 1895; H. Töpsöe and C. Christiansen, *Ann. Chim. Phys.*, (5), 1. 21, 30, 1874; B. Wagner, *Tabellen zum Einwauchrefraktometer*, Sondershausen, 1907; W. Hallwachs, *Wied. Ann.*, 53. 1, 1894; E. Forster, *Mitt. Nat. Bern*, 3, 1878; *Untersuchungen über die Beziehungen die zwischen dem spezifischen Brechungsvermögen und der Concentration der Salzlösungen bestehen*, Bern, 1878; P. Barbier and L. Roux, *Bull. Soc. Chim.*, (3), 3. 255, 419, 424, 1890; (3), 4. 9, 614, 620, 1890; D. Dijken, *Zeit. phys.*

Chem., **24**, 81, 1897; J. Forchheimer, *ib.*, **34**, 20, 1900; G. Wyruboff, *Bull. Soc. Min.*, **12**, 75, 369, 1889; P. Bary, *Compt. Rend.*, **130**, 776, 1900; J. Dinkhauser, *Anz. Akad. Wien*, **143**, 1905; *Sitzber. Akad. Wien*, **114**, 1001, 1905; O. Pulvermacher, *Zeit. anorg. Chem.*, **113**, 141, 1920.

¹⁷ W. C. D. Whetham, *Proc. Roy. Soc.*, **71**, 332, 1903; G. N. Lewis and G. A. Linhart, *Journ. Amer. Chem. Soc.*, **41**, 1951, 1919; G. N. Lewis and M. Randall, *ib.*, **43**, 1112, 1921; A. Benrath and K. Drekopf, *Zeit. phys. Chem.*, **99**, 57, 1921; J. Kendall, H. Adler, and A. W. Davidson, *Journ. Amer. Chem. Soc.*, **43**, 1846, 1921; E. Klein, *Wied. Ann.*, **27**, 151, 1886; C. Heim, *ib.*, **27**, 643, 1886; P. Walden, *Zeit. phys. Chem.*, **1**, 529, 1887; W. Bein, *ib.*, **27**, 1, 1898; K. Hopfgartner, *ib.*, **25**, 115, 1898; R. B. Denison, *ib.*, **44**, 575, 1903; O. Masson, *ib.*, **29**, 501, 1898; *Phil. Trans.*, **192**, 331, 1899; B. D. Steele, *ib.*, **193**, 105, 1902; *Journ. Chem. Soc.*, **79**, 414, 1901; *Zeit. Elektrochem.*, **7**, 618, 1901; *Zeit. phys. Chem.*, **40**, 689, 1902; H. C. Jones, *The Electrical Conductivity, Dissociation, and Temperature Coefficients of Conductivity of Solutions*, Washington, 1912; W. Hittorf, *Pogg. Ann.*, **106**, 337, 513, 1859; A. Chassy, *Ann. Chim. Phys.*, (6), **21**, 241, 1890; K. Hopfgartner, *Zeit. phys. Chem.*, **25**, 115, 1898.

¹⁸ G. Quincke, *Wied. Ann.*, **24**, 347, 1885; **34**, 401, 1888; S. Meyer, *ib.*, **68**, 325, 1899; **69**, 236, 1899; *Ann. Physik*, (4), **1**, 664, 668, 1900; G. Meslin, *Ann. Chim. Phys.*, (8), **7**, 145, 1906; C. K. Studley, *Phys. Rev.*, (1), **24**, 22, 1907; C. Borel, *Arch. Sciences Genève*, (3), **30**, 131, 1893; *Recherches des constantes diélectriques de quelques substances cristallisées*, Genève, 1883; A. de Gramont, *Bull. Soc. Min.*, **7**, 235, 1884; J. Grailich and V. von Lang, *Sitzber. Akad. Wien*, **33**, 58, 1858; P. Pascal, *Compt. Rend.*, **173**, 144, 1921.

¹⁹ J. B. Richter, *Anfangsgründe der Stöchiometrie*, Breslau, **2**, 245, 1794; H. von Blücher, *Pogg. Ann.*, **50**, 541, 1840; G. Clemm, *Bull. Soc. Chim.*, (2), **1**, 297, 1864; O. Boudouard, *ib.*, (3), **25**, 284, 1901; J. L. Gay Lussac, *Ann. Chim. Phys.*, (2), **63**, 431, 1836; F. G. Reichel, *Journ. prakt. Chem.*, (2), **12**, 65, 1875; E. Jacquemin, *Compt. Rend.*, **46**, 1164, 1858; E. H. Riesenfeld, *Journ. prakt. Chem.*, (2), **100**, 115, 1920; E. Kunheim, *Ueber die Einwirkung des Lichtbogens auf Gemische von Sulfaten mit Kohle*, Berlin, **25**, 1900; C. Hensgen, *Ber.*, **10**, 259, 1877; V. Merz and W. Weith, *ib.*, **13**, 718, 1880; A. d'Heureuse, *Pogg. Ann.*, **75**, 255, 1848; C. J. B. Karsten, *Lehrbuch der Salinenkunde*, Berlin, **2**, 50, 280, 1847; *Philosophie der Chemie*, Berlin, **176**, 1843; C. W. Scheele, *Acta Acad. Stockholm*, **1**, 1771; P. Berthier, *Ann. Chim. Phys.*, (2), **22**, 236, 1823; K. Stammer, *Dingler's Polyt. Journ.*, **156**, 40, 1860; **153**, 42, 131, 1860; **165**, 45, 135, 1862; L. A. Planche, *Journ. Pharm.*, **12**, 131, 1826; S. J. Thugutt, *Zeit. anorg. Chem.*, **2**, 149, 1892; A. B. Prescott, *Chem. News*, **36**, 179, 1877; J. Zawadzky, K. Kossak, and H. Narbut, *Przemysl Chem.*, **5**, 225, 1922.

§ 13. The Complex and Double Salts of Magnesium Sulphate

At least three double sulphates of sodium and magnesium occur in the Stassfurt salt deposits, namely, *vanthoffite*, $\text{MgSO}_4 \cdot 3\text{Na}_2\text{SO}_4$; *blödite* or *astrakanite*, or *simonyte*, $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; and *löweite*, $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. R. Nacken,¹ S. Takegami, and A. S. Ginsberg have studied the equilibrium conditions in the binary system, MgSO_4 — Na_2SO_4 , and the probable results are shown graphically in Fig. 23. The equilibrium is somewhat complicated. The f.p. curve has a eutectic at 44.2 molar per cent. of MgSO_4 , and 670°; and there is a break at 71.3 molar per cent. and 814°. α -Sodium sulphate forms solid soln. containing up to 35.8 mols per cent. MgSO_4 . The compound **disodium trimagnesium tetrasulphate**, $\text{Na}_2\text{SO}_4 \cdot 3\text{MgSO}_4$, melts with decomposition at 814°. Magnesium sulphate does not form solid soln. The existence of the two other compounds, **disodium magnesium disulphate**, $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$ and **hexasodium magnesium tetrasulphate**, $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$, formed only in the solid state, is also indicated.

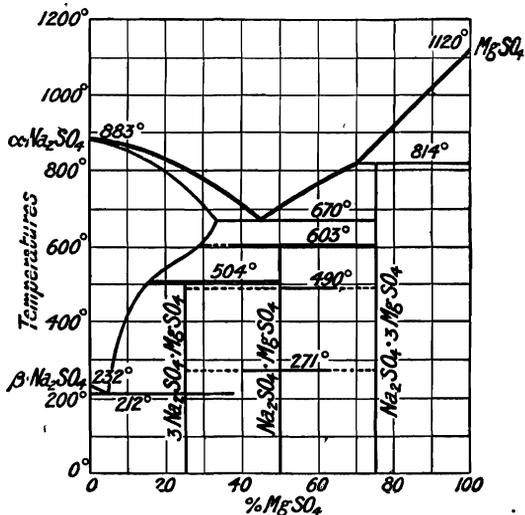


FIG. 23.—Freezing-point Curves of the Binary System, Na_2SO_4 — MgSO_4 .

These compounds are identical with anhydrous blödite and vanthoffite respectively, the former existing in α -, β -, and γ -modifications. Sodium sulphate only forms two modifications, the transition point being at 232°. H. le Chatelier placed the maximum at $\text{Na}_2\text{SO}_4 \cdot 2\text{MgSO}_4$, but this is wrong. Some early work on the mutual solubilities of the sodium and magnesium sulphates has been previously indicated.

Crystals of löweite, *i.e.* **pentahemihydrated sodium magnesium disulphate**, $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, or $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, were found in masses associated with the anhydrite at the Ischl salt mine, Austria; and they were described by W. Haidinger in 1846, and analyzed by K. von Hauer. Löweite occurs in yellowish-white or reddish-white compact masses. J. H. van't Hoff and G. Just prepared this salt by dissolving 10.5 grms. of sodium chloride in a litre of water, and mixing this with a second soln. containing eq. proportions of magnesium and sodium sulphates. The mixed soln. is then slowly evaporated at 55° to 60°, when astrakanite begins to crystallize out. The soln. is then seeded with löweite, the vessel closed, and kept for several days at the same temp. Crystals of löweite appear. According to J. H. van't Hoff and A. O'Farely, astrakanite is transformed into löweite at 71°; and a soln. which contains eq. proportions of the component salts, at a temp. exceeding 71° first gives astrakanite, which then passes into löweite. The transition temp. is lowered when other salts are present —*e.g.* it is 43° in the presence of a soln. containing 25 grms. of heptahydrated magnesium sulphate, 7 grms. of sodium chloride, 3 grms. of leonite, and one gm. of astrakanite. The optical properties of the crystals show that they belong to the tetragonal system. W. Haidinger found the sp. gr. of löweite to be 2.376 to 2.42; and the hardness $2\frac{1}{2}$ to 3 on Mohs' scale.

Reddish translucent masses of a mineral from the salt mines of Ischl (Austria) were analyzed by J. F. John in 1811, and found to be eq. to **tetrahydrated sodium magnesium sulphate**, $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, or $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The mineral was called *blödite*, after M. Blöde. G. Rose obtained imperfect crystals from the salt lakes of Astrakan, east of the mouth of the Volga, and he called the mineral *astrakanite*; analyses showed that the two minerals have virtually the same composition. Crystals also occur in the soil near Mendoza, and east of San Juan, and at Stassfurt; and Munos y Luna found prismatic crystals in the dry beds of some Toledo lakes in summer. The salt has also been analyzed by K. von Hauer, A. A. Hayes, G. vom Rath, A. Brezina, etc. G. Tschermak obtained crystals of a mineral, which he called *simonyite*, resembling those of astrakanite, and of the same composition, but unlike the latter, the crystals of simonyite do not effloresce in air; and P. Groth and C. Hintze's blödite, which was unalterable in air, was probably simonyite; they assumed that the efflorescence of ordinary blödite was due to the presence of some efflorescent salt as impurity. H. F. Link regarded the double salt as a hexahydrate.

A. R. Arrott probably prepared tetrahydrated sodium magnesium sulphate in 1844, by evaporating at 50° a soln. containing eq. proportions of the component salts. J. Koppel, H. W. B. Roozeboom, J. H. van't Hoff and W. Meyerhoffer, and C. M. van Deventer and J. H. van't Hoff have studied the conditions under which the double salt is formed in aq. soln. The transition temp. for the reaction: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + 13\text{H}_2\text{O}$, is about 21.5°; and, according to the latter, if finely powdered astrakanite be mixed with water in the proportion represented by this equation, at a temp. below 21.5°, the thin paste soon sets to a dry solid mixture of the two sulphates, but above 21.5° this does not occur. Similarly, a finely powdered mixture of the two hydrated sulphates remains unchanged if kept in a closed flask below 21.5°, but above that temp. astrakanite is formed, and this is evidenced by the appearance of partial fusion produced by the liberated water. A mixture of heptahydrated magnesium sulphate and of decahydrated sodium sulphate melts at 26°. The formation of astrakanite is accelerated if some of the last-named salt be added at the beginning. The transi-

tion point is lowered by sodium chloride such that a mixture of eq. proportions of decahydrated sodium sulphate, heptahydrated magnesium sulphate, and sodium chloride melts at 15°, the system contracts, and monohydrated sodium sulphate separates out; after a time, the vol increases, and astrakanite is formed. When this point is reached, the reverse reaction occurs below 5°—*cf.* Fig. 6, 2, 20, 3. The formation of astrakanite by the reaction symbolized: $2\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 2\text{NaCl} = \text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + 4\text{H}_2\text{O}$, was found to occur above 30.6°.

Astrakanite is somewhat deliquescent in a moderately moist atm. J. Murray said the crystals are permanent in air. W. H. Miller found the axial ratios to be $a : b : c = 1.3492 : 1 : 0.6717$, and $\beta = 100^\circ 48'5''$. This salt is one member of an isomorphous group in which manganese (ous), iron (ous), and zinc replace the magnesium of astrakanite; but it is not isomorphous with potassium-astrakanite. The crystals of astrakanite have a negative double refraction; the sp. gr. is 2.223 to 2.244; and the hardness 2.5 to 3.5 on Mohs' scale. According to J. H. van't Hoff and A. O'Farely, astrakanite passes into löweite at 71°; and, according to J. H. van't Hoff and G. Just, in the presence of sodium chloride, and seeding with vanthoffite and löweite, the transition temp. is lowered to 59°. G. Tschermak found that the crystals lose about three-eighths of their water—*i.e.* 7.33 per cent. in weight—when heated on a water-bath; but P. Groth and C. Hintze found 8.8 per cent. is lost at 100°, and 10.12 per cent. at 150°; and G. vom Rath found 10.05 per cent. is lost between 100° and 130°; 10.09 per cent. between 130° and 300°; and the remaining 1.16 per cent. at a red heat. E. Reichardt also made observations on the dehydration of astrakanite. G. Tschermak found the dehydrated mass melts to a clear liquid which glows when it begins to freeze. J. H. van't Hoff and A. O'Farely represented the vap. press., p , of astrakanite at a temp. θ , by the expression $\log p = \log p_w - (166.79 - 2.017\theta)/(273 + \theta)$, where p_w represents the vap. press. of water. J. Murray said that the double sulphate is soluble in three times its wt. of water. According to H. W. B. Roozeboom, 100 mols of water hold in sat. soln.:

	22°	24.5°	30°	35°	47°
Astrakanite $(\text{Na}_2\text{SO}_4$	2.95	3.45	3.60	3.69	3.60 mols
$(\text{MgSO}_4$	4.70	3.68	3.60	3.69	3.60 „

If an excess of either component be present, the solubility of astrakanite is lowered a little. According to J. H. van't Hoff and A. O'Farely, the heat of soln. of astrakanite is 1456 Cals. per kgrm. mol, and of löweite, 7998 Cals.; the heat of transformation of löweite to astrakanite is 6542 Cals. per kgrm. mol.

K. Kubierschky deduced indirectly that anhydrous **hexasodium magnesium tetrasulphate**, $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$, or $\text{Na}_6\text{Mg}(\text{SO}_4)_4$, occurs in the salts from Wilhelmshall in the Magdeburg-Halberstadt salt district, and he gave it the name *vanthoffite*. J. H. van't Hoff found that the salt is produced artificially by heating the crystals of blödite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, deposited at 22° from a soln. containing equi-mol. proportions of the component sulphates, which when heated to 70° in the mother liquor, lose some of their water, and are transformed into löweite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, and at a still higher temp. crystals of the anhydrous salt, $\text{Na}_6\text{Mg}(\text{SO}_4)_4$, appear. Among other methods of preparation, J. H. van't Hoff showed that the salt can be made by digesting on a water-bath a mixture of 154 grms. of water, 54 grms. of sodium chloride, 252 grms. of decahydrated sodium chloride, and 103 grms. of heptahydrated magnesium sulphate; the sodium sulphate first deposited gradually gives way to vanthoffite, and when all is transformed, the crystals are collected on a hot-water suction filter, washed first with 50 per cent. and then with absolute alcohol and dried. According to J. H. van't Hoff and G. Just, 46° is the lowest temp. at which vanthoffite is formed from astrakanite and sodium sulphate in a soln. simultaneously saturated with sodium chloride and glaserite. The crystals of vanthoffite resemble those of löweite; their sp. gr. is 2.7; and the hardness of the natural mineral, containing 10 per cent. of sodium chloride, is 3 on Mohs' scale.

C. H. Pfaff² found that magnesium and potassium sulphates unite together,

producing differently formed crystals—thus H. F. Link said that the crystals are long prisms which crumble in air; and C. L. Berthollet, that the crystals are rhombohedral and permanent in air. There are at least three double salts of magnesium and potassium sulphates in the Stassfurt salt deposits, namely, *langbeinite*, $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$; *leonite*, $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; and *picromerite* or *schönite*, $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. G. J. Mulder, and J. H. van't Hoff and N. Kassatkin prepared **pentahydrated potassium tetramagnesium pentasulphate**, $\text{K}_2\text{SO}_4 \cdot 4\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$, or $\text{K}_2\text{Mg}_4(\text{SO}_4)_5 \cdot 5\text{H}_2\text{O}$; the latter, by warming a mixture of hexahydrated magnesium sulphate with astrakanite at 72° , or by evaporating a soln. containing a mol of potassium sulphate and four mols of magnesium sulphate when needle-like crystals of leonite are first formed. The leonite finally disappears and the whole mass solidifies. Leonite alone does not form this compound. The transition point is given as 72.5° . It is regarded as a double salt of the hydrate $\text{MgSO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$.

The mineral *langbeinite* was so named by S. Zuckschwerdt from specimens which he found near Halberstadt (Prussian Saxony). It occurs in the polyhalite regions at Wilhelmshall, and accompanies the sylvite at Westeregeln. The analyses agreed with anhydrous **potassium dimagnesium trisulphate**, $2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$, or $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$. G. J. Mulder made this compound in 1864; and F. R. Mallet

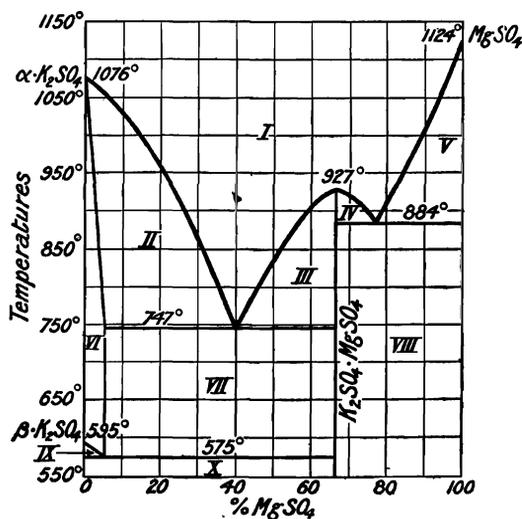


FIG. 24.—Freezing-point Curves of the Binary System, K_2SO_4 — MgSO_4 .

obtained well-defined crystals by fusing together at a full red heat mol. proportions of the two components. The clear liquid, on cooling, generally intumescens. The best crystals were obtained by pouring the fused salt into a hot nickel crucible, and allowing the mass to cool. A. S. Ginsberg, and R. Nacken have studied the equilibrium conditions in the binary system, K_2SO_4 — MgSO_4 , and the results are shown graphically in Fig. 24.

The two components are completely miscible in the molten state—region I; in region II, mixed crystals are in equilibrium with the melt; and in region VI the mixed crystals are alone stable. The first eutectic at 747° — 750° corresponds with 38 to 40 molar per cent. of MgSO_4 ; the second eutectic at 884° has 78 molar per cent. of MgSO_4 . In regions III and IV, the melt and langbeinite are coexistent, and in region VII langbeinite is in equilibrium with the mixed crystals of VI. In region V the melt and magnesium sulphate crystals are coexistent; and in region VIII langbeinite and magnesium sulphate are in equilibrium. Mixed crystals of VI are in equilibrium with β - K_2SO_4 in region IX, and, in region X, langbeinite is in equilibrium with β - K_2SO_4 .

According to J. H. van't Hoff, W. Meyerhoffer, and F. G. Cottrell, the salt crystallizes from a soln. of the component salts at 85° , and at a lower temp. in the presence of dehydrating salts like magnesium chloride; they recommended evaporating a boiling soln. of 17 grms. of potassium sulphate, 49 grms. of heptahydrated magnesium sulphate, and 75 grms. of hexahydrated magnesium chloride, until the langbeinite which is formed no longer dissolves, and then further evaporating on a water-bath until magnesium chloride begins to separate. The product is washed with 50 per cent. alcohol, and is then nearly free from chlorides and water. Although the transformation temp. of leonite to langbeinite is 89° , the transformation of leonite to langbeinite is extremely slow at 100° , and requires a temp. of

120°. The temp. of formation of langbeinite from a mixture of leonite and hexahydrated magnesium chloride is 61°. The presence of hexahydrated magnesium sulphate depresses the temp. of formation of langbeinite from leonite, down to 61°; but this temp. may be easily passed without the change taking place, and at 72° the unstable $K_2Mg_4(SO_4)_5 \cdot 5H_2O$ is formed and readily passes into langbeinite when a little of the latter is present. The presence of sodium chloride lowers the temp. of formation still further.

According to O. Luedecke, crystals from Bernburg belong to the tetartohedral class in the cubic system; the octahedra obtained by F. R. Mallet are therefore supposed to be compounded of two tetrahedrons of opposite sign. The corresponding salts of zinc, manganese, and cobalt have the tetrahedron predominant. According to R. Naeken, the sp. gr. of the artificial salt is 2.829 at 25°; and O. Luedecke gives for the natural crystals 2.827 to 2.830. From the maximum in Fig. 24, the m.p. is 927°. The crystals are singly refracting, and, according to O. Luedecke, the index of refraction is 1.5281 for the Li-line, 1.5329 for the Na-line, and 1.5343 for the Tl-line. The crystals do not rotate the plane of polarization of light. F. R. Mallet observed that the salt gradually absorbs moisture from the atm. and decomposes into picromerite and epsomite: $K_2SO_4 \cdot 2MgSO_4 + 13H_2O = MgSO_4 \cdot K_2SO_4 \cdot 6H_2O + MgSO_4 \cdot 7H_2O$. According to O. Schumann, when the double sulphate of magnesium and potassium is heated in a stream of hydrogen, hydrogen sulphide, sulphur, and water are formed, and a mixture of magnesium oxide and potassium sulphide remains. F. R. Mallet prepared **rubidium dimagnesium trisulphate**, $Rb_2SO_4 \cdot 2MgSO_4$, or $Rb_2Mg_2(SO_4)_3$ —this is *rubidium langbeinite*—in a similar way to that which he employed for langbeinite, and he found that it had similar properties.

No compound of the type *potassium magnesium disulphate*, $K_2SO_4 \cdot MgSO_4$, or $K_2Mg(SO_4)_2$, appears on the thermal diagram, Fig. 24, although M. Berthelot and L. Ilosvay de N. Ilosva claimed to have made it by fusing the component salts in the right proportions, and F. R. Mallet likewise claimed to have made this compound as well as rubidium magnesium disulphate by a similar process. He also made some measurements on the hygroscopic crystals. L. Playfair and J. P. Joule gave 2.676 for the sp. gr. of the crystals, and H. G. F. Schröder, 2.743.

According to A. Naupert and W. Wense, crystals of **tetrahydrated potassium magnesium disulphate**, $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, or $K_2Mg(SO_4)_2 \cdot 4H_2O$, occur in the kainite beds of Westeregeln, and they are readily distinguished from the surrounding kainite; they also occur associated with the blue rock salt. At Leopoldshall, the mineral occurs as thick tabular crystals along with kainite and rock salt. The colour varies from a very pale yellow to a reddish, greyish-yellow. Analyses have been made by A. Naupert and W. Wense, C. A. Tenne, and J. E. Strandmark; the results are in agreement with the formula—the massive variety usually contains chlorides as impurities. This salt was obtained by J. K. van der Heide, by evaporating an aq. soln. of schönite and sodium chloride at 60°, or a soln. of magnesium and potassium sulphates at 100°. He called the salt *potassium astrakanite*, and it has also been called kaliblödite, but C. A. Tenne showed that there is no crystallographic relation between this mineral and blödite or astrakanite, and he therefore prefers the name *leonite*. The monoclinic prisms were found by C. A. Tenne to have axial ratios $a : b : c = 1.03815 : 1 : 1.23349$, and the axial angle $\beta = 84^\circ 50'$. The optical axial angle is perpendicular to the plane of symmetry, and makes an angle $29^\circ 30'$ with the base. There is no distinct cleavage, and the fracture is conchoidal. J. E. Strandmark said that leonite is isomorphous with the artificial salt, $K_2Mn(SO_4)_2 \cdot 4H_2O$, but not with astrakanite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$. Twinned crystals are found in the artificial preparations. The salt is soluble in water.

In his examination of the crystals of a salt produced at the eruption of Vesuvius in 1855, A. Scacchi found crystals of a mineral which was called *picromerite* in allusion to the magnesium present. The same crystals occur in the Stassfurt salt deposits along with kieserite and carnallite. Most of the impurities present as

chlorides can usually be removed by washing with alcohol. E. Reichardt called the mineral *schönite*—C. F. Zincken proposed kainite, but that name is reserved for another mineral. Analyses by M. Graf, E. Reichardt, R. Phillips, C. F. Rammelsberg, and others show that the composition is in agreement with **hexahydrated potassium magnesium disulphate**, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, or $K_2Mg(SO_4)_2 \cdot 6H_2O$. The crystals were obtained by A. Marcet from the bittern of sea-water, and by G. Busch from the mother liquid of the Lüneburg and Schönebeck springs. Schönite is obtained from soln. of potassium chloride and kieserite; from the leaching of kainite with water; and by evaporating the mixed soln. of the component salts to the point of crystallization.

According to T. C. McKay, when schönite is dissolved in water, it is decomposed more or less into its components, and from conductivity measurements, it follows that in conc. soln. some undecomposed double salt is still present, while in dil. soln., the salt is completely decomposed. The same conclusion follows from observations on the sp. gr. of aq. soln. which is smaller than that calculated for the components. The limits of existence and solubility relations have been described by J. K. van der Heide, J. H. van't Hoff, and H. S. van Klooster. The latter found that in aq. soln. of the two salts at 25° , the solid phase is $K_2Mg(SO_4)_2 \cdot 6H_2O$ for conc. between 26.39 grms. of $MgSO_4$ and 7.02 grms. of K_2SO_4 per 100 grms. of sat. soln., where the solid phases are $MgSO_4 \cdot 7H_2O$ and $K_2Mg(SO_4)_2 \cdot 6H_2O$, and 12.68 grms. $MgSO_4$ and 10.70 grms. K_2SO_4 , where the solid phases are $K_2Mg(SO_4)_2 \cdot 6H_2O$ and K_2SO_4 —*vide* the solubility of magnesium sulphate in soln. of potassium sulphate. J. K. van der Heide showed that schönite decomposes into its components below -3° , and above 72° ; at 72° , in the presence of hexahydrated magnesium sulphate, schönite passes into leonite, and in the presence of potassium sulphate, the transition point is 92° . J. H. van't Hoff and P. Williams found that schönite passes into leonite at 47.5° , provided that an excess of potassium sulphate is present; at 41° if heptahydrated magnesium sulphate is present; and at 20° if the latter salt and also potassium chloride are present. Some equilibrium relations have been discussed in connection with Figs. 2-6, 2, 20, 3. According to W. D. Bancroft:

If one solid phase can be converted into one of the others by addition of water the inversion point is a maximum or a minimum temp. for one of those phases, and is neither a maximum nor a minimum for the third solid phase. For example, in the system: potassium sulphate, magnesium sulphate and water, at 47.2° , two of the phases are $MgSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 6H_2O$, the third is $K_2Mg(SO_4)_2 \cdot 6H_2O$. This is a minimum temp. for the hexahydrate. The hydrated double salt exists both above and below the temp. of the inversion point. At 72° two of the solid phases are the hydrated double salts, $K_2Mg(SO_4)_2 \cdot 6H_2O$ and $K_2Mg(SO_4)_2 \cdot 4H_2O$, while the third is heptahydrated magnesium sulphate. At 92° two of the solid phases are the same two hydrated double salts and the third is potassium sulphate. The first temp. is a minimum for the double salt with four units of water, and the second a maximum for the one with six of water. If the temp. are not given it can only be told by experiment which point is which. If the compositions of the soln. are known, the direction of the temp. change can be foretold from the theorem of A. C. van Rijn van Alkemade that the temp. rises along the boundary curve in the direction of the line connecting the m.p. of the two solid phases. The higher temp. will necessarily be a maximum for the double salt with a larger amount of water of crystallization.

A. E. H. Tutton prepared the corresponding **hexahydrated rubidium magnesium disulphate**, $Rb_2Mg(SO_4)_2 \cdot 6H_2O$, and **hexahydrated caesium magnesium disulphate**, $Cs_2Mg(SO_4)_2 \cdot 6H_2O$, by the evaporation of soln. of the component salts. The crystals have been measured by H. J. Brooke, C. F. Rammelsberg, A. Murmann and L. Rotter, H. Töpsöe and C. Christiansen, J. C. Heusser, F. L. Perrot, etc. They belong to the monoclinic system. The ammonium, potassium, rubidium, and caesium salts form an isomorphous series. A. E. H. Tutton has made an exhaustive examination of the crystal constants of this series of salts and the corresponding series with zinc in place of magnesium, and with selenates in place of sulphates. He found the habit of the potassium salt is a stout primary prism with a large basal plane; that of the caesium salt is a clinodome-prism with a narrow

basal plate; and that of the ammonium salt gives all varieties. The axial ratios, the axial angle β , and the topic axes or distance ratios are indicated in Table I. The values for the ammonium salt are included.

TABLE I.—AXIAL RATIOS, TOPIC PARAMETERS, AND ANGLES OF THE SALTS :
 $M_2Mg(SO_4)_2 \cdot 6H_2O$.

	$a : b : c$	β	$\chi : \psi : \omega$	Sp. gr.	Mol. vol.
$K_2Mg(SO_4)_2 \cdot 6H_2O$	0·7413 : 1 : 0·4993	104° 48'	6·0711 : 8·1899 : 4·0892	2·034	196·58
$Rb_2Mg(SO_4)_2 \cdot 6H_2O$	0·7400 : 1 : 0·4975	105° 59'	6·1803 : 8·3518 : 4·1550	2·386	206·18
$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	0·7400 : 1 : 0·4918	107° 6'	6·2320 : 8·4217 : 4·1418	1·723	207·78
$Cs_2Mg(SO_4)_2 \cdot 6H_2O$	0·7279 : 1 : 0·4946	107° 6'	6·2608 : 8·6012 : 4·2541	2·676	218·96

A. E. H. Tutton deduces the following relations: (1) The value of the axial angle β in the rubidium salt is approximately midway between the values of the axial angles of the potassium and caesium salts. (2) The relative amounts of change brought about in the axial-angle by replacing the alkali metal potassium by rubidium, and the rubidium in turn by caesium, are approximately directly proportional to the relative differences in the at. wt. of the metals interchanged. (3) The axial angle increases with the increase in the at. wt. of the alkali metal. (4) The values of all the angles of the rubidium salt lie between the corresponding values of the potassium and caesium salts, except in very rare cases, where more or less neutrality is produced owing to the changes in adjacent angles being of opposite sign. (5) The relative amounts of change in the angles other than the axial angle are rarely in direct simple proportion to the changes in at. wt. The maximum deviation from direct proportionality occurs in the prism zone at right angles to the zone containing the basal plane and orthopinacoid, and the relative amounts of change here bear the ratio of one to three. (6) The magnitude of the differences between most of the angular values of the three salts is surprisingly large, exceeding a whole degree in the cases of several important angles, and indicates a preponderating influence on the part of the alkali metals in determining the geometrical form of these double salts. (7) No indication of the full nature of the change brought about on replacing one metal by another in this isomorphous series is afforded by a comparison of the axial ratios, as simultaneous changes, which more or less neutralize each other, occur in the inclinations of the planes which determine them. The angles themselves alone furnish complete information concerning the change of external form. E. Blasius studied the corrosion figures of the ammonium salt.

J. W. Retgers found that the **specific gravity** of the mixed crystals of ammonium and potassium zinc sulphates varies linearly with the relative proportions of the two salts. The sp. gr. of the hexahydrated potassium salt has been found by L. Playfair and J. P. Joule to be 2·076 to 2·05319 at 4°; H. Schiff gave 1·995; H. Töpsöe and C. Christiansen, 2·204; H. Gerhart, 2·029; and H. G. F. Schröder, 2·039. The latter's values for the sp. gr. of the potassium salt which has been dehydrated without melting, range from 2·735 to 2·750. F. L. Perrot found 2·41 for the sp. gr. of the rubidium salt, and G. Wulff, 2·672 for the caesium salt. L. Playfair and J. P. Joule found for the hexahydrated ammonium salt 1·71686 at 4°; H. Schiff, 1·608; H. J. Buignet, 1·762; H. Töpsöe and C. Christiansen, and F. L. Perrot, 1·720; G. Wulff, 1·721; and H. G. F. Schröder, 1·725. A. E. H. Tutton's values, for the sp. gr., at 20°, referred to water at 4°, and **molecular volumes** of the potassium, rubidium, ammonium, and caesium series, are indicated in Table I. The rate of **diffusion** has been measured by C. Porlezza; and the heat of admixture of soln. of the component salts by R. Dubrisay.

The **refractive indices** have been determined by H. Töpsöe and C. Christiansen, F. L. Perrot, and A. E. H. Tutton. The last-named has given the results in Table II.

TABLE II.—REFRACTIVE INDICES OF THE SALTS $M_2Mg(SO_4)_2 \cdot 6H_2O$ at 20°.

	Li-line.	C-line.	Na-line.	Tl-line.	F-line.	G-line.	
α	K	1.4581	1.4585	1.4607	1.4631	1.4658	1.4699
	Rb	1.4646	1.4650	1.4672	1.4695	1.4724	1.4762
	NH_4	1.4685	1.4689	1.4716	1.4740	1.4771	1.4814
	Cs	1.4828	1.4832	1.4857	1.4880	1.4912	1.4956
β	K	1.4603	1.4607	1.4629	1.4652	1.4678	1.4720
	Rb	1.4664	1.4668	1.4689	1.4713	1.4743	1.4782
	NH_4	1.4701	1.4705	1.4730	1.4755	1.4786	1.4831
	Cs	1.4830	1.4834	1.4858	1.4881	1.4912	1.4957
γ	K	1.4727	1.4731	1.4755	1.4778	1.4810	1.4853
	Rb	1.4755	1.4759	1.4779	1.4805	1.4835	1.4876
	NH_4	1.4756	1.4760	1.4786	1.4811	1.4842	1.4888
	Cs	1.4888	1.4892	1.4916	1.4940	1.4970	1.5015

The mean values for the refractive index and of the positive **double refraction** $\gamma - \alpha$ for Na-light, at 20°, are :

Mean refractive index	K-salt.	Rb-salt.	NH_4 -salt.	Cs-salt.
Double refraction	0.0148	0.0107	0.0070	0.0059

A. E. H. Tutton found the refractive indices of the potassium salt decrease by 0.0015 to 0.0022 in raising the temp. from 20° to 70°; with the rubidium salt the decrease is about 0.0015; with the caesium salt about 0.0016; and with the ammonium salt 0.0015 to 0.0019. The mean **molecular refractions** for the C-ray—Gladstone and Dale's formula—are 91.23 for the potassium salt, 96.74 for the rubidium salt, 98.03 for the ammonium salt, and 106.25 for the caesium salt.

When the potassium salt is heated to 100°, it loses about 18.48 per cent. of water; and T. Graham found all the water of crystallization is expelled at 132°. S. U. Pickering found the **heat of solution** of the dihydrated potassium salt to be 11.47 Cals. at 18°; and of the hexahydrate, -9.96 Cals. J. Thomsen also gave for the heat of soln. of a mol of the salt $K_2SO_4 \cdot MgSO_4 \cdot nH_2O$, in 400 mols of water at 18°:

n	0	1	2	3	4	5	6 mols
Heat of soln.	10.60	6.122	0.741	-2.038	-5.160	-7.954	-10.024 Cals.

J. F. Daniell and W. A. Miller gave data for the **transport numbers** of the ions.

E. Erlenmeyer represents the constitution of $MgSO_4 \cdot K_2SO_4$ by $KO \cdot SO_2 \cdot O \cdot Mg \cdot O \cdot SO_2 \cdot OK$, otherwise expressed by $Mg(KSO_4)_2$. W. Meyerhoffer and F. G. Cottrell prepared what they called an acid triple salt, $KHMg(SO_4)_2 \cdot 2H_2O$, or **potassium magnesium monohydro-disulphate**, $Mg(KSO_4)(HSO_4) \cdot 2H_2O$, by dissolving leonite, $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, in 85 per cent. nitric acid and allowing the mixture to crystallize. The prismatic crystals are washed with absolute alcohol and ether, and dried at 60°. The crystals are doubly refracting. They are immediately decomposed by water, forming schönite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$.

K. Kubierschky assumed the existence of a triple salt *potassium sodium magnesium sulphate*, and possibly related to the *sodium-potassium-simonyites* in the salt deposits of Wilhelmshall; but J. H. van't Hoff and H. Barschall showed that isomorphous mixtures of astrakanite and leonite are involved, but no compound is formed.

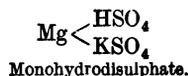
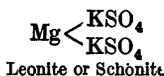
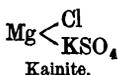
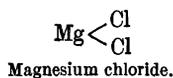
E. Bechi³ found ammonium sulphate with part of the alkali replaced by magnesium about the boric acid fumaroles of Tuscany; and he named the mineral *boussingaultite*; it has been described by O. Popp, who re-christened it *cerbolite*. It seldom occurs in a high degree of purity, but when recrystallized from water, analyses agree with its being **hexahydrated ammonium magnesium disulphate**, $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, or $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$. According to J. J. Berzelius, the salt is readily precipitated as a crystalline powder on mixing conc. soln. of the

component salts; or by passing ammonia into a soln. of magnesium sulphate in dil. sulphuric acid; and its preparation and composition were studied by C. J. B. Karsten, T. Graham, etc. The crystallographic data, sp. gr., and optical constants have been discussed in connection with the corresponding potassium salt with which it is isomorphous. C. Borel found the dielectric constant of magnesium ammonium sulphate for $\lambda = \infty$, to be 8.54 for the symmetry axis. According to H. Rheineck, at 120°, the crystals lose 25.8–26.1 per cent. of water, and at a higher temp. they melt and decompose. The crystals, dried at 100°, were found by T. Graham to lose all their water and become anhydrous at 132°. H. G. F. Schröder gave 2.105 for the sp. gr. of the dehydrated salt. The crystals are less soluble in water than either of their component salts; G. J. Mulder stated that at 13°, 100 parts of water dissolved 15.9 parts of $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2$; and, according to E. Tobler, 100 grms. of water dissolve at:

	0°	10°	20°	30°	45°	50°	60°	75°
$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2$	9.0	14.2	17.9	19.1	25.6	30.0	36.1	45.8 grms.

J. Lothian obtained rather higher results; he found that 100 grms. of water dissolved 18.22 grms. of the double salt at 1.1°; 20.72 grms. at 5°; 22.48 grms. at 10°; 24.08 grms. at 15°; 24.81 grms. at 15.5°; 28.26 grms. at 20.5°; and 33.33 grms. at 27.2°. According to C. F. Lindsay, the electrical conductivity of a conc. soln. is smaller than that of either of the components at the same conc.; and H. C. Jones and B. P. Caldwell estimate that the salt is completely dissociated at a conc. of a 0.005*N*-soln. F. Rüdorff, D. M. Torrance and N. Knight, H. L. Maxwell, and C. Porlezza studied the dissociation of the salt by diffusion experiments. A. Weston studied the quaternary system: $\text{K}_2\text{SO}_4 - \text{Mg}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$. G. Spacu and R. Ripan prepared **magnesium tetraquodiamminosulphate**, $[\text{Mg}(\text{NH}_3)_2(\text{H}_2\text{O})_4]\text{SO}_4$, as a crystalline powder; **magnesium triaquotriamminosulphate**, $[\text{Mg}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{SO}_4$, in colourless crystals; **magnesium diaquodiamminosulphate**, $[\text{Mg}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{SO}_4$, as a white powder. They also made complexes with piperidine, and benzylamine. G. Spacu made a complex with triethylenediamine.

The mineral *kainite* occurs as yellowish-greyish or greenish masses in the salt deposits of Stassfurt, Westeregeln, Kalucz in Galicia, etc.; its name is derived from *καίνος*, recent. Analyses correspond with **trihydrated potassium magnesium chlorosulphate**, $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, or possibly with $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The former was recommended by W. Meyerhoffer,⁴ G. Tschermak, A. de Schulten, and E. Erlenmeyer, and the latter by A. Frank. The formula may also be written $\text{Mg}(\text{KSO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$.



In 1843, C. J. B. Karsten noticed that no precipitation occurs on mixing conc. soln. of potassium chloride and magnesium sulphate, but crystals appear when the soln. has stood for some hours. A. de Schulten prepared kainite by evaporating on a water-bath a mixed soln. of 40 grms. of potassium sulphate and 80–90 grms. of magnesium sulphate with a great excess (500 grms.) of hexahydrated magnesium chloride. The crystals are removed from the mother liquid by press. or suction, and washed with absolute alcohol. If a smaller proportion of magnesium sulphate is employed, the product is contaminated with carnallite. The conditions of formation of kainite have been studied by J. H. van't Hoff and W. Meyerhoffer. The former showed that what he called a *tetragenic salt*—i.e. one with four different elements or radicles, exclusive of the water of crystallization—must have at least two and it may have three temp. of formation; the temp. of formation of kainite are 76° and 85°, and the *polytherms*, or the equilibrium relationships of kainite at different temp., show that besides the above primary temp. of formation, other lower secondary temp. of formation exist.

The crystals of kainite were shown by P. Groth to be monoclinic prisms with axial ratios $a : b : c = 1.2186 : 1 : 0.5863$, and $\beta = 94^\circ 54' 30''$. For this sp. gr. of kainite, C. F. Zincken gave 2.131; E. Reichardt, 2.133 to 2.154; V. von Zepharovich, 2.151; and A. de Schulten, 2.120, at 15° , for the artificial product. The hardness is 2.5 to 3.0. The double refraction is negative. According to C. F. Rammelsberg, kainite effloresces on standing over conc. sulphuric acid. C. F. Zincken, and A. Frank observed that kainite loses water and hydrogen chloride when heated. In moist air, water is absorbed, magnesium chloride is washed out, and schönite remains; water and alcohol decompose it in a similar way. According to G. Krause, 100 parts of water at 18° dissolve 79.56 parts of kainite; and J. G. Lehmann noted that a mixture of equal parts of alcohol and ether, which dissolves magnesium chloride, does not dissolve kainite.

The triple salts, *polyhalite*, $2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and *krugite*, $4\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, occur in the Stassfurt salt deposits. Polyhalite was named by F. Stromeyer⁵ from $\pi\omicron\lambda\upsilon\varsigma$, many, $\acute{\alpha}\lambda\varsigma$, salt, in reference to the number of the component salts which make up the mineral. It occurs associated with gypsum, anhydrite, and rock salt in the salt deposits at Ischl, Ebensee, Aussee, Hallstadt, and Hallein in Austria; at Berchtesgaden in Bavaria; at Vic in Lorraine; and the various Stassfurt deposits. Analyses have been reported by F. Stromeyer, C. F. Rammelsberg, W. Dexter, C. A. Joy, K. von Hauer, P. Berthier, J. B. Schober, G. Jenzsch, F. Bischof, E. Reichardt, etc. In the main, these agree with the composition: $2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, **dihydrated magnesium potassium dicalcium sulphate**. M. Rosza has shown that the occurrence of polyhalite in different parts of the salt deposits is in good agreement with the work of J. H. van't Hoff. A. Goebel found nodules of a white mineral resembling polyhalite, and associated with the carnallite of the salt mines at Maman (Persia), and hence named *mamanite*. The ratio of the calcium, magnesium, and potassium sulphates is as 3 : 2 : 1. According to J. H. van't Hoff and G. L. Voerman, *mamanite* is an impure polyhalite. According to E. E. Basch, polyhalite is formed at 25° in a soln. containing syngenite, gypsum, and epsomite. The region of its existence is narrow. Soln. containing per litre:—

K_2SO_4	MgSO_4	Solid phases.
3.5	56.7	Polyhalite, gypsum, syngenite
3.6	55.7	Polyhalite, gypsum, epsomite
5.1	58.1	Polyhalite, syngenite, epsomite

The equilibrium conditions are illustrated diagrammatically in Fig. 25, although H. S. van Klooster has shown that there is probably something wrong in E. E. Basch's

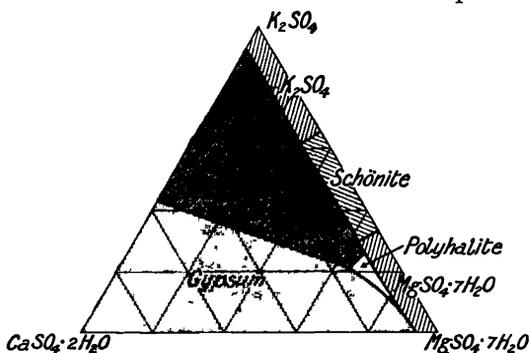


FIG. 25.—Conditions for the Formation of Polyhalite (25°).

results. Polyhalite is probably rhombic, its sp. gr. is 2.769, and its hardness 2.5 to 3. According to H. Rose, it melts when heated, and on cooling solidifies to an amorphous mass. Polyhalite is decomposed with difficulty by cold water, and leaves a residue of calcium sulphate, while potassium and magnesium sulphates pass into soln. It is more rapidly decomposed by hot water. The dehydrated salt hardens when mixed with water, and forms a voluminous mass, which is readily separated into its constituents by water. J. H. van't Hoff, F. Farup, and J. d'Ans have further studied the formation of polyhalite in the presence of "sea-salts."

H. Precht analyzed a crystalline mineral resembling polyhalite, which he found at the salt-works of New Stassfurt. Its analysis corresponds with $4\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, **dihydrated magnesium potassium tetracalcium sulphate**, and it is supposed to be a mixture of polyhalite and anhydrite, even though it appears homogeneous under the microscope. It was named *krugite* after the mining director, D. Krug von Nidda. The sp. gr. of *krugite* is 2·801, and its hardness 3·5. With cold water, magnesium sulphate is dissolved, and a double salt, $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$, remains insoluble, and with hot water, it acts like polyhalite, dissolving magnesium and potassium sulphates, and leaving the gypsum undissolved.

According to J. H. van't Hoff and A. P. Saunders,⁶ if an aq. soln., containing the sulphates and chlorides of potassium, sodium, and magnesium, and sat. with sodium chloride, be evaporated at 25°, sodium and potassium chlorides; carnallite, $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$; bischoffite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; hexa- and hepta-hydrates of magnesium sulphate; schönite, $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$; penta- and tetra-hydrates of magnesium sulphate; thenardite, Na_2SO_4 ; and astrakanite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, crystallize from the soln., but not langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$; Glauber's salts, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; nor löweite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. The formation of potassium sulphate; kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$; kainite, $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$; and leonite, $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, occurs only under special conditions; for example, J. H. van't Hoff and P. Williams state that supersaturation phenomena prevent the appearance of leonite. J. H. van't Hoff and co-workers have shown that at 25°, soln. with 1000 mols of water sat. with one, two, three, or four other salts have the compositions, and vap. press. in mm. of mercury, shown in Table III.

TABLE III.—LIMITS OF EXISTENCE OF SALT MINERALS.

1000 mols $\text{H}_2\text{O} \rightarrow$	Na_2Cl_2	MgCl_2	K_2Cl_2	Na_2SO_4	MgSO_4	mm.
$\text{NaCl}; \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	2·5	103 (24·9°)	—	—	—	7·63
$\text{NaCl}; \text{KCl}$	44·5	—	19·5	—	—	16·844
$\text{NaCl}; \text{Na}_2\text{SO}_4$	51	—	—	12·5	—	17·5
$\text{NaCl}; \text{MgCl}_2 \cdot 6\text{H}_2\text{O}; \text{carnallite}$	1	103·5	0·5	—	—	7·52
$\text{NaCl}; \text{Carnallite}; \text{KCl}$	2	70·5	5·5	—	—	12·66
$\text{NaCl}; \text{KCl}; \text{glaserite}$	44	—	20	4·5	—	16·841
$\text{NaCl}; \text{Glaserite}; \text{Na}_2\text{SO}_4$	44·5	—	10·5	14·5	—	17
$\text{NaCl}; \text{Na}_2\text{SO}_4; \text{astrakanite}$	46	—	—	3	16·5	17·1
$\text{NaCl}; \text{Astrakanite}; \text{epsomite}$	26	7	—	—	34	15·1
$\text{NaCl}; \text{Epsomite}; \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	10·5	53	—	—	15	12
$\text{NaCl}; \text{MgSO}_4 \cdot 6\text{H}_2\text{O}; \text{MgSO}_4 \cdot 5\text{H}_2\text{O}$	2	83·5	—	—	9	10·6
$\text{NaCl}; \text{MgSO}_4 \cdot 5\text{H}_2\text{O}; \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	1	86	—	—	8	9·3
$\text{NaCl}; \text{MgSO}_4 \cdot 4\text{H}_2\text{O}; \text{MgCl}_2 \cdot 4\text{H}_2\text{O}$	1	102	—	—	5	7·55
$\text{NaCl}; \text{Glaserite}; \text{schönite}; \text{KCl}$	23	21·5	14	14	15·9	—
$\text{NaCl}; \text{Leonite}; \text{schönite}; \text{KCl}$	14	37	11	14·5	14·9	—
$\text{NaCl}; \text{Leonite}; \text{MgSO}_4 \cdot 6\text{H}_2\text{O}; \text{KCl}$	17	30·5	13	13·5	13·2	—
$\text{NaCl}; \text{MgSO}_4 \cdot 6 \text{ and } 5\text{H}_2\text{O}; \text{KCl}$	8	63	6·5	5	—	—
$\text{MgSO}_4 \cdot 5 \text{ and } 4\text{H}_2\text{O}; \text{carnallite}; \text{KCl}$	2·5	68	6	5	12·4	—
$\text{MgSO}_4 \cdot 5 \text{ and } 4\text{H}_2\text{O}; \text{carnallite}; \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0	100	0·5	5	7·4	—
$\text{NaCl}; \text{Na}_2\text{SO}_4; \text{astrakanite}; \text{glaserite}$	40	2	8	8	14	—
$\text{NaCl}; \text{Astrakanite}; \text{glaserite}; \text{schönite}$	27·5	16·5	10·5	—	18·5	—
$\text{NaCl}; \text{Astrakanite}; \text{schönite}; \text{leonite}$	22	23	10·5	—	19	—
$\text{NaCl}; \text{Epsomite}; \text{astrakanite}; \text{leonite}$	10·5	42	7·5	—	19	—

J. H. van't Hoff represented these results graphically, and applied them to the phenomena which occur during the evaporation of sea-water, and which were studied by J. Usiglio. Kainite and kieserite did not appear owing to supersaturation; and when the effects of this phenomenon were eliminated, the compositions of the soln. sat. with different salts are shown in Table IV.

TABLE IV.—LIMITS OF EXISTENCE OF SALT MINERALS.

1000 mols H ₂ O sat. with	Na ₂ Cl ₂	MgCl ₂	K ₂ Cl ₂	MgSO ₄
Kainite; NaCl; epsomite; leonite . . .	9	45	7.9	19.5
Kainite; NaCl; KCl; leonite . . .	9.5	47	9.5	14.5
Kainite; NaCl; KCl; carnallite . . .	2.5	68	6	5
Kainite; NaCl; MgSO ₄ .6H ₂ O; carnallite . . .	0.5	85.5	1	8
Kainite; NaCl; MgSO ₄ .6H ₂ O; epsomite . . .	3.5	65.5	4	13
Kieserite; NaCl; MgSO ₄ .6H ₂ O . . .	2.5	79	—	9.5
Kieserite; NaCl; carnallite; kainite . . .	0.5	85.5	1	8
Kieserite; NaCl; MgSO ₄ .6H ₂ O; kainite . . .	1.5	77	2	10
Kieserite; NaCl; carnallite; MgCl ₂ .6H ₂ O . . .	—	100	0.5	5

The graphic representation of the results has been discussed by J. H. van't Hoff and W. Meyerhoffer, J. H. van't Hoff and F. Farup; J. H. van't Hoff, H. Sachs, and O. Biach; and E. Jänecke—the last-named also in his work: *Gesättigte Salzlösungen vom Standpunkt der Phasenlehre* (Halle, 1908).

The limits of existence of the different minerals with respect to temp. are indicated in Table V. In studying the *paragenesis*—παρά, beside; γένος, birth—

TABLE V.—TRANSFORMATION TEMPERATURES OF SALT MINERALS.

Mineral.	Presence.	Absence.	Product.
Glauber's salt, Na ₂ SO ₄ .10H ₂ O . . .	18°	32.5°	Thenardite, NaSO ₄
Schönite, K ₂ Mg(SO ₄) ₂ .6H ₂ O . . .	26°	47.5°	Leonite, K ₂ Mg(SO ₄) ₂ .4H ₂ O
Epsomite, MgSO ₄ .7H ₂ O . . .	31°	48°	MgSO ₄ .6H ₂ O
MgSO ₄ .6H ₂ O . . .	35.5°	67.5°	Kieserite, MgSO ₄ .H ₂ O
Astrakanite, Na ₂ Mg(SO ₄) ₂ .4H ₂ O . . .	59°	71°	Löweite, Na ₂ Mg(SO ₄) ₂ .2½H ₂ O
Leonite, K ₂ Mg(SO ₄) ₂ .4H ₂ O . . .	61.5°	89°	Langbeinite, K ₂ Mg ₂ (SO ₄) ₃
Kainite, KCl.MgSO ₄ .3H ₂ O . . .	83°	85°	Hard salt, MgSO ₄ .H ₂ O and KCl

i.e. the origin of the salt minerals between 25° and 83°, it was found convenient to divide the temp. interval into three periods. The first ranges from 25° to 37°, and here the limits for the phases schönite, epsomite, and MgSO₄.6H₂O gradually become less, or disappear, as illustrated diagrammatically in the schemes I to V, Fig. 26. The appearance or disappearance of a new phase is represented by a blackened circle. In the second period, between 37° and 55°, langbeinite, löweite, and vanthoffite appear as new phase, as illustrated in VI to VIII, Fig. 26. In the third period, ranging from 55° to 83°, astrakanite, löweite, and kainite disappear, as illustrated IX to XII, Fig. 26. Below 25°, many of the phases disappear, and at 18°, Glauber's salt appears, and kieserite disappears; at 13.5°, thenardite disappears; and at 13°, the hexahydrate, MgSO₄.6H₂O, disappears.

J. H. van't Hoff and co-workers⁷ have also studied systems containing potassium, sodium, and magnesium chlorides and sulphates with calcium sulphate in addition. The range of existence of the different salt minerals is indicated. The limiting soln. for syngenite and polyhalite at 83° are indicated in Table VI.

TABLE VI.—LIMITS OF EXISTENCE OF THE SALT MINERALS AT 83°.

1000 mols of H ₂ O→	Na ₂ Cl ₂	K ₂ Cl ₂	MgCl ₂	MgSO ₄	Na ₂ SO ₄	CaSO ₄	CaCl ₂
NaCl; anhydrite; glauberite . . .	18	—	47.5	13.5	—	0.28	—
NaCl; glauberite; syngenite . . .	40.5	33.5	—	—	6.5	small	—
Syngenite; K ₂ SO ₄ .5CaSO ₄ .H ₂ O . . .	40.5	38.5	—	—	2	0.18	—
Anhydrite; K ₂ SO ₄ .5CaSO ₄ .H ₂ O . . .	32	31	—	—	—	0.07	20.5
Glauberite; polyhalite . . .	43	23.5	—	7.5	5.5	0.08	—
Glauberite; polyhalite; syngenite . . .	41.5	32	—	4.2	2.7	0.14	—
Syngenite; polyhalite . . .	40.5	37	—	3	2	0.14	—
Syngenite; polyhalite; K ₂ SO ₄ .5CaSO ₄ .H ₂ O . . .	40.5	38	—	2.5	0.5	0.14	—

J. H. Hildebrand studied the systems $KCl-MgCl_2-K_2SO_4-MgSO_4$ at 25° ; $NaCl-KCl-MgCl_2-MgSO_4-Na_2SO_4$ at 25° , and at 83° ; and $NaCl-MgCl_2-MgSO_4-Na_2SO_4$ at 25° . W. C. Blasdale studied the system with water and the

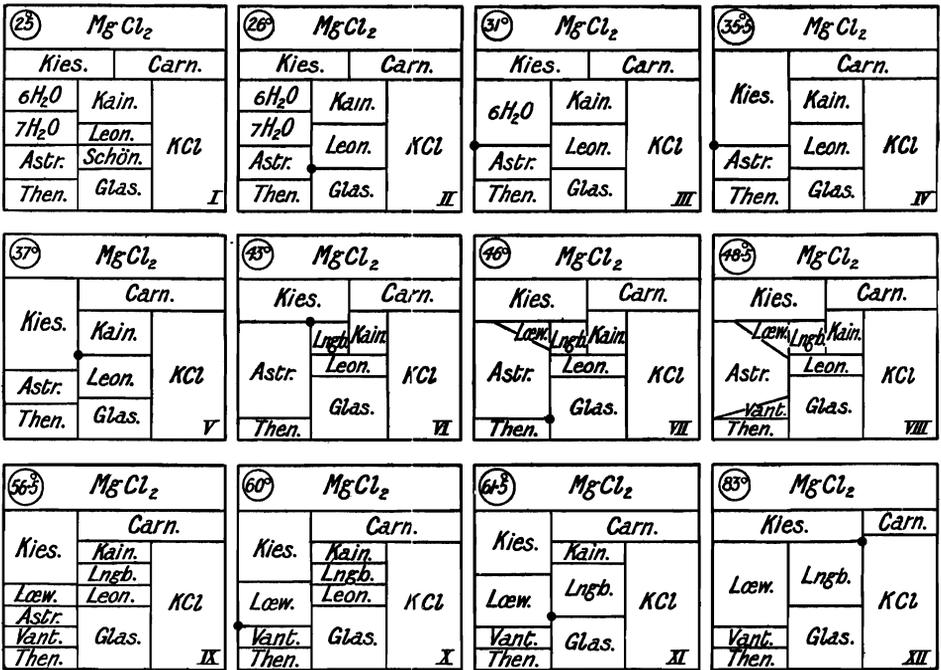


FIG. 26.—Paragenetic Relations of the Salt Minerals between 25° and 83° .

(Kies. = kieserite; Carn. = carnallite; $6H_2O$ and $7H_2O$ stand respectively for $MgSO_4 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$; Astr. = astrakanite; Then. = thenardite; Kain. = kainite; Leon. = leonite; Schön. = schönite; Glas. = glaserite; Vant. = vanthoffite; Loew. = löwite; and Lngb. = langbeinite.)

sulphates and chlorides of sodium and magnesium at different temp. S. Takegami studied the equilibrium of salt pairs—sodium and magnesium chlorides and sulphates at 25° .

REFERENCES.

¹ A. S. Ginsberg, *Proc. Polyt. Inst. St. Petersburg*, **6**, 493, 1906; *Zeit. anorg. Chem.*, **61**, 122, 1909; R. Nacken, *Gött. Nachr.*, 602, 1907; H. le Chatelier, *Ann. Mines*, (9), **11**, 209, 1897; J. H. van't Hoff and G. Just, *Sitzber. Akad. Berlin*, 499, 1903; K. Kubierschky, *ib.*, 404, 1902; J. H. van't Hoff, *ib.*, 414, 1902; J. H. van't Hoff and A. O'Farely, *ib.*, 370, 1902; J. H. van't Hoff and W. Meyerhoffer, *ib.*, 678, 1903; J. H. van't Hoff and C. M. van Deventer, *Ber.*, **19**, 2144, 1886; *Zeit. phys. Chem.*, **1**, 170, 1887; *Rec. Trav. Chim. Pays-Bas*, **6**, 36, 1887; H. W. B. Roozeboom, *ib.*, **6**, 333, 1887; G. Tschermak, *Sitzber. Akad. Wien*, **60**, i, 14, 1869; P. Groth and C. Hintze, *Zeit. deut. geol. Ges.*, **23**, 670, 1871; E. Reichardt, *Neues Jahrb. Min.*, 856, 1871; F. Millosevich, *Atti Accad. Lincei*, (5), **29**, i, 344, 1920; J. Murray, *Trans. Roy. Soc. Edin.*, **8**, 205, 1818; W. H. Miller, *Phil. Mag.*, (3), **31**, 540, 1847; S. Takegami, *Journ. Chem. Soc. Japan*, **42**, 441, 1921; J. Koppel, *Zeit. phys. Chem.*, **52**, 418, 1905; A. R. Arrott, *Phil. Mag.*, (3), **24**, 502, 1844; Munos y Luna, *Journ. Pharm. Chim.*, (3), **26**, 125, 1854; W. Haidinger, *Abhand. Ges. Wiss. Prag.*, **5**, 4, 1846; *Sitzber. Akad. Berlin*, 266, 1847; K. von Hauer, *Jahresb. Geol. Reichsanst. Wien*, 605, 1856; J. F. John, *Chemische Untersuchungen*, Berlin, 1811; G. Rose, *Reise nach dem Ural, dem Altai, und dem kaspischen Meere*, Berlin, **2**, 270, 1842; G. vom Rath, *Pogg. Ann.*, **144**, 586, 1871; A. Brezina, *Tschermak's Mitt.*, (1), **2**, 20, 1872; A. A. Hayes, *Proc. Nat. Hist. Soc. Boston*, **5**, 391, 1846; H. F. Link, *Crell's Ann.*, **1**, 30, 1796.

² R. Nacken, *Gött. Nachr.*, 602, 1907; A. S. Ginsberg, *Proc. Polyt. Inst. St. Petersburg*, **6**, 493, 1906; *Zeit. anorg. Chem.*, **61**, 122, 1909; J. H. van't Hoff and N. Kassatkin, *Sitzber. Akad. Berlin*, 951, 1899; J. H. van't Hoff, W. Meyerhoffer, and F. G. Cottrell, *ib.*, 276, 1902; J. H. van't

Hoff and P. Williams, *ib.*, 808, 1898; K. Kubierschky, *ib.*, 404, 1902; J. H. van't Hoff and H. Barschall, *ib.*, 366, 1903; G. J. Mulder, *Bijdragen tot de geschiedenis van het scheikundig gebonden water*, Rotterdam, 189, 1864; S. Zuckschwerdt, *Zeit. angew. Chem.*, 4, 356, 1891; O. Luedecke, *Zeit. Kryst.*, 29, 255, 1898; J. E. Strandmark, *ib.*, 36, 465, 1902; G. Wulff, *ib.*, 36, 4, 1902; E. Blasius, *ib.*, 10, 236, 1885; F. R. Mallet, *Min. Mag.*, 12, 159, 1899; *Journ. Chem. Soc.*, 77, 219, 1900; 81, 1548, 1902; A. E. H. Tutton, *ib.*, 63, 337, 1893; 69, 355, 1896; 87, 1160, 1905; *Proc. Roy. Soc.*, 67, 58, 1900; *Phil. Trans.*, 197, A, 255, 1901; T. Graham, *Mem. Chem. Soc.*, 1, 106, 1843; 2, 51, 1845; L. Playfair and J. P. Joule, *ib.*, 2, 401, 1845; *Journ. Chem. Soc.*, 1, 138, 1849; S. U. Pickering, *ib.*, 49, 260, 1886; M. Berthelot and L. Ilosva de N. Ilosva, *Ann. Chim. Phys.*, (5), 29, 329, 1883; O. Schumann, *Liebig's Ann.*, 187, 306, 1877; H. Schiff, *ib.*, 113, 183, 1860; 107, 64, 1858; A. Naupert and W. Wense, *Ber.*, 26, 873, 1893; J. K. van der Heide, *ib.*, 26, 414, 1893; *Zeit. phys. Chem.*, 12, 416, 1893; H. G. F. Schröder, *Ber.*, 7, 1117, 1879; *Dichtigkeitsmessungen*, Heidelberg, 1873; *Journ. prakt. Chem.*, (2), 19, 226, 1879; J. Thomsen, *ib.*, (2), 1, 165, 1878; H. F. Link, *Crell's Ann.*, 1, 30, 1796; C. H. Pfaff, *Schweigger's Journ.*, 45, 380, 1825; A. Marcet, *Phil. Trans.*, 97, 296, 1807; 109, 161, 1819; 112, 448, 1822; G. Busch, *Arch. Pharm.*, 28, 257, 1829; C. L. Berthollet, *Arceuil. Mém. Phys.*, 3, 453, 1817; H. J. Brooke, *Ann. Phil.*, 23, 117, 1823; H. Gerhart, *Tschermak's Mitt.*, 24, 380, 1905; H. Töpsöe and C. Christiansen, *Kgl. Danske Vid. Selsk. Skr.*, (5), 9, 737, 1873; *Ann. Chim. Phys.*, (5), 1, 88, 1874; J. F. Daniell and W. A. Miller, *Phil. Trans.*, 134, i, 1844; R. Phillips, *Ann. Phil.*, (2), 6, 339, 1823; R. Dubrisay, *Compt. Rend.*, 170, 1582, 1920; A. Murmann and L. Rotzer, *Sitzber. Akad. Wien*, 34, 142, 1859; F. L. Perrot, *Arch. Sciences Genève*, (3), 25, 26, 669, 672, 1891; J. H. van't Hoff, *Vorlesungen über Bildung und Spaltung von Doppelsalzen*, Leipzig, 1897; *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen insbesondere des Stassfurter Salzlagers*, Leipzig, 1912; *Zur Bildung der ozeanischen Salzablagerungen*, Braunschweig, 1905; H. S. van Klooster, *Journ. Phys. Chem.*, 21, 513, 1917; W. D. Bancroft, *ib.*, 1, 337, 1897; H. J. Buiznet, *Journ. Pharm. Chim.*, (2), 40, 161, 337, 1860; E. Erlenmeyer, *Ber.*, 2, 289, 1869; W. Meyerhoffer and F. G. Cottrell, *Zeit. anorg. Chem.*, 27, 442, 1901; J. W. Retgers, *Zeit. phys. Chem.*, 6, 193, 1890; A. C. van Rijn van Alkemade, *ib.*, 11, 289, 1893; C. A. Tenne, *Zeit. deut. geol. Ges.*, 48, 632, 1896; C. F. Rammelsberg, *ib.*, 17, 649, 1865; *Arch. Pharm.*, (2), 127, 46, 1866; A. Scacchi, *Memoria sullo incendio Vesuviano del mese di maggio*, Napoli, 191, 1855; M. Graf, *Berg. Hütt. Ztg.*, 24, 288, 1865; C. F. Zincken, *ib.*, 24, 79, 1865; E. Reichardt, *Neues Jahrb. Min.*, 602, 1865; 340, 1866; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 281, 1860; *Handbuch der kristallographischen Chemie*, Berlin, 268, 1855; J. C. Heusser, *Pogg. Ann.*, 91, 506, 1854; T. C. McKay, *Zeit. Elektrochem.*, 6, 111, 1899; C. Porlezza, *Gazz. Chim. Ital.*, 50, ii, 285, 1920.

³ E. Bechi, *Compt. Rend.*, 58, 583, 1864; O. Popp, *Liebig's Ann. Suppl.*, 8, 1, 1872; C. Schmidt, *Liebig's Ann.*, 98, 273, 1856; E. Tobler, *ib.*, 95, 193, 1855; C. J. B. Karsten, *Philosophie der Chemie*, Berlin, 101, 1843; H. Rheineck, *Dingler's Journ.*, 202, 271, 1871; T. Thomson, *Phil. Mag.*, 17, 401, 1840; T. Graham, *Trans. Roy. Soc. Edin.*, 13, 297, 1836; *Phil. Mag.*, (3), 6, 327, 417, 1835; F. Rüdorff, *Ber.*, 20, 3044, 1888; C. F. Lindsay, *Amer. Chem. Journ.*, 25, 62, 1901; H. C. Jones and B. P. Caldwell, *ib.*, 25, 349, 1901; D. M. Torrance and N. Knight, *Chem. News*, 117, 270, 1918; H. L. Maxwell, *ib.*, 116, 247, 1917; C. Porlezza, *Gazz. Chim. Ital.*, 50, ii, 285, 1920; R. Dubrisay, *Compt. Rend.*, 170, 1582, 1920; A. Weston, *Journ. Chem. Soc.*, 121, 1223, 1922; J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, 2, i, 648, 1826; G. J. Mulder, *Scheikunde Verhandl.*, Rotterdam, 226, 1864; H. G. F. Schröder, *Journ. prakt. Chem.*, (2), 19, 266, 1879; J. Lothian, *Pharm. Journ.*, (4), 30, 546, 1910; C. Borel, *Compt. Rend.*, 116, 1509, 1893; G. Spacu, *Bul. Soc. Stiinta Cluj*, 1, 247, 267, 1922.

⁴ J. H. van't Hoff and W. Meyerhoffer, *Sitzber. Akad. Berlin*, 424, 1901; 1106, 1902; W. Meyerhoffer, *Zeit. anorg. Chem.*, 34, 145, 1903; P. Groth, *Pogg. Ann.*, 137, 442, 1869; *Chemische Krystallographie*, Leipzig, 2, 443, 1908; A. de Schulten, *Bull. Soc. Chim.*, (3), 17, 165, 1897; *Compt. Rend.*, 111, 928, 1890; C. J. B. Karsten, *Philosophie der Chemie*, Berlin, 107, 171, 1843; G. Tschermak, *Sitzber. Akad. Wien*, 63, 311, 1871; A. Frank, *Ber.*, 1, 121, 1868; E. Erlenmeyer, *ib.*, 2, 289, 1869; E. Reichardt, *Arch. Pharm.*, (2), 127, 41, 1866; C. F. Rammelsberg, *ib.*, (2), 127, 58, 1866; G. Krause, *ib.*, (3), 6, 326, 1875; C. F. Zincken, *Neues Jahrb. Min.*, 310, 602, 859, 1865; V. von Zepharovich, *Zeit. Kryst.*, 6, 324, 1882; J. G. Lehmann, *Isis*, 75, 1868.

⁵ F. Stromeyer, *Untersuchungen über die Mischung der Mineralkörper*, Göttingen, 1, 144, 1821; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 283, 1862; *Pogg. Ann.*, 68, 512, 1846; H. Rose, *ib.*, 93, 1, 1854; W. Dexter, *ib.*, 93, 1, 1854; G. Jenzsch, *ib.*, 97, 175, 1856; C. A. Joy, *ib.*, 93, 1, 1854; *Miscellaneous Chemical Researches*, Göttingen, 1853; K. von Hauer, *Sitzber. Akad. Wien*, 11, 385, 1853; E. Reichardt, *Neues Jahrb. Min.*, 345, 1886; *Arch. Pharm.*, (2), 109, 204, 1862; (2), 139, 11, 1869; F. Bischof, *Ann. Chim. Phys.*, (4), 5, 312, 1865; P. Berthier, *Ann. Mines*, (1), 10, 260, 1825; A. Goebel, *Bull. Acad. St. Petersburg*, 9, 16, 1865; H. Precht, *Ber.*, 14, 2138, 1881; J. B. Schöber, *Repert. Pharm.*, 17, 129, 1868; J. H. van't Hoff, *Zeit. anorg. Chem.*, 47, 244, 1905; M. Rosza, *ib.*, 105, 167, 1919; J. H. van't Hoff and F. Farup, *Sitzber. Akad. Berlin*, 1008, 1903; J. H. van't Hoff and G. L. Voerman, *ib.*, 984, 1904; J. H. van't Hoff and J. d'Ans, *ib.*, 412, 1906; J. H. van't Hoff and W. C. Blasdale, *ib.*, 712, 1906; E. E. Basch, *Die künstliche Darstellung und die Bildungsverhältnisse der Polyhalit*, Berlin, 1901; H. S. van Klooster, *Journ. Phys. Chem.*, 21, 513, 1917.

⁶ J. H. van't Hoff and A. P. Saunders, *Sitzber. Akad. Berlin*, 387, 1898; J. H. van't Hoff and P. Williams, *ib.*, 808, 1908; J. H. van't Hoff and W. Meyerhoffer, *ib.*, 814, 1898; 372, 1899; 420, 1901; 678, 1903; 1418, 1904; J. H. van't Hoff and H. Barschall, *ib.*, 369, 1903; J. H. van't Hoff and H. von Euler, *ib.*, 1018, 1900; W. A. Wilson, *ib.*, 954, 1899; J. H. van't Hoff and F. Farup, *ib.*, 1000, 1903; J. H. van't Hoff, W. Meyerhoffer, and N. Smith, *ib.*, 1039, 1901; J. H. van't Hoff, N. Grassi, and R. B. Denison, *ib.*, 518, 1904; J. H. van't Hoff, H. Sachs, and O. Biach, *ib.*, 576, 1904; J. H. van't Hoff, *Zeit. angew. Chem.*, 14, 537, 1901; J. Usiglio, *Ann. Chim. Phys.*, (3), 27, 92, 172, 1849; E. Jänecke, *Zeit. anorg. Chem.*, 51, 132, 1907; 52, 358, 1907; 53, 319, 1907; 54, 319, 1907.

⁷ J. H. van't Hoff and F. Farup, *Sitzber. Akad. Berlin*, 1000, 1903; J. H. van't Hoff and W. C. Blasdale, *ib.*, 712, 1906; J. H. van't Hoff, F. Farup, and J. d'Ans, *ib.*, 218, 1906; J. H. van't Hoff and J. d'Ans, *ib.*, 412, 1906; J. H. van't Hoff, *Zeit. anorg. Chem.*, 47, 244, 1905; *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen insbesondere des Stassfurter Salzlagers*, Leipzig, 1912; *Zur Bildung der ozeanischen Salzablagerungen*, Braunschweig, 1905; J. H. Hildebrand, *Journ. Ind. Eng. Chem.*, 10, 96, 1918; W. C. Blasdale, *ib.*, 10, 344, 1918; 12, 164, 1920; S. Takegami, *Journ. Tokyo Chem. Soc.*, 41, 831, 1920.

§ 14. Magnesium Carbonate

Anhydrous normal magnesium carbonate, $MgCO_3$, occurs in nature as the mineral *magnesite*. This was discovered at Hrubšütz (Moravia), and named *Kohlensaurer Talkerde* by W. A. Lampadius (1800);¹ and *reine Talkerde*, or *Talcum carbonatum*, by C. F. Ludwig (1803). J. C. Delamétherie (1795) applied the term *magnesite* to a series of magnesium salts—carbonate, sulphate, nitrate, and chloride; and A. Brongniart applied the same term to a group of minerals including magnesium carbonate, and a series of siliceous varieties. The carbonate came first in both series of *magnesites*, and the term *magnesite* was formally reserved for the carbonate by D. L. G. Karsten in 1808. This was gradually accepted by the German mineralogists, though, in France, F. S. Beudant's term *giobertite* for the carbonate, and his *magnesite* for the silicate prevailed for a long time. J. C. Delamétherie used *baudisserite* for a siliceous earthy variety from Baudissero near Turin which was analyzed by G. A. Giobert; this variety of *magnesite* resembles chalk, and sticks to the tongue.

There are two main types of *magnesite*—the one type is amorphous or a gel colloid, and is represented by the compact, granular, and cleavable forms; and the other type occurs in distinct rhombohedral or trigonal crystals. A. Breithaupt called the former *magnesite* and the latter *magnesite spar*; but *magnesite* is now applied to both forms. *Magnesite* usually contains some iron, possibly as ferrous carbonate, siderite, and the colour may be white, yellow, brown, or rarely black.

The light-coloured ferruginous *magnesites* often become brown on exposure; hence the name brown spar. A variety containing 5–10 per cent. ferrous oxide was called by W. Haidinger, after M. Breuner, *breunnerite*; and a variety analyzed by L. P. Walmstedt, containing a little more manganese oxide than usual was called *walmstedtite* by K. C. Leonard. A. Breithaupt named one variety *mesitile* or *mesitine*— $\mu\epsilon\sigma\iota\tau\eta\varsigma$, a go-between—being intermediate in composition between siderite and *magnesite*; and another variety, with a little more iron and nearer the mean composition of *magnesite* and siderite, was called *pistomexite*— $\pi\iota\sigma\tau\omicron\varsigma$, truly.

Magnesite is formed in nature as a product of the action of carbonated waters on the more easily decomposed magnesium rocks—*e.g.* peridotites and serpentines.² The *magnesia* is dissolved as carbonate and may be deposited elsewhere along with more or less opaline silica formed at the same time. Ferrous carbonate may also be formed and produce a mixed carbonate. Instead of depositing their contained magnesium carbonate, these waters may act on limestone or dolomite, replacing the calcium by magnesium. *Magnesite* may also be formed as a sedimentary deposit, for H. S. Gale observed that near Bisnell, California, *magnesian salt soln.* mix with sodium carbonate, and deposit basic magnesium carbonate.

No deposits of *magnesite* of any industrial importance are known in the British Isles. Large deposits of crystalline *magnesite* occur in Austria and Hungary—principally

at Veitsch, and other places in Styria, and about Jolsva and Nyusta in N.-W. Hungary; they follow a N.-E. and N.-W. line crossing Vienna and Budapest. Deposits are also worked at Kraljevo, Serbia. There are very important deposits of chalk-like magnesite in the northern part of the Island of Eubœa, Greece; and there are deposits on the Chalcidice peninsula, Macedonia. In Italy, compact magnesite has been quarried at Castiglioneello, Monterufoti on the Island of Elba, and also in Turin. In Norway, spathic magnesite is worked at Snarum, Modum. In Russia, at Mt. Boltscheja, there are quarries of magnesite resembling that from Austria. There is a small output of compact magnesite from Spain—Esperanza and San Jose, Santander, and La Papa, Almeria. Large deposits of compact magnesite occur in the Barberton district, Eastern Transvaal, S. Africa. In India, compact magnesite is mined in the Chalk Hills of the Salem district, Madras; and there are deposits at Dod Kanya and Dod Katur, Mysore. Compact magnesite occurs in many parts of Australia—Fifield, N.S.W.; Heathcote, Victoria; Marlborough and Kunwarara, Queensland; Tumby Bay, South Australia; and at Bulong, Western Australia. In Canada there are large deposits of lenticular masses of magnesite in the Grenville district, Quebec; and in British Columbia there are deposits of compact magnesite and of hydromagnesite. Most of the magnesite mined in the United States is of the Grecian type and comes from California, where it occurs on the western side of the Sierra Nevada in the Tulare, Sonoma, Santa Clara, and Kern counties; and crystalline magnesite occurs in Stevens County, Washington. Compact magnesite occurs on the Island of Margarita, Venezuela. Compact magnesite also occurs in Manchuria. Bibliographies have been published by the Imperial Mineral Resources Bureau, etc.³ There are many of the deposits in which the magnesite may occur in veins too thin to work profitably, and many would be workable if more favourably situated for transport.

Numerous analyses of selected specimens have been reported.⁴ The material is blasted from the sides of the quarry, and broken to one-man pieces, and the particles of gangue—dolomite, quartz, serpentine, calcite, and other impurities—are removed by cobbing, etc. The extremes in some commercial samples of raw magnesite are indicated in Table VII. Small proportions of manganese oxide,

TABLE VII.—COMMERCIAL ANALYSIS OF MAGNESITE.

	Austro-Hungarian.	Grecian.	Indian.	Callifornian
SiO ₂ . . .	0.45-5.83	0.20-1.63	0.22-1.17	0.73-7.67
Al ₂ O ₃ . . .	0.14-0.48	0.15-0.40	0.10-0.14	0.03-0.26
Fe ₂ O ₃ . . .	1.54-7.70	0.08-0.40	0.40-0.65	0.08-0.29
CaO . . .	0.20-1.20	0.51-1.68	-0.83	0.04-1.32
MgO . . .	39.54-45.00	45.45-47.11	46.28-47.35	44.73-46.61
CO ₂ . . .	47.99-50.44	49.88-51.77	50.10-51.44	48.08-51.52

phosphoric acid, calcium carbonate, alkalis, and combined water may be present. F. Accum discussed the separation of argillaceous matter from magnesia.

Magnesite is marketed in three forms: (i) *Crude or raw magnesite* as produced at the mine. (ii) *Caustic magnesite* has been calcined at a red heat. It consists mainly of magnesia, and it still retains 2 to 4 per cent. of carbon dioxide. It slakes in contact with water, and combines with magnesium chloride to form Sorel's cement. The calcination of the purer forms of magnesite has at times been effected in retorts so as to obtain the carbon dioxide for making effervescent beverages. (iii) *Dead-burned magnesite* is calcined at as high a temp. as is practicable. It contains less than one per cent. of carbon dioxide. It is hard, dense, and non-plastic and is chemically inert, for it does not slake in air or in water; but it tends to disintegrate when exposed to steam.⁵ The shrinkage in making dead-burned magnesite approaches 50 per cent., and the product, if the calcination has been adequately performed, has lost nearly all its shrinking power. It is mainly used for the manufacture of magnesia (*i.e.* magnesite) bricks.

The preparation of normal magnesium carbonate.—T. Bergman,⁶ in his essay *De acido aëreo* (Upsala, 1774), described the formation of magnesium carbonate. There is a tendency for magnesium carbonate to separate from its aq. soln. in a hydrated form, or if precipitated it undergoes more or less hydrolysis and appears

as basic carbonate. W. Bramley and W. P. Cochrane heated a soln. of an alkali or ammonium hydro-carbonate or sesqui-carbonate in a closed vessel with magnesia. Hydrated magnesium carbonate is formed, and the hydro- or sesqui-carbonate is converted into normal carbonate. Magnesium carbonate and magnesia alba were found by J. J. Berzelius to contain alkali carbonate and occluded chlorides or sulphates. The alkali carbonate cannot be removed by repeated extraction with boiling water, but W. A. Davis purified the carbonate by dissolving it in water through which carbon dioxide was passing; and decomposing the filtered soln. by boiling. If necessary the treatment is repeated on the washed product. H. de Sénarmont obtained a granular mass of crystals of anhydrous magnesium carbonate by the action of sodium carbonate on magnesium sulphate in a sealed tube between 160° and 175° ; he also obtained a similar product from a soln. of magnesium carbonate in carbonic acid at about 155° . R. Marc and A. Simek made anhydrous rhombohedral crystals of magnesite by heating 10 grms. of the precipitated carbonate with 300 c.c. of water and a few grms. of solid carbon dioxide in a sealed tube, in an autoclave at 185° and a press. of 20-30 atm. H. Rose found that if the soln. be evaporated to dryness crystals of magnesite resembling aragonite are produced as well as the basic carbonate—magnesia alba. If this be correct, magnesium carbonate is dimorphous like calcium carbonate. L. Bourgeois found that precipitated magnesium carbonate furnishes crystals of magnesite when heated with urea in a sealed tube at 140° ; if ammonium nitrate be used in place of urea, the crystallization does not take place. O. Brill obtained a flocculent form of anhydrous magnesium carbonate by heating the basic carbonate; or precipitation by alkali carbonate from a soln. of a magnesium salt, between 150° and 220° , in an atm. of dry carbon dioxide. C. Heyer proposed to remove the alkali, which adheres very tenaciously to the precipitate, by heating the mass, and then washing out the alkali. A. Röhrig, and J. Treumann heated under press. a soln. of a magnesium salt with calcium carbonate. R. Engel obtained crystals of magnesite by heating ammonium magnesium carbonate, $(\text{NH}_4)_2\text{Mg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, in a stream of dry air between 130° and 140° . The corresponding potassium salt furnishes a similar result at 200° , and the alkali carbonate can be washed out with cold water.

C. Neuberg and B. Rewald⁷ prepared **colloidal magnesium carbonate** by passing a stream of carbon dioxide into a methyl alcohol soln. of magnesium oxide; the opaque liquid clears in about 24 hrs. Water flocculates the colloidal soln.

The physical properties of anhydrous magnesium carbonate.—The natural crystals belong to the trigonal system⁸ and have the axial ratio $a:c=1:0.8095$ with $\alpha=103^{\circ} 21\frac{1}{2}'$. Magnesium carbonate is the first member of a series of isomorphous carbonates, including calcium, manganous, ferrous, zinc, and cadmium carbonates. If G. Rose's statement—*vide supra*—be correct, magnesium carbonate, like calcium carbonate, is dimorphous. A. W. Hull⁹ studied the **X-radiogram**. The **specific gravity** has been determined by many observers, and the reported values for crystalline magnesite range from A. Breithaupt's, and R. F. Marchand and T. Scheerer's 3.017, to A. Jentsch's 3.076. The best representative value approaches 3.037; for amorphous magnesite W. Beck, and R. F. Marchand and T. Scheerer give 2.934; K. Grünberg gives 2.822 for the sp. gr. of magnesium carbonate, and 3.27 for that of ferrous carbonate; and the sp. gr. of isomorphous mixtures of the two changes linearly between these limits. W. Beck's value for the **molecular volume** is 27.38. The **hardness** of crystalline magnesite ranges between $3\frac{1}{2}$ and $4\frac{1}{2}$; amorphous magnesite, with more or less silica, may be still harder than this. This subject has been discussed by A. Reis and L. Zimmermann.

H. Fizeau found the **coefficient of thermal expansion** in the direction of the principal axis to be $\alpha=0.00002130$, and in a direction normal to this, $\alpha'=0.00000599$. R. Ulrich and I. Wollny found the **specific heat** of magnesite to be 0.2438 between 17° and 99° ; and, for artificial magnesium carbonate, 0.2456. A. S. Herschel gave 0.24 for the sp. ht. of magnesite. The **heat of formation**, according to M. Berthelot for the precipitated carbonate ($\text{Mg}, 3\text{O}, \text{C}$)= 266.6 Cals., or $(\text{CO}_{2\text{aq.}}, \text{MgO}_{\text{aq.}})=17.9$

Cals.; and $K_2CO_{3aq.} + MgSO_{4aq.} = MgCO_3 + K_2SO_{4aq.} + 2.1$ Cals. R. de Forcrand gives $(MgO, CO_2) = 28.9$ Cals. R. Marc and A. Simek give -23.2 Cals. for the heat of dissociation of magnesium carbonate. J. Johnston gives for the **free energy** of the dissociation carbonate to oxide 11,700 cal. at 25° . E. Mallard gave for the **index of refraction** of natural crystals for Na-light $\omega = 1.717$ for the ordinary ray, and $\epsilon = 1.515$ for the extraordinary ray; the **double refraction** is strongly negative. W. Orloff's value for the **refraction equivalent** for the ordinary ray is 19.63, and for the extraordinary ray, 14.10, when calculated from Gladstone and Dale's formula. According to P. Bary, magnesite exhibits no fluorescence with **Bequerel's rays** or **Röntgen's rays**. L. Knobloch found the **contact electricity** of powdered magnesite with a plate of platinum, paraffin, or sulphur was negative, and positive with a plate of glass.

The action of heat on magnesium carbonate.—The conclusions drawn by different observers are not always in agreement. H. Rose¹⁰ stated that magnesium carbonate begins to lose carbon dioxide between 200° and 300° , and that when heated to a dull red heat all the carbon dioxide is lost; *au contraire*, R. F. Marchand and T. Scheerer stated that after a prolonged calcination at a bright red heat, the product still retains carbon dioxide. W. C. Anderson found the lowest temp. at which magnesite begins to lose carbon dioxide is 405° ; with the so-called heavy carbonate, the temp. is 368° , with light carbonate, 352° , and with crystal carbonate, 271.5° ; in the case of light and crystal carbonates, the expulsion of carbon dioxide was stated to be complete at about 750° , while the heavy carbonate retains a little of its carbon dioxide at temp. over 810° . H. le Chatelier found under atm. press. carbon dioxide is given off from magnesite at 680° ; and J. A. Hedvall gave 546° for the **dissociation temperature**. K. Friedrich and L. G. Smith found the decomposition of magnesite begins about 570° , and a maximum thermal change in the heating curve occurs at about 600° . A. Vesterberg found that magnesite decomposes more readily than dolomite; that magnesite first gives off carbon dioxide at 448° , and loses virtually all that gas when heated for an hour at 500° , whereas dolomite loses but little if any carbon dioxide at that temp. E. Wülfing also found that the temp. at which magnesite decomposes rapidly is but little over 500° , while with dolomite the temp. is much higher than this. J. Johnston gives for the **dissociation pressure** at 25° , 2.6×10^{-9} atm., and for the dissociation temp. 230° at 760 mm.; for the latter, R. Marc and A. Simek give 402° .

O. Brill studied the dissociation of artificial normal magnesium carbonate and, starting with 68.70 grms., he measured the loss in weight after heating 10 mins. at different temp. ranging from 135° to 630° . The following is a selection from a few of his measurements of the weight after heating to different temp.:

	135°	237°	265°	300°	340°	360°	435°	465°	500°	630°
Grms.	68.70	67.90	64.65	64.10	63.45	62.90	59.75	41.10	38.15	32.95

The whole of the results are plotted in Fig. 27. There appears to be a series of breaks in the curve. He considers that this proves that the decomposition of magnesium carbonate takes place in a series of stages corresponding with the formation of a series of basic carbonates each of which has a definite dissociation temp. The carbonates with their dissociation temp. are as follows:—

$10MgO.9CO_2$	$9MgO.8CO_2$	$8MgO.7CO_2$	$7MgO.6CO_2$	$6MgO.5CO_2$	$5MgO.4CO_2$	$7MgO.CO_2$
265°	295°	325°	340°	380°	405°	510°

As W. A. Davis has pointed out, the fact that O. Brill worked with a hygroscopic magnesium carbonate having the composition $MgCO_3 \cdot \frac{1}{2}H_2O$, deprives his results of real significance as examples of the dissociation of magnesium carbonate. The presence of water caused the material to break down at 230° , a much lower temp. than that required for the dissociation of magnesite, but approaching the temp. required for the decomposition of the trihydrate. R. Marc and A. Simek also emphasize the fact that precipitated magnesium carbonate retains water very

tenaciously. K. Friedrich and L. G. Smith observed no discontinuities. Accordingly, the breaks are probably due to some cause other than the formation of basic carbonates. Measurements of the dissociation of dried magnesium carbonate are unsatisfactory because of the slowness of the change; the presence of water vapour accelerates the change without disturbing the results because magnesium hydroxide dissociates at 180° at atm. press. The presence of fused potassium nitrate also stimulates the reaction. According to K. Grünberg, when a mixture of artificial magnesite, dolomite, and calcite is heated in a stream of hot air, in a silica vessel, the magnesite is completely decomposed at 410° ; the dolomite loses carbon dioxide corresponding with the magnesia content at 500° , and with the lime content at 530° ; and finally the calcite is decomposed at 570° . E. Reichardt and T. P. Blumtrill found that 100 grms. of magnesium carbonate absorb 720 c.c. of gas from the air, and the vol. composition of the gas is 64 per cent. nitrogen, 7 per cent. oxygen, and 29 per cent. carbon dioxide.

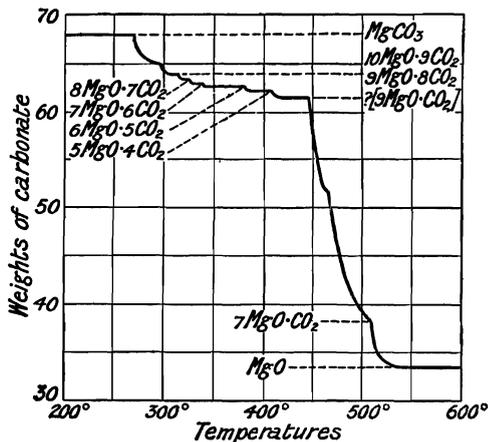


FIG. 27.—The Action of Heat on Magnesium Carbonate.

REFERENCES.

- W. A. Lampadius, *Sammlung praktisch-chemischer Abhandlungen*, Dresden, 3, 241, 1800; A. G. Werner, *Handbuch der Mineralogie*, Leipzig, C. F. Ludwig's edit., 2, 154, 1803; A. Brongniart, *Traité élémentaire de minéralogie*, Paris, 2, 489, 1807; D. L. G. Karsten, *Mineralogische Tabellen*, Berlin, 48, 92, 1808; J. C. Delamétherie, *Théorie de la terre*, Paris, 2, 93, 1795; *Leçons de minéralogie*, Paris, 1812; F. S. Beudant, *Traité élémentaire de minéralogie*, Paris, 410, 1824; K. C. Leonhard, *Handbuch der Oryktognosie*, Heidelberg, 297, 1826; G. A. Giobert, *Journ. Mines*, 20, 291, 401, 1803; A. Breithaupt, *Vollständiges Handbuch der Mineralogie*, Dresden, 2, 323, 1847; *Pogg. Ann.*, 11, 170, 1827; 70, 146, 1847; W. Haidinger, *Handbuch der bestimmenden Mineralogie*, Wien, 1845; L. P. Walmstedt, *Schweigger's Journ.*, 35, 398, 1822; H. Leitmeier, *Neues Jahrb. Min. B.B.*, 40, 655, 1916.
- F. W. Clarke, *The Data of Geochemistry*, Washington, 572, 1920; H. S. Gale, *Bull. U.S. Geol. Sur.*, 540, 483, 1914; H. Leitmeier, *Neues Jahrb. Min. B.B.*, 40, 655, 1915; S. H. Dolbear, *Min. Scientific Press*, 114, 237, 1917.
- Anon., *Magnesite*, London, 1920; K. A. Redlich, *Fortschr. Min.*, 4, 6, 1914; W. Donald, *Trans. Cer. Soc.*, 17, 486, 1918; T. Crook, *ib.*, 18, 67, 1919; C. D. Dolman, *Bull. Amer. Inst. Min. Eng.*, 1193, 1919.
- G. Magnus, *Pogg. Ann.*, 10, 145, 1827; W. Gibbs, *ib.*, 71, 366, 1847; C. Fritsche, *ib.*, 70, 147, 1847; P. S. Calderon, *Los minerales de Espana*, Madrid, 2, 65, 1910; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 1875; R. F. Marchand and T. Scheerer, *Journ. prakt. Chem.*, (1), 50, 95, 1850; H. J. Brooke, *Ann. Phil.*, (2), 5, 382, 1823; K. von Hauer, *Jahrb. Geol. Reichsanst. Wien*, 3, 154, 1852; H. Hofer, *ib.*, 445, 1866; F. von Foullon, *ib.*, 38, 2, 1888; C. von John, *ib.*, 50, 686, 1900; 57, 427, 1907; A. Jentzsch, *Neues Jahrb. Min.*, 535, 1853; M. von Miklucho-Maclay, *ib.*, i, 70, 1885; E. Monaco, *ib.*, i, 333, 1906; K. Sommer, *ib.*, 456, 1866; Anon., *Min. Ind.*, 20, 408, 1911; W. Beck, *Proc. Min. Soc. St. Petersburg*, 1, 1862; A. Saytzeff, *ib.*, 24, 1, 1887; J. Antipoff, *ib.*, 27, 487, 1890; N. von Kokscharoff, *Die Mineralien Russlands*, St. Petersburg, 1878; J. Rumpf, *Tschermak's Mitt.*, 263, 1873; F. Uhlick, *ib.*, 263, 1873; K. A. Redlich, *Zeit. prakt. Geol.*, 17, 306, 1909; M. F. Hedde, *Min. Mag.*, 2, 9, 106, 1878; K. Haushofer, *Sitzber. Bayer. Akad.*, 11, 225, 1881; L. Weiss, *Jahrb. preuss. geol. Lands.*, 113, 1885; R. Pöhlmann, *Verh. deut. wiss. Ver. St. Jago*, 2, 320, 1893; A. Schwager and C. W. Gümbel, *Geognost. Jahresh.*, 7, 57, 1899; A. Vesterberg, *Bull. Geol. Inst. Upsala*, 110, 1900; A. G. Maitland, *Bull. Imp. Inst.*, 19, 100, 1921; E. D. de Lome and C. F. M. de Borbon, *Bol. Inst. Geol. Espana*, 39, 255, 1918; F. H. Ascher, *Zeit. prakt. Geol.*, 66, 1917; J. Loczka, *Zeit. Kryst.*, 35, 282, 1902; K. Eisenhut, *ib.*, 35, 595, 1902; C. Zengels, *Berg. Hutt. Ztg.*, 61, 453, 1902; A. Christomanos, *Zeit. anal. Chem.*, 42, 606, 1903; G. d'Achiardi, *Mem. Soc. Toscana*, 20, 86, 1903; G. Piolti, *Atti Accad. Torino*, 41, 800, 1906; R. Canaval, *Karinthia*, 9, 1904;

D. Kalcinsky, *Jahr. ungar. Geol.*, 294, 1907; F. Meijnan, *Eng. Min. Journ.*, 86, 962, 1908; D. E. McGinley, *ib.*, 68, 665, 1899; H. Dains, *Journ. Soc. Chem. Ind.*, 28, 503, 1909; W. Meigen, *Ber. Ver. Oberrhein. geol. Ver.*, 79, 1910; H. Stromeyer, *Kastner's Archiv.*, 4, 432, 1825; P. Meyer, *Liebig's Ann.*, 115, 129, 1860; L. B. G. de Morveau, *Dans. Chim. Phys.*, (1), 47, 85, 1803; A. Dufrenoy, *Traité de minéralogie*, Paris, 1847; H. Wedding, *Stahl Eisen*, 13, 283, 1893; C. Bischof, *Oester. Zeit. Berg. Hütt.*, 41, 27, 1893; F. Accum, *Nicholson's Journ.*, 2, 83, 1797.

⁸ L. C. Morganroth, *Bull. Amer. Inst. Min. Eng.*, 93, 2351, 1914; R. H. Youngman, *Met. Chem. Eng.*, 12, 620, 1914.

⁹ H. de Sénarmont, *Ann. Chim. Phys.*, (3), 30, 137, 1850; (3), 32, 129, 1851; L. Bourgeois, *Compt. Rend.*, 103, 1086, 1886; R. Engel, *ib.*, 100, 911, 1885; 101, 814, 1885; 129, 598, 1899; *Bull. Soc. Chim.*, (2), 44, 355, 1885; T. C. N. Bröksmit, *Pharm. Weekbl.*, 58, 210, 1921; R. Marc and A. Simek, *Zeit. anorg. Chem.*, 82, 17, 1913; J. J. Berzelius, *Handl. Akad. Stockholm*, 334, 1824; *Ann. Phil.*, 12, 116, 1826; E. A. Nörsgaard, *Kgl. Danske Vidensk., Selsk. Skr.*, (5), 2, 65, 1851; C. Heyer, *German Pat.*, D.R.P. 37597, 1886; O. Brill, *ib.*, 164882, 1905; *Zeit. anorg. Chem.*, 45, 285, 1905; A. Röhrig and J. Treumann, *Zeit. öffent. Chem.*, 6, 241, 1900; G. Rose, *Pogg. Ann.*, 42, 366, 1837; H. Rose, *ib.*, 83, 432, 1851; W. Bramley and W. P. Cochrane, *Brit. Pat. No.* 13762, 1886; W. A. Davis, *Journ. Soc. Chem. Ind.*, 25, 788, 973, 1906.

¹⁰ C. Neuberg and B. Rewald, *Biochem. Zeit.*, 9, 545, 1908; *Zeit. Koll.*, 2, 354, 1908.

¹¹ P. Groth, *Chemische Krystallographie*, Leipzig, 2, 200, 1908.

¹² F. E. Neumann, *Pogg. Ann.*, 23, 1, 1831; C. Fritsche, *ib.*, 70, 147, 1847; T. Scheerer, *ib.*, 69, 535, 1846; 70, 407, 1847; *Liebig's Ann.*, 110, 237, 1858; W. Beck, *Proc. Min. Soc. St. Petersburg*, 1, 1862; V. von Zepharovich, *Sitzber. böhm. Ges. Wiss.*, 72, 1865; A. Jentsch, *Neues Jahrb. Min.*, 535, 1853; K. Eisenhut, *Zeit. Kryst.*, 35, 595, 1902; R. F. Marchand and T. Scheerer, *Journ. prakt. Chem.*, (1), 50, 95, 1850; K. von Hauer, *Jahrb. Geol. Reichsanst. Wien*, 3, 154, 1852; A. Breithaupt, *Vollständiges Handbuch der Mineralogie*, Dresden, 1847; F. Mohs, *Grundriss der Mineralogie*, Dresden, 1824; K. Grünberg, *Beitrag zur Kenntnis der natürlichen kristallisierten Karbonate des Calciums, Magnesiums, Eisens und Mangans*, Leipzig, 1913; *Zeit. anorg. Chem.*, 80, 337, 1913; R. Marc and A. Simek, *ib.*, 82, 17, 1913; A. W. Hull, *Journ. Amer. Chem. Soc.*, 41, 1169, 1919; W. Diesel, *Ueber isomorphe Mischsalze von wasserfreien Kalk-, Magnesium- und Eisen-carbonat*, Leipzig, 1911; R. Ulrich and E. Wolny, *Forsch. Geb. Agrik. Phys.*, 17, 1, 1894; A. S. Herschel, *B.A. Rep.*, 58, 1879; H. Fizeau in A. des Cloizeaux' *Manuel de minéralogie*, Paris, 2, 158, 1894; M. Berthelot, *Ann. Chim. Phys.*, (5), 4, 165, 1875; E. Mallard, *Compt. Rend.*, 107, 302, 1888; P. Bary, *ib.*, 130, 776, 1900; R. de Forcrand, *ib.*, 146, 512, 1908; W. Ortlöf, *Zeit. phys. Chem.*, 19, 217, 1896; A. Reis and L. Zimmermann, *ib.*, 102, 298, 1922; L. Knobloch, *ib.*, 29, 231, 1902; J. Johnston, *Journ. Amer. Chem. Soc.*, 30, 1357, 1908.

¹³ H. Rose, *Pogg. Ann.*, 83, 423, 1851; A. Vesterberg, *Bull. Geol. Inst. Upsala*, 127, 1900; R. F. Marchand and T. Scheerer, *Journ. prakt. Chem.*, (1), 50, 385, 1850; E. Wülfing, *Jahresb. Ver. Vaterland Nat. Württemberg*, 56, 1, 1900; O. Brill, *Zeit. anorg. Chem.*, 45, 282, 1905; J. A. Hedvall, *ib.*, 98, 47, 1916; R. Marc and A. Simek, *ib.*, 82, 17, 1913; K. Grünberg, *ib.*, 80, 337, 1913; H. le Chatelier, *Bull. Soc. Chim.*, (2), 47, 300, 1887; K. Friedrich and L. G. Smith, *Met.*, 9, 409, 1912; K. Friedrich, *Centr. Min.*, 616, 651, 684, 1912; W. C. Anderson, *Journ. Chem. Soc.*, 87, 257, 1905; J. Johnston, *Journ. Amer. Chem. Soc.*, 30, 1357, 1908; W. A. Davis, *Journ. Soc. Chem. Ind.*, 25, 788, 1906; E. Reichardt and T. P. Blumtrill, *Journ. prakt. Chem.*, (1), 98, 476, 1866.

§ 15. Hydrated Magnesium Carbonates

Several hydrates of normal magnesium carbonate, $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$, have been reported, where n may be 1; 2, 3, $3\frac{1}{2}$, 4, and 5. It is, however, by no means clear if all of them are chemical individuals, and it has been argued that the trihydrate is a hydrated basic hydrocarbonate. H. Beckurts¹ succeeded in making only the trihydrate. It is fairly obvious that the equilibrium relations of the hydrated normal carbonates require examination in the light of the phase rule.

E. A. Nörsgaard is the authority for the report of the first two of these hydrates; he claimed to have made monohydrated magnesium carbonate, $\text{MgCO}_3 \cdot \text{H}_2\text{O}$, as a granular precipitate, by heating a dil. or conc. soln. of magnesium carbonate in carbonic acid, or in a soln. of magnesium sulphate, but not sufficiently high for the evolution of carbon dioxide. He said the precipitate is not changed by washing. The analysis 38.03 per cent. MgO agrees as well with a mixture of $\text{Mg}(\text{OH})_2 + \text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ as with $\text{MgCO}_3 \cdot \text{H}_2\text{O}$. E. A. Nörsgaard made dihydrated magnesium carbonate, $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$ by precipitation, by adding sodium carbonate to an excess of a soln. of magnesium sulphate—between 18° and 20° the precipitate is amorphous. The temp. falls from 20° to 3.5° during its formation, and rises 3.5° to 5° during its passage to the crystalline state. The analysis 34.06 per cent. MgO agrees with a mixture of $\text{Mg}(\text{OH})_2 + \text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ as well as with $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$. From the work of W. A. Davis, it is probable that the so-called monohydrated magnesium

carbonate is magnesium hydroxycarbonate, $\text{Mg}(\text{HCO}_3)(\text{OH})$, and the so-called dihydrated magnesium carbonate is a mixture of anhydrous magnesium hydroxycarbonate and of its dihydrate, $\text{Mg}(\text{HCO}_3)\text{OH}\cdot 2\text{H}_2\text{O}$. According to T. C. W. Bröksmit, the amorphous precipitate obtained by adding sodium, potassium, or ammonium carbonate, or hydrocarbonate to a soln. of magnesium sulphate, and generally supposed to be a basic carbonate, becomes crystalline after some time, and may be trihydrated magnesium carbonate, $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$.

The rare mineral *nesquehonite*, trihydrated magnesium carbonate, $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$, was discovered in the anthracite mine of Nesquehoning, Lansford, Pa., and described by F. A. Genth and S. L. Penfield (1890). The mineral was first observed as being formed as stalactites in one of the galleries. It was also found by G. Friedel at Isère (France), and by H. Leitmeier as a deposit from the mineral springs at Rohitsch-Sauerbrunn (Untertiermark) at about 6°. According to J. J. Berzelius, the trihydrate is formed when a soln. of magnesium carbonate in aq. carbonic acid is allowed to evaporate spontaneously in air; or, according to J. Fritzsche, when the soln. sat. with carbon dioxide under press. is kept above 20°—the Salzbergwerk Neu-Stassfurt has a number of patents involving modifications of these processes. H. Leitmeier found the soln. furnishes the basic carbonate, $\text{Mg}_4\text{C}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$, from the b.p. down to 60°–65°; from 60°–55°, the basic carbonate is mixed with the trihydrate, $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$; at still lower temp. the trihydrate forms alone; and below 10°, the pentahydrate, $\text{MgCO}_3\cdot 5\text{H}_2\text{O}$, appears. C. Kippenberger found that crystals of his $\text{MgCO}_3\cdot 3\frac{1}{2}\text{H}_2\text{O}$ form the trihydrate when allowed to stand in dry air, or over sulphuric acid. J. Fritzsche observed that the pentahydrate loses two-fifths of its water and forms the trihydrate when exposed in a glass tube to sunlight; and when treated in other ways—*vide infra*. According to A. F. de Fourcroy, and V. Rose, a mixture of aq. soln. of magnesium sulphate and sodium or potassium hydrocarbonate is initially clear, but it deposits crystals of the trihydrate when allowed to stand for some time; according to J. B. J. D. Boussingault, sodium sesquicarbonate can be used in place of the hydrocarbonate. Again, J. Fritzsche, E. Soubeiran, and P. A. Favre found that the precipitate which normal sodium carbonate gives with a soln. of magnesium sulphate is converted into crystals of the trihydrate if allowed to stand for a few days at a temp. between 0° and 10°—E. A. Nörsgaard added that it is best to use an excess of magnesium sulphate, and if the temp. is below 22°, the pentahydrate is formed. According to a patent of the Salzbergwerk Neu-Stassfurt, a soln. of potassium magnesium carbonate reacts with magnesia: $2(\text{MgCO}_3\cdot \text{KHCO}_3\cdot 4\text{H}_2\text{O}) + \text{MgO} = \text{K}_2\text{CO}_3 + 3(\text{MgCO}_3\cdot 3\text{H}_2\text{O})$ at temp. between 20° and 50°.

According to W. A. Davis, the salt which is supposed to be the trihydrated normal carbonate is really a dihydrated magnesium hydroxycarbonate,



This opinion is based on the fact that the salt loses only two-thirds of its water when heated at 100° in a current of air, or boiled with a liquid like xylene (b.p. 137°); the remaining third of the water is expelled only at a much higher temp., and always together with some carbon dioxide.

W. A. Davis prepared dihydrated magnesium hydroxycarbonate, the so-called trihydrated magnesium carbonate, by mixing cold soln. of eq. quantities of sodium carbonate and magnesium sulphate, each dissolved in 15 parts of water. The precipitate first formed was left in contact with the mother liquor when it became entirely crystalline. The mother liquid, after standing for three months, had deposited a further crop of needle-like crystals. In both cases, the crystals had the composition $\text{Mg}(\text{HCO}_3)\text{OH}\cdot 2\text{H}_2\text{O}$. The conversion of the dihydrate into the anhydrous salt, $\text{Mg}(\text{HCO}_3)\text{OH}$, is effected as previously indicated.

The mode of formation of this salt shows that a basic carbonate cannot be produced by the decomposition of the hydroxyhydrocarbonate by water at the ordinary temp.; the crystals separated from the mother liquor remained in contact with water containing a slight excess of alkaline carbonate during three months,

and yet contained magnesia and carbon dioxide in the ratio corresponding with a normal carbonate. Water, free from alkali, is practically without action on magnesium hydroxyhydrocarbonate at ordinary temp. W. A. Davis supposes that the formation of the hydroxyhydrocarbonate in a soln. of magnesium carbonate in carbonic acid, when the partial press. of the carbon dioxide is low enough, is due to hydrolysis: $\text{Mg}(\text{HCO}_3)_2 + \text{H}_2\text{O} = \text{Mg}(\text{OH})(\text{HCO}_3) + \text{H}_2\text{CO}_3$. When this compound is boiled with water, two actions take place simultaneously: $\text{Mg}(\text{HCO}_3)\text{OH} \cdot 2\text{H}_2\text{O} = \text{Mg}(\text{HCO}_3)\text{OH} + 2\text{H}_2\text{O}$; and $\text{Mg}(\text{HCO}_3)\text{OH} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{H}_2\text{O} + \text{CO}_2$, so that the product is a mixture of magnesium hydroxide and hydroxycarbonate. The change is slow because a coating of magnesium hydroxide protects the interior of the crystals from the water.

Needle-like crystals of the trihydrate were obtained by W. A. Davis. According to F. A. Genth and S. L. Penfield, the natural salt belongs to the rhombic system with axial ratios $a : b : c = 0.6450 : 1 : 0.4568$; and their values for the **specific gravity** of nesquehonite range from 1.83 to 1.852; H. Leitmeier gave 1.854; and for the artificial crystals, G. von Knorre gave 1.808, and H. Beckurts, 1.875. Well-developed crystals of magnesite are rare. R. W. G. Wyckoff tried to get Laue's patterns with some short six-sided prisms, but the results were not satisfactory. **X-radiograms** of the powder by W. P. Davey and E. O. Hoffman showed that the space lattice is like that of sodium chloride. A. W. Hull also studied the subject. According to F. A. Genth and S. L. Penfield, the **hardness** of the mineral is $2\frac{1}{2}$; and the **indices of refraction** for Na-light are $\mu_a = 1.495$, $\mu_\beta = 1.501$, and $\mu_\gamma = 1.526$. P. Pascal gave 727×10^{-7} for the mol. **coefficient of magnetization**.

J. Fritzsche said the crystals are stable in air; and J. J. Berzelius said the crystals effloresce in dry air. Observations on the solubility of the salt are indicated below. The crystals were found by E. Soubeiran to have an alkaline taste, and to colour a decoction of violets green. H. Beckurts said the salt loses 15.27 per cent. of water and carbon dioxide at 100° —H. Rose assumed that water alone was lost at this temp.—at 200° more water and carbon dioxide are given off; and at 300° , all these gases have not been driven off; but all can be driven off at a higher temp. leaving residual magnesium oxide. J. J. Berzelius, and E. Soubeiran found the soln. gives off carbon dioxide when boiled, and deposits *magnesia alba*; H. Rose also noted the loss of carbon dioxide when the soln. is boiled, although J. Fritzsche found boiling water did not decompose the salt. J. J. Berzelius, and A. Bineau observed that when cold water dissolves the trihydrate a basic salt is precipitated and an acid salt remains in soln. According to V. A. Jacquelin, the salt loses carbon dioxide in a stream of moist air, or at 90° or 100° in a stream of water vapour.

C. Kippenberger prepared what he regarded as **pentadecatetrahydrated magnesium carbonate**, $\text{MgCO}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, by dissolving freshly precipitated magnesium carbonate in an aq. soln. of potassium or sodium hydrocarbonate, and allowing the soln. to stand for some time. The crystals are said to pass readily into the trihydrate, on standing in dry air, or over sulphuric acid. J. C. G. de Marignac obtained fine prismatic crystals of **tetrahydrated magnesium carbonate**, $\text{MgCO}_3 \cdot 4\text{H}_2\text{O}$, by very slowly evaporating a soln. of magnesium hydrocarbonate. The crystals belong to the monoclinic system, and have the axial ratios $a : b : c = 1.6366 : 1 : 0.9653$, and $\beta = 101^\circ 33'$. A. Damour obtained the same product, but E. A. Nørgaard supposed it to be a mixture and not a chemical individual, even though J. C. G. de Marignac's analysis of an isolated crystal gave numbers in agreement with $\text{MgCO}_3 \cdot 4\text{H}_2\text{O}$.

J. Fritzsche found that when a sat. soln. of magnesium carbonate in carbonic acid is exposed to the cold of winter in a loosely covered vessel, a mixture of tri- and **pentahydrated magnesium carbonate**, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$, is formed, and the proportion of the higher hydrate increases the lower the temp. of formation. E. A. Nørgaard prepared the pentahydrate by adding normal sodium carbonate to a soln. of magnesium sulphate at 0° until it begins to appear turbid, and allowing the mixture to stand for some time. G. Moressée dissolved magnesium oxide in water at 10° , sat. with carbon dioxide under a press. of 5–6 atm. The filtrate deposits

monoclinic crystals of the pentahydrate; the analyses sometimes show a somewhat higher percentage of magnesia, presumably owing to a partial decomposition.

The mineral *lansfordite* was reported by F. A. Genth and S. L. Penfield, from the anthracite mines of Nesquehoning, Lansford, Pa., where it has probably been formed by the percolation of ground waters rich in magnesia and carbon dioxide. Lansfordite occurs in prismatic crystals which were stated to belong to the triclinic system, the axial ratios being $a : b : c = 0.5493 : 1 : 0.5655$. The chemical analysis corresponds with $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 21\text{H}_2\text{O}$. H. J. Brooke gave for the axial ratios of the monoclinic tabular crystals of the pentahydrate $a : b : c = 1.1156 : 1 : 1.7817$, and $\beta = 107^\circ 40'$, but there appears to be some mistake here. The crystals of the pentahydrate obtained by G. Moressée were found by G. Cesaro to be hexagonal prisms belonging to the monoclinic system with axial ratios $a : b : c = 1.6393 : 1 : 0.96676$, and $\beta = 77^\circ 50' 58''$; and the latter claimed that the crystalline form of the pentahydrate is identical with that of lansfordite, and that the smaller proportion of carbon dioxide in the analysis of lansfordite is really due to the decomposition of the unstable mineral during analysis. The sp. gr. of lansfordite was found to vary from 1.692 to 1.540; H. Leitmeier gave 1.688, and he also concluded that lansfordite is really partially decomposed pentahydrated magnesium carbonate, and that the crystallographic data of F. A. Genth and S. L. Penfield were defective owing to the imperfections in the specimen available for measurement. G. Cesaro gave 1.73 (19⁵) for the sp. gr. of the pentahydrate, and he stated that the crystals are harder than gypsum, but softer than calcite; F. A. Genth and S. L. Penfield gave $2\frac{1}{2}$ for the hardness of lansfordite.

According to E. A. Nörgaard, there are two forms of the pentahydrate—tabular and columnar. The former is produced below 16° , the latter below 10° . J. Fritzsche found the crystals of the pentahydrate part with two-fifths of their combined water when exposed to air, and more rapidly on exposure to sunlight; the same result is obtained by keeping the pentahydrate for a long time in water at 50° ; and when heated to 75° , they lose carbon dioxide as well as water. E. A. Nörgaard said that the tabular crystals pass into the trihydrate if heated under water at 20° – 25° ; and when warmed under water to about 100° , they begin to lose carbon dioxide provided contact with the walls of the vessel is avoided; if the temp. be raised slowly, the pentahydrate swells at about 50° , and passes into the trihydrate; if the temp. be raised very rapidly to 90° , the tabular crystals pass into the monohydrate. The columnar crystals effloresce on exposure to air, and decompose when boiled in water more readily than the tabular crystals. The solubility of the pentahydrate is indicated in the next section. According to G. Cesaro, the aq. soln. is alkaline to litmus and phenolphthalein, and he found that the residue obtained by the spontaneous evaporation of its aq. soln. seems to contain both the original substance and a small quantity of nesquehonite, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. A soln. of G. Moressée's carbonate becomes turbid when heated to boiling, but the precipitate redissolves on cooling the liquid to 10° , and the latter, when evaporated, leaves an amorphous residue containing crystals of both $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ and of nesquehonite. H. Leitmeier found the heating curve of the pentahydrate to show a well-defined break at about 50° corresponding with its transformation into the trihydrate. The tetrahydrate of J. C. G. de Marignac gives no such break.

REFERENCES.

- ¹ E. A. Nörgaard, *Kgl. Danske Vid. Seisk. Skr.*, (5), 2. 65, 1851; H. Beckurts, *Arch. Pharm.*, (3), 18. 429, 1881; J. Fritzsche, *Pogg. Ann.*, 37. 310, 1836; H. Rose, *ib.*, 83. 443, 1851; E. Soubeiran, *Journ. Pharm.*, 13. 598, 1827; P. A. Favre, *Ann. Chim. Phys.*, (3), 10. 483, 1844; J. B. J. D. Boussingault, *ib.*, (2), 29. 285, 1825; V. A. Jacquelin, *ib.*, (3), 32. 195, 1851; A. Bineau, *ib.*, (3), 51. 301, 1857; A. F. de Fourcroy, *Crell's Ann.*, i, 451, 1792; *Ann. Chim. Phys.*, (1), 2. 278, 1789; A. W. Hull, *Journ. Franklin Inst.*, 188. 131, 1919; P. Pascal, *Compt. Rend.*, 173. 144, 1921; R. W. G. Wyckoff, *Amer. Journ. Science*, (4), 50. 317, 1920; W. P. Davey and E. O. Hoffman, *Phys. Rev.*, (2), 15. 333, 1920; C. Kippenberger, *Zeit. anorg. Chem.*, 6. 190, 1894; G. von

Knorre, *ib.*, **34**, 263, 1903; J. J. Berzelius, *Schweigger's Journ.*, **31**, 258, 1821; Salzbergwerk Neu-Stassfurt, *German Pat.*, D.R.P.P. 143594, 144742, 1901; 159870, 1902; 172313, 1903; W. A. Davis, *Journ. Soc. Chem. Ind.*, **28**, 788, 973, 1906; A. Damour, *Compt. Rend.*, **44**, 561, 1857; J. C. G. de Marignac, *Arch. Sciences Genève*, **14**, 252, 1855; H. J. Brooke, *Ann. Phil.*, **22**, 375, 1823; F. A. Genth and S. L. Penfield, *Amer. Journ. Science*, (3), **39**, 121, 1890; H. Leitmeier, *Neues Jahrb. Min. B.B.*, **40**, 655, 1915; T. C. W. Bröksmit, *Pharm. Weekbl.*, **58**, 210, 1921; *Zeit. Kryst.*, **47**, 104, 1909; G. Friedel, *Bull. Soc. Min.*, **14**, 60, 1891; G. Cesaro, *Bull. Acad. Roy. Belg.*, **234**, 1910; G. Moressée, *Bull. Soc. Géol. Belg.*, **37**, 151, 1910; F. A. Genth, *Zeit. Kryst.*, **255**, 1888; H. Leitmeier in C. Doelter, *Handbuch der Mineralchemie*, Dresden, **1**, 269, 1912; V. Rose, *Scherer's Journ.*, **6**, 50, 1800; *Gehlen's Journ.*, **3**, 546, 1807.

§ 16. The Solubility of Magnesium Carbonate

The available data for the solubility of normal magnesium carbonate in water are not satisfactory. T. Bergman¹ made some observations on this subject in 1775. P. Butini found that "an ounce of distilled water dissolves from 1.0 to 1.5 grains of magnesia, whereas the same quantity of aerated water takes up 13 grains." According to A. M. Pleischl, and M. Pichard, when powdered magnesite is moistened with water, it gives an alkaline reaction with vegetable colouring matters. N. Ljubavin reported that at 26°, 100 grms. of water dissolve 0.27 grm. of normal magnesium carbonate, and 8.12 grms. of trihydrated magnesium carbonate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$; on the other hand, W. A. Davis stated that magnesite and dolomite are as resistant to the solvent action of water as is calcium carbonate. Magnesite is insoluble in water, and is not affected to an appreciable extent by boiling it with water or with an aq. soln. of an alkali carbonate. F. Gothe says water free from carbon dioxide dissolves 94.4 mgrms. of magnesium carbonate per litre; and R. C. Wells, that a soln. of distilled water in equilibrium with atm. air, at 20°, dissolves 0.083 mgrm. of magnesite. The diversity of the data indicated below has been explained by assuming the existence of various modifications of magnesium carbonate which slowly pass into stable forms.

The anhydrous magnesium carbonate prepared by R. Engel by heating to 130° double ammonium magnesium carbonate, is sensitive towards water, for it slakes in moist air, and readily forms the trihydrate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$; 100 c.c. of water was also found to dissolve 0.2 grm. of the carbonate. According to E. A. Nørgaard, 100 parts of water, between 0° and 7°, dissolve about 0.167 part of both forms of the pentahydrate, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$; and, according to G. Cesaro, 100 parts of cold water dissolve 0.374 of the pentahydrate prepared by G. Moressée. A. Bineau, R. Engel, and H. Beckurts noted the solubility of the trihydrate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, in water, and E. A. Nørgaard found that 100 grms. of soln. between 0° and 16°, contained:

	0°	6.5°	8°	16°	15°	25°	35°
$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	0.15	0.153	0.155	0.179;	0.141	0.129	0.105 grm.

The data between 15° and 35° are by F. Auerbach. F. Kohlrausch and F. Rose did not get constant results by measuring the conductivity of sat. soln., but later F. Kohlrausch obtained 794×10^{-6} rec. ohms for the sp. conductivity of a soln. sat. at 18°. According to E. Soubeiran, when an aq. soln. of magnesium carbonate is boiled, carbon dioxide is evolved, and *magnesia alba* is precipitated. A. Cavazzi showed that while the dissociation of calcium carbonate in boiling water is limited when a certain proportion of calcium hydroxide has been dissolved, no limit occurs with the dissociation of magnesium carbonate under these conditions—magnesium hydroxide is a weak base nearly insoluble in water, while calcium hydroxide is a strong base fairly soluble in water; the former, too, has little affinity for carbon dioxide, while the latter has a strong affinity for that gas.

N. Ljubavin observed that the solubility of magnesium carbonate in water is augmented by the presence of *calcium chloride*, or of *sodium chloride*. R. C. Wells also studied the solubility of magnesium carbonate in natural waters. E. Fleischer

found an aq. soln. of *calcium sulphate* readily decomposes magnesium carbonate, particularly if some sodium chloride is present. According to F. K. Cameron and A. Seidell, in air free from carbon dioxide, the solubility of magnesium carbonate increases to a maximum and then decreases with increasing conc. of sodium chloride; thus, expressing the results in grams per litre, at 23°,

NaCl	. . . 0 0	28.0	59.5	106.3	147.4	231.1	272.9	331.4
MgCO ₃	. . . 0.176	0.418	0.527	0.585	0.544	0.460	0.393	0.293

but, when in contact with an atm. of carbon dioxide, under normal press., the solubility of magnesium carbonate decreases regularly with increasing conc. of sodium chloride.

NaCl	. . . 7.0	56.5	119.7	163.9	224.8	306.6
MgCO ₃	. . . 30.64	30.18	27.88	24.96	20.78	10.75

F. K. Cameron and A. Seidell added: "This appears to be a real exception to the hypothesis of electrolytic dissociation for which no explanation based upon that hypothesis can be offered." C. Kippenberger explains the phenomenon by assuming that the products of a reaction between the two salts suffer hydrolysis. The solubility of magnesium carbonate in soln. of *sodium sulphate*, at 24°, has been measured by F. K. Cameron and A. Seidell. In an atm. free from carbon dioxide, the solubility increases with increasing conc. of sodium sulphate:

Na ₂ SO ₄	. . . 0.00	25.12	54.76	95.68	160.8	191.9	254.6	305.1
MgCO ₃	. . . 0.216	0.586	0.828	1.020	1.230	1.280	1.338	1.388

The solubilities at 35.5° are less, showing that the solubility of magnesium carbonate in soln. of sodium sulphate, with soln. exposed to an atm. of carbon dioxide, under normal press., increases slightly and then decreases with increasing conc. of sodium sulphate. W. A. Davis found the presence of *potassium sulphate*, *potassium nitrate*, or *potassium chloride* favours the soln. of magnesium carbonate, and he believes the increased solubility is due to the formation of mixed salts, KSO₄.Mg.CO₃K; NO₃.Mg.KCO₃; Cl.Mg.KCO₃, etc. According to F. Gothe, the solubility of magnesium carbonate is increased by the presence of *alkali chlorides*, *nitrates*, and *sulphates* in the water, but decreased by *alkali carbonates*, and by the *alkaline earth chlorides*, *nitrates*, and *sulphates*; *ammonium salts* decompose the carbonate and the effect on the solubility cannot be determined. The solubility is increased when the water contains *organic (humus) substances*, especially when alkali salts are also present, but is decreased in the presence of alkali-earth salts. According to R. C. Wells, certain natural waters, freely exposed to the atm., seem to be super-saturated with respect to magnesite, but none of them approaches very closely to the point of sat. of the trihydrate. A. Frébault and A. Destrem have studied the action of *disodium hydrophosphate* on magnesium carbonate. G. C. Wittstein found magnesium carbonate is readily soluble in cold soln. of the *alkali borates*, and when heated, the soln. forms a precipitate which redissolves on cooling.

Freshly precipitated magnesium carbonate is soluble in soln. of *magnesium chloride* or *magnesium sulphate*. According to E. A. Nørgaard, the solubility of magnesium carbonate is raised in the presence of magnesium sulphate, and with a mol of the latter salt per litre,

		0°	10°	20°	30°
MgCO ₃	. . .	0.20	0.15	0.11	0.18 mol.

T. S. Hunt was able to dissolve 5 grms. of magnesium carbonate in a litre of water containing 60 grms. of heptahydrated magnesium sulphate and a little sodium chloride; when the alkaline soln. is heated a precipitate is formed which redissolves as the soln. cools. According to E. A. Nørgaard, freshly prepared tabular crystals of pentahydrated magnesium carbonate, dissolve in a 4 per cent. soln. of magnesium

sulphate or sodium carbonate, but the prismatic form is insoluble in these menstrua.

W. A. Davis supposes a mixed salt of the type $Mg < \begin{smallmatrix} SO_4 \\ CO_3 \end{smallmatrix} > Mg$ is formed.

According to C. Kippenberger, soln. of *sodium carbonate* readily dissolve freshly precipitated magnesium carbonate. F. K. Cameron and A. Seidell found for soln. in equilibrium with an atm. free from carbon dioxide at 25°, when the results are expressed in grams per litre,

Na_2CO_3 . . .	0·00	23·12	50·75	86·42	127·3	160·8	181·9	213·2
$MgCO_3$. . .	0·223	0·288	0·510	0·879	1·314	1·636	1·972	2·317

Except for the lower conc., the increase in solubility of the magnesium carbonate with increase in the amount of sodium carbonate is represented by an approximately straight line. The sp. gr. of the soln. were also determined. F. Auerbach found at 15°, 25°, and 35° for soln. of *potassium hydrocarbonate*, when the results are expressed in mols per litre, at 25°:

$KHCO_3$. . .	0	0·0985	0·2210	0·3434	0·4985	0·3906	0·5893	0·6406	1·125
$MgCO_3$. . .	0·0087	0·0115	0·0149	0·0181	0·0217	0·0196	0·0128	0·0117	0·0061

Solid phases . . . $MgCO_3 \cdot 3H_2O$ $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$

The solubility thus increases as the conc. of the alkali hydrocarbonate increases until the double salt, $MgCO_3 \cdot KHCO_3 \cdot 4H_2O$, is formed, and thereafter the solubility diminishes. The solubility of *magnesia alba* was found by P. Butini,² T. Bergman, C. L. Berthollet, and F. Gothe to be raised by the presence of *carbon dioxide* in soln. A similar remark applies to magnesium carbonate.

P. Butini stated that water may be over-saturated with magnesia and yet pass through the filter-paper and remain clear; such a soln. is obtained by immediately filtering the water in which epsom salt has been decomposed; and if heated to 20° (which may be done in the palm of the hand), it lets fall its earth, which is redissolved when the liquid cools to about 15°. This is a very amusing experiment.

According to E. Soubeiran, the sat. soln. contains twice as much carbon dioxide as the normal carbonate. It was assumed by A. Cossa, C. Kippenberger, etc., that **magnesium hydrocarbonate**, $Mg(HCO_3)_2$, is formed, but the salt has not been isolated; and, according to F. P. Treadwell and M. Reuter, the hydrocarbonate exists in aq. soln. only in the presence of a large excess of carbon dioxide; if the partial press. of this gas falls below 2 per cent., the soln. loses all its free carbon dioxide and part of that present as hydrocarbonate. At 15°, a litre of a soln. is estimated to contain 1·9540 grms. of hydrocarbonate, and 0·7156 gm. of carbonate. The conclusion is supported by R. Rinne; and P. N. Raikow found that a soln. of magnesium nitrate precipitated by a definite amount of potassium hydroxide, absorbed enough carbon dioxide to form the hydrocarbonate. M. Monhaupt tried to precipitate the hydrocarbonate by adding alcohol to the sat. soln., but he obtained only the trihydrated carbonate, $MgCO_3 \cdot 3H_2O$. W. A. Davis also found that the solid phase which separated from a soln. of the so-called hydrocarbonate is trihydrated magnesium carbonate, a result confirmed by F. K. Cameron and W. O. Robinson. The latter also measured the vap. press. of carbon dioxide, expressed in p cms. of mercury, when w grms. of carbon dioxide are successively added to wet magnesium hydroxide:

w . . .	0·00	0·1519	0·1953	0·2170	0·3038	0·3255	0·3906	0·5642
p . . .	76	78	80	88	90	112	142	275

The results are plotted in Fig. 28, which shows a curve consisting of three parts. The portion AB remains constant, and it corresponds with the formation of normal magnesium carbonate; the portion BC corresponds with the absorption of carbon dioxide—some of the solid phase appeared to pass into soln.; and the portion CD in which the addition of carbon dioxide has no influence on the solid phase. When the excess of carbon dioxide is allowed to escape until p has reached atm. press.,

the molar ratio $MgO : CO_2$ in the solid is nearly that required for the hydrocarbonate. F. K. Cameron and W. O. Robinson regard the solid as a soln. of carbon dioxide in trihydrated magnesium carbonate. The soln. of magnesium carbonate in carbonic acid containing "13 grains per ounce" is the *fluid magnesia* or the *liquor magnesiæ carbonatæ* of the British Pharmacopœia.

H. Leitmeier found a litre of water sat. with carbon dioxide at ordinary temp. dissolves 0.08 grm. of crystalline magnesite, and 0.22 grm. of amorphous magnesite. The solubility of magnesium carbonate in aq. soln. of carbon dioxide depends on the slowness of the conversion of one modification into another—say, the basic carbonate into trihydrated normal carbonate—and this, in turn, depends on the source of the solid employed, and on the time of contact. Thus, R. Engel found the following values for the solubilities starting with different materials, and after the elapse of different periods of time :

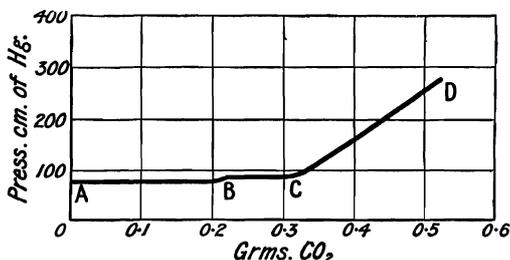


FIG. 28.—Pressure of Carbon Dioxide over Magnesium Hydroxide.

Time in hrs.	Magnesium oxide.	Trihydrated normal carbonate.	Hydrocarbonate.
0.15	3.5	4.3	1.25
1.00	6.4	6.4	2.50
1.30	6.4	6.4	3.75
9.00	6.4	6.4	5.00

Before the importance of this was recognized, the results were very discordant ; thus, a litre of water sat. with carbon dioxide was found by J. R. von Wagner, and G. Merkel to dissolve 1.31 grms. of magnesium carbonate ; H. Beckurts, 8.39 grms. ; and A. Bineau, 23.3 grms. R. Engel and J. Ville give for the solubility of magnesium carbonate, in grams per litre, in water at 19.5°, sat. with carbon dioxide at various press. expressed in atm. :

CO_2	:	1	2.1	3.2	4.7	5.6	6.2	7.5	9.0 atm.
$MgCO_3$:	25.79	33.11	37.30	43.50	45.20	48.50	51.20	56.59

They also gave for the solubility of magnesium carbonate in water sat. with carbon dioxide at various temp. at a press. of one atm., when the results are expressed in grams per litre :

	13.4°	19.5°	29.3°	46.0°	62.0°	70.0°	82.0°	90°	100°
$MgCO_3$	28.45	25.79	21.95	15.7	10.35	8.1	4.9	2.4	0.0

T. Schlösing represented the solubility of magnesium carbonate in water at different press. p of carbon dioxide, by the empirical formula $p^{0.362} = 0.0398y$, where y denotes the amount of magnesium hydrocarbonate in the soln. expressed in grams per litre. R. Engel obtained good results with the empirical formula $p^{0.333} = 0.814y$, i.e. with $y = 1.934\sqrt[3]{p}$, or, at a definite temp., the quantity of magnesium carbonate dissolved by water with carbon dioxide in soln., is proportional to the cube root of the press. of the carbon dioxide.

G. Bodländer attempted to obtain a formula of the same form as that employed to represent the solubility of calcium carbonate in water containing carbon dioxide, but he found it necessary to assume the presence of ions in soln. of the form $\{(MgCO_3)_n \cdot MgOH\}$. F. P. Treadwell and M. Reuter have also shown that, at the lower conc., there is less carbon dioxide in soln. than corresponds with the formula $Mg(HCO_3)_2$, a conclusion which was confirmed by R. Rinne. In the opinion of J. Johnston, the results of F. P. Treadwell and M. Reuter, and of J. W. Leather and J. N. Sen on the ternary system, $MgCO_3 - H_2CO_3 - H_2O$, and the quaternary system, $CaCO_3 - MgCO_3 - H_2CO_3 - H_2O$, are vitiated by defective analyses or by the

uncertainty whether equilibrium was really attained. J. Johnston calculated the **solubility product**, at 18°, to be $[Mg^{..}][CO_3^{..}] = 1.2 \times 10^{-4}$, or else $[Mg^{..}][OH']^2 = 1.2 \times 10^{-11}$.

According to J. Johnston, (1), $[Mg^{..}][CO_3^{..}] = K$; (2), $[H_2CO_3] = k'[CO_2] = c'p$, where p is the partial press. of the carbon dioxide; (3), $[H^+][HCO_3'] = k_1[H_2CO_3]$; (4), $[H^+][CO_3^{..}] = k_2[HCO_3']$; (5), $[H_2CO_3] = nk[CO_2] = ncp$, where $c = a/22.4$, and n , from the work of J. Walker and W. Cormack on the proportion of the total carbon dioxide in soln. existing as H_2CO_3 , is greater than 0.5. By dividing (3) by (4), it follows (6), $[HCO_3']^2/[CO_3^{..}][H_2CO_3] = k_1/k_2 = r$; and when combined with (5), there remains (7), $[HCO_3']^2/[CO_3^{..}]cp = nr$. Consequently, (8), $[Mg^{..}][HCO_3']^2 = nrKcp$, or $nrK = [Mg^{..}][HCO_3']^2/cp$; (9), $[OH']/[HCO_3'] = K_w/nk_1cp$, where K_w is the constant for water; (10), $[OH']^2/[CO_3^{..}] = K_w^2/nr_1K_2cp$. At 18°, for partial press. ranging from 0.0002 to 0.0005 atm., J. Johnston calculated from R. Engel's measurements (7), $nrKcp = 229.6p$; (8), $nrKcp = 2.755 \times 10^{-2}p$; (9), $K_w/nk_1cp = 4.012 \times 10^{-2}p$; (10), $K_w^2/nk_1k_2cp = 3.694 \times 10^{-11}p$; and either (11), $[Mg^{..}][CO_3^{..}] = K = 1.2 \times 10^{-4}$; or (12), $[Mg^{..}][OH']^2 = 1.2 \times 10^{-11}$. By combining (1) and (10), or (8) and (9), it follows that at 18° $[Mg^{..}][OH']^2 = 4.433 \times 10^{-15}/p$, a value which exceeds (12) when p is less than 0.000369.

When $p < 0.000369$, at 18°, the solid phase is not $MgCO_3 \cdot 3H_2O$, but $Mg(OH)_2$. At the transition press. 0.000369, both solid phases are in equilibrium. If the press. of the carbon dioxide is kept constant at p atm., and water be evaporated from the soln. so slowly at 18° that equilibrium conditions are continuously maintained, the following amounts of magnesium hydroxide, or trihydrated carbonate, will be obtained (grams per litre):

p	0	0.00030	0.00030	0.00035	0.00040	0.00045	0.00050 atm.
Total [Mg]	0.00015	0.01934	0.02486	0.02742	0.02868	0.02924	0.02976 mols
Grms.	0.0087	1.13	1.45	1.60	3.97	4.05	4.12
		Mg(OH) ₂			MgCO ₃ ·3H ₂ O		

The transition press. increases rapidly with temp. because K_w^2/nk_1k_2 increases rapidly whilst K/c varies but little; the increase cannot be calculated because the rate of change of k_2 with temp. is not known.

It follows, adds J. Johnston, that the ordinary methods of preparing magnesium carbonate (in which, it is safe to say, a state of equilibrium is not attained continuously) will yield a product contaminated with hydroxide, the amount of which will depend upon the mode of working generally, and upon the prevailing partial press. of CO_2 over the liquid in particular: moreover, that this contamination can be avoided completely by working with a partial press. p greater than a certain limit.

J. Johnston continues: In soln. sat. with both calcium and magnesium carbonates, the ratio of the conc. of $Mg^{..}$ and $Ca^{..}$ must have a definite value; thus, at 16°

$$\frac{[Mg^{..}]}{[Ca^{..}]} = \frac{[Mg^{..}][CO_3^{..}]}{[Ca^{..}][CO_3^{..}]} = \frac{K_{Mg}}{K_{Ca}} = \frac{1.4 \times 10^{-4}}{1 \times 10^{-8}} = 14,000$$

Hence, if a soln. of the two carbonates in carbonic acid is evaporated, or if the partial press. of the carbon dioxide be gradually reduced, at 16°, calcium carbonate will be precipitated so long as the above ratio is less than 14,000, as would normally be the case in natural waters when the press. of the carbon dioxide is sufficient to prevent the precipitation of magnesium hydroxide. The order of precipitation will be reversed if the relative conc. of the magnesium ions be greater than 14,000, as could be the case when a soluble magnesium salt is present. These deductions are valid when $CaCO_3$ and $MgCO_3 \cdot 3H_2O$ are the only solid phases which separate; if a solid soln. of the two be formed at certain conc., these deductions would have to be modified accordingly. If the partial press. of carbon dioxide is such that magnesium hydroxide may precipitate, it follows that:

$$\frac{[Mg^{..}]}{[Ca^{..}]} = \frac{[Mg^{..}][OH']^2}{[Ca^{..}][OH']^2} = \frac{1.2 \times 10^{-11}p}{3.43 \times 10^{-19}} = 3.5 \times 10^7 p$$

a ratio which decreases steadily as p is reduced. Hence calcium carbonate precipi-

tated from a soln. containing magnesium may be very readily contaminated with appreciable proportions of magnesium hydroxide, which would be removed only slowly by repeated re-precipitations. J. C. Hostetter, for example, has emphasized how difficult it is to get calcium carbonate free from magnesia. This difficulty may be obviated very easily, namely, by conducting the operations in such a way that the liquid is always sat. with CO_2 at a press. above a certain limiting value; this limit, which increases with the temp., cannot at present be specified very accurately, but is in all probability not greater than 1 atm. for any conditions likely to be encountered in actual practice.

According to C. L. Berthollet, the soln. of magnesium carbonate has a bitter taste, and an alkaline reaction, and C. H. Pfaff, A. M. Pleischl, and C. L. Berthollet stated that the alkalinity towards vegetable colouring matters—tincture of logwood, tumeric, red litmus, etc.—is maintained even when a great excess of carbon dioxide is in soln., but, according to the last-named, the soln. gives a green colour with tincture of violets, and he also stated that the soln. becomes turbid when heated to 75° , but recovers its transparency on cooling. According to J. J. Berzelius, and J. Fritzsche, when the soln. is heated to 50° , or, according to E. Soubeiran, when evaporated in vacuo, trihydrated normal carbonate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, is deposited. According to W. Weldon, and E. Bohlig, when sodium chloride is added to a sat. soln. of magnesium carbonate and carbon dioxide, sodium hydrocarbonate is precipitated, and magnesium chloride remains in soln.

Magnesite is not quickly attacked by cold *hydrochloric acid* or *sulphuric acid*, but it dissolves readily in the warm acids. According to K. Haushofer, and A. Vesterberg, compact magnesite is more quickly dissolved by *acetic acid* than crystallized magnesite; and the solubility of crystallized magnesite decreases with increasing conc. of the acid. A. Vesterberg, and T. S. Hunt found that magnesite dissolves more slowly than dolomite in acetic acid; K. Haushofer came to the opposite conclusion. F. W. Pfaff found that powdered magnesite is very slightly soluble in a soln. of *hydrogen sulphide* in water; and its solubility in an aq. soln. of *ammonium sulphide* is small. L. Naudin and F. de Montholon have studied the action of hydrogen sulphide on magnesite suspended in water. J. A. Hedvall and J. Heuberger found the reaction temp. and the thermal value of the reaction between magnesium carbonate and *calcium oxide* to be respectively 300° and 2.5 Cals.; with *strontium oxide*, 240° and 11.5 Cals.; and with *barium oxide*, 230° and 19 Cals.

REFERENCES.

- ¹ A. M. Pleischl, *Zeit. Phys.*, 5, 59, 1829; W. A. Davis, *Journ. Soc. Chem. Ind.*, 25, 788, 1897; N. Ljubavin, *Journ. Russ. Phys. Chem. Soc.*, 24, 389, 1892; R. Engel, *Compt. Rend.*, 129, 598, 1899; 100, 445, 1885; M. Pichard, *ib.*, 87, 797, 1878; G. C. Wittstein, *Arch. Pharm.*, (3), 6, 40, 1875; E. Fleischer, *Journ. prakt. Chem.*, (2), 6, 273, 1870; E. A. Nörsgaard, *Kgl. Danske Vid. Selsk. Skr.*, (5), 2, 65, 1851; A. Bineau, *Ann. Chim. Phys.*, (3), 51, 301, 1857; A. Cavazzi, *Gazz. Chim. Ital.*, 47, ii, 49, 1917; J. R. von Wagner, *Journ. prakt. Chem.*, (1), 102, 233, 1867; A. Frébault and A. Destrem, *Bull. Soc. Chim.*, (2), 27, 499, 1879; G. Cesaro, *Ann. Acad. Roy. Belg.*, 234, 1910; H. Beckurts, *Arch. Pharm.*, (3), 18, 429, 1881; F. Auerbach, *Zeit. Elektrochem.*, 10, 161, 1904; F. Kohrausch and F. Rose, *Sitzber. Akad. Berlin*, 453, 1893; *Zeit. phys. Chem.*, 12, 234, 1893; F. Kohrausch, *ib.*, 44, 197, 1903; G. Bodländer, *ib.*, 35, 29, 1900; W. A. Davis, *Journ. Soc. Chem. Ind.*, 25, 788, 973, 1905; T. S. Hunt, *Amer. Journ. Science*, (2), 42, 49, 1866; C. Kippenberger, *Ber. deut. pharm. Ges.*, 5, 245, 1895; *Zeit. anorg. Chem.*, 6, 177, 1894; F. K. Cameron and A. Seidell, *Journ. Phys. Chem.*, 7, 578, 1903; R. C. Wells, *Journ. Amer. Chem. Soc.*, 37, 1704, 1915; P. Butini, *Novelles observations et recherches analytiques sur la magnésie du sel d'Epsom, suivies de réflexions sur l'union chimique des corps*, Genève, 1781; T. Bergman, *De magnesia*, Upsala, 1775; F. Gothe, *Chem. Ztg.*, 39, 305, 326, 1915; G. Moressée, *Bull. Soc. Géol. Belg.*, 37, 151, 1910.
- ² C. L. Berthollet, *Mém. L'Inst.*, 229, 1806; *Gehlen's Journ.*, 3, 263, 1807; F. P. Treadwell and M. Reuter, *Zeit. anorg. Chem.*, 17, 171, 1898; C. Kippenberger, 6, 177, 1894; J. Walker and W. Cormack, *Journ. Chem. Soc.*, 77, 13, 1900; J. Walker, *ib.*, 83, 182, 1903; R. Engel and J. Ville, *Compt. Rend.*, 93, 340, 1881; M. Pichard, *ib.*, 87, 797, 1878; L. Naudin and F. de Montholon, *ib.*, 138, 760, 1876; *Bull. Soc. Chim.*, (2), 28, 71, 1876; A. Frébault and A. Destrem, *ib.*, (2), 27, 499, 1877; T. Schlösing, *ib.*, 74, 1552, 1872; 75, 70, 1872; R. Engel, *ib.*, 100, 352,

444, 1885; *Ann. Chim. Phys.*, (6), 13. 349, 1888; A. Bineau, *ib.*, (3), 51. 301, 1857; M. Monhaupt, *Chem. Ztg.*, 28. 868, 1904; P. Butini, *Nouvelles observations et recherches analytiques sur la magnésie du sel d'Epsom suivies de réflexions sur l'union chimique des corps*, Genève, 1781; T. Bergman, *De magnesia*, Upsala, 1775; H. Leitmeier, *Neues Jahrb. Min. B.B.*, 40. 655, 1916; W. Weldon, *Mechanic's Mag.*, (2), 16. 150, 1866; E. Bohlig, *Dingler's Journ.*, 224. 621, 1877; G. Bodländer, *Zeit. phys. Chem.*, 35. 23, 1900; A. M. Pleischl, *Zeit. phys.*, 5. 59, 1829; F. K. Cameron and A. Seidell, *Journ. Phys. Chem.*, 7. 578, 1903; F. K. Cameron and L. J. Briggs, *ib.*, 5. 537, 1902; F. K. Cameron and W. O. Robinson, *ib.*, 12. 561, 1908; W. A. Davis, *Journ. Soc. Chem. Ind.*, 25. 788, 973, 1905; F. W. Pfaff, *Neues Jahrb. Min. B.B.*, 9. 490, 1894; C. H. Pfaff, *Schweigger's Journ.*, 35. 428, 1822; J. J. Berzelius, *ib.*, 31. 258, 1821; *Gilbert's Ann.*, 40. 255, 1812; K. Haushofer, *Sitzber. Bayr. Akad.*, 11. 225, 1881; J. Johnston, *Journ. Amer. Chem. Soc.*, 37. 2001, 1915; A. Vesterberg, *Bull. Geol. Inst. Upsala*, 110, 1900; J. W. Leather and J. N. Sen, *Mem. Dept. Agric. India*, 3. 203, 219, 1914; T. S. Hunt, *Amer. Journ. Science*, (2), 28. 181, 371, 1859; J. C. Hostetter, *Journ. Ind. Eng. Chem.*, 6. 392, 1914; A. Cossa, *Ber.*, 2. 697, 1869; E. A. Nörsgaard, *Kgl. Danske Vid. Selsk. Skr.*, (5), 2. 54, 1850; G. Merkel, *Wagner's Jahresh.*, 213, 1867; J. R. von Wagner, *Journ. prakt. Chem.*, (1), 102. 233, 1867; H. Beckurts, *Arch. Pharm.*, (3), 18. 429, 1881; R. Rinne, *Chem. Ztg.*, 31. 125, 1907; P. N. Raikow, *ib.*, 31. 55, 1907; E. Soubeiran, *Journ. Pharm.*, 13. 598, 1827; J. Fritzsche, *Pogg. Ann.*, 37. 310, 1836; J. A. Hedvall and J. Heuberger, *Zeit. anorg. Chem.*, 122. 181, 1922.

§ 17. The Basic Magnesium Carbonates—Magnesium Oxycarbonates

A considerable number of distinct basic magnesium carbonates have been reported:

Representing the proportions of $MgO : CO_2 : H_2O$ by numerals in that order, J. Fritzsche¹ prepared the (1), 3 : 2 : 3-carbonate; also the (2), 4 : 3 : 4-carbonate; H. Rose the (3), 4 : 3 : 7-carbonate; J. J. Berzelius, the (4), 4 : 3 : 8-carbonate; J. Fritzsche and H. Rose, the (5), 5 : 4 : 5-carbonate; H. Rose, the (6), 5 : 4 : 6-, (7), 5 : 4 : 7-, (8), 5 : 4 : 8-, and (9), 5 : 4 : 9-carbonates; H. Rose, and V. A. Jacquelin (10), 5 : 4 : 10-carbonate; H. Rose (11), 5 : 4 : 11-, and (12), 5 : 4 : 12-carbonate; G. Kittel (13), 5 : 4 : 16-carbonate; H. Beckurts (14), 7 : 5 : 9; H. Rose (15), 6 : 4 : 6-carbonate, and V. A. Jacquelin (16), 6 : 5 : 14-carbonate. There are also the native basic carbonates 2 : 1 : 3; 2 : 1 : 4; 4 : 3 : 3; and 4 : 3 : 4; and the anhydrous basic carbonates. With $MgO : CO_2$, viz. 10 : 9; 9 : 8; 8 : 7; 7 : 6; 6 : 5; 5 : 4; and 9 : 7-carbonates.

This confusing variety of the basic magnesium carbonates is usually regarded as a consequence of the more or less incomplete hydrolysis of the normal carbonate; and this view can be traced back to H. Rose's work in 1851-2, *Ueber den Einfluss des Wassers bei chemischen Zersetzungen*, whereby it was shown that water acting as a weak acid is able to decompose more or less completely the salts of the weak carbonic acid. Indeed, said M. Roloff,

Die Zusammensetzung des Gemisches ist dabei von den zufälligen Nebenumständen abhängig; die bestimmte Formel eines basischen Carbonates aufzustellen ist daher von vornherein aussichtslos.

The *magnesia alba* of pharmacy is a basic carbonate of very indefinite composition; it is obtained by precipitating soln. of the sulphate, chloride, or nitrate with alkali carbonate. A soln. of magnesium sulphate may be employed, also many mineral waters, salt springs, or the mother liquor of sea-water. If these liquids likewise contain calcium salts these must be first removed by adding an alkali sulphate to the liquid. E. Durand, and E. Schmidt have described the preparation of *magnesia alba* in detail. W. Esch made it by the action of ammonia and carbon dioxide on a paste made of water and calcined magnesia. F. Oswald described the preparation from the mineral waters at Bilin; H. Endemann from the residue remaining after the calcination of magnesite for its carbon dioxide. For the preparation from dolomite, *vide supra*.

The light white powder obtained by mixing soln. of 10 parts of magnesium sulphate and 12 parts of sodium carbonate crystals, each dissolved in 80 parts of water; boiling for 15 mins.; washing; draining; and drying, is the so-called *light magnesium carbonate*, or the *magnesi carbonas levis* of the pharmacopœia. Under

the microscope it consists of amorphous granules and slender prismatic crystals. In the preceding operations, if 20 instead of 80 parts of water be employed; the mixture evaporated to dryness; the residue washed until all the soluble sulphate is removed; and dried, the resulting white granular powder is the *heavy magnesium carbonate*, or the *magnesi carbonas ponderosus* of the pharmacopœia. Both products are basic carbonates. W. C. Anderson's analyses of commercial samples of heavy carbonate correspond with 41 : 20 : 83, or approximately $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$; of the light carbonate, 39 : 19 : 85, or approximately $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$; and of the so-called crystal carbonate, 24 : 14 : 85, or approximately $3\text{MgCO}_3 \cdot 2\text{Mg}(\text{OH})_2 \cdot 16\text{H}_2\text{O}$.

The mineral *hydromagnesite*, analyzed by T. Wachtmeister, F. von Kobell, J. L. Smith and G. J. Brush, G. C. Hoffmann, and G. Tschermak, is a basic magnesium carbonate with a composition 4 : 3 : 4, or $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ —a kind of native *magnesia alba*. J. D. Dana considered the crystals belonged to the monoclinic system, with axial ratios $a : b : c = 1.0379 : 1.04652$, and $\beta = 90^\circ$. E. Weinschenk and P. Groth also place the crystals in the monoclinic system, but G. Tschermak and L. Brugnatelli favour the rhombic system. J. L. Smith and G. J. Brush found the sp. gr. of a sample from Texas to be 2.145–2.180; E. Weinschenk found with a sample from Lancaster, 2.32; and L. Brugnatelli found with a sample from Aostatal, 2.196–2.210. The latter also gave the index of refraction $\mu_\beta > 1.530$, and $\mu_\gamma > 1.538$. The hardness on Mohs' scale is $3\frac{1}{2}$. G. A. Young has reported on the large deposits of hydromagnesite near Atlin, British Columbia, where it occurs as a white soft mineral which falls to powder on drying. The so-called *lancasterite* of B. Silliman is considered by J. L. Smith and G. J. Brush to be a mixture of brucite and hydromagnesite. The amorphous mineral *giorgiosite* found by A. Lacroix at Vesuvius is a 4 : 3 : 3-carbonate, or $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. The mineral *hydrogiobertite* found by E. Scacchi near Pollena (Vesuvius) has a composition corresponding with 2 : 1 : 3-carbonate, or $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Its sp. gr. is 2.149 to 2.174; L. Brugnatelli's optical study of this mineral inclines him to the opinion that it is a mixture of at least two other minerals. F. Zambonini identified hydrogiobertite with hydromagnesite. L. Brugnatelli found monoclinic prismatic crystals of the Italian mineral *artinite*—named after E. Artini, at Val Brutta, Val Malenco, and Val Lanterna. Analyses correspond with the 2 : 1 : 3-carbonate, or $2\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$; its sp. gr. is 2.028 at 21.6° , and 2.013 at 22° ; and its hardness is about $2\frac{1}{2}$.

J. J. Berzelius showed that the composition of *magnesia alba* is influenced (i) *by the relative quantity of the precipitant*—if an excess of the alkali carbonate is used, the precipitate is more dense than when the magnesium salt is in excess; (ii) *by the concentration of the solutions*—the more conc. the two soln., the denser the precipitate, and the more normal carbonate does it contain; and (iii) *on the temperature*—the precipitate formed in the cold is lighter than when the soln. are warm, and the utmost degree of lightness is obtained by allowing the precipitate to freeze while still moist. J. J. Berzelius continued: the precipitate formed in the cold approaches more nearly to the composition of the normal salt than that formed in hot soln.; at the same time, a quantity of magnesia remains in soln., because the normal salt is hydrolyzed by water into an insoluble basic salt, and a soluble acid salt. When heated, carbon dioxide is given off by the soln., and the greater part of the magnesia is precipitated from the soln., and the precipitate becomes more basic owing to the escape of carbon dioxide. The composition of the precipitate also depends on (iv) *the time the precipitate is in contact with the mother liquid*. J. J. Berzelius showed that when boiled for a long time, the precipitate has the composition $\text{MgO} : \text{CO}_2 : \text{H}_2\text{O} = 4 : 3 : 4$. According to J. Fritzsche, if moderately boiled, the precipitate is converted into the 5 : 4 : 4-carbonate, but if long boiled, it becomes mixed with a constantly increasing proportion of the 4 : 3 : 4 and the 3 : 2 : 3-carbonates. In general, it may be said that *every alteration in the conditions of preparation of magnesia alba tends to modify the composition of the product*. W. A. Davis found traces of alkali in the soln. caused "a wide variation in the results."

Analyses of *magnesia alba* have been made by J. Fritzsche, J. J. Berzelius, H. Rose, O. Brill, K. Kraut, H. Beckurts, E. A. Nørgaard, W. C. Anderson, etc., and many of the results have been represented by chemical formulæ and assumed to be definite compounds without the application of any criterion as to whether

mixtures or individuals are in question. J. J. Berzelius favoured the formula 4 : 3 : 4; but J. Fritzsche and R. Rinne showed that while the original precipitate approaches 5 : 4 : 5 in composition, this by the prolonged action of boiling water approaches 4 : 3 : 4, and afterwards 3 : 2 : 3. G. Rose observed that the product obtained by evaporating the acid carbonate on a water-bath includes spherules of *magnesia alba* with crystals of the normal salt resembling aragonite. E. A. Nörsgaard failed to obtain a definite crystalline basic carbonate. L. Joulin argued that *magnesia alba* is a mixture of magnesium hydroxide and carbonate in proportions dependent on the conc., temp., and the relative proportions of the reacting salts. As previously indicated, W. A. Davis has shown that trihydrated magnesium carbonate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, may be regarded as **dihydrated magnesium hydroxyhydrocarbonate**, $\text{Mg}(\text{HCO}_3)\text{OH} \cdot 2\text{H}_2\text{O}$, which is produced by the hydrolysis of a soln. of magnesium hydrocarbonate. The dihydrate is readily converted into anhydrous **magnesium hydroxyhydrocarbonate**, $\text{Mg}(\text{HCO}_3)\text{OH}$, as indicated in connection with trihydrated magnesium carbonate, where the preparation and properties of the hydroxycarbonates are therefore discussed. When the dihydrated hydroxycarbonate is suspended in boiling water, it slowly decomposes into magnesium hydroxide. The solid at any intermediate stage has a composition ranging between $\text{Mg}(\text{HCO}_3)\text{OH} \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$, and the mixed character of the product is evident from a microscopic examination of the mass. Excluding the hydroxycarbonate and its hydrate, W. A. Davis shows good reasons for believing that all the varieties of basic magnesium carbonate, *magnesia alba*, light, heavy, and crystal magnesium carbonates are not definite salts, but mixtures of the anhydrous and dihydrated magnesium hydroxycarbonates and hydroxide in varying proportions.

Hydromagnesite, and *magnesia alba*, decompose at a lower temp. than magnesite (*q.v.*); the latter decomposes into magnesium oxide and carbon dioxide at 300°. According to P. Kremers, a litre of water at 15° dissolves 0.197 part of *magnesia alba*; and, according to A. Bineau, 0.10 part in cold or boiling water. According to A. M. Pleischl, the aq. soln. has an alkaline reaction. S. Merkel found that with a soln. of carbon dioxide in a litre of water and at different press. :

Press. of CO_2	.	1	2	4	5	6 atm.
MgO dissolved	.	1.314	1.344	7.46	9.09	13.1 grms.

so that the solubility increases with increasing press. of carbon dioxide when the temp. is constant. G. C. Wittstein found the solubility in water is much raised in the presence of ammonium nitrate, and, according to A. Vogel, in the presence of ammonium chloride. *Magnesia alba* does not dissolve so quickly after it has been heated to 100°; according to A. Vogel, the sat. soln. does not become turbid on exposure to air or by boiling; but it is precipitated by potassium hydroxide. *Magnesia alba* is readily soluble in acids. According to T. S. Hunt, *magnesia alba* precipitates calcium carbonate from its soln. in carbonated waters; and G. Bauck found that when *magnesia alba* is boiled with a dil. soln. of calcium chloride the precipitate contains $\text{CaCO}_3 : \text{Mg}(\text{OH})_2$ in the mol. proportion 3 : 1. According to C. A. Gössmann, if carbon dioxide be passed into a soln. of sodium chloride containing calcium sulphate and *magnesia alba*, magnesium chloride, sodium sulphate, and calcium carbonate are formed. E. Fleischer digested eq. quantities of *magnesia alba*, calcium sulphate, and a soln. of sodium chloride (1 : 6) for an hour at 80°, and found 30 per cent. of the calcium sulphate was transformed into carbonate; the change is less complete if the salt soln. be more dil., if some magnesium sulphate be present, and if the mixture be kept cold.

REFERENCES.

- ¹ H. Rose, *Pogg. Ann.*, **34**, 137, 1835; **83**, 132, 417, 423, 597, 1851; **84**, 52, 461, 547, 1851; **85**, 107, 304, 1852; **86**, 99, 279, 1852; G. Rose, *ib.*, **42**, 366, 1837; J. Fritzsche, *ib.*, **37**, 310, 1836; P. Kremers, *ib.*, **85**, 247, 1852; M. Roloff, *Die Theorie der elektrolytischen Dissoziation*, Berlin, 1902; E. Durand, *Ann. Chim. Phys.*, (2), **54**, 312, 1833; A. Bineau, *ib.*, (3), **51**, 299, 1857;

L. Joulin, *ib.*, (4), 30. 271, 1873; V. A. Jaquelain, *ib.*, (3), 32. 196, 1850; G. Longchamp, *ib.*, (2), 12. 255, 1819; G. A. Young, *Rep. Geol. Sur. Canada*, Ottawa, 50, 1915; B. H. Paul and A. J. Coanley, *Pharm. Journ.*, 61. 389, 1898; H. Deane, *ib.*, 8. 266, 1848; J. H. Gladstone, *ib.*, 8. 273, 1848; E. A. Nørgaard, *Kgl. Danske Vid. Selsk. Skr.*, (5), 2. 54, 1850; W. A. Davis, *Journ. Soc. Chem. Ind.*, 25. 788, 973, 1906; H. Endemann, *ib.*, 14. 127, 1895; C. W. Scheele, *Acta Acad. Stockholm.*, 172, 1785; W. Esch, *German Pat.*, D.R.P. 325141, 1914; P. Kremers, *Pogg. Ann.*, 85. 247, 1852; E. Fleischer, *Journ. prakt. Chem.*, (2), 6. 274, 1872; J. J. Berzelius, *Gilbert's Ann.*, 40. 255, 1812; *Schweigger's Journ.*, 31. 258, 1821; C. H. Pfaff, *ib.*, 35. 428, 1822; H. Beckurts, *Archiv. Pharm.*, (3), 18. 429, 1881; (3), 19. 13, 1881; K. Kraut, *ib.*, (3), 20. 80, 1882; G. Lemoine, *Bull. Soc. Enc.*, (2), 20. 362, 1873; R. Rinne, *Chem. Ztg.*, 31. 125, 1907; F. Zambonini, *Mineralogica Vesuviana*. Neapel, 95, 1910; O. Brill, *Zeit. anorg. Chem.*, 45. 282, 1905; G. Bauck, *Analyse der Salzsoolen von Colberg nebst Beiträgen zur analytischen Chemie*, Göttingen, 1860; A. Vogel, *Journ. prakt. Chem.*, (2), 7. 455, 1836; F. von Kobell, *ib.*, (1), 4. 80, 1835; A. M. Pleischl, *Zeit. Phys.*, 5. 59, 1829; G. Kittel, *Pharm. Viertelj.*, 6. 421, 1857; C. A. Gössmann, *Amer. Chemist*, 1. 442, 1871; A. Fyfe, *Edin. Phil. Journ.*, 5. 305, 1821; G. C. Wittstein, *Repert. Pharm.*, 57. 67, 1836; C. J. B. Karsten, *Philosophie der Chemie*, Berlin, 190, 1843; *Lehrbuch der Salinenkunde*, Berlin, 2. 304, 1847; W. C. Anderson, *Journ. Chem. Soc.*, 87. 261, 1905; J. D. Dana, *Amer. Journ. Science*, (2), 17. 84, 1854; B. Silliman, *ib.*, (2), 9. 216, 1850; J. L. Smith and G. J. Brush, *ib.*, (2), 15. 214, 1853; T. S. Hunt, *ib.*, (2), 26. 109, 1858; P. Groth, *Chemische Kristallographie*, Leipzig, 2. 216, 1908; G. Tschermak, *Tschermak's Mitt.*, 113, 1871; L. Brugnatelli, *Rend. Ist. Lombardo*, 36. 824, 1903; *Centr. Min.*, 663, 1906; *Rend. Accad. Lincei*, (1), 18, 3, 1909; *Zeit. Kryst.*, 31. 54, 1899; E. Weinschenk, *ib.*, 27. 570, 1897; S. Merkel, *Zeit. Chem.*, (2), 3. 697, 1867; T. Wachtmeister, *Akad. Stockholm*, 18, 1827; E. Scacchi, *Rend. Accad. Napoli*, 12, 1885; G. C. Hoffmann, *Ann. Rep. Geol. Sur. Canada*, Ottawa, 1900; A. Lacroix, *Bull. Soc. Min.*, 28. 198, 1908; F. Oswald, *Arch. Pharm.*, (2), 70. 242, 1852; E. Schmidt, *Pharm. Centr.*, 1. 667, 1860.

§ 18. Complex or Double Salts with Magnesium Carbonate

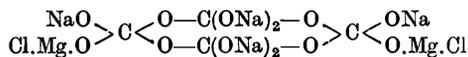
According to J. J. Berzelius,¹ an aq. soln. of magnesium nitrate or chloride, when mixed with an excess of sodium hydrocarbonate, furnishes crystals similar to those obtained when potassium hydrocarbonate is used as precipitant, and presumably misled by analogy, he assumed the crystals to be *sodium magnesium hydrocarbonate*, $\text{MgCO}_3 \cdot \text{NaHCO}_3 \cdot 4\text{H}_2\text{O}$. He added that the crystals are not so readily decomposed by water as the *potassium magnesium hydrocarbonate*, $\text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O}$. H. St. C. Deville, J. Fritzsche, H. Rose, E. A. Nørgaard, and G. von Knorre did not succeed in verifying Berzelius' assumed sodium salt; nor did they obtain the tetrahydrate, $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$. G. Mosander treated a warm soln. of a magnesium salt with an excess of sodium carbonate, and obtained a granular precipitate containing about 21 per cent. of sodium carbonate, and 79 per cent. of magnesium carbonate. The solid dissolved in water as a whole without separating the sodium salt, but, added J. J. Berzelius, if the compound be decomposed by ignition, the sodium salt may be leached out. The alkali magnesium carbonates are decomposed by water. K. Kippenberger mixed freshly precipitated magnesium carbonate with a soln. of sodium or potassium hydrocarbonate at ordinary temp., and found much magnesium carbonate dissolves, and crystallizes from the filtered soln. in about 24 hrs. The crystals approximate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. It is assumed that an alkali magnesium double carbonate is formed and afterwards decomposed.

G. Bollmann prepared what were regarded as hexagonal plates of **lithium magnesium tricarbonate**, $2\text{Li}_2\text{CO}_3 \cdot \text{MgCO}_3$, by dropping 4.6 c.c. of a 10 per cent. soln. of magnesium chloride into 100 c.c. of a sat. soln. of lithium carbonate. After the mixture has stood 4-6 weeks, the turbid soln. is clear, the hydrated magnesium carbonate has disappeared, and six-sided plates of this double salt appear. The crystals are but slowly decomposed by water. The crystals are hard enough to scratch glass.

H. St. C. Deville digested magnesia alba with an aq. soln. of sodium hydrocarbonate at 60°-70°, and obtained anhydrous **sodium magnesium carbonate**, $\text{Na}_2\text{Mg}(\text{CO}_3)_2$; G. von Knorre obtained the same salt by digesting trihydrated magnesium carbonate with an aq. soln. of sodium sesquicarbonate for 24 hrs. between 63°-65°, filtering the warm mixture, and washing well the solid. A. de

Schulten prepared the same compound by heating on a water-bath for 4-5 hrs. a mixture of soln. of 100 grms. of anhydrous sodium carbonate in 400 grms. of water, and 20 grms. of magnesium nitrate in 50 grms. of water, rhombohedral or tetragonal crystals are formed which, he said, were uniaxial, and had a sp. gr. of 2·729 at 15°—G. von Knorre stated that his crystals were doubly refracting, and probably belonged to the tetragonal system. Both A. de Schulten and G. von Knorre agreed that the double salt is very slowly decomposed by cold water; and even at 100° the speed of decomposition is not fast. According to H. St. C. Deville, carbon dioxide and traces of water are lost when the crystals are ignited and the double salt is therefore assumed to be anhydrous. E. A. Nörgaard obtained the **pentadecahydrated sodium magnesium carbonate**, $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot 15\text{H}_2\text{O}$, in rhombic prismatic crystals, by cooling to a low temp. a soln. of magnesium sulphate made just turbid with sodium carbonate. The crystals are decomposed by water, and should be washed with the clear mother liquid and then pressed. Magnesia alba is formed when the crystals are boiled with water. Attempts made by H. St. C. Deville, E. A. Nörgaard, J. Fritzsche, H. Rose, V. A. Jacquelin, G. Kittel, K. Kippenberger, G. von Knorre, and G. Bollmann furnished a basic magnesium carbonate.

Crystals corresponding with **sodium magnesium chlorocarbonate**, $\text{NaCl} \cdot \text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$, were found by G. W. Leighton on the inside of an iron boiler in which the vapour of ammonium carbonate was passed through a lye containing sodium and magnesium chlorides; C. Winkler found them on the inside of the cooling apparatus of the Solvay soda process; and J. H. Pratt found them native at Borax Lake, San Bernadino County, Cal., and called the mineral *northupite*. A. de Schulten obtained the salt by heating a mixture of soln. of 15 grms. of magnesium chloride in 50 c.c. of water, and of 20 grms. anhydrous sodium carbonate and 150 of sodium chloride in 500 c.c. of water. The flocculent precipitate gradually forms regular octahedral crystals which are washed with the mother liquid, and dried at 100°. The crystals belong to the cubic system. C. Winkler represented the salt by the formula $\text{Na}_3(\text{MgCl})(\text{CO}_3)_2$, and S. L. Penfield and G. L. Jamieson, by



A. de Schulten gives 2·377 for the sp. gr. of the artificial crystals at 15°; and J. H. Pratt, 2·380 for *northupite*. The hardness of the mineral is 4. The crystals melt at a red heat, forming an enamel-like mass from which water extracts sodium carbonate and chloride, leaving magnesium oxide as a residue. J. H. Pratt gives 1·5117 for the index of refraction in Li-light; 1·5144 in Na-light; and 1·5180 in TI-light. The crystals are stable in air, but slowly decomposed by cold or hot water.

The sodium and potassium magnesium carbonates are fundamentally different, so that H. St. C. Deville was led to say:

Dans aucun cas la soude et la potasse, dont les analogies sont si intimes, ne se séparent d'une manière plus complète que lorsqu'elles sont mises dans les conditions nécessaires pour former les mêmes carbonates double métalliques.

The double carbonates with rubidium, caesium, and thallium show more analogies. P. A. von Bonsdorff, and H. Rose treated a warm soln. of a magnesium salt with an excess of potassium carbonate, and obtained a precipitate which is slightly soluble in water, and separates from its soln. as a crystalline powder. If the soln. are mixed at the b.p., magnesium carbonate is alone precipitated. J. J. Berzelius prepared crystals of what were probably **tetrahydrated potassium magnesium carbonate**, $\text{K}_2\text{Mg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, by treating a cold aq. soln. of magnesium nitrate or chloride with an excess of potassium sesquicarbonate, and allowing the mixture to stand for a few days. H. St. C. Deville made small rhombic prisms of the same salt by digesting magnesia alba with an aq. soln. of potassium hydrocarbonate for 12 to

15 hrs. at 60° to 70°; G. von Knorre prepared crystals of the salt by digesting 9 grms. of trihydrated magnesium carbonate and 50 grms. of potassium hydrocarbonate, with 50 c.c. of water for 21 hrs. at 60° to 70°, and by digesting 20 grms. of hexahydrated magnesium chloride and 40 grms. of potassium carbonate for two days at ordinary temp. If magnesium sulphate be used the precipitate is contaminated with sulphates. H. St. C. Deville found that the crystals are decomposed by cold water; and he gives for the axial ratios of the rhombic crystals $a : b : c = 0.7563 : 1 : 0.6068$.

J. J. Berzelius found that if an excess of potassium hydrocarbonate be added to a cold aq. soln. of magnesium chloride or nitrate, large crystals of **tetrahydrated potassium magnesium hydrocarbonate**, $\text{KHMg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, or $\text{Mg}(\text{KCO}_3)(\text{HCO}_3) \cdot 4\text{H}_2\text{O}$, are formed. In his study of the solubility of magnesium carbonate in soln. of potassium hydrocarbonate, F. Auerbach obtained the same salt. G. von Knorre made this salt by adding a very conc. soln. of 6 grms. of magnesium chloride to 50 c.c. of a soln. with 10 grms. of potassium hydrocarbonate, and 7 grms. of the normal carbonate—crystals are formed when the mixture is allowed to stand. R. Engel obtained this salt by the action of carbon dioxide on a soln. of potassium chloride and trihydrated magnesium carbonate; and the Salzbergwerk Neustassfurt has some patents on the subject.

In R. Engel's *magnesia-potash process*, magnesium carbonate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, is suspended in a sat. soln. of potassium chloride, and the mixture sat. with carbon dioxide. A crystalline double salt, $\text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O}$, separates from the soln.: $3(\text{MgCO}_3 \cdot 3\text{H}_2\text{O}) + 2\text{KCl} + \text{CO}_2 = \text{MgCl}_2 + 2(\text{KHCO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O})$. When the crystalline mass is treated with water at 140° under press., carbon dioxide is evolved, magnesium hydroxide is precipitated, and potassium carbonate remains in soln.: $2(\text{KHCO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}) = \text{K}_2\text{CO}_3 + 2\text{Mg}(\text{OH})_2 + 7\text{H}_2\text{O} + 3\text{CO}_2$. Sodium carbonate cannot be formed in the same way since the corresponding sodium salt, $\text{MgCO}_3 \cdot \text{NaHCO}_3 \cdot 4\text{H}_2\text{O}$, does not precipitate.

According to J. C. G. de Marignac, the crystals belong to the triclinic system and have the axial ratios $a : b : c = 0.4261 : 1 : 0.5945$, and the axial angles $\alpha = 111^\circ 9'$, $\beta = 114^\circ 26'$, and $\gamma = 74^\circ 33'$. G. von Knorre gives for the sp. gr. 1.984 at 18°. J. C. G. de Marignac found the crystals to be stable in air. J. J. Berzelius added that the crystals are tasteless at first, but after a few seconds exhibit an alkaline flavour. When heated to 100° the crystals become opaque and lose water; and when strongly heated they soften and give off bubbles of carbon dioxide leaving a mixture of magnesium oxide and normal potassium carbonate. The crystals are soluble in water, but not without decomposition, for a basic magnesium carbonate is precipitated and a mixture of potassium hydrocarbonate and magnesium hydrocarbonate passes into soln. J. Fritzsche said that the precipitate is trihydrated magnesium carbonate mixed with the pentahydrate, and the proportion of the latter increases as the temp. of the water falls. G. von Knorre said that the salt is stable in water sat. with carbon dioxide.

R. Engel has investigated the conditions under which normal magnesium carbonate combines with potassium hydrocarbonate, and finds that for the same soln. of potassium hydrocarbonate the velocity of the reaction decreases as the temp. rises. If the temp. remains constant, the velocity increases with the initial conc. of the potassium soln. Combination ceases when it attains a certain limit, which is measured by the conc. of the soln. of the potassium salt remaining in contact with excess of magnesium carbonate without combining with it. This limit increases with the temp., and its variation is given by the formula $y = 2.5236 + 0.00517t + 0.003108t^2$, where y is the number of c.c. of standard sulphuric acid required to neutralize the carbonates remaining in soln. The product of the combination, $\text{MgCO}_3 \cdot \text{KHCO}_3 + 4\text{H}_2\text{O}$, is decomposed by water, and the decomposition tends towards a limit which is not identical with the limit of combination, but is always inferior to it by a quantity which is practically the same for all temp. P. Duhem regards this as an example where *la région des faux équilibres* separates two regions corresponding respectively to two reactions which are the inverse of one another.

The reaction was also investigated by E. H. Büchner, and he considers that R. Engel's systems were not in equilibrium, nor could M. Nanty confirm the existence of two distinct limits in the formation and decomposition of the system: $\text{KHCO}_3 + \text{MgCO}_3 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{MgCO}_3 \cdot \text{KHCO}_3 \cdot 4\text{H}_2\text{O}$, at 20° – 30° ; since he found at the same temp. and press., the two reactions converge towards a common limit. F. Auerbach studied the conditions of stability as indicated in connection with the solubility of magnesium carbonate in soln. of potassium hydrocarbonate.

H. Erdmann and P. Köthner prepared **tetrahydrated rubidium magnesium hydrocarbonate**, $\text{MgRbH}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, by heating on a water-bath at 60° in a current of carbon dioxide, a soln. of rubidium hydrocarbonate, and magnesium carbonate. The salt is very efflorescent. G. Bollmann prepared the same salt, and he also obtained microscopic rhombic plates of tetrahydrated **rubidium magnesium carbonate**, $\text{MgCO}_3 \cdot \text{Rb}_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, mixed with trihydrated magnesium carbonate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, by adding rubidium carbonate to a well-cooled soln. of magnesium chloride. He likewise obtained tetrahydrated **caesium magnesium carbonate**, $\text{MgCO}_3 \cdot \text{Cs}_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$. Both salts are readily decomposed by water. G. Bollmann also speaks of a possible *copper magnesium carbonate*.

According to A. F. de Fourcroy,² the addition of even a large excess of aq. ammonia to a soln. of a magnesium salt never precipitates more than half the magnesia present; and, according to N. J. B. G. Guibourt, one part of ammonium sesquicarbonate precipitates half the magnesium as carbonate from a soln. of two parts of magnesium sulphate; and two parts of ammonium sesquicarbonate precipitate all the magnesium as tetrahydrated **ammonium magnesium carbonate**, $(\text{NH}_4)_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}$. F. Schaffgotsch said the precipitate is at first flocculent, but later becomes crystalline. When a mixture of cold aq. soln. of magnesium sulphate or chloride and ammonium sesquichloride is allowed to stand for several hours, A. F. de Fourcroy and C. F. Bucholz observed that crystals of the double salt are formed. G. C. Wittstein also found a soln. of magnesia in an aq. soln. of ammonium sesquicarbonate furnishes a crop of crystals of the double salt in a short time. P. A. Favre observed similar results on shaking magnesia alba with an aq. soln. of ammonium carbonate, and allowing the filtered soln. to crystallize. According to F. Schaffgotsch, soln. of ammonium carbonate, with or without free ammonia, furnish the double salt on being treated with a magnesium compound; and E. Divers added that if a soln. with one mol of magnesium sulphate be treated with less than four mols of ammonium carbonate, magnesium carbonate first precipitates, and the double salt is afterwards deposited: if the soln. contains two mols of ammonium chloride for every mol of magnesium sulphate, no magnesium carbonate is precipitated. If the ammonium carbonate is added slowly, the double salt is formed, and all the magnesium is precipitated as the double salt when four mols of ammonium carbonate have been added; if a larger proportion of ammonium chloride is present, more ammonium carbonate is required for the complete precipitation of the magnesium. R. Weber and F. Schaffgotsch studied the occlusion of salts by the precipitated ammonium magnesium carbonate; they find potassium salts are occluded so tenaciously as not to be removed by washing—sodium salts are not so occluded. According to J. W. Döbereiner, the crystals form translucent rhombohedrons. N. J. B. G. Guibourt observed that the damp crystals give off ammonia when exposed to air, but not if the crystals have been well dried over calcium chloride. E. Divers found that the dry distillation of the double salt gives a liquid which deposits crystals of ammonium sesquicarbonate, $(\text{NH}_4)_4\text{H}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$, and a sublimate of the same salt. The ignition of the salt yields magnesium oxide. According to C. F. Bucholz, the crystals are decomposed by water; and P. A. Favre, N. J. B. G. Guibourt, and E. Divers found that with cold water, magnesium carbonate is formed, and with hot water, magnesia alba. According to E. Divers, the double salt is sparingly soluble in an aq. soln. of ammonium carbonate, and very soluble in an aq. soln. of ammonium chloride. If a magnesium salt be treated with a large excess of ammonium hydrocarbonate, H. St. C. Deville obtained

tetrahydrated **magnesium ammonium hydrocarbonate**, $\text{Mg}(\text{NH}_4\text{CO}_3)(\text{HCO}_3)\cdot 4\text{H}_2\text{O}$, as a crystalline powder which forms normal ammonium magnesium carbonate by the loss of ammonia and water. A higher hydrate, $\text{Mg}(\text{NH}_4\text{CO}_3)(\text{HCO}_3)\cdot 5\frac{1}{2}\text{H}_2\text{O}$, is produced by working at a low temp. R. Engel could not make this salt, but G. von Knorre succeeded in doing so.

The term *dolomite* is employed somewhat loosely for limestones containing notable quantities of magnesium carbonate; and it is also employed in a more specific sense for the double **calcium magnesium carbonate**, $\text{CaMg}(\text{CO}_3)_2$, which occurs as a crystallized mineral and as a massive rock, and in which the ratio $\text{CaO} : \text{MgO}$ is as 1 : 1. H. B. Saussure³ first named the mineral *dolomie* after D. Dolomieu, who observed many of the peculiar properties of what he called *pierres calcaires très-peu effervescentes avec les acides*; R. Kirwan called it *dolomite*. Normal dolomite has also been called *dolomite spar*, *bitter spar*, or *bitter salt spar*. In some cases part of the magnesium has been replaced by iron to furnish *ferruginous dolomites*, which, when coloured brown, are called *brown spar*, and, when coloured a pale brown, *pearl spar*; while varieties approximating to $2\text{CaCO}_3\cdot\text{MgCO}_3\cdot\text{FeCO}_3$ are called *ankerite*, after M. Anker of Styria. Varieties of dolomite of minor importance have been named after particular localities—e.g. *miemite* from Miemo (Tuscany), *tharandite* from Tharand (Dresden), and *gurhofite* from Gurhof (Austria). The latter was analyzed by A. Baumgarten and J. R. von Holger in 1837, and was shown by H. von Foullon to be most probably a mixture. L. Blum found what he regarded as $2\text{MgCO}_3\cdot\text{CaCO}_3$ in an iron mine in Lothringen, and he regarded it as a new mineral species, *lessbergite*; but W. Bruhns showed that lessbergite is probably a mixture. Several more or less ephemeral names have been used for varieties of dolomite—*conite*, *brossite*, *tautocline*, etc. What appears to have been a kind of ankerite was analyzed by P. Woulfe in 1779. Similarly also manganese carbonate may replace magnesium carbonate, furnishing *manganiferous dolomites*—a specimen from Kuttenberg (Bohemia) was named *kutnohorite* by A. Bukowsky. A *nickeliferous dolomite* from Taraps (Switzerland) has been called *taraspite* by C. von John; a *cobaltiferous dolomite* was reported by W. Gibbs from Przibram; and a zinciferous dolomite by K. Monheim from Altenberg. There are also *dolomitic marbles*. The magnesium limestones are presumably mixtures of dolomite and calcite, although brucite is sometimes present—e.g. *predazzite* and *pencatite* are mixtures of calcite and brucite.

Dolomite, like limestone, is found in large beds covering whole tracts of country and mountain ranges, as in the North of England, Tyrol, and many other places. Numerous analyses have been made of normal dolomites and dolomites with a low proportion of iron; ⁴ of ferruginous dolomites, including ankerite and brown spar; ⁵ and of manganiferous dolomites.⁶

The formation of dolomite in nature.—In the formation of marine dolomites in nature, (i) the mixed carbonates may be directly precipitated in shallow waters, by changes of temp., of conc. of atm. carbon dioxide, or by ammonium carbonate derived from the decomposition of marine organisms. This hypothesis has been advocated by G. Leube,⁷ C. W. Gümbel, T. Scheerer, T. S. Hunt, etc. (ii) The limestone formed by the accumulation of the shells or skeletons of marine organisms is magnesian. This statement is emphasized by A. G. Högbom's analyses of oceanic oozes; and by F. W. Clarke and W. C. Wheeler's analyses of the inorganic parts of marine organisms, etc. The more soluble calcium carbonate may be leached away by percolating waters until the dolomitic ratio is approximated. H. Grandjean, A. G. Högbom, J. D. Dana, and others have produced evidence of this action. The borings on the atoll of Funafuti, examined by J. W. Judd, showed a marked enrichment in magnesium carbonate near the surface, owing presumably to the leaching out of the lime salts. The coralline rock may also be enriched by the magnesium salts contained in sea-water. The precipitation of magnesium carbonate from its soln. in sea-water by calcium carbonate has been established by the experiments of T. Scheerer and F. Hoppe-Seyler. T. Scheerer noted that powdered chalk

precipitates magnesium carbonate from a soln. of the hydrocarbonate, and carbonated waters can dissolve calcium carbonate out of magnesian limestones.

The synthesis of dolomite.—J. C. G. de Marignac obtained dolomite artificially by heating calcium carbonate with a soln. of magnesium chloride to 200° under 15 atm. press. After 2 hrs.' heating a little of the calcium carbonate was dolomitized, but after 6 hrs.' heating, the product was richer in magnesite than is dolomite itself. A. von Morlot heated powdered calcite with a soln. of magnesium sulphate in a sealed tube at 200° and found that a mixture of dolomite and gypsum was formed; W. Haidinger pointed out that these two minerals are in frequent association. This reaction appears to be reversible because H. C. Sorby obtained efflorescences of magnesium sulphate in Permian limestones, and they are not uncommon in gypsum quarries. J. Durocher heated fragments of porous limestone with dry magnesium chloride to dull redness in a closed gun-barrel so that the vapour of the chloride impregnated the carbonate. The limestone was partially changed to dolomite. H. St. C. Deville saturated chalk or corals with a soln. of magnesium chloride, and heated the mixture on a sand-bath. The lime was partially replaced by the magnesia. K. Spangenberg heated vaterite with a soln. of sodium carbonate and magnesium chloride at 180°–200° in an autoclave under a press. of 50 atm. of carbon dioxide, and obtained dolomite. G. Linck effected the synthesis of dolomite by adding calcium chloride to a mixture of soln. of magnesium chloride, magnesium sulphate, and ammonium sesquicarbonate, when the amorphous precipitate becomes crystalline, with the composition and optical properties of dolomite, when gently heated in a sealed tube. W. Meigen failed to verify G. Linck's result. L. Bourgeois and H. Traube obtained dolomite by heating a mixture of magnesium and calcium chlorides with potassium cyanate in a sealed tube at 130°. F. W. Pfaff found that the products of organic decay—ammonium carbonate and sulphide, hydrogen sulphide, etc.—probably assist in the dolomitic process; he found that when a current of carbon dioxide is passed for a long time through a warm soln. of the sulphates and chlorides of magnesium and calcium, the slow evaporation of the soln. at 20°–25°, yields a residue containing a double carbonate insoluble in dil. hydrochloric acid. It is suggested that these conditions might be approximately paralleled in the case of sea-water and thus dolomite might be formed.

C. J. B. Karsten found magnesium carbonate dissolves slowly in a conc. soln. of calcium chloride, and the freshly precipitated carbonate was found by T. S. Hunt to dissolve copiously in that menstruum. According to C. A. Gössmann, the soln. decomposes when boiled, forming a precipitate of calcium carbonate and magnesium chloride. The spontaneous evaporation of a soln. of calcium and magnesium carbonates in carbonated water mixed with calcium chloride was found by A. Bineau to give a precipitate of calcium carbonate, and if evaporated by the aid of heat, a precipitate of calcium carbonate mixed with a little magnesium carbonate. G. Bauck boiled a soln. of equal parts of magnesium and calcium carbonates in carbonated water along with some calcium and magnesium chlorides, and found the precipitate contained a larger proportion of calcium than magnesium the more prolonged the boiling. With slow heating very little, and with rapid heating a lot, of magnesium salt is precipitated; when the alkaline liquid is allowed to stand some days, the magnesium precipitate is redissolved. According to T. S. Hunt, sodium hydrocarbonate precipitates at first almost wholly calcium carbonate from a mixed soln. of calcium and magnesium chlorides; and then follows hydrated magnesium carbonate. T. S. Hunt precipitated mixtures of calcium and magnesium carbonates from hydrocarbonate soln. by alkali carbonates; when the pasty mass formed by precipitation was heated to a temp. exceeding 120°, combination occurred, and dolomite was formed. T. Scheerer obtained mixtures but no dolomite when a soln. of calcium and magnesium hydrocarbonates is evaporated spontaneously at ordinary temp. Temp. is evidently an important factor in the formation of dolomite. F. Hoppe-Seyler obtained no dolomite by allowing a soln. of magnesium chloride to act on calcium carbonate for many months; nor by allowing sea-water,

sat. with carbon dioxide, to stand in contact with an excess of calcium carbonate, for four months in a closed flask; but when magnesium salts or sea-water were heated with calcium carbonate in sealed tubes, dolomite and magnesite were formed. Calcium carbonate heated to over 100° with a soln. of magnesium hydrocarbonate gave a similar result.

C. Klement tried aragonite, the less stable form of calcium carbonate, in place of calcite, and he found that a conc. soln. of magnesium sulphate at 60° will partially transform coral or aragonite into magnesium carbonate under conditions where calcite is but slightly attacked; a mixed soln. of magnesium sulphate and sodium chloride at 90° attacked aragonite rapidly, forming a product with 41.5 per cent. of magnesium carbonate. Magnesium chloride was not so active as the sulphate. Although the product of these reactions is not dolomite, but rather a mixture of the carbonates, he believed that in time mixtures of this kind would combine and crystallize into dolomite. He attributed the formation of dolomite to the action of sea-water in closed lagoons on the aragonite of coral rock. Pseudomorphs of dolomite after calcite have been reported by R. Blum, and others.

The deposition of crystalline dolomite, and of magnesian travertine, from natural waters has been observed, as well as, what might be called, the accidental formation of dolomite crystals. Thus, J. Girardin noted that the travertine deposited by the mineral spring of St. Allyre (Clermont) is rich in magnesium carbonate, but whether present as dolomite has not been ascertained. A. Moitessier found that crystals of dolomite were deposited inside a badly closed bottle containing mineral water; and A. Terreil found similar crystals were formed in a sealed tube containing water from a hot spring near the Dead Sea. Hence, L. Lartet concluded that the dolomites in the region of the Dead Sea were probably formed by the impregnation of limestones by magnesian waters. E. von Gorup-Besanez also found spring water from the dolomitic (1:1) ratio, to deposit the mixed salts and not the double compound. Although in the laboratory, a moderately high temp. is needed for the combination of the mixed carbonates to form the double salt, it may be that union between the moist particles does actually take place very slowly in the cold and possibly under a moderate press.

The properties of dolomite.—The crystals of dolomite are shown by P. Groth⁸ to belong to the trigonal system and to have the axial ratio $a : c = 1 : 0.8322$, and $\alpha = 102^\circ 53'$. H. Baumhauer, P. Koller, etc., have studied the corrosion figures. G. Tschermak has pointed out that the corrosion figures show that dolomite is not hemihedral like calcite, but rather tetartohedral; and this is in agreement with F. Becke's observations on the twinning of dolomite crystals. In order to explain the magnesia in calcites, P. Groth assumed an isomorphism between calcite and dolomite, and he regarded the latter as a true double salt; but F. Becke, *au contraire*, showed that while the crystals of calcite and magnesite belong to the scalenohedral class, dolomite crystallizes in the rhombohedral class. The **X-radiograms** of dolomite have been studied by H. Haga and F. M. Jäger, F. Rinne, and A. Johnsen.

The **specific gravity** of dolomite has been determined on most of the samples which have been analyzed—*vide supra*—and the results range from 2.75 to 3.10. Most of these samples were not of a high degree of purity. F. E. Neumann's value⁹ is 2.916; F. Ott's, 2.89; G. Tschermak's, 2.924; E. Madelung and R. Fuchs' 2.8735 (0°); and F. Senft's 2.85. The best representative value for dolomite is taken by J. W. Retgers to be 2.872; for calcite, 2.712; and for magnesite, 3.017. The mean sp. gr. calculated on the assumption that dolomite is a mechanical mixture is 2.843, a difference of 0.029. The contraction which occurs in the formation of dolomite is therefore taken by J. W. Retgers to indicate that dolomite is a chemical individual, a true double salt. This double salt does not form isomorphous mixtures with either calcite or magnesite, but stands isolated in its physical properties outside the series of mixtures. The primitive forms of calcite and magnesite are two rhombohedra with slightly different angles; and these angles vary with the temp.

and elastic actions. Calcium carbonate, however, can form a very small range of mixed crystals with a little magnesium carbonate, and these crystals are isomorphous with those of calcite, so that the magnesite here occurs as a labile dimorphous modification which does not belong to the same class as calcite. Similarly also with respect to the admixture of a little calcite with magnesite, the calcite is present as a labile modification isomorphous with magnesite. To summarize, it is probable, though not yet established, that dolomite is a double salt; but there is yet no further evidence of the assumed isodimorphism of calcite and magnesite, *vid* two unknown labile phases. The **hardness** of dolomite on Mohs' scale is 3.5 to 4.0. W. Voigt found the **elastic modulus** to be 14,600 kgrms. per sq. mm. in the direction of the principal axis; 8330 kgrms. per sq. mm. in a direction perpendicular to that axis; 14,400 and 18,700 kgrms. per sq. mm. respectively in directions inclined at angles -21.5° and $+21.5^\circ$ to the principal axis. E. Madelung and R. Fuchs gave 1.21×10^{-6} megabars per sq. cm. for the **compressibility** of dolomite.

According to F. Findeisen¹⁰ when dolomite is heated, the magnesium carbonate first decomposes, and then the calcium carbonate. G. A. Bole and J. B. Shaw obtained similar results. K. Friedrich and L. G. Smith found that different specimens of dolomite began to decompose at from 730° to 745° , and the heating curves showed a maximum thermal change at about 750° or 760° . According to J. A. Hedvall and J. Heuberger, if the oxides of the alkaline earths and magnesium be arranged in order of increasing basicity, MgO, CaO, SrO, BaO, then the oxide of the more basic metal will on heating with the carbonate of the less basic element be changed into the carbonate without the evolution of gas and at a temp. well below the temp. of dissociation of the carbonate taken. The temp. of the reaction decreases and the heat effect increases with increasing difference of basicity, for example, $\text{MgCO}_3 + \text{BaO} = \text{BaCO}_3 + \text{MgO} + 19$ cal. at 230° ; $\text{SrCO}_3 + \text{BaO} = \text{BaCO}_3 + \text{SrO} + 6.14$ cal. at 280° . According to H. St. C. Deville, and A. Hauenschild, dolomite which has been heated to 360° – 400° and made into a paste with water, hardens under water like a cement; but if pre-heated to redness, it disintegrates when placed in water.

The thermal properties of dolomite have not been closely examined, but the same remark applies to the physical properties generally. It is remarkable, said H. Leitmeier, that so little is known about the physical properties of a substance on which so much work, relating to its genesis and constitution, has been expended. H. Fizeau measured the **coefficient of linear expansion**, and found $\alpha = 0.0001968$ in a direction parallel to the chief axis, and 0.0000367 when vertical to the chief axis. H. Kopp found the coeff. of cubical expansion to be 0.000035 per degree between 13° and 43° . H. Kopp found the **specific heat** to be 0.206 between 18° and 47° ; H. V. Regnault, 0.21743 between 26° and 99° ; and R. Ulrich and E. Wollny, 0.2218 between 18° and 98° .

According to H. Fizeau, the **double refraction** is strongly negative $\omega - \epsilon = 0.189$; and the **index of refraction** for Na-light is $\omega = 1.68174$ for the ordinary ray, and $\epsilon = 1.50256$ for the extraordinary ray. K. Eisenhut¹¹ measured the refractive indices of eight specimens of dolomite with gradually increasing proportions of iron, and found that the index of refraction increases. W. Schmidt found the **dielectric constant** of a crystal of dolomite in a direction parallel to the chief axis to be 6.70 , and normal to that axis 7.77 . W. Voigt studied the **magnetic properties** of crystals of dolomite.

The solubility of dolomite.—According to A. Cossa,¹² a litre of distilled water sat. at 18° and 750 mm. press. with carbon dioxide, dissolves 0.320 grm. of dolomite, 0.15 grm. of magnesite, and 1.0 to 1.2 grms. of calcite. H. Leitmeier found that at ordinary temp. a litre of water sat. with carbon dioxide dissolves 0.11 grm. of dolomite. C. G. C. Bischof found that if the dolomite contains a little magnesite or calcite, these are first dissolved. T. Scheerer found that the calcium carbonate was dissolved much faster than magnesium carbonate. C. Doelter and R. Hoernes, and E. von Gorup-Besanez did not find much difference, though the calcium

carbonate dissolved a little more quickly. When the soln. is evaporated, the dissolved carbonates do not reform dolomite, although F. Hoppe-Seyler showed that at temp. near 200°, dolomite can be recrystallized from carbonated water.

The early reports on the action of acids on dolomite and magnesian limestones appear contradictory; possibly some cases can be explained by the presence of forms of magnesium carbonate which dissolve, in acids—some slowly, some quickly. In 1791, D. Dolomieu stated that cold dil. *mineral acids* do not act very well on dolomite. C. J. B. Karsten treated a magnesian limestone with cold dil. acetic acid and obtained an undissolved residue of dolomite; in another limestone, he obtained a residue of magnesium carbonate *ohne Spur von Kalk*; and therefore inferred that the former was a mixture of calcite and dolomite, the latter a mixture of calcite and magnesite. A. Damour similarly treated a limestone from Mt. Somma and found that it all dissolved even though the proportions of calcium and magnesium carbonates were as 4 : 1. C. Schmidt also obtained a similar result with a Russian limestone. P. Forchhammer found that dil. *acetic acid* removed the excess of calcite from a dolomitic limestone, but scarcely affected the dolomite. C. Doelter and R. Hoernes, A. Vesterberg, and F. Hoppe-Seyler obtained a similar result. On the other hand, F. W. Pfaff, J. Roth, and T. S. Hunt found a considerable proportion of magnesium salt was dissolved. K. Haushofer made an extensive study of the solubility of dolomite in acetic acid, and found that the duration of the treatment, the conc. of the acid, and the temp. are of great importance. The effect of temp. and the time of treatment are usually greater with dil. than with conc. acetic acid. With normal dolomites, the magnesia dissolves more readily than the lime, while with dolomites containing an excess of calcite, the calcium salt dissolves faster than the magnesium salt. Citric acid acts more energetically than acetic acid. T. Liebe found that a dolomitic limestone was enriched by treatment with cold dil. *hydrochloric acid* owing to the preferential dissolution of the calcium carbonate, and C. E. Schafhäütl made a similar observation with *nicht allzu* conc. hydrochloric acid. For the action of *carbonic acid*, that is, carbonated water, or a soln. of carbon dioxide in water, see the decalcification of dolomite. A. Vesterberg found that magnesium carbonate in some cases dissolves as fast as the calcium carbonate; and that the presence of magnesium chloride depresses the speed of dissolution of magnesium carbonate in carbonated water.

According to H. Reinsch, dolomite is not decomposed by boiling it with calcium sulphate and water, but if calcined dolomite is treated with carbon dioxide and again exposed to the action of calcium sulphate and water, F. Findeisen found that magnesium sulphate is formed. According to C. J. B. Karsten, dolomite behaves like magnesite towards an aq. soln. of *sodium chloride*, and it is not decomposed by an aq. soln. of *calcium chloride*. P. Berthier fused a mixture of four mols of *sodium carbonate* with one of dolomite, and on cooling obtained a clear mass with a crystalline fracture. If a very high temp. be employed carbon dioxide is evolved, and with a smaller proportion of sodium carbonate, the evolution of gas occurs as soon as the mixture begins to soften.

The so-called *hydrodolomite* or *hydromagnocalcite* found in stalagmitic and concretionary forms at Mt. Somma, Vesuvius, is a calcium magnesium carbonate with 6 to 17 per cent. water of hydration. R. Hermann¹³ called a similar mineral *pernite*. C. U. Shepard found a variety which he called *hydronicke magnesite* tinted with nickel in Texas, Pa. A variety called *hydromanganocalcite* contains manganese. According to C. F. Rammelsberg, and F. von Kobell, hydrodolomite is really a mixture of hydromagnesite and dolomite. T. S. Hunt obtained what he regarded as a hydrated calcium magnesium carbonate, $\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot 5\text{H}_2\text{O}$, by the action of a small excess of sodium carbonate on a soln. containing equi-mol. proportions of magnesium and calcium chlorides. If this precipitate is kept in contact with sea-water for some days, it forms small transparent prismatic crystals; and by using insufficient sodium carbonate for complete precipitation, he obtained prismatic crystals of what he regarded as $7\text{MgCO}_3 \cdot 10\text{CaCO}_3 \cdot 21\text{H}_2\text{O}$.

It is difficult to *distinguish calcite from dolomite*. J. Lemberg¹⁴ tried ferric chloride, and silver nitrate soln. The latter stains the two minerals unequally after ignition; and E. Hinden has stated that limestone is coloured reddish-brown by a soln. of ferric chloride,

and blue by a soln. of cupric sulphate, while dolomite is not affected—O. Mahler got poor results with ferric chloride, but good ones with the cupric sulphate. According to J. Lemberg, a soln. of aluminium chloride and hæmatoxylin or extract of logwood—*Lemberg's solution*—deposits a violet coating on calcite surfaces, but leaves dolomite uncoloured. F. Cornu has pointed out that if the powdered minerals are covered with water with a few drops of phenolphthalein, calcite gives an intense coloration while dolomite is not affected.

G. Bollmann allowed a soln. of calcium chloride or nitrate to act for 1–8 hrs. on hydrated magnesium carbonate at 120°–200°, but did not get any sign of the formation of dolomite, and he assumed that the reaction requires a long time; on the other hand, he found that the formation of trihydrated **distrontium magnesium carbonate**, $2\text{SrCO}_3 \cdot \text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, proceeds more quickly when carbon dioxide is passed into a sat. soln. of strontium nitrate with magnesium carbonate in suspension, for 2 hrs. at 150°–170°. When the action is allowed to continue for a longer time, the product approximates to a *strontia-dolomite*, $\text{SrCO}_3 \cdot \text{MgCO}_3$. When a soln. of barium nitrate is treated in a similar manner, **barium magnesium carbonate**, $\text{BaCO}_3 \cdot \text{MgCO}_3$, is formed.

W. F. Foshag¹⁵ groups the following minerals of the general formula $\text{MgCO}_3 \cdot 5\text{Mg}(\text{OH})_2 \cdot 2\text{R}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, as **hydrotalcites**. C. Hochstetter, R. Hermann, C. U. Shepard, C. F. Rammeisberg, and W. R. Johnson described the mineral *hydrotalcite*, $\text{MgCO}_3 \cdot 5\text{Mg}(\text{OH})_2 \cdot 2\text{Al}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$. C. U. Shepard called it *houghite*, and R. Hermann, *völkernite*; W. F. Petterd, L. K. Ward, L. Hezner, and A. Himmelbauer described *stichtite*, $\text{MgCO}_3 \cdot 5\text{Mg}(\text{OH})_2 \cdot 2\text{Cr}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$; L. J. Igelström, H. Sjögren, R. Mauzelius, and G. Flink, *pyroaurite*, $\text{MgCO}_3 \cdot 5\text{Mg}(\text{OH})_2 \cdot 2\text{Fe}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$; and E. Artini, and A. Pelloux, *brugnatellite*, $\text{MgCO}_3 \cdot 5\text{Mg}(\text{OH})_2 \cdot \text{Fe}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$ —but whose composition has not yet been definitely established. A comparison of the properties of these minerals is indicated in Table VIII.

TABLE VIII.—COMPARISON OF THE PROPERTIES OF THE HYDROTALCITES.

Hydrotalcite.	Pyroaurite.	Stichtite.	Brugnatellite.
White	Light brown	Lavender purple	Rose, light brown
Translucent	Translucent	Translucent	Translucent
Uniaxial	Uniaxial	Uniaxial	Uniaxial
Cleavage basal	Cleavage basal	Cleavage basal	Cleavage basal
Sp. gr. 2.04–2.09	Sp. gr. 2.07	Sp. gr. 2.12	Sp. gr.
n. 1.510	n. 1.55 (approx.)	n. 1.542	n. 1.533
Biref, weak	Biref. weak	Biref. 0.026	—
Pleochroism, none	Pleochroism, none	Very slightly pleochroic	Pleochroic

REFERENCES.

¹ J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, 4. 311, 1835; *Ann. Chim. Phys.*, (2), 14. 370, 1820; V. A. Jacquelin, *ib.*, (3), 32. 196, 1851; H. St. C. Deville, *ib.*, (3), 33. 75, 1851; P. A. von Bonsdorff, *ib.*, (2), 20. 12, 1822; *Pogg. Ann.*, 18. 26, 1830; G. Mosander, *ib.*, 5. 505, 1825; H. Rose, *ib.*, 83. 411, 1851; 84. 461, 1851; J. Fritzsche, *ib.*, 37. 310, 1836; G. von Knorre, *Zeit. anorg. Chem.*, 34. 278, 1903; K. Kippenberger, *ib.*, 6. 177, 1894; E. A. Nörsgaard, *Kgl. Danske Vid. Selsk. Skr.*, (5), 2. 54, 1850; A. de Schulten, *Bull. Soc. Chim.*, (3), 15. 1145, 1896; *Compt. Rend.*, 122. 1427, 1896; 123. 1025, 1896; 143. 403, 1906; M. Nanty, *ib.*, 151. 1352, 1910; G. W. Leighton, *Chem. News*, 57. 3, 1888; G. Kittel, *Pharm. Viertelj.*, 6. 421, 1857; C. Winkler, *Zeit. angew. Chem.*, 6. 445, 1893; Salsbergwerk Nue-Stassfurt, *German Pat.*, D.R.P.P. 125897, 1901; 143480, 1900; 143595, 1901; R. Engel, *ib.*, 50786, 53574, 55182, 57721, 1890; *Deut. Patentschr.* 15218, 1881; R. Engel, *Compt. Rend.*, 100. 1224, 1885; 101. 749, 1885; *Bull. Soc. Chim.*, (2), 44. 358, 1885; F. Auerbach, *Zeit. Elektrochem.*, 10. 161, 1904; E. H. Büchner, *ib.*, 14. 63, 1908; J. C. G. de Marignac, *Ann. Mines*, (5), 12. 59, 1857; J. H. Pratt, *Amer. Journ. Science*, (4), 2. 125, 1896; S. L. Penfield and G. L. Jamieson, *ib.*, (4), 20. 222, 1905; P. Duhem, *Thermodynamique et chimie*, Paris, 413, 1902; H. Edmann and P. Köthner, *Liebig's Ann.*, 294. 71, 1896; G. Bollmann, *Beiträge zur Kenntnis der Magnesiumverbindungen*, Berlin, 1905.

² A. F. de Fourcroy, *Ann. Chim. Phys.*, (1), 2. 278, 1789; H. St. C. Deville, *ib.*, (3), 35. 454, 1852; P. A. Favre, *ib.*, (3), 10. 474, 1844; C. F. Bucholz, in F. A. C. Gren, *Grundriss der Chemie*,

Halle, 1. 274, 1809; N. J. B. G. Guibourt, *Journ. Chim. Méd.*, 1. 478, 1825; F. Schaffgotsch, *Pogg. Ann.*, 104. 482, 1858; E. Divers, *Journ. Chem. Soc.*, 15. 196, 1862; G. C. Wittstein, *Repert. Pharm.*, 57. 67, 1837; J. W. Döbereiner, *Schweigger's Journ.*, 13. 320, 1815; R. Weber, *Pharm. Viertelj.*, 8. 161, 1839; R. Engel, *Compt Rend.*, 129. 600, 1899; G. von Knorre, *Zeit. anorg. Chem.*, 34. 283, 1903.

² D. Dolomieu, *Journ. Phys.*, 39. 1, 1791; H. B. Saussure, *Voyages dans les Alpes*, Neuchatel, 1796; R. Kirwan, *Elements of Mineralogy*, London, 1. 111, 1794; P. Woulfe, *Phil. Trans.*, 68. 29, 1779; W. Gibbs, *Pogg. Ann.*, 71. 564, 1847; K. Monheim, *Verh. naturhist. Ver. Rheinlande*, 5. 41, 1849; A. Bukowsky, *Neues Jahrb. Min.*, ii, 338, 1903; C. von John, *Verh. Geol. Reichsanst. Wien*, 68, 1899; A. Baumgarten and J. R. von Holger, *Zeit. Phys.*, 5. 65, 1837; H. von Foullon, *Jahrb. Geol. Reichsanst. Wien*, 38. 14, 1883; W. Bruhns, *Mitt. Geol. Landes. Elsass-Lothringen*, 6. 303, 1908; L. Blum, *Ann. Soc. Géol. Belg.*, 34. 118, 1907.

⁴ C. Doelter, *Jahresb. Geol. Reichsanst. Wien*, 25. 317, 1875; C. von John, *ib.*, 57. 425, 1907; H. W. F. Wackenroder, *Schweigger's Journ.*, 65. 41, 1832; D. John, *ib.*, 5. 13, 1812; M. H. Klaproth, *Beiträge zur chemischen Kenntnis der Mineralkörper*, Berlin, 1. 300, 1795; 2. 397, 1796; A. Grubenmann, *Mitt. Nat. Ges. Frauenfeld*, 8. 1, 1888; A. W. Rothrock and J. B. Shumaker, *Chem. News*, 120. 29, 1920; C. L. Harding, J. B. Shumaker, and A. W. Rothrock, *ib.*, 121. 59, 1920; P. Koller, *Neues Jahrb. Min. B.B.*, 42. 457, 1913; L. R. McKay and W. A. Moore, *Chem. News*, 125. 10, 1922; G. d'Achiardi, *Proc. Soc. Toscana*, 11. 156, 1899; L. Colomba, *Atti Soc. Toscana*, 33. 779, 1898; A. Wankel, *Ber. Nat. Ver. Regensburg*, 10. 101, 1904; F. Ammon, *Beiträge zur Kenntnis der Speckstein- und Pseudophitbildung*, Erlangen, 1902; N. Knight, *Geol. Mag.*, (5), 1. 491, 1904; *Amer. Geol.*, 34. 64, 1904; J. Rumpf, *Tschermak's Mitt.*, 33, 1873; C. Doelter, *ib.*, 178, 1875; F. Heddle, *Min. Mag.*, 2. 9, 106, 1878; V. von Zepharovich, *Zeit. Kryst.*, 3. 100, 1879; L. Buchrucker, *ib.*, 19. 139, 1891; C. Schiffer, *ib.*, 33. 209, 1900; K. Eisenhut, *ib.*, 35. 584, 1902; L. Loczka, *ib.*, 35. 282, 1902; F. J. Wijk, *Oefvers. Finska Vet. Soc. Förh.*, 22. 91, 1880; K. Haushofer, *Sitzber. Bayr. Akad.*, 11. 220, 1881; A. Brun, *Mineralogische Notizen*, Genf, 1881; D. F. Wisser, *Neues Jahrb. Min.*, 580, 1845; A. Saytzeff, *Proc. Geol. Soc. St. Petersburg*, 4, 1887; A. H. Chester, *Amer. Journ. Science*, (3), 33. 294, 1887; H. Hirzel, *Zeit. Pharm.*, 2. 24, 1850; A. Sella, *Rend. Accad. Lincei*, (4), 3. 455, 1887; T. Bentivoglio, *Atti Soc. Nat. Modena*, 26. ii, 84, 1892; F. W. Pfaff, *Neues Jahrb. Min. B.B.*, 9. 499, 1894; A. Vesterberg, *Bull. Geol. Inst. Upsala*, 5. 111, 1900; H. Arsandaux, *Bull. Soc. Min.*, 24. 472, 1901; E. T. Allen, *Bull. U.S. Geol. Sur.*, 220, 1903; L. Dürr, *Mitt. Geol. Elsass-Lothringen*, 6. 183, 1907; K. Hutchinson, *B.A. Rep.*, 701, 1908; G. Suckow, *Journ. prakt. Chem.*, (1), 8. 403, 1836; J. Roth, *ib.*, (1), 58. 82, 1853; S. von Waltershausen, *Pogg. Ann.*, 94. 115, 1854; A. Göbel, *ib.*, 20. 586, 1830; T. Scheerer, *ib.*, 65. 283, 1845; C. F. Karamelsberg, *Handbuch der Mineralchemie*, Leipzig, 213, 1860; *Handwörterbuch der chemischen Theils der Mineralogie*, Berlin, *Suppl.*, 2. 25, 1845.

⁶ E. Boricky, *Jahrb. Geol. Reichsanst. Wien*, 26. 47, 1876; K. A. Redlich, *ib.*, 53. 288, 1903; F. Sandberger, *Untersuchungen über Erzgänge*, Wiesbaden, 159, 1885; *Sitzber. Bayr. Akad.*, 24. 231, 1894; J. Heddle, *Min. Mag.*, 2. 9, 106, 1878; H. Schmeisser, *Jahrb. Geol. Landesanst.*, ii, 126, 1882; C. J. Woodward, *Journ. Geol. Soc.*, 38. 466, 1883; A. Genth, *Amer. Phil. Soc.*, 2, 1885; L. Buchrucker, *Zeit. Kryst.*, 19. 139, 1891; K. Eisenhut, *ib.*, 35. 593, 1902; T. Bentivoglio, *Atti Soc. Nat. Modena*, 26. ii, 84, 1892; G. Spezia, *Atti Accad. Toscana*, 34. 705, 1890; A. F. Rogers, *Univ. Quart. Kansas*, 8. 183, 1890; A. Bukowsky, *Neues Jahrb. Min.*, ii, 338, 1903; O. Fahrenheit, *Zeit. Naturwiss.*, 73. 375, 1900; H. Arsandaux, *Bull. Soc. Min.*, 24. 472, 1901; A. Uhlemann, *Tschermak's Mitt.*, 28. 461, 1909; G. Flinck, *Arkiv. Kem. Min. Geol.*, 3. 154, 1910; O. B. Kühn, *Liebig's Ann.*, 59. 363, 1846; J. Pelletier, *Ann. Chim. Phys.*, (2), 14. 192, 1816; J. Roth, *Journ. prakt. Chem.*, (1), 58. 82, 1853; H. Hirzel, *Zeit. Pharm.*, 2. 24, 1850.

⁶ A. Bukowsky, *Neues Jahrb. Min.*, ii, 338, 1903; C. J. Woodward, *Journ. Geol. Soc.*, 38. 466, 1883; H. B. von Foullon, *Jahrb. Geol. Reichsanst. Wien*, 36. 342, 1886; T. Bentivoglio, *Atti Soc. Nat. Modena*, 26. ii, 84, 1892; W. H. Weed, *Ann. Rep. U.S. Geol. Sur.*, 20. 257, 1890; O. Fahrenheit, *Zeit. Naturwiss.*, 73. 375, 1900; K. Eisenhut, *Zeit. Kryst.*, 35. 593, 1902; C. Etiling, *Liebig's Ann.*, 99. 204, 1856.

⁷ J. C. G. de Marignac, *Arch. Sciences Genève*, 10. 177, 1848; J. Durocher, *Compt. Rend.*, 33. 64, 1851; P. A. Favre, *ib.*, 28. 364, 1849; H. St. C. Deville, *ib.*, 47. 91, 1858; A. von Morlet, *ib.*, 26. 311, 1848; *Pogg. Ann.*, 74. 591, 1848; *Haidinger's Mitt. Naturv.*, 305, 1847; C. W. Gümbel, *Sitzber. Akad. Wiss. München*, 45, 1871; T. S. Hunt, *Chemical and Geological Essays*, Boston, 80, 1875; *Amer. Journ. Science*, (2), 26. 109, 1858; (2), 28. 170, 365, 1859; (2), 42. 49, 1866; C. G. C. Bischof, *Lehrbuch der chemischen und physikalischen Chemie*, Bonn, 3. 89, 1871; F. W. Clarke and W. C. Wheeler, *Proc. Paper U.S. Geol. Sur.*, 90, 1914; J. D. Dana, *Coral and Coral Islands*, London, 1875; J. W. Judd, *The Atoll of Funafofi*, London, 1904; C. J. B. Karsten, *Handbuch der Salinenkunde*, Berlin, 2. 304, 1847; A. Bineau, *Ann. Chim. Phys.*, (3), 51. 301, 1857; G. Bauck, *Analyse der Salzsoolen von Colberg nebst Beiträgen zur analytischen Chemie*, Göttingen, 1860; C. A. Gössmann, *Liebig's Ann.*, 99. 373, 1856; L. Bourgeois and H. Traube, *Bull. Soc. Min.*, 15. 9, 1892; F. Hoppe-Seyler, *Zeit. deut. geol. Ges.*, 27. 509, 1875; H. C. Sorby, *Journ. Geol. Soc.*, 35. 56, 1879; *B.A. Rep.*, 77, 1856; A. Moitessier, *Proc. Acad. Montpellier*, 18, 1863; G. Linck, *Monats. deut. geol. Ges.*, 230, 1909; W. Meigen, *Geol. Rudschau*, 1. 131, 1900; K. Spangenberg, *Zeit. Kryst.*, 52. 529, 1913; J. Girardin, *Ann. Mines*, (3), 11. 460, 1837; L. Lartet, *Bull. Soc. Géol.*, (2), 23. 750, 1866; A. Terrell, *ib.*, (2), 23. 570, 1866; T. Scheerer, *Neues Jahrb. Min.*, 1, 1866; *Beiträge zur Erklärungen der Dolomitbildung*, Dresden, 13, 1865; E. T. Hardman, *Proc. Roy. Irish Acad.*, 2. ii, 705, 1877; E. von Gorup-Besanez, *Liebig's Ann.*

Suppl., 8. 230, 1872; C. Klement, *Bull. Soc. Belg. Géol.*, 8. 219, 1894; 9. 3, 1895; *Tschermak's Mitt.*, 14. 526, 1894; O. Mahler, *Ueber das chemische Verhalten von Dolomit und Kalkspat*, Freiburg, 1906; T. S. Hunt, *Amer. Journ. Science*, (2), 42. 49, 1866; G. Leube, *Neues Jahrb. Min.*, 371, 1840; A. G. Högbom, *ib.*, 1, 262, 1894; H. Grandjean, *ib.*, 543, 1844; W. Haidinger, *ib.*, 862, 1847; H. Leitmeier, *ib.*, 1, 49, 1910; *Neues Jahrb. Min. B.B.*, 40. 655, 1915; R. Blum, *Die Pseudomorphosen des Mineralreichs*, Stuttgart, 1843; B. B. Reed and W. Knight, *Iowa Acad. Science*, 26. 377, 1919; L. M. Parsons, *Geol. Mag.*, 59. 51, 104, 1921; F. W. Pfaff, *ib.*, 9. 485, 1895; 23. 529, 1907; *Centr. Min.*, 659, 1903; F. Tucan, *ib.*, 506, 1909; E. Philippi, *Neues Jahrb. Min. Festband*, 397, 1907; E. Steidtmann, *Journ. Geol.*, 19. 323, 1911; for full discussions on the formation of native dolomite, see F. W. Clarke, *The Data of Geochemistry*, Washington, 1920; F. M. van Tuyl, *Ann. Rep. Iowa Geol. Sur.*, 25. 251, 1916; C. Doelter, *Handbuch der Mineralchemie*, Dresden, 1. 396, 1912; H. H. Thomas, A. F. Hallimond, and E. G. Radley, *Refractory Materials*, London, 79, 1920.

⁸ P. Groth, *Chemische Krystallographie*, Leipzig, 2. 207, 1908; *Tabellarische Uebersicht der Mineralien*, Braunschweig, 45, 1882; H. Baumhauer, *Die Resultate der Aetzmethode in der krystallographischen Forschung*, Leipzig, 1894; G. Tschermak, *Tschermak's Mitt.*, 4. 99, 1881; F. Becke, *ib.*, 10. 93, 1889; 11. 224, 1890; H. Haga and F. M. Jager, *Proc. Acad. Amsterdam*, 17. 430, 1915; F. Rinne, *Ber. Sächs. Ges. Wiss.*, 67. 303, 1915; P. Koller, *Neues Jahrb. Min. B.B.*, 42. 457, 1918; A. Johnsen, *Fortschr. Min.*, 5. 17, 1916.

⁹ F. E. Neumann, *Pogg. Ann.*, 23. 1, 1831; G. Tschermak, *Sitzber. Geol. Reichsanst. Wien*, 8. 760, 1857; F. Madelung and R. Fuchs, *Ann. Physik*, (4), 65. 289, 1921; F. Ott, *Haidinger's Ber.*, 2. 403, 1847; F. Senft, *Zeit. deut. geol. Ges.*, 14. 160, 1862; J. W. Retgers, *Zeit. phys. Chem.*, 6. 227, 1880; V. Goldschmidt, *Ann. Naturhis. Hofmuseums*, 1. 129, 1886; H. Leitmeier, in C. Doelter, *Handbuch der Mineralchemie*, Dresden, 1. 335, 1912; W. Voigt, *Wied. Ann.*, 40. 642, 1890.

¹⁰ H. Kopp, *Liebig's Ann.*, 81. 1, 1852; *Pogg. Ann.*, 86. 156, 1852; *Liebig's Ann. Suppl.*, 3. 289, 1865; *Phil. Trans.*, 155. 71, 1865; H. V. Regnault, *Ann. Chim. Phys.*, (3), 1. 129, 1841; R. Ulrich and E. Wollny, *Forsch. Geb. Agric. Phys.*, 17. 1, 1894; H. Fizeau in A. des Cloiseaux, *Manuel de minéralogie*, Paris, 2. 132, 1874; A. Hauenschild, *Anz. Akad. Wien*, 38, 1870; H. St. C. Deville, *Compt. Rend.*, 61. 975, 1865; F. Findeisen, *Polyt. Notizblatt*, 81, 1860; K. Friedrich and L. G. Smith, *Centr. Min.*, 616, 651, 684, 1912; *Met.*, 9. 409, 1912; H. Leitmeier in C. Doelter, *Handbuch der Mineralchemie*, 1. 360, 1912; J. A. Hedvall and J. Heuberger, *Zeit. anorg. Chem.*, 122. 181, 1922; G. A. Bole and J. B. Shaw, *Journ. Amer. Cer. Soc.*, 5. 817, 1922.

¹¹ K. Eisenhut, *Zeit. Kryst.*, 35. 607, 1902; W. Schmidt, *Ann. Physik*, (4), 9. 919, 1902; W. Voigt, *Gött. Nachr.*, 1, 1901.

¹² A. Cossa, *Ber.*, 2. 697, 1869; C. G. C. Bischof, *Lehrbuch der chemischen und physikalischen Geologie*, Bonn, 3. 78, 1871; E. von Gorup-Besanez, *Liebig's Ann. Suppl.*, 3. 230, 1872; F. Hoppe-Seyler, *Zeit. deut. geol. Ges.*, 27. 509, 1875; J. Roth, *ib.*, 4. 565, 1852; T. Liebe, *ib.*, 7. 433, 1855; P. Forchhammer, *Journ. prakt. Chem.*, (1), 49. 52, 1849; H. Leitmeier, *Neues Jahrb. Min. B.B.*, 40. 655, 1916; T. Scheerer, *Neues Jahrb. Min.*, 11, 1866; C. E. Schafhäütl, *ib.*, 812, 1864; C. Doelter and R. Hoernes, *Jahrb. Geol. Reichsanst. Wien*, 25. 293, 1875; T. S. Hunt, *Amer. Journ. Science*, (2), 28. 181, 371, 1850; W. Pfaff, *Pogg. Ann.*, 32. 487, 1851; D. Dolomieu, *Journ. Phys.*, 39. 1, 1791; A. Vesterberg, *Bull. Geol. Inst. Upsala*, 5. 97, 1900; 6. 253, 1901; H. Reinsch, *Neues Jahrb. Pharm.*, 33. 204, 1870; F. Findeisen, *Polyt. Notizbl.*, 81, 1850; C. J. B. Karsten, *Lehrbuch der Salinenkunde*, Berlin, 2. 280, 1847; K. Haushofer, *Sitzber. Bayr. Akad.*, 11. 220, 1881; A. Wankel, *Ber. Nat. Ver. Regensburg*, 10. 101, 1905; F. W. Pfaff, *Neues Jahrb. Min. B.B.*, 23. 553, 1907; P. Berthier, *Ann. Chim. Phys.*, (2), 38. 249, 1828; E. A. Wülfing, *Jahresb. Ver. Nat. Württemberg*, 56. 1, 1900; A. Damour, *Bull. Soc. Géol.*, (2), 6. 313, 1849; C. J. B. Karsten, *Arch. Min.*, 22. 592, 1848; C. Schmidt, *Bull. Acad. St. Petersburg*, 16. 205, 1871.

¹³ F. von Kobell, *Journ. prakt. Chem.*, (1), 36. 304, 1845; J. F. L. Hausmann, *Handbuch der Mineralogie*, Göttingen, 1404, 1847; C. U. Shepard, *Amer. Journ. Science*, (2), 6. 250, 1848; C. F. Rammelsberg, *Handbuch der Mineralchemie*, Leipzig, 234, 1860; T. S. Hunt, *Amer. Journ. Science*, (2), 42. 49, 1866; R. Hermann, *Journ. prakt. Chem.*, (1), 47. 13, 1849.

¹⁴ J. Lemberg, *Zeit. deut. geol. Ges.*, 23. 226, 1872; 39. 489, 1887; 40. 357, 1888; O. Meyer, *ib.*, 31. 445, 1879; E. Steidtmann, *Bull. Amer. Geol. Soc.*, 28. 431, 1917; F. Cornu, *Centr. Min.*, 550, 1906; E. Hinden, *Verh. Naturforsch. Ges. Basel*, 15. 201, 1903; K. Spagenberg, *Zeit. Kryst.*, 52. 529, 1913; O. Mahler, *Über das chemische Verhalten von Dolomit und Kalkspat*, Freiburg, 1906; G. Bollmann, *Beiträge zur Kenntnis der Magnesiumverbindungen*, Berlin, 1905.

¹⁵ W. F. Foshag, *Proc. U.S. Nat. Museum*, 58. 147, 1920; C. Hochstetter, *Journ. prakt. Chem.*, (1), 27. 378, 1842; R. Hermann, *ib.*, 40. 11, 1847; (1), 46. 257, 1849; C. U. Shepard, *Amer. Journ. Science*, (2), 12. 209, 1851; W. R. Johnson, *ib.*, (2). 12. 361, 1851; W. F. Petter, *Catalogue of the Minerals of Tasmania*, Hobart, 167, 1910; L. K. Ward, *ib.*, 169, 1910; L. Hezner, *Centr. Min.*, 18, 1912; A. Himmelbauer, *Tschermak's Mitt.*, (2), 31. 32, 1912; L. J. Igelström, *Oefvers. Akad. Stockholm*, 22. 608, 1865; H. Sjögren, *Bull. Geol. Inst. Upsala*, 2. 59, 1894; G. Flink, *ib.*, 5. 87, 1900; E. Artini, *Rend. Accad. Lincei*, 18. 3, 1909; A. Pelloux, *Museo Civico di Storia Naturale Genova*, 46. 34, 1913; C. F. Rammelsberg, *Pogg. Ann.*, 97. 296, 1856; R. Mauzelius, *Bull. Geol. Inst. Upsala*, 2. 85, 1894.

§ 19. Magnesium Nitrates

The so-called *nitromagnesite* is said to occur as an efflorescent mass of hexahydrated magnesium nitrate besides the so-called nitrocalcite. A soln. of **magnesium nitrate**, $\text{Mg}(\text{NO}_3)_2$, is obtained by the action of nitric acid on magnesium carbonate, hydroxide, or oxide. As T. Graham¹ showed, when this soln. is evaporated on a water-bath, and cooled to ordinary temp. crystals of **hexahydrated magnesium nitrate**, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, are formed; but if the soln. be cooled below -20° , crystals of **enneahydrated magnesium nitrate**, $\text{Mg}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, appear. R. Funk found the transition point for the ennea- and hexa-hydrates to be -18° . The relation between these hydrates appears from the solubility curves. The following results by R. Funk refer to the **solubility** of the hexahydrated salt in grams per 100 grms. of sat. soln :

	-4.5°	0°	18°	40°	80°	90°	89°	77.5°	67°
$\text{Mg}(\text{NO}_3)_2$	39.50	39.96	42.33	45.87	53.69	57.81	63.14	65.67	66.55

where 90° , according to J. M. Ordway, represents the m.p. of the hexahydrate, and the succeeding numbers give a reversed curve. This means that soln. can be prepared with less water than is contained in the hexahydrate which occurs as the solid phase; and they can be regarded as soln. of the hexahydrate in the anhydrous salt. The numbers for the enneahydrate are likewise

	-7.8°	-20°	c. -29°	-23°	-20°	18°
$\text{Mg}(\text{NO}_3)_2$	15.00	27.4	34.6	35.44	36.19	38.03

where -18° is the transition point for the ennea- and hexa-hydrates, and the first two pairs in the series refer to the ice-line with the eutectic at *circa* -29° , according to F. Rüdorff. According to A. Ditte, if an aq. soln. of magnesium nitrate be heated carefully until a few gas bubbles begin to develop, the remaining colourless liquid is in a state of supersaturation at ordinary temp., and on shaking heat is developed, and crystals of **trihydrated magnesium nitrate**, $\text{Mg}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, are deposited. According to H. Lesœur, the same hydrate is formed from a sat. soln. of the nitrates mixed with an equal vol. of nitric acid; and he found that when the hexahydrate is heated to 65° , the vap. press. suddenly falls from 80 mm. to 25 mm., corresponding with the formation of the trihydrate. A. Ditte also claimed to have prepared short prismatic crystals of **dihydrated magnesium nitrate**, $\text{Mg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, by heating the trihydrate a little above the m.p., but not sufficiently high for the evolution of red vapours; and dissolving the residue in monohydrated nitric acid which dissolves 5 per cent. of the salt at 2° , and 11 per cent. at 80° . The hot sat. soln. furnishes crystals of the dihydrate. A. Chodneff prepared this hydrate as a white hygroscopic powder by allowing the hexahydrate to stand over conc. sulphuric acid. R. Funk was unable to confirm the preparation of the dihydrate. Still further, T. Graham obtained what was regarded as **monohydrated magnesium nitrate**, $\text{Mg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, by heating the hexahydrate to 100° ; and A. Ditte by heating magnesium nitrate until red fumes began to appear, dissolving the residue in as little hot monohydrated nitric acid as possible. Fine crystals of the monohydrate appear when the soln. is cooled.

According to A. Chodneff, the **crystals** of the hexahydrate belong to the triclinic system, but J. C. G. de Marignac found they are really monoclinic prisms, with axial ratios $a : b : c = 0.5191 : 1 : 0.9698$, and $\beta = 92^\circ 56'$. L. Playfair and J. P. Joule gave 1.464 for the **specific gravity** of hexahydrated magnesium nitrate. F. Mylius and R. Funk found that at 18° a sat. soln. of magnesium nitrate contained 43.08 per cent. $\text{Mg}(\text{NO}_3)_2$, and had a sp. gr. 1.394. A. C. Oudemans gave for the sp. gr. of soln. containing

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1	5	10	20	30	40	45	49
Sp gr. at 14°	1.0034	1.0202	1.0418	1.0869	1.1347	1.1909	1.2176	1.2397

Measurements have also been made by H. C. Jones, H. Schiff, by D. Dijken, and by

H. T. Barnes and A. P. Scott. The vol. of a soln. in 100 mols of H_2O at θ° between 0° and 60° was represented by N. S. Tschernay by the equation $v=1+0\cdot0001552\theta+0\cdot000003483\theta^2$. J. Wagner found the **viscosity** of N -, $\frac{1}{2}N$ -, $\frac{1}{4}N$ -, and $\frac{1}{8}N$ -soln. of magnesium nitrate at 25° to be respectively 1.1706, 1.0824, 1.0396, and 1.0198. Measurements were also made by S. Arrhenius, and K. Mützel. A. Strickler and J. H. Mathews studied the electric endosmose of magnesium nitrate.

According to A. Chodneff, the crystals of the hexahydrate lose 28.25 per cent.—nearly two-thirds—of water of crystallization when confined over conc. sulphuric acid; and he stated that the **melting point** of the hexahydrate is 100° ; J. M. Ordway, and W. A. Tilden gave 90° . A. Chodneff found that the hexahydrate loses 34.14 per cent. of water at its m.p. and congeals to a glass-like mass. A. Chodneff found that the percentage loss on calcination:

	110°-115° (6 hrs.)	115°-120° (6 hrs.)	120°-125° (23 hrs.)	140°-150° (28 hrs.)	150°-155° (6 hrs.)	210° (5 hrs.)
Loss	20.87	28.97	31.05	34.72	35.10	35.32

T. Graham was unable to drive off all the water at 400° , and at a dull red heat it loses the remainder of the water, and at the same time gives off nitrogen peroxide and oxygen. D. Gernez found that in air free from carbon dioxide, nitric acid is given off when magnesium nitrate is heated to 150° ; and J. C. G. de Marignac found the crystals to be stable in dry air.

According to A. Ditte, when trihydrated magnesium nitrate is melted and heated to the temp. at which red fumes are evolved, and the product leached with water, **magnesium trioxynitrate**, $3MgO.Mg(NO_3)_2$, remains as white tabular crystals. A. Chodneff heated the hexahydrate with stirring until the mass melted and lost all its water. The product was washed with water, and there remained a white basic nitrate, **magnesium dioxynitrate**, $2MgO.Mg(NO_3)_2$, which is insoluble in alcohol and water, but soluble in acids. There is really nothing to establish the individuality of those, although G. Didier made crystals of **pentahydrated magnesium dioxynitrate** by dissolving 200 grms. of hexahydrated magnesium nitrate in 150 c.c. of water at 100° , and adding 10 grms. of magnesia prepared at a low temp. $-350^\circ-400^\circ$. The temp. is gradually raised to 150° and the filtrate, preserved in a closed vessel, deposits a flocculent precipitate in a few days. The precipitate is isolated by suction and press. keeping it as much as possible out of contact with the carbon dioxide of the atm. The microscopic crystals consist of doubly refracting needles which are rapidly decomposed by cold water or absolute alcohol, with the separation of magnesium hydroxide.

J. C. G. de Marignac found for the **specific heat** of a soln. of a mol of $Mg(NO_3)_2$ in n mols of water, between 21° and 52° ,

n	15	25	50	100	210
Sp. ht.	0.6777	0.7568	0.8517	0.9145	0.9537
Mol. ht.	283.7	453	893	1782	3575

H. C. Jones and co-workers measured the lowering of the **freezing point** of aq. soln. of magnesium nitrate and found for soln. with 1.142, 0.921, and 32.07 grms. of $Mg(NO_3)_2$ per 100 grms. of water, the f.p. were respectively -0.370° , -3.559° , and -22.500° , and the mol. lowering of the f.p. respectively 4.8° , 5.75° , and 10.40° .

According to J. Thomsen, the **heat of formation**, $(Mg, O_2, N_2O_4, 6H_2O)=214.53$ Cals.; and, according to M. Berthelot, $Mg(OH)_2+2HNO_{3aq.}=27.6$ Cals. J. Thomsen gave -4.22 Cals. for the **heat of solution** of a mol of the hexahydrate in 400 mols of water, and S. U. Pickering, -4.547 ; the latter found 0.936 Cal. for the heat of soln. in alcohol. D. Dijken found the following difference in the **refractive indices** of the soln. and water for a mol. of $Mg(NO_3)_2$ in v litres of water between 15° and 16.5° :

v	1	4	13	32	64	128
Diff.	0.012258	0.003086	0.0007890	0.0003982	0.0001991	0.0001020

According to C. Chéneveau, the value of $(\mu_D - 1)D$ in dil. soln., decreases with the

press. of the solute. W. N. Hartley found that the **absorption spectrum** for a soln. with 256.4 grms. per litre, and thickness 4 mm., gave bands λ^{-1} , 3069 to 3772; and for a thickness 2 mm., absorption bands for λ^{-1} , 3069 to 3772; and for a thickness 2 mm., absorption bands for λ^{-1} , 3149 to 3504. J. R. Collins measured the ultra-red absorption spectrum of aq. soln. of the nitrate. F. Kohlrausch and L. Holborn give for the **equivalent conductivity**, λ , of magnesium nitrate, at 25°; H. C. Jones gives for the mol. conductivity, μ , at 0°, the percentage **ionization** α , and the temp. coeff., k , of soln. of a mol. of the salt in v litres of water at 0°:

v
λ (25°)
μ (0°)
α (0°)
k (0°–12.5°)
		8	32	64	128	256	512	1024
		—	104.6	111.0	115.7	119.0	122.9	125.6
		88.91	101.55	110.78	119.01	120.68	123.34	122.89
		72.1	82.4	89.9	96.5	97.9	100.0	99.7
		2.76	3.23	3.58	3.74	3.97	3.99	4.06

C. A. Kraus and J. E. Bishop measured the conductivity of soln. of magnesium nitrate in mixtures of propyl alcohol and water. A. Chassy gave data for the **transport numbers** of the ions.

J. W. Thomas found that **hydrogen chloride** reacts vigorously with heated magnesium nitrate and red fumes of nitrogen peroxide are evolved. T. Graham found the hydrates of magnesium nitrate are all hygroscopic, and readily soluble in **alcohol**, and he found that a hot sat. soln. of anhydrous magnesium nitrate, in alcohol, forms a double compound $\text{Mg}(\text{NO}_3)_2 \cdot 4\frac{1}{2}\text{C}_2\text{H}_5\text{OH}$; and A. Chodneff represented the composition $\text{Mg}(\text{NO}_3)_2 \cdot 3\text{C}_2\text{H}_5\text{OH}$. E. C. Franklin and C. A. Kraus found magnesium nitrate to be soluble in **liquid ammonia**, and the soln. immediately gives a precipitate with ammonium chloride; one is formed more slowly with ammonium bromide, and none at all with ammonium iodide; ammonium sulphide gives a precipitate of $(\text{NH}_4)_2\text{S} \cdot 2\text{MgS} \cdot n\text{NH}_3$; ammonium chromate, and borate also give precipitates with the liquid ammonia soln. of magnesium nitrate. D. N. Jackman and A. Browne studied the ternary systems, $\text{Mg}(\text{NO}_3)_2$ — NaNO_3 — H_2O , and MgSO_4 — $\text{Mg}(\text{NO}_3)_2$ — H_2O , at 25°, and found that no double salts or solid soln. are formed.

REFERENCES.

- ¹ F. Rüdorff, *Pogg. Ann.*, **145**, 617, 1872; R. Funk, *Zeit. anorg. Chem.*, **20**, 395, 1899; *Ber.*, **32**, 96, 1899; J. Thomsen, *ib.*, **11**, 1021, 1878; **12**, 2062, 1879; *Journ. prakt. Chem.*, (2), **17**, 165, 1878; F. Mylius and R. Funk, *Ber.*, **30**, 1718, 1897; *Wiss. Abhand. Phys. Tech. Reichsanst.*, **3**, 437, 1900; J. M. Ordway, *Amer. Journ. Science*, (2), **27**, 16, 1859; A. Chodneff, *Bull. Acad. St. Petersburg*, **8**, 137, 1841; *Liebig's Ann.*, **71**, 241, 1849; P. Einbrodt, *ib.*, **65**, 115, 1848; H. Schiff, *ib.*, **108**, 326, 1858; **110**, 70, 1859; T. Graham, *Phil. Mag.*, (3), **4**, 265, 331, 1828; G. Didier, *Compt. Rend.*, **122**, 935, 1896; D. Gernez, *ib.*, **64**, 606, 1867; C. Chéneveau, *ib.*, **172**, 1408, 1921; A. Ditte, *ib.*, **89**, 576, 641, 1879; *Ann. Chim. Phys.*, (5), **18**, 320, 1879; A. Chassy, *ib.*, (6), **21**, 241, 1890; H. Lescœur, *ib.*, (7), **7**, 419, 1896; J. C. G. de Marignac, *ib.*, (5), **8**, 410, 1876; *Ann. Mines*, (5), **9**, 29, 1856; *Arch. Sciences Genève*, **55**, 113, 1876; J. W. Thomas, *Chem. News*, **37**, 246, 1878; *Journ. Chem. Soc.*, **33**, 367, 1878; W. A. Tilden, *ib.*, **45**, 266, 1884; S. U. Pickering, *ib.*, **53**, 865, 1888; W. N. Hartley, *ib.*, **81**, 556, 1902; M. Berthelot, *Bull. Bur. Longitudes*, **395**, 1877; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **21**, 1, 1899; H. C. Jones and J. N. Pearce, *ib.*, **38**, 683, 1907; H. T. Barnes and A. P. Scott, *Journ. Phys. Chem.*, **2**, 536, 1898; A. C. Oudemans, *Zeit. anal. Chem.*, **7**, 419, 1868; H. C. Jones and F. H. Getman, *Zeit. phys. Chem.*, **49**, 385, 1904; J. Wagner, *ib.*, **5**, 31, 1890; S. Arrhenius, *ib.*, **1**, 285, 1887; D. Dijken, *ib.*, **24**, 81, 1897; N. S. Tschernay, *Journ. Russ. Phys. Chem. Soc.*, **21**, 176, 1889; C. A. Kraus and J. E. Bishop, *Journ. Amer. Chem. Soc.*, **43**, 1568, 1921; A. Strickler and J. H. Mathews, *ib.*, **44**, 1647, 1922; D. N. Jackman and A. Browne, *Journ. Chem. Soc.*, **121**, 694, 1922; K. Mützel, *Wied. Ann.*, **43**, 15, 1891; L. Playfair and J. P. Joule, *Mem. Chem. Soc.*, **2**, 401, 1843; H. C. Jones, *Hydrates in Aqueous Solution*, Washington, 1907; H. C. Jones, *The Electrical Conductivity, Dissociation, and Temperature Coefficients of Conductivity from 0° to 65°*, Washington, 1912; F. Kohlrausch and L. Holborn, *Das Leitvermögen der Electrolyte insbesondere der Lösungen*, Leipzig, 1898; J. R. Collins, *Phys. Rev.*, (2), **20**, 486, 1922.

§ 20. Magnesium Orthophosphates

Analyses of the guano mineral *bobierrite* or *hautefeullite* from Chile by A. Lacroix,¹ and from Bambe by L. Michel, show that it has a composition corresponding closely to that required for normal **hexahydrated magnesium orthophosphate**, $Mg_3(PO_4)_2 \cdot 8H_2O$. According to C. Stein and B. Tollens, it also separates from pathological and from normal urine; small quantities have also been reported in the cereals, in bones, in urinary calculi, and in the intestinal concretions of some animals. T. Graham,² and W. Gregory prepared what has been regarded as hydrated normal magnesium phosphate, $Mg_3(PO_4)_2$, by treating a soln. of magnesium sulphate with normal sodium phosphate; the precipitate dried at 100° contains the eq. of $5H_2O$. C. Stein and B. Tollens used disodium hydrophosphate, and employed as well conc. soln. made slightly alkaline with sodium hydrocarbonate. A crystalline precipitate forms in 12–24 hrs. K. Kraut recommended mixing magnesium sulphate or chloride with a mixed soln. of disodium hydrophosphate, or of disodium hydrophosphate and borax, the flocculent precipitate soon becomes crystalline. L. Schaffner boiled magnesium hydrophosphate repeatedly with water so long as this acquired an acid reaction, and obtained the normal phosphate; and H. Debray heated the same compound with water in a sealed tube at 120° . G. A. Daubrée prepared rhombic plates of magnesium phosphate by heating magnesium oxide in an atm. of phosphorus pentachloride: $8MgO + 2PCl_5 = Mg_3(PO_4)_2 + 5MgCl_2$. A. de Schulten mixed a soln. of 20 grms. of heptahydrated magnesium sulphate in two litres of water and cooled at 10° , with a soln. of 19.4 grms. of dodecahydrated disodium hydrophosphate and 4 grms. of sodium hydrocarbonate in a litre of water, and, after diluting the mixture with a litre of water, allowed it to stand at 20° – 25° for a long time. Crystals of *bobierrite* were slowly formed. He also obtained crystals without using the sodium hydrocarbonate.

Bobierrite occurs in colourless and white needles. A. de Schulten found the artificially prepared **crystals** of the octohydrate, $Mg_3(PO_4)_2 \cdot 8H_2O$, to be monoclinic prisms, with axial ratios $a : b : c = 0.076 : 1 : 0.74$, and β is about 106° . A. Sachs supposed *bobierrite* to be isomorphous with *vivianite* and *symplesite*. A. Lacroix gave 2.41 for the **specific gravity** of *bobierrite*, and A. de Schulten, 2.195 at 15° , for the artificial product. The latter also found that the synthesized octohydrate did not lose its water of crystallization at 100° , while the hydrated precipitate lost about 82 per cent. of its water at 100° , and still more with a prolonged heating. According to K. Kraut, if precipitated magnesium phosphate be dried over conc. sulphuric acid, the product contains 43.8 per cent. of water; if at 100° , 10.86 per cent.; and if calcined at a red heat 4.77 per cent. of water. L. Schaffner found a very small loss at 100° , a loss of 23 per cent. at 180° , and a further loss of 9.10 per cent. at a red heat, and his analysis of the original phosphate corresponded with $Mg_3(PO_4)_2 \cdot 7H_2O$; C. Stein and B. Tollens' and H. Debray's analyses of the crystals corresponded with $Mg_3(PO_4)_2 \cdot 5H_2O$; C. Stein and B. Tollens, and K. Kraut's analyses of the air-dried precipitate, with $Mg_3(PO_4)_2 \cdot 22H_2O$; and A. de Schulten's analysis of artificial *bobierrite*, with $Mg_3(PO_4)_2 \cdot 8H_2O$. Both T. Graham, and W. Gregory found that the phosphate has a **melting point** near a white heat, and the resulting clear glass is easily soluble in acids. According to M. Berthelot, the **heat of formation** of colloidal normal magnesium phosphate from its elements is 910–6 Cals.; and from magnesium sulphate and normal sodium phosphate is compounded of two factors—the initial formation of an amorphous precipitate, 4.86 Cals., followed by its transformation into crystals which in 5–6 mins. liberate 8.12 Cals. With magnesium chloride, the numbers are respectively –4.44 Cals. and 12.18 Cals. The **heat of neutralization** is $Mg(OH)_2 + H_3PO_4 \text{ aq.} = Mg_3(PO_4)_2 \text{ aq.} + 57.80$ Cals. for the amorphous, and 83.00 Cals. for the crystalline precipitate. *Bobierrite* has a positive **double refraction**.

According to F. K. Cameron and J. M. Bell, the behaviour of the magnesium phosphates in contact with **water** is quite similar to that of the calcium phosphates.

A. Lacroix found bobierite to be insoluble in water, while J. A. Völcker stated that a litre of water dissolves in 7 days 0.205 grm. of the freshly precipitated normal phosphate, and 0.100 grm. of the calcined. J. von Liebig found a litre of water containing 2 grms. of **sodium chloride** dissolves 75.8 mgrms. of the precipitated phosphate; and a litre of water with 3 grms. of sodium nitrate dissolves 61.9 mgrms. According to A. Lacroix, bobierite is soluble in **nitric acid**, and, according to L. Schaffner, normal magnesium phosphate is easily soluble in **acetic acid**. According to B. W. Gerland, when normal magnesium phosphate is suspended in water, it rapidly absorbs **sulphur dioxide**, and forms an oily liquid; if an excess of the phosphate is present it does not alter its composition. A soln. containing a mol of $Mg_3(PO_4)_2$ and 4.3 mols of sulphur dioxide furnishes crystals of trihydrated magnesium hydrophosphate when allowed to stand in vacuo, and a similar product, but less hydrated, is gradually deposited in needle-like crystals on adding sodium carbonate; or on boiling the soln. According to L. Grandeau, a double alkali magnesium phosphate is produced when the phosphate is fused with an **alkali sulphate**, but no magnesium oxide is formed. E. Erlenmeyer has shown that an acid **ammonium citrate** soln. dissolves normal magnesium phosphate quite readily, but not so readily in a neutral citrate soln. A. Chizynsky studied the distribution of phosphoric acid between magnesium and **calcium salts**.

According to L. B. G. de Morveau, magnesium oxide forms a white vitrifiable substance when ignited with two parts of sodium ammonium phosphate. J. J. Berzelius also noted the solubility of magnesia in fused sodium ammonium phosphate before the blowpipe. H. Rose also made a **sodium magnesium phosphate**, $NaMgPO_4$, by fusing equimolar parts of magnesium pyrophosphate with sodium carbonate; the analysis corresponded with $3MgO \cdot 3Na_2O \cdot 2P_2O_5$. L. Ouvrard obtained a substance with the same composition by fusing normal sodium phosphate with magnesium oxide, and extracting the slowly cooled mass with water. The dendritic crystals have a sp. gr. 2.5 at 20°, and they are doubly refracting. H. Rose made anhydrous **potassium magnesium phosphate**, $KMgPO_4$, by calcining a mixture of magnesium pyrophosphate and potassium carbonate. R. Weber's analyses of a similar product were found by H. Rose to be too low in alkali for $KMgPO_4$, but H. Rose pointed out that R. Weber washed the material with ammoniacal water which by hydrolytic decomposition removed the alkali and left magnesium hydrophosphate behind. L. Grandeau obtained the same compound by heating for many hours at 800° an intimate mixture of magnesium pyrophosphate with 25 times its weight of potassium sulphate, and extracting the cold mass with hot water. A white powder consisting of needle-like crystals remained. According to L. Ouvrard, potassium pyrophosphate or orthophosphate yields rhombic prisms of the salt $P_2O_5, 2MgO, K_2O$, previously described by L. Grandeau. Magnesium phosphate yields the same products as the oxide, but the chloride yields a chlorophosphate unless the alkaline phosphate is present in considerable excess. L. Ouvrard's potassium magnesium phosphate had a sp. gr. 2.6 at 20°, and was easily soluble in acids. H. Erdmann and P. Köthner prepared **hexahydrated rubidium magnesium phosphate**, $RbMgPO_4 \cdot 6H_2O$, by mixing soln. of magnesium sulphate and of rubidium phosphate. The crystalline precipitate is not decomposed by boiling water, and it is soluble in cold dil. hydrochloric acid.

M. Berthelot, and A. Quartaroli studied the equilibrium conditions between phosphoric acid, magnesium oxide, and the alkali hydroxides. The latter found that the behaviour of the magnesium oxide is different from that of barium or calcium oxides. Thus, on adding one eq. of magnesia and two eq. of sodium hydroxide to one mol of phosphoric acid, only magnesium oxide is precipitated, whilst if the sodium hydroxide is replaced by potassium hydroxide, a portion of the latter passes into the insoluble state. On adding one eq. of sodium or potassium hydroxide to monomagnesium phosphate, the amount of phosphoric acid precipitated is much less than in the other cases and only amounts to about one-sixth of the total quantity; seeing that dimagnesium phosphate, like the dicalcium salt,

is only very slightly soluble and that the alkali hydroxide present is sufficient to precipitate it, it is probable that soluble double phosphates are formed. M. Schröcker and M. Violet prepared **enneahydrated sodium magnesium phosphate**, $\text{NaMgPO}_4 \cdot 9\text{H}_2\text{O}$, by heating a soln. of equimolar parts of phosphoric acid and sodium carbonate until carbon dioxide is expelled, and to the cold soln., adding magnesia, which has been heated to the lowest possible temp., until the liquid has a neutral reaction. After the mixture has stood some days, microscopic prisms are formed which are freed from the mother liquid by press. The crystals belong to the triclinic system, and, according to K. Haushofer, they have the axial ratios $a : b : c = 1.2588 : 1 : 1.4380$, and $\alpha = 89^\circ 42'$, $\beta = 93^\circ 13'$, $\gamma = 89^\circ 31'$. M. Schröcker and M. Violet prepared **hexahydrated potassium magnesium phosphate**, $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$, in a similar manner; K. Haushofer found the crystals belong to the rhombic system and have the axial ratios $a : b : c = 0.5584 : 1 : 0.9001$. The crystals lose five-sixths of their water at 100° , and they are decomposed by water. A. Metz obtained crystals of this double salt by adding potassium carbonate to beer.

K. Haushofer prepared an acid double phosphate which he regarded as decapentahydrated *potassium dimagnesium hydrodiphosphate*, but did not describe the method; he said that the crystals were triclinic plates with axial ratios and angles $a : b : c = 0.9418 : 1 : 0.5003$, and $\alpha = 90^\circ 7'$, $\beta = 92^\circ 4'$, and $\gamma = 95^\circ 48'$. L. Chevron and A. Droihe prepared crystals of what they regarded as acid phosphates: $\text{K}_2\text{O} \cdot 4\text{MgO} \cdot 2\text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$, and $\text{K}_2\text{HMg}_2(\text{PO}_4)_2 \cdot 4\frac{1}{2}\text{H}_2\text{O}$, from mixtures of soln. of potassium dihydrophosphate, potassium hydrocarbonate, and magnesium sulphate of different conc.; but there is no evidence of the chemical individuality of the products.

Crystals of **hexahydrated ammonium magnesium phosphate**, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$, were found by G. L. Ulex³ in some old soil, under quantities of cattle dung, in the neighbourhood of Hamburg, and the mineral was called *struvite*, after a Russian statesman; and E. F. Teschemacher called it *guanite*. F. de la Provostaye found the mineral in guano from Patagonia, and it has been reported in guano from other localities. E. P. Pittman, R. W. E. MacIvor and G. vom Rath reported it in the bat guano from the Skipton Caves (Victoria); H. Ludwig found it in intestinal concretions; and it is deposited from decomposing urine. O. B. Böggild found crystals of struvite in extracts from fossil plants; peat extracts, etc.

A. F. de Fourcroy first made the salt by treating magnesium phosphate with ammonium hydrophosphate; J. J. Berzelius mixed a neutral magnesium salt with ammonium hydrophosphate. In both these cases, G. F. Wach found the soln. becomes acidic. L. Blum also preferred sodium phosphate as precipitating agent because the precipitate settles more quickly; while C. Mohr, and W. Gibbs preferred sodium ammonium phosphate because it precipitates more rapidly and completely. A. Riffault mixed a magnesium salt first with ammonium carbonate, and then with disodium hydrophosphate. According to C. A. Lesueur, magnesium hydroxide or carbonate is transformed into ammonium magnesium phosphate when it is allowed to stand in contact with a soln. of ammonium hydrophosphate; and likewise also when magnesium hydrophosphate is treated with aq. ammonia, ammonium sulphide, or ammonium carbonate; C. Stein, and B. Tollens observed a similar result with normal magnesium phosphate. J. W. C. Davis also prepared this salt. A. de Schulten obtained good crystals of the double salt by mixing a soln. of 28 grms. of diammonium hydrophosphate, 10 grms. of ammonium sulphate, and 12 grms. of phosphoric acid in 80 c.c. of water with a soln. of 16 grms. of heptahydrated magnesium sulphate in 20 c.c. of water. Comparatively large crystals were produced by H. Vohl, O. Richter, and E. Monier by slowly mixing the soln. separated by a permeable diaphragm. A. Millot and L. Maquenne obtained large crystals in acid or neutral soln. in the presence of ammonium citrate; and K. Haushofer from a soln. of the double phosphate in ammonium citrate. R. H. Solly, and A. Arzruni have reported the formation of crystals of struvite in certain culture media for bacteria, and in peptone soln.

M. Berthelot has studied the equilibrium between soln. of magnesium chloride,

and of ammonium phosphate. Hexahydrated magnesium ammonium phosphate is precipitated whenever a neutral magnesium salt is brought in contact with a soln. containing ammonia and phosphoric acid. According to J. J. Berzelius, the salt is slowly precipitated, and the precipitation is never complete unless an excess of phosphate is present in the soln. W. H. Wollaston noticed that the precipitate is deposited on the sides of the glass containing vessel, especially where the stirring rod has scratched it. This salt is usually the form in which magnesium is precipitated in analytical work, and reciprocally also, it is often the form in which phosphoric acid is precipitated. According to H. Neubauer, the precipitation is practically complete even in the presence of comparatively large quantities of ammonium salts, but the composition of the precipitate is largely determined by the nature of the soln., e.g. (i) the precipitate contains a lower proportion of magnesium than the normal phosphate in neutral and ammoniacal soln.; (ii) the precipitate has the normal composition if an excess of the magnesium salt is present; and (iii), the precipitate contains more magnesium than the normal phosphate in the presence of an excess of both magnesium salt and ammonia. R. Reidenbach believes the third observation is not correct, and that the precipitate contains less, not more, magnesium than the normal phosphate.

A. Gawalowsky obtained large crystals with the composition $(\text{NH}_4)_2\text{O} \cdot \frac{1}{2}\text{MgO} \cdot 2\text{P}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$, by crystallization from a soln. of the normal phosphate in acetic acid. The analyses of C. Lindbergson led J. J. Berzelius to assume that another ammonium magnesium phosphate exists containing less magnesium than $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$; and J. Tünnermann supposed the existence of even six varieties of this salt, but T. Graham and G. F. Wach showed that there is only one double magnesium ammonium phosphate. F. A. Gooch and M. Austin have confirmed the existence of a compound $(\text{NH}_4)_2\text{H}_2\text{Mg}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, whose production is favoured by the presence of an excess of a soluble phosphate or of ammonium salts in the soln. R. W. E. MacIvor reported three minerals in the bat guano of the Skipton Caves (Victoria)—*hannayite*, $\text{Mg}_2\text{H}_2(\text{PO}_4)_2 \cdot \text{MgH}_2(\text{NH}_4)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, in triclinic crystals with $a : b : c = 0.6990 : 1 : 0.9743$; *schertelite*, $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, in small ill-defined crystals; and *ditmarite*, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 2\text{MgH}_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, in rhombic crystals. H. Neubauer and K. Bube also inferred that a compound *magnesium tetrammonium diphosphate*, $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$, i.e. $(\text{NH}_4)_3\text{PO}_4 \cdot \text{Mg}(\text{NH}_4)\text{PO}_4$, is formed in neutral or ammoniacal soln. because, when the precipitate is ignited, some phosphoric acid is volatilized, which is not the case when the normal double salt is ignited under similar conditions. It is assumed that during the ignition of the tetrammonium salt, magnesium metaphosphate is first formed: $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2 \rightarrow \text{Mg}(\text{PO}_3)_2 + 4\text{NH}_3 + 2\text{H}_2\text{O}$; and that on further ignition, the metaphosphate decomposes into pyrophosphate and volatile phosphoric oxide: $2\text{Mg}(\text{PO}_3)_2 \rightarrow \text{Mg}_2\text{P}_2\text{O}_7 + \text{P}_2\text{O}_5$.

Disturbances also arise in the presence of alkali salts, so that it is usual to dissolve the precipitate in dil. nitric acid, and reprecipitate it from a soln. which will give the normal phosphate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. Many other observations have been made on this subject by W. Heintz, F. G. Jörgensen, C. Stünkel, T. Wetzke, and F. Wagner, O. Popp, T. R. Ogilvie, E. W. Parnell, W. Kubel, L. Brünner, etc.

Struvite is sometimes colourless, or it may have a yellowish or brownish tinge. K. Haushofer established the identity of the crystals of struvite and of hexahydrated ammonium magnesium phosphate. According to A. Sadebeck, the pyramidal crystals belong to the rhombic system, and have axial ratios $a : b : c = 0.5667 : 1 : 0.9121$. H. Haga and F. M. Jäger have studied the **X-radiograms** of crystals of struvite. E. F. Teschemacher gave 1.65 for the **specific gravity** of struvite; O. B. Böggild, 1.715; A. de Schulten, 1.711. The **hardness** is about 2 on Mohs' scale. M. Berthelot gave for the **heat of formation** of crystalline ammonium magnesium phosphate MgNH_4PO_4 from its elements as 898.8 Cals. The crystals of struvite have a positive **double refraction**, and, according to O. B. Böggild, the **indices of refraction** are $\mu_\alpha = 1.4954$, $\mu_\beta = 1.4963$, and $\mu_\gamma = 1.5043$. K. Bube measured the **electrical conductivities** of aq. soln. of mono- and hexa-hydrated magnesium ammonium phosphate at different temp. K. Hausmann, and E. Kalkowsky have studied the **pyroelectrical effects** produced by the crystals.

According to C. H. Pfaff, hexahydrated ammonium magnesium phosphate loses ammonia when exposed to air at ordinary temp.; and, according to G. F. Wach,

it loses both water and ammonia when dried for several days in *vacuo* over conc. sulphuric acid. T. Graham reported that when heated to 100°, in a retort, it loses five-sixths of its water of crystallization but no ammonia, while H. Struve maintained, on the contrary, that some ammonia is evolved; L. Chevron and A. Droihe stated that the residue left on drying at 100° is $\frac{2}{3}\text{NH}_3 \cdot 2\text{MgO} \cdot \text{P}_2\text{O}_5 \cdot 2\frac{1}{2}\text{H}_2\text{O}$. P. Griessmayer reported that the hexahydrate loses some ammonia when boiled with water.

K. Bube found the transition temp. for the conversion of the hexahydrate to **monohydrated ammonium magnesium phosphate**, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$, under water is between 48° and 49°; and under its own mother liquid, between 56° and 57°. A. Millot and L. Maquenne boiled equimolar proportions of MgSO_4 and $(\text{NH}_4)_2\text{HPO}_4$, and found that the normal phosphate, $\text{Mg}_3(\text{PO}_4)_2$, is first formed, and that this then takes up ammonia and water, forming plates and cubes of the monohydrate, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$. The crystals are not doubly refracting, they remain unchanged at 100°, and dissolve neither in water nor in a soln. of ammonium citrate.

According to A. F. de Fourcroy and J. J. Berzelius, when hexahydrated ammonium magnesium phosphate is strongly heated, it loses all its ammonia and water and is reduced to a powder which fuses at a higher temp. forming a clear glass of magnesium pyrophosphate; if, when all the water and ammonia have been expelled at a moderate heat, the residue be subsequently exposed to a greater degree of heat, it becomes slightly incandescent in consequence of an intramolecular change—according to O. Popp, owing to the passage of the pyrophosphate from a crystalline to an amorphous condition—because no change in weight can be detected before and after the material has glowed. H. Struve, and O. Popp found that the incandescence occurs if the magnesium pyrophosphate be contaminated with calcium or other magnesium compounds, and, particularly so, with silica. Analyses confirmatory of the conversion of the double salt into magnesium pyrophosphate: $2\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + 13\text{H}_2\text{O}$, were made by G. F. Wach, A. Riffault, C. Lindbergson, J. J. Bergson, F. Stromeyer, C. H. Pfaff, etc. The hexahydrated magnesium ammonium phosphate precipitated in analysis is weighed as magnesium pyrophosphate.

J. J. Berzelius said that hexahydrated ammonium magnesium phosphate is slightly soluble in water, and C. R. Fresenius found that a litre of water at 10° dissolves 0.065 grm. of ammonium magnesium phosphate. E. Ebermayer gave 0.074 grm. per litre at 20.5°–22.5°; J. von Liebig gave 0.107 grm.; and J. A. Völcker, 0.106 grm. P. Wenger gave for the solubility of NH_4MgPO_4 in grams per litre at different temp.:

	0°	20°	40°	50°	60°	70°	80°
NH_4MgPO_4	0.023	0.052	0.036	0.030	0.040	0.016	0.019

The irregularity in the results shows that equilibrium was not attained. The results are also probably complicated by hydrolysis, and by the transition from the hexa- to the mono-hydrate. K. Bube also measured the solubility of the mono- and hexa-hydrates in water. The double salt is much less soluble in water containing ammonia, thus, C. R. Fresenius found a litre of an aq. soln. of ammonia dissolves 0.0226 grm. of the double salt; while, according to F. G. Jörgensen, the solubility of the double salt in 2½ per cent. aq. ammonia is approximately eq. to 0.0006 grm. MgO per litre; and, according to C. Stünkel, T. Wetzke, and F. Wagner aq. soln. of 1, 2, and 3 per cent. ammonia dissolve respectively the eq. of 0.00050, 0.00023, and 0.00008 grm. of MgO . E. Ebermayer found that between 20.5° and 22.5°, a litre of aq. ammonia dissolves:

Per cent. NH_3	0	1.98	2.48	4.95	6.64	7.43	9.91
Grm. $(\text{NH}_4)\text{MgPO}_4$	0.0741	0.0322	0.0272	0.0232	0.0221	0.0191	0.0164

The solubility increases with rise of temp. Expressing the results in grams of NH_4MgPO_4 per 1000 grms. of a mixture of one part aq. ammonia (sp. gr. 0.96) and 4 parts of water, P. Wenger found:

	0°	20°	40°	50°	60°	70°	80°
$(\text{NH}_4)\text{MgPO}_4$	0.087	0.098	0.136	0.153	0.174	0.178	0.145

The decrease in the solubility at the higher temp. may be connected with the transition from the hexa- to the mono-hydrate. C. R. Fresenius found the double salt is more soluble in the presence of 20 per cent. *ammonium chloride*, for a litre of the soln. dissolved 0.132 grm. of the double salt. F. G. Jörgensen also noted that the solubility of the double salt is increased in the presence of ammonium chloride, so that a litre of $2\frac{1}{2}$ per cent. ammonia with a gram of ammonium chloride dissolves the eq. of 0.013 grm. of MgO. P. Wenger gives for the solubility of the double salt in a 5 per cent. soln. of ammonium chloride, in grams of NH_4MgPO_4 per 1000 grms. of solvent:

	0°	20°	30°	40°	50°	60°	70°	80°
NH_4MgPO_4 . . .	0.60	1.05	1.13	0.71	0.93	1.73	1.24	1.91

Here again there is every indication that equilibrium was not attained. When the ammonium chloride soln. of the double salt is boiled, K. Kraut found that ammonia is evolved. According to C. R. Fresenius, a litre of a soln. of ammonium chloride and ammonia dissolved 0.064 grm. of the double salt; P. Wenger from 100 grms. of a 5 per cent. soln. of ammonium chloride with 4 of ammonia per 100 dissolved 0.165 and 0.274 grm. per litre at 20° and 60°. P. Wenger's values for the solubilities of the double salt in a 5 per cent. soln. of *ammonium nitrate* resemble those with ammonium chloride:

	0°	20°	30°	40°	50°	60°	70°	80°
NH_4MgPO_4 . . .	1.10	0.46	0.54	0.64	0.72	0.85	0.83	1.01

J. von Liebig found that an aq. soln. of *ammonium sulphate* containing 2.2, 3.0, and 10 grms. $(\text{NH}_4)_2\text{SO}_4$ per litre, dissolved respectively 0.0717, 0.1130, and 0.147 grm. of the double salt. A. Bolis found that 2 grms. of hexahydrated ammonium magnesium phosphate in contact with 100 c.c. of a soln. of *ammonium citrate* (400 grms. citric acid per litre) loses, by soln., 0.457 per cent. in weight at ordinary temp., and 0.587 per cent. at 50°. A. Millot found a boiling soln. of ammonium citrate dissolves the double salt, which re-crystallizes out on cooling. J. Ville noted that a soln. of ammonium citrate dissolves only traces of the double salt, while soln. of *calcium citrate* dissolve larger amounts. J. von Liebig found that water containing 2 grms. of *sodium chloride* per litre dissolves 0.1234 grm. of the double salt per litre, and an aq. soln. containing 3 grms. of *sodium nitrate* per litre dissolves 0.0931 grm. of the double salt. When the double salt is precipitated in the presence of alkali salts, the latter are occluded or adsorbed and the resulting increase in weight more than counterbalances the solubility losses.

Hexahydrated ammonium magnesium phosphate is readily soluble in **acetic acid** and in other dil. acids, and, as C. H. Pfaff showed, the dissolution is accompanied by partial decomposition. J. von Liebig found a litre of water sat. with **carbonic acid** dissolves 1.425 grms. of the double salt; B. W. Gerland studied the solubility of the double salt in **sulphurous acid**. According to A. Marcet, a soln. of the double salt in **hydrochloric acid**, when evaporated to dryness and heated, furnishes a sublimate of ammonium chloride. When digested with **glycerol**, especially at an elevated temp., the ammonium double salt is converted into magnesium hydrophosphate. According to M. Märcker, and P. Griessmayer, when the double salt is boiled with magnesium oxide, part of the ammonia is expelled; and C. H. Pfaff found that the **fixed alkalis** liberate ammonia from the double salt, although H. Rose found the salt is but incompletely decomposed by **alkali carbonates**. C. H. Pfaff found that when ignited with **carbon**, some phosphorus is evolved. H. Struve, and R. Weber found that when ignited in the presence of **reducing agents**—*e.g.* carbon, hydrogen, unburnt gases from the source of heat, etc.—at a high temp., phosphorus, phosphorus oxide, or hydride are evolved, and, as shown by W. C. Heraeus, W. P. Headden, etc., these vapours attack the platinum crucible.

A rare mineral found in the quartz and clay slate of Höllgraben in Salzburg (Austria), and having a superficial resemblance to topaz,⁴ was shown by J. N. von Fuchs to be a magnesium fluophosphate, and was named *wagnerite*. A. Breithaupt

called it *pleuroclase*. Analyses by J. N. von Fuchs, and C. F. Rammelsberg are in agreement with the formula, $Mg_3(PO_4)_2 \cdot MgF_2$. P. Groth regards it as a salt of orthophosphoric acid, $Mg(MgF)PO_4$; and G. Tschermak as a salt of HMg_2PO_4 , namely, $Mg_2F \cdot PO_4$, in which the hydrogen can be replaced by fluorine :



Monoclinic crystals, with a composition approximating to wagnerite, were found by A. Scacchi near Massa di Somma and San Sebastiano (Vesuvius), and regarded as a distinct mineral species which was called *cryphiolite*; but F. Zambonini showed that cryphiolite and wagnerite are really the same. F. von Kobell found a mineral at Kjerulfin, near Bambe (Norway), which he regarded as $2Mg_3(PO_4)_2 \cdot CaF_2$, and named *kjerulfine*, but G. C. Wittstein, M. Bauer, and W. C. Brögger and E. Reusch showed that the optical properties of kjerulfine are identical with those of wagnerite, and this conclusion is in agreement with analyses by F. Pisani, C. F. Rammelsberg, F. Friederici, etc. It is probable that calcium can replace magnesium in wagnerite, forming *calcium-wagnerite*, and these have been synthesized by H. St. C. Deville and H. Caron, etc. H. Winter prepared *strontium-wagnerite* and *barium-wagnerite*. H. St. C. Deville and H. Caron also prepared *chloro-wagnerite* in which the fluorine is replaced by chlorine; and *ferro-wagnerite* and *manganowagnerite*, where ferrous oxide and manganous oxide respectively replace the magnesium oxide of normal wagnerite. A. Ditte has made an analogous series of *bromo-wagnerite*; while H. Debray, and H. Lechartier prepared *arsenico-wagnerite*, and P. Hautefeuille, *vanadium wagnerite*.

In H. St. C. Deville and H. Caron's synthesis of normal wagnerite, 132 parts of ammonium dihydrophosphate and 60 parts of magnesium fluoride were heated with a great excess of magnesium chloride in a carbon crucible at a red heat. The soluble matter was leached with water from the cold mass; by fusing one part of calcium fluoride with ten parts of normal magnesium phosphate and a large excess of calcium chloride, calcium chloro-wagnerite was formed: $(Ca, Mg)_3(PO_4)_2 \cdot (Ca, Mg)(F, Cl)_2$. H. Winter made wagnerite by melting equimolar parts of normal magnesium phosphate and magnesium fluoride.

The colour of wagnerite is yellowish- or reddish-white. The prismatic crystals are holohedral, and belong to the monoclinic system with axial ratios $a : b : c = 1.9145 : 1 : 1.5059$, and $\beta = 71^\circ 53'$. The **specific gravity** is 3.07 to 3.15; J. N. von Fuchs gave 3.13 at 15° ; C. F. Rammelsberg, 3.026 at 15° ; F. Pisani, 3.12; F. von Kobell, 3.15; and H. St. C. Deville and H. Caron, 3.12 for artificial wagnerite. The **hardness** is 5 to $5\frac{1}{2}$. Wagnerite fuses in the blowpipe flame to a grey glass. The **double refraction** is negative; the dispersion feeble; and, according to M. Levy and A. Lacroix, the **indices of refraction** are $\alpha = 1.569$; $\beta = 1.570$; and $\gamma = 1.582$. The mineral is soluble in nitric and hydrochloric acids.

REFERENCES.

¹ A. Lacroix, *Compt. Rend.*, **106**, 631, 1888; L. Michel, *Bull. Soc. Min.*, **16**, 40, 1893; C. Stein and B. Tollens, *Liebig's Ann.*, **187**, 79, 1877.

² G. A. Daubrée, *Ann. Mines*, (4), **19**, 684, 1851; A. de Schulten, *Bull. Soc. Min.*, **26**, 81, 1903; A. Sachs, *Centr. Min.*, **198**, 1906; F. K. Cameron and J. M. Bell, *Journ. Phys. Chem.*, **11**, 363, 1907; A. Chizynsky, *Liebig's Ann. Suppl.*, **4**, 226, 1866; T. Graham, *Phil. Mag.*, (3), **2**, 30, 1827; W. Gregory, *Trans. Roy. Soc. Edin.*, **16**, 47, 1845; C. Stein and B. Tollens, *ib.*, **187**, 79, 1877; L. Schaffner, *ib.*, **50**, 145, 1844; J. von Liebig, *Liebig's Ann.*, **106**, 185, 1858; H. Erdmann and P. Köthner, *ib.*, **294**, 71, 1896; E. Erlenmeyer, *Ber.*, **14**, 1253, 1881; M. Berthelot, *Compt. Rend.*, **103**, 911, 1886; L. Grandeau, *ib.*, **95**, 921, 1882; **100**, 1134, 1885; A. Lacroix, *ib.*, **106**, 631, 1888; H. Debray, *Ann. Chim. Phys.*, (3), **61**, 430, 1860; M. Berthelot, *ib.*, (6), **11**, 353, 1887; B. W. Gerland, *Journ. prakt. Chem.*, (2), **4**, 126, 1871; A. Pavesi and E. Rotondi, *Ber.*, **15**, 1441, 1882; J. A. Völcker, *B. A. Rep.*, **169**, 1862; H. Rose, *Pogg. Ann.*, **77**, 296, 1849; R. Weber, *ib.*, **73**, 137, 1847; L. Ouyard, *Compt. Rend.*, **106**, 1729, 1888; *Ann.*

Chim. Phys., (6), 16. 311, 1889; L. Grandeau, *ib.*, (6), 8. 202, 1886; M. Berthelot, *ib.*, (7), 25. 187, 1902; *Compt. Rend.*, 133. 5, 1901; M. Schröcker and M. Violet, *Liebig's Ann.*, 140. 232, 1866; A. Quartaroli, *Gazz. Chim. Ital.*, 35. ii, 290, 1905; K. Haushofer, *Zeit. Kryst.*, 7. 259, 1883; L. Chevron and A. Droiexhe, *Bull. Acad. Belg.*, (3), 16. 477, 1888; A. Metz, *Bayr. Bierbrauer*, 7. 49, 1872; K. Kraut, *Liebig's Ann.*, 182. 165, 1876; L. B. G. de Morveau, *Ann. Chim. Phys.*, (1), 30. 1, 1799; J. J. Berzelius, *Om Blåsörtes Användande i Kemien och Mineralogen*, Stockholm, 1820.

³ G. L. Ulex, *Liebig's Ann.*, 66. 41, 1848; *Neues Jahrb. Min.*, 53, 1851; E. P. Pittman, *Contributions to the Mineralogy of Victoria*, Melbourne, 56, 1870; G. vom Rath, *Sitzber. Niederrhein. Ges. Bonn.*, 1, 1878; *Bull. Soc. Min.*, 2. 81, 1879; R. W. E. MacIvor, *Chem. News*, 55. 215, 1887; 85. 181, 1902; E. F. Teschemacher, *Phil. Mag.*, (3), 28. 546, 1846; F. de la Provostaye, *Compt. Rend.*, 53. 442, 1861; C. A. Lesueur, *ib.*, 59. 191, 1864; E. Monier, *ib.*, 78. 300, 1874; H. Ludwig, *Arch. Pharm.*, (1), 143. 136, 1858; G. F. Wach, *Schweigger's Journ.*, 59. 297, 1830; C. H. Pfaff, *ib.*, 35. 428, 1822; C. Lindbergson, *ib.*, 30. 437, 1830; A. F. de Fourcroy, *Système des connaissances chimiques, et de leurs applications aux phénomènes de la nature et de l'art*, Paris, 3. 268, 1801; *Ann. Chim. Phys.*, (1), 2. 278, 1789; M. Berthelot, *ib.*, (7), 25. 200, 1902; A. Riffault, *ib.*, (2), 19. 90, 1821; T. Graham, *Phil. Mag.*, (3), 2. 20, 1827; J. J. Berzelius, *Pogg. Ann.*, 4. 275, 1825; F. Stromeyer, *ib.*, 11. 170, 1827; C. Stein and B. Tollens, *Liebig's Ann.*, 187. 79, 1877; H. Vohl, *ib.*, 88. 114, 1853; C. R. Fresenius, *ib.*, 55. 109, 1845; A. Pavesi and E. Rotondi, *Ber.*, 15. 1441, 1882; A. Millot and L. Maquenne, *Bull. Soc. Chim.*, (2), 23. 238, 1875; A. Millot, *ib.*, (2), 18. 20, 1872; A. de Schulten, *Bull. Soc. Min.*, 26. 95, 1905; H. Neubauer, *Ueber die Zuverlässigkeit der Phosphorsäurebestimmung als Magnesiumpyrophosphat*, Rostock, 1893; *Journ. Amer. Chem. Soc.*, 16. 289, 1894; R. Reidenbach, *Ueber die quantitative Bestimmung des Magnesiums als Magnesiumpyrophosphat*, Kusel, 1910; W. Heintz, *Zeit. Chem.*, (2), 6. 479, 1870; O. Popp, *ib.*, (2), 6. 395, 1870; F. G. Jørgensen, *Mém. Acad. Roy. Soc. Danemark*, (7), 2. 141, 1905; T. R. Ogilvie, *Chem. News*, 31. 274, 1875; 32. 5, 12, 70, 1875; E. W. Parnell, *ib.*, 23. 145, 1871; 32. 222, 1875; C. Stünkel, T. Wetzke, and F. Wagner, *Zeit. anal. Chem.*, 21. 353, 1882; H. Struve, *ib.*, 36. 289, 1897; 37. 485, 1898; O. Popp, *ib.*, 13. 305, 1874; P. Griessmayer, *ib.*, 11. 45, 1872; M. Märcker, *ib.*, 10. 277, 1871; W. Kubel, *ib.*, 8. 125, 1869; E. Kiesel, *ib.*, 8. 164, 1869; L. Brünner, *ib.*, 11. 30, 1872; L. Blum, *ib.*, 28. 452, 1889; C. Mohr, *ib.*, 12. 36, 1873; K. Bube, *ib.*, 49. 525, 1910; *Ueber Magnesiumammoniumphosphat*, Wiesbaden, 1910; W. H. Wollaston, *Phil. Trans.*, 103. 51, 1813; A. Gawalowsky, *Chem. Centrbl.*, (1), 16. 721, 1885; K. Haushofer, *Zeit. Kryst.*, 4. 43, 1880; A. Arzruni, *ib.*, 13. 60, 1891; E. Kalkowsky, *ib.*, 11. 2, 1886; R. H. Solly, *Min. Mag.*, 8. 279, 1889; H. Haga and F. M. Jäger, *Versl. Akad. Amsterdam*, 24. 400, 443, 1135, 1403, 1410, 1916; A. Sadebeck, *Jahresb. Geol. Reichsanst. Wien*, 27. 113, 1877; O. B. Böggild, *Medd. geol. Ferening*, 13. 25, 1907; O. Richter, *Tschermak's Mitt.*, 20. 89, 1901; K. Hausmann, *Gött. Nachr.*, 121, 1846; W. Gibbs, *Chem. News*, 28. 51, 1873; *Amer. Journ. Science*, (3), 5. 114, 1873; F. A. Gooch and M. Austin, *ib.*, (4), 7. 3, 1899; J. Tündermann, *Neues Journ. Pharm.*, 26. 1, 6, 1833; E. Ebermayer, *Journ. prakt. Chem.*, (1), 60. 41, 1853; B. W. Gerland, *ib.*, (2), 4. 127, 1871; J. A. Völeker, *B.A. Rep.*, 169, 1862; J. Ville, *Compt. Rend.*, 75. 344, 1872; *Bull. Soc. Chim.*, (2), 18. 317, 1872; A. Bolis, *Chem. Ztg.*, 27. 1151, 1904; M. Berthelot, *Ann. Chim. Phys.*, (6), 11. 364, 1887; K. Kraut, *Arch. Pharm.*, (2), 111. 101, 1862; W. P. Headen, *Proc. Colorado Scient. Soc.*, 8. 45, 1905; W. C. Heraeus, *Zeit. angew. Chem.*, 15. 917, 1902; *Chem. News*, 97. 108, 1903; J. W. C. Davis, *ib.*, 25. 249, 258, 1872; A. Marcet, *Phil. Trans.*, 112. 448, 1822; P. Wenger, *Étude sur la solubilité des phosphates et arsénates ammoniaco-magnésiens et du phosphate ammoniaco-magnésien*, Genève, 1911; W. Weber, *Pogg. Ann.*, 73. 137, 1847; 84. 310, 1851; H. Rose, *ib.*, 77. 296, 1849; J. von Liebig, *Liebig's Ann.*, 106. 185, 1858; L. Chevron and A. Droiexhe, *Bull. Acad. Belg.*, (3), 16. 477, 1888.

⁴ C. E. von Moll, *Ephemeriden der Berg- und Hüttenkunde*, München, 1. 209, 1805; K. C. Leonhard, *Taschenbuch für die gesammte Mineralogie*, Frankfurt, 5. 233, 1811; A. Breithaupt, *Vollständige Charakteristik der Mineral-Systeme*, Dresden, 50, 193, 1823; J. N. von Fuchs, *Schweigger's Journ.*, 33. 269, 1821; F. von Kobell, *Journ. prakt. Chem.*, (2), 7. 272, 1873; F. Friederici, *Neues Jahrb. Min.*, ii, 77, 1880; M. Bauer, *ib.*, ii, 75, 1880; *Zeit. deut. geol. Ges.*, 27. 230, 1875; W. C. Brögger and E. Reusch, *ib.*, 27. 675, 1875; C. F. Rammelsberg, *ib.*, 31. 107, 1879; *Handbuch der Mineralchemie*, Suppl., Leipzig, 1. 265, 1886; *Pogg. Ann.*, 64. 251, 405, 1845; *Liebig's Ann.*, 56. 210, 1845; W. C. Brögger, *Zeit. Kryst.*, 3. 474, 1879; F. Pisani, *Bull. Soc. Min.*, 2. 43, 1879; *Compt. Rend.*, 88. 241, 1879; H. Lechartier, *ib.*, 65. 172, 1867; H. Debray, *ib.*, 52. 44, 1861; A. Ditte, *ib.*, 99. 794, 1884; P. Hautefeuille, *ib.*, 77. 986, 1874; A. Scacchi, *Atti Ist. Napoli*, (4), 1. 5, 1883; F. Zambonini, *Mineralogie Vesuviana*, Napoli, 313, 1910; H. Winter, *Versuche zur Bildung von Apatiten und wagneritähnlichen Verbindungen des Magnesiums, Bariums, und Strontiums*, Leipzig, 1913; H. St. C. Deville and H. Caron, *Ann. Chim. Phys.*, (3), 67. 456, 1863; G. C. Wittstein, *Vierteljahr prakt. Pharm.*, 22. 448, 1873; P. Groth, *Chemische Kristallographie*, 2. 817, 823, 1908; G. Tschermak, *Lehrbuch der Mineralogie*, Wien, 647, 1915; A. Michel-Lévy and A. Lacroix, *Les minéraux des roches*, Paris, 1888.

§ 21. Magnesium Hydrophosphates

Anhydrous magnesium hydrophosphate, MgHPO_4 , has not been made, but four hydrates have been reported, $\text{MgHPO}_4 \cdot n\text{H}_2\text{O}$, where n is 1, 3, $4\frac{1}{2}$, or 7. Magnesium hydrophosphate occurs in human fæces; and trihydrated magnesium hydrophosphate occurs as a guano mineral, *newberyite*. A specimen of the latter from the bat guano in the Skipton Caves (Victoria), was reported by G. vom Rath,¹ and R. W. E. MacIvor; while a mineral, which appeared to be a mixture of newberyite and struvite, from Quarz Creek (Dawson City, Yukon), was analyzed by G. C. Hoffmann.

A. de Schulten² obtained microscopic crystals of **monohydrated magnesium hydrophosphate**, $\text{MgHPO}_4 \cdot \text{H}_2\text{O}$, by heating a soln. of magnesium carbonate in an excess of phosphoric acid for some hours in a sealed tube at 225° . A. F. de Fourcroy, A. Riffault, T. Graham, L. Schaffner, and C. G. Reischauer prepared **trihydrated magnesium hydrophosphate**, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, in needle-like crystals, by the mixing of a soln. of, say, 2 parts of magnesium sulphate in 32 parts of water, with 3 parts of decahydrated disodium hydrophosphate in 32 parts of water, and allowing the soln. to stand 24 hrs. at a temp. above 36° . H. Rose stated that if very dil. soln. are employed, the normal phosphate is produced. H. Debray made this compound by neutralizing an aq. soln. of phosphoric acid with magnesium carbonate, the precipitated heptahydrate was filtered off. On boiling the filtrate, small crystals of this salt separated from the soln. H. Struve added that only the trihydrate is produced if the boiling soln. of phosphoric acid is treated with magnesium oxide or carbonate, until the liquid has only a feeble acid reaction. J. Stocklasa made the trihydrate by heating dihydrated magnesium tetrahydrophosphate in the solid state or in alcoholic soln. at 100° . B. W. Gerland also made the trihydrate from a soln. of the normal phosphate in sulphurous acid. A. de Schulten mixed a soln. of 16 grms. of heptahydrated magnesium sulphate in 120 c.c. of water with a soln. of 20 grms. of diammonium hydrophosphate, 10 grms. of ammonium sulphate, and 12 grms. of phosphoric acid in 80 c.c. of water, and in 24 hrs. obtained crystals of struvite, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$, which when left in contact with the mother liquid did not change; but when a more conc. soln. of the magnesium sulphate was employed, a mixture of crystals of struvite and newberyite, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, was formed, and when allowed to stand in contact with the mother liquid, the latter increased at the expense of the former.

According to F. K. Cameron and J. M. Bell, when mixtures of phosphoric acid and magnesium oxide are agitated for two months, the clear soln. contains, per litre, at 25° ,

MgO	. 0.207	2.23	26.09	75.5	122.6	146	160	87.1	70.6
P_2O_5	. 0.486	7.35	93.09	281.8	498	623	700	779.6	835.1
Sp. gr.	—	1.006	1.109	1.285	1.470	1.595	—	1.626	1.654
Solid phases	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$						$\text{Mg}(\text{H}_2\text{PO}_4) \cdot n\text{H}_2\text{O}$		

The graph of the results is shown in Fig. 29 in connection with magnesium dihydrophosphate.

H. Debray claimed to have made crystals of **enneahemihydrated magnesium hydrophosphate**, $\text{MgHPO}_4 \cdot 4\frac{1}{2}\text{H}_2\text{O}$, by allowing magnesium carbonate to stand for some days in contact with phosphoric acid. A. F. de Fourcroy, T. Graham, C. G. Reischauer, A. Riffault, and L. Schaffner prepared **heptahydrated magnesium hydrophosphate**, $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, by the process employed for the trihydrate, but keeping the mixture at a temp. below 36° . T. Bergmann probably also made this salt by evaporating a soln. of magnesium oxide in phosphoric acid, and J. J. Berzelius by evaporating a mixed soln. of magnesium acetate and phosphoric acid. L. Chevron and A. Droixhe prepared the heptahydrate by digesting a soln. of potassium dihydrophosphate with magnesium oxide or hydroxide, and allowing the filtered soln. to stand at ordinary temp. According to J. Percy,

the amorphous precipitate of the heptahydrate becomes crystalline when exposed to the action of carbon dioxide.

The **crystals** of the monohydrate were stated by A. de Schulten to behave in polarized light as if they belonged to the rhombic system, but that they are really monoclinic twinned complexes, and resemble the trihydrated pyrophosphate. The trihydrate forms acicular crystals or rhombic six-sided plates, which, in the natural state, according to A. Schmidt, belong to the rhombic system, and have the axial ratios $a : b : c = 0.9548 : 1 : 0.9360$. The heptahydrate also forms small six-sided columnar or acicular crystals which, according to K. Haushofer, are monoclinic prisms with axial ratios $a : b : c = 0.4451 : 1 : 0.2177$, and $\beta = 94^\circ 18'$. A. de Schulten found that the **specific gravity** of the monohydrate is 2.326 at 15° ; the natural trihydrate, according to A. Schmidt, has a sp. gr. 2.10, and **hardness** 3.

A. de Schulten stated that the monohydrate loses no water when heated to 100° . According to H. Struve, the trihydrate loses water when heated above 100° , while T. Graham found that the trihydrate loses its water of crystallization at 170° , and at a higher temp. it forms the pyrophosphate. T. Graham, and L. Schaffner found that the heptahydrate rapidly effloresces in dry air, and loses three-sevenths of its water of crystallization at 100° , and at a higher temp. the pyrophosphate is formed; according to A. F. de Fourcroy, the salt melts to a transparent glass when heated to a still higher temp. H. Struve found that the heptahydrate, according to the mode of preparation, loses 4 to 4.5 mols of water at 100° . C. G. Reischauer stated that when the heptahydrate, dried over sulphuric acid, is heated in a closed vessel, it passes into the trihydrate, and appears to become moist; but the undried heptahydrate loses 5.5 mols over sulphuric acid, and the product does not absorb quite enough water to produce the trihydrate when it is exposed to moist air. According to M. Berthelot, the **heat of formation** of crystalline MgHPO_4 from its elements is 413.6 Cals., and from magnesium sulphate and disodium hydrogen phosphate is -0.79 Cal. when the amorphous salt is produced, and when this becomes crystalline, 1.80 Cals. are set free, so that the total heat of formation of the crystalline salt is 1.01 Cals. The **heat of neutralization** of phosphoric acid with magnesium hydroxide to form MgHPO_4 is 25.30 or 27.10 Cals. depending on whether the amorphous or crystalline salt is produced. A. Schmidt found newberyite has the **index of refraction** $\mu_\beta = 1.5196$ for Na-light, and the **double refraction** is positive. P. Bary stated that the heptahydrate does not fluoresce either in **X-rays** or in **Becquerel's rays**.

According to H. Struve, 100 parts of water dissolve 0.025 part of the trihydrate; and F. Graham found that after several days' digestion 100 parts of cold water dissolve 0.3106 part of the heptahydrate; the soln. becomes turbid at 49° , and milky at 100° in consequence of the separation of the unchanged salt; a boiling sat. soln. contains 0.2008 part of the salt in 100 parts of water. Any salt which has been deposited from the soln. by raising the temp., is re-deposited on cooling. L. Schaffner found that digestion with boiling water frequently renewed converts the hydrophosphate into the normal salt (*q.v.*), and the soln. contains the dihydrophosphate, $\text{Mg}(\text{H}_2\text{PO}_4)_2$. H. Debray also heated the hydrophosphate with water in a sealed tube at 120° , and obtained the normal salt. A. Riffault, however, said that boiling water decomposes the hydrophosphate into a soluble acid salt and an

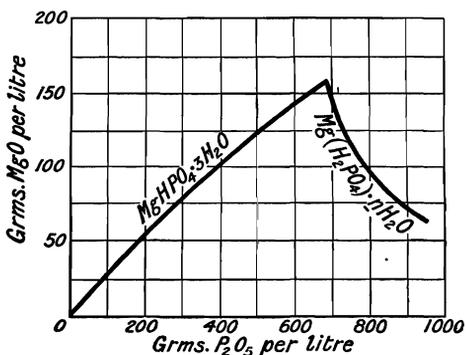


FIG. 29.—Equilibrium between Magnesium Oxide and Phosphoric Acid in Aqueous Solutions at 25° .

insoluble basic salt. According to T. Graham, magnesium hydrophosphate is much more soluble in water containing a trace of one of the acids—phosphoric, sulphuric, hydrochloric, nitric, oxalic, or acetic acid—and the soln. thus obtained does not become turbid when boiled. *Vide supra* for B. W. Gerland's observations on the solubility of magnesium hydrophosphate in **sulphurous acid**. C. A. Lesueur found that precipitated hydrophosphate absorbs **ammonia**, and is transformed into ammonium magnesium phosphate; A. Pavesi and E. Rotondi said that the absorption is incomplete; and H. Iutschak, that the precipitate dried at 100° does not absorb ammonia. According to A. Joannis, when magnesium hydrophosphate is left for three days in contact with liquid ammonia, only an insignificant amount is absorbed.

J. Stoklasa³ prepared **dihydrated magnesium dihydrophosphate**, $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, by digesting on a water-bath magnesium oxide in a conc. soln. of phosphoric acid of sp. gr. 1.4, so that the product contains from 5 to 7 per cent. of free phosphoric acid; the soln. is evaporated until crystallization begins, then cooled, and the crystals washed with ether, pressed between filter-paper, again washed with ether until no more phosphoric acid is removed, and then dried in a stream of air. F. K. Cameron and J. M. Bell treated trihydrated magnesium hydrophosphate with soln. of phosphoric acid of varying conc. The stable solid in contact with the more dil. soln. is $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, but with conc. soln. containing over 700 grms. P_2O_5 per litre, the solid phase is $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$. The observed results are indicated in connection with magnesium hydrophosphate. For soln. in contact with magnesium hypophosphate the proportion of magnesium oxide in soln. increases regularly with increased conc. of phosphoric acid, whilst for those in equilibrium with the latter salt, the conc. of magnesium oxide diminishes with increasing phosphoric acid conc. Some evidence has been obtained that a magnesium phosphate more basic than the diphosphate exists at 25° in contact with very dil. soln. of phosphoric acid.

The radial aggregates of the crystals are not particularly hygroscopic, they absorb about one per cent. of water from the air of a room, and from an atm. sat. with water-vapour, in 24 hrs. 6–7 per cent. of water which is given off again in dry air. When dehydrated at 100°–170°, J. Stoklasa found that anhydrous **magnesium dihydrophosphate**, $\text{Mg}(\text{H}_2\text{PO}_4)_2$, is formed as a white opaque crystalline mass, which remains unchanged in air, and is non-hygroscopic. At 175°, the dihydrophosphate decomposes: $4\text{Mg}(\text{H}_2\text{PO}_4)_2 = 3\text{Mg}(\text{H}_2\text{PO}_4)_2 + \text{MgH}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}$; at 184°, $4\text{Mg}(\text{H}_2\text{PO}_4)_2 = 2\text{Mg}(\text{H}_2\text{PO}_4)_2 + 2\text{MgH}_2\text{P}_2\text{O}_7 + 2\text{H}_2\text{O}$; at 196°, $4\text{Mg}(\text{H}_2\text{PO}_4)_2 = \text{Mg}(\text{H}_2\text{PO}_4)_2 + 3\text{MgH}_2\text{P}_2\text{O}_7 + 3\text{H}_2\text{O}$; and at 205°, $4\text{Mg}(\text{H}_2\text{PO}_4)_2 = 4\text{MgH}_2\text{P}_2\text{O}_7 + 4\text{H}_2\text{O}$ —*vide infra* for the dihydroxyphosphate—100 c.c. of water dissolve 20 grms. of anhydrous dihydrophosphate, without decomposition, and thus the behaviour is different from the corresponding calcium salt; nor does an aq. soln. of magnesium dihydrophosphate decompose at 60°; but with alcohol the salt is decomposed: $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O} = \text{MgHPO}_4 \cdot 3\text{H}_2\text{O} + \text{H}_3\text{PO}_4$; the reaction progresses rapidly at 100°, and with a great excess of alcohol is quantitative.

REFERENCES.

¹ G. vom Rath, *Sitzber. Niederrhein. Ges. Bonn* 1, 1878; *Bull. Soc. Min.*, 2, 81, 1879; R. W. E. MacIvor, *Chem. News*, 55, 215, 1887; 85, 181, 1902; G. C. Hoffmann, *Amer. Journ. Science*, (4), 11, 149, 1901.

² A. de Schulten, *Bull. Soc. Min.*, 26, 95, 1903; *Compt. Rend.*, 100, 877, 1885; P. Bary, *ib.*, 130, 776, 1900; C. A. Lesueur, *ib.*, 59, 191, 1864; A. Joannis, *ib.*, 163, 1202, 1919; M. Berthelot, *ib.*, 103, 911, 1886; *Ann. Chim. Phys.*, (6), 11, 333, 1887; A. F. de Foureroy, *Ann. Chim. Phys.*, (1), 2, 278, 1789; A. Riffault, *ib.*, (2), 29, 24, 1839; H. Debray, *ib.*, (3), 61, 430, 1860; T. Graham, *Phil. Mag.*, (3), 2, 20, 1827; J. Percy, *ib.*, (3), 36, 194, 1850; C. G. Reischauer, *Repert. Pharm.*, 12, 43, 1865; 14, 57, 1865; L. Schaffner, *Liebig's Ann.*, 50, 145, 1844; H. Rose, *Pogg. Ann.*, 76, 24, 1849; J. J. Berzelius, *ib.*, 4, 275, 1825; H. Struve, *Zeit. anal. Chem.*, 36, 290, 1897; J. Stocklasa, *Zeit. anorg. Chem.*, 3, 74, 1893; B. W. Gerland, *Journ. prakt. Chem.*, (2), 4, 127, 1871; K. Haushofer, *Zeit. Kryst.*, 7, 259, 1887; T. Bergmann, *De magnesia*, Upsala, 1775;

L. Chevron and A. Droixhe, *Bull. Acad. Belg.* (3), 16 473, 1888; A. Pavesi and E. Rotondi, *Ber.*, 7. 818, 1874; H. Lutschak, *ib.*, 5. 31, 1872; F. K. Cameron and J. M. Bell, *Journ. Phys. Chem.*, 11. 363, 1907; A. Schmidt, *Zeit. Kryst.*, 7. 26, 1883.

* J. Stoklassa, *Zeit. anorg. Chem.*, 1. 307, 1892; 3. 67, 1893; F. K. Cameron and J. M. Bell, *Journ. Phys. Chem.*, 11. 363, 1907.

§ 22. Magnesium Pyrophosphates

When magnesium hydrophosphate or ammonium magnesium phosphate is heated, normal **magnesium pyrophosphate**, $Mg_2P_2O_7$, remains as a transparent glass. Z. Karaoglanoff and P. Dimitroff¹ found that if the ammonium magnesium phosphate is precipitated slowly while boiling, the conversion to pyrophosphate by ignition is not attended by incandescence; the converse obtains if the salt is precipitated rapidly at a lower temp. Traces of organic matter are also necessary for the incandescent effect. According to H. Rose, an aq. soln. of pyrophosphoric acid gives a precipitate of **trihydrated magnesium pyrophosphate**, $Mg_2P_2O_7 \cdot 3H_2O$ —according to the analyses of the crystalline and amorphous salts by A. Schwarzenberg—when added to a soln. of magnesium sulphate in the presence of ammonium chloride and ammonia; this salt is soluble in much water; while normal sodium pyrophosphate gives a precipitate with magnesium sulphate which is soluble in an excess of both agents; when the mixture is boiled, a precipitate again forms which does not redissolve on cooling. G. F. Wach stated that sodium dihydropyrophosphate gives no precipitate with magnesium sulphate until further addition of ammonium carbonate, and the precipitate which is then formed contains but a trace of ammonia, and is dissolved by an excess of either magnesium sulphate or the sodium dihydropyrophosphate: According to A. Schwarzenberg, when a soln. of magnesium oxide in one of sodium dihydropyrophosphate is heated, gelatinous magnesium pyrophosphate, resembling aluminium hydroxide, separates out; when this is dissolved in sulphurous acid, and boiled, it appears as a crystalline powder.

O. Andersen found that colourless glass-like tabular **crystals** were readily obtained by cooling fused magnesium pyrophosphate; the monoclinic crystals have the axial ratios $a : b : c = 0.7947 : 1 : 1.0880$, and $\beta = 75^\circ 49'$. By twinning, the crystals often approximate to the rhombic form. Z. Karaoglanoff and P. Dimitroff said that if the pyrophosphate is produced with incandescence by the ignition of ammonium magnesium phosphate, it is hard, grey to black, and lava-like; if not produced with incandescence, it is an amorphous powder, loose in texture. F. W. Clarke found the **specific gravity** of the anhydrous, probably amorphous, normal pyrophosphate is 2.559 at 18° , and 2.598 at 22° ; H. G. F. Schröder gave 2.20. O. Andersen showed that the crystals have a sp. gr. 3.058 at $25^\circ/4$. The **hardness** is a little below 4. A. Schwarzenberg noted that both the amorphous and crystalline salt lose all the water of crystallization at 100° . O. Andersen measured the **indices of refraction** for Na-light, and found $\mu_\alpha = 1.615 \pm 0.003$; $\mu_\beta = 1.604 \pm 0.003$; $\mu_\gamma = 1.602 \pm 0.003$; and the maximum positive **double refraction** is $\alpha - \gamma = 0.013 \pm 0.005$. P. Bary stated that the salt does not fluoresce when exposed to the **X-rays**, or to **Becquerel's rays**.

H. Struve found that when heated white hot in a stream of **hydrogen**, magnesium pyrophosphate is reduced developing phosphorus and phosphine. C. R. Fresenius stated that the salt is easily soluble in **hydrochloric acid**; while T. Graham said that it is dissolved with difficulty by that acid. According to R. Weber, and C. R. Fresenius, magnesium pyrophosphate is not completely precipitated as ammonium magnesium phosphate, when the acid soln. is neutralized with ammonia. R. Weber stated that when boiled with **sulphuric acid**, it is converted into the normal salt, while H. Pellet stated that it is transformed into **magnesium pyrosulphosphate**. Magnesium pyrophosphate is readily dissolved in nitric acid, and the soln. behaves towards ammonia like the soln. in hydrochloric acid. According to D. Campbell,

the soln. in **nitric acid** furnishes crystals of magnesium nitrate when evaporated to a syrupy consistence by standing over conc. sulphuric acid; and, according to E. Luck, if the soln. is evaporated to complete dryness, a white gum-like mass remains which has an acid reaction, and which is regarded by D. Campbell, and E. Luck, as a magnesium nitritophosphate, $2\text{MgO} \cdot \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot \text{NO}_2$. H. Rose found that the pyrophosphate is completely converted into the normal phosphate by fusion with **sodium carbonate**.

According to J. Stoklasa, when magnesium dihydrophosphate is heated to 205° , **magnesium dihydroxyphosphate**, $\text{MgH}_2\text{P}_2\text{O}_7$, is formed; and he also found when $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ is heated for 2 hrs. at

	210°	220°	240°	260°	280°	295°	303°
Per cent. loss . . .	22.4	22.42	23.28	23.64	23.66	26.99	28.50

The calculated loss for the formation of $\text{MgH}_2\text{P}_2\text{O}_7$ is 21.26 per cent. and for $\text{Mg}(\text{PO}_3)_2$, 28.35 per cent.

A. Beer, and H. Ludwig prepared **sodium magnesium pyrophosphate** by gradually adding magnesium chloride to a boiling soln. of sodium pyrophosphate. The amorphous precipitate is washed with water containing ammonia. The precipitate is soluble in water, and readily soluble in hydrochloric or nitric acid; J. F. Persoz, and A. Schwarzenberg obtained a similar precipitate which dissolved in an excess of the sodium pyrophosphate furnishing a liquid which soon became turbid and congealed to a gelatinous solid on standing. L. Ouvrard obtained crystals of $\text{Na}_3\text{MgP}_2\text{O}_7$ by slowly cooling a soln. of magnesium oxide, chloride, or phosphate in fused sodium orthophosphate or pyrophosphate, and extracting the mass with water. The dendritic crystals probably belong to the cubic system; their sp. gr. is 2.2 at 20° . K. A. Wallroth obtained transparent prisms with the composition $\text{Mg}_{10}\text{Na}_{16}(\text{P}_2\text{O}_7)_9$ by dissolving the metallic oxide in microcosmic salt heated to a bright red heat; the glass so formed is maintained in a state of fusion until the crystals have separated out. On cooling, the mass is digested with water, and then with dil. hydrochloric acid. L. Ouvrard obtained the same compound. The transparent prisms are probably monoclinic; their sp. gr. is 2.7 at 20° ; they fuse to a transparent glass; and are readily soluble in acids. M. Berthelot and G. André prepared the triple salt **ammonium sodium magnesium pyrophosphate**, $(\text{NH}_4)_3\text{NaMg}_6(\text{P}_2\text{O}_7)_4$, by precipitation from a soln. of normal sodium pyrophosphate with magnesia mixture; the precipitate is dissolved by adding a great excess of ammonium chloride, and the soln. acidified with acetic acid. When boiled for a long time, the compound in question separates out. It is insoluble in, and undecomposed by water; but a prolonged washing with acetic acid extracts magnesium. No ammonia is lost at 110° . There is doubt about the individuality of these products.

T. Fleitmann and W. Henneberg* prepared **magnesium tetrphosphate**, $3\text{MgO} \cdot 2\text{P}_2\text{O}_5$, by precipitation from a soln. of magnesium sulphate by adding the sodium salt; or by fusing together the salts and leaching the product with water. The white insoluble crystalline powder becomes insoluble in acids when heated to a high enough temp. M. Stange prepared **sodium magnesium triphosphate**, $\text{Na}_3\text{MgP}_3\text{O}_{10} \cdot 13\text{H}_2\text{O}$, by adding a soln. of magnesium chloride to one of sodium triphosphate until a permanent precipitate begins to form; this is quickly redissolved by the addition of sufficient triphosphate, and the salt then at once commences to separate. It crystallizes in very slender needles, is decomposed by exposure to air, losing water of crystallization, and, when heated, intumescs like borax, and melts at a red heat to a clear glass easily soluble in acids.

REFERENCES.

- * H. Rose, *Pogg. Ann.*, 76, 1849; R. Weber, *ib.*, 73, 137, 1847; A. Beer, *ib.*, 75, 168, 1848; O. Popp, *Zeit. Chem.*, (2), 6, 305, 1870; A. Schwarzenberg, *Liebig's Ann.*, 65, 146, 1847; *Untersuchungen über die pyrophosphorsäuren Salzen*, Göttingen, 1847; J. F. Persoz, *Liebig's Ann.*, 65, 169, 1847; H. Ludwig, *Arch. Pharm.*, (1), 143, 136, 265, 1858; Z. Karaoglanoff and P. Dimitroff, *Zeit. anal. Chem.*, 57, 353, 1918; G. F. Wach, *Schweigger's Journ.*, 59, 297,

1830; J. Stoklasa, *Zeit. anorg. Chem.*, **3**, 70, 1893; F. W. Clarke, *Amer. Journ. Science*, (3), **14**, 381, 1877; P. Bary, *Compt. Rend.*, **130**, 776, 1900; H. Moissan, *ib.*, **116**, 1429, 1893; L. Ouvrard, *ib.*, **106**, 1729, 1888; *Ann. Chim. Phys.*, (6), **16**, 311, 1889; M. Berthelot and G. André, *ib.*, (7), **11**, 186, 190, 1897; K. A. Wallroth, *Bull. Soc. Chim.*, (2), **39**, 318, 1883; O. Andersen, *Journ. Washington Acad. Sciences*, **4**, 318, 1914; H. G. F. Schröder, *Dichtigkeitsmessungen*, Heidelberg, 1873; H. Struve, *Journ. prakt. Chem.*, (1), **79**, 349, 1860; A. Pavesi and E. Rotondi, *Ber.*, **7**, 818, 1874; H. Pellet, *Ann. Chim. Anal. App.*, **6**, 211, 1901; D. Campbell, *Phil. Mag.*, (4), **24**, 380, 1862; E. Luck, *Zeit. anal. Chem.*, **13**, 255, 1874; T. Graham, *Phil. Mag.*, (3), **2**, 20, 1827; *Phil. Trans.*, **123**, 253, 1833; A. F. de Fourcroy and C. R. Fresenius, *Anleitung zur quantitativen Analyse*, Braunschweig, **1**, 159, 1873.

² T. Fleitmann and W. Henneberg, *Liebig's Ann.*, **65**, 331, 1847; M. Stange, *Zeit. anorg. Chem.*, **12**, 453, 1896.

§ 23. Magnesium Metaphosphates

According to R. Maddrell,¹ **magnesium metaphosphate** is formed by dissolving magnesium carbonate in an excess of dil. phosphoric acid, evaporating the soln. to dryness, and heating the residue to 316°; or, according to J. Stoklasa, by heating magnesium dihydrophosphate to 305°. It appears as a glassy mass, which, according to T. Fleitmann, is not changed by digestion for a day with soln. of alkali carbonate or phosphate, and it is therefore not clear to which particular metaphosphate this product belongs.

A. Glatzel made anhydrous **magnesium dimetaphosphate**, MgP_2O_6 , by evaporating a soln. of magnesium carbonate in aq. phosphoric acid, with about one per cent. in excess, first on a water-bath, then on a sand-bath, and finally at 400°. The pulverized mass was washed with cold water slightly acidified with nitric acid. The resulting crystalline powder is strongly attacked by sulphuric, nitric, or hydrochloric acid. T. Fleitmann prepared **hydrated magnesium dimetaphosphate**, $MgP_2O_6 \cdot nH_2O$ —where $n=4$ according to A. Glatzel, and 4.5 according to T. Fleitmann—by mixing conc. soln. of his ammonium dimetaphosphate, $(NH_4)_2P_2O_6$, with an excess of magnesium chloride, and allowing the mixture to stand for some time. The resulting crystals do not dissolve in water, and are not decomposed by acids; but conc. sulphuric acid was found by A. Glatzel to dissolve readily the salt, forming, when boiled, normal phosphoric acid. T. Fleitmann found that the calcined salt is not changed by soln. of alkali carbonates or phosphates. At 100°, the hydrated salt loses about 2 per cent. of water, and the remainder on calcination. T. Fleitmann stated that some phosphoric oxide is lost at the same time, but A. Glatzel said that this is wrong.

A. Glatzel prepared tetrahydrated **sodium magnesium dimetaphosphate**, $Na_2Mg(P_2O_6)_2 \cdot 4H_2O$, as a crystalline powder by mixing conc. soln. of sodium dimetaphosphate and magnesium chloride. The complex salt loses its water of crystallization completely at a dull red heat, sinters at a higher temp., and passes without melting into polymerized phosphoric acid. Before calcination, the salt is readily soluble in sulphuric, hydrochloric, and nitric acids, but after conc., it is soluble only in conc. sulphuric acid. 100 c.c. of water dissolve 4 grms. of the salt. A. Glatzel prepared the corresponding tetrahydrated **potassium magnesium dimetaphosphate**, $K_2Mg(P_2O_6)_2 \cdot 4H_2O$, in a manner similar to that employed for the sodium salt. It loses its water of crystallization at 150°, and after heating to redness, it is not affected by soln. of alkali carbonates. It does not fuse at a bright red heat. 100 parts of water dissolve 9.84 parts of salt. The salt is readily decomposed by acids—particularly boiling sulphuric acid—forming phosphoric acid. According to L. Ouvrard, when magnesia is dissolved in potassium metaphosphate, the sole product is the compound $K_2Mg_2(P_2O_6)_3$, which crystallizes in large, monoclinic prisms, very soluble in dil. acids; sp. gr. at 20°=2.4. It is analogous to the double magnesium sodium phosphate obtained by T. Fleitmann and W. Henneberg in the wet way.

T. Fleitmann prepared hydrated **ammonium magnesium dimetaphosphate**, $(\text{NH}_4)_2\text{Mg}(\text{P}_2\text{O}_6)_2 \cdot n\text{H}_2\text{O}$, by mixing soln. of ammonium dimetaphosphate and magnesium chloride. A. Glatzel found the crystals lose all their water at 150° . T. Fleitmann said that the hydrate contains 6 mols of water, and effloresces in air; *au contraire*, A. Glatzel said the crystals contain 4 mols of water, and do not lose weight even when confined over conc. sulphuric acid. The latter also stated that the crystals lose ammonia at a dull red heat, and at a bright red heat, phosphoric oxide; at a still higher temp. the product melts and forms magnesium tetrametaphosphate. The double salt is easily attacked by acids.

According to G. F. Wach, when a soln. of recently ignited metaphosphoric acid in aq. ammonia is added to one of magnesium sulphate, the precipitate first formed is redissolved so long as an excess of the latter is present, but when the former is in excess, the precipitate remains undissolved. Alcohol precipitates the portion still remaining in soln. An excess of magnesium chloride, nitrate, or acetate gives the same precipitate, but does not dissolve it so readily. The precipitate forms feathery flakes which unite to form a stringy viscid mass which, after being washed with water and dried, becomes transparent and brittle like glass. When the product is heated in a glass tube, it swells up, forming an opaque spongy mass with the evolution of water at first, and afterwards ammonia. The residue does not fuse at the temp. at which glass softens; it dissolves in water with difficulty to form a soln. with an acid reaction, but is itself slightly soluble in acids. The undecomposed double salt dissolves somewhat freely in cold water, but is precipitated on the addition of alcohol. The cold soln. has an acid reaction towards litmus, and deposits the salt as a viscid mass, when heated, but re-dissolves it on cooling. In boiling water, the salt swells to an opaque frothy mass, without any considerable proportion passing into soln. The analyses of the double salt do not correspond with a definite magnesium ammonium meta- or pyro-phosphate.

G. Tammann has argued that the so-called magnesium dimetaphosphate is really **hydrated magnesium trimetaphosphate**, $\text{Mg}_3(\text{P}_3\text{O}_9)_2 \cdot 14\text{H}_2\text{O}$. C. G. Lindbom prepared dodeca- and pentadeca-hydrated trimetaphosphates by crystallization from a mixed soln. of two parts of hexahydrated magnesium chloride, and one part of sodium trimetaphosphate, at 20° to 30° —either the one or the other hydrate appears. When the crystals are dried on the water-bath they retain about 10.5 mols of water, which is all lost at a red heat, without melting. The residue is insoluble in boiling hydrochloric acid. The salt is sparingly soluble in water, and the soln. is neutral. When the aq. soln. is treated with aq. ammonia and normal sodium phosphate, the salt is precipitated. T. Fleitmann and W. Henneberg, and C. G. Lindbom have prepared sodium magnesium trimetaphosphate, $\text{Na}_4\text{Mg}(\text{P}_3\text{O}_9)_2 \cdot 5\text{H}_2\text{O}$. The latter evaporated a mixed soln. of hexahydrated magnesium chloride with about four times its weight of sodium trimetaphosphate at 20° to 30° , and obtained a crystalline crust, which was washed with a little water. Over conc. sulphuric acid, about one-tenth of the water of crystallization was removed, and all was expelled at a high temp. The product melts at a red heat, forming an opaque white mass which deliquesces in air, and furnishes a soln. of sodium hexametaphosphate when treated with water, and magnesium metaphosphate remains. The double salt dissolves slowly in water, the soln. is neutral, and is not precipitated by sodium carbonate or disodium hydrophosphate unless ammonia has been previously added.

According to A. Glatzel, when magnesium dimetaphosphate is melted, and slowly cooled, **magnesium tetrametaphosphate**, $\text{Mg}_2\text{P}_4\text{O}_{12}$, is formed. The salt crystallizes in stellate aggregates. It is insoluble in water, and is attacked by hydrochloric acid, still more by nitric acid, and quite vigorously by conc. sulphuric acid. When digested for a day with a soln. of alkali carbonate, the alkali tetrametaphosphate is formed. When a dil. soln. of ammonium tetrametaphosphate is treated with an excess of magnesium chloride, small white crystals of **decahydrated magnesium tetrametaphosphate**, $\text{Mg}_2\text{P}_4\text{O}_{12} \cdot 10\text{H}_2\text{O}$, are formed. 100 parts of water dissolve 1.43 parts of the salt. The hydrate is decomposed by acids, particularly conc. sulphuric acid. When calcined, the whole of the water is driven off, and the molten mass is glassy when rapidly cooled. According to H. Rose, an aq. soln. of hexametaphosphoric acid gives a precipitate of **magnesium hexametaphosphate**, when

added to a soln. of magnesium and ammonium chlorides. The precipitate is soluble in much water. T. Graham found that a gum-like precipitate is obtained when sodium hexametaphosphate is added to a soln. of magnesium acetate, but not to one of magnesium sulphate. H. Rose obtained no precipitate by adding aq. ammonia to a soln. of magnesium sulphate mixed with a sufficient quantity of sodium hexametaphosphate.

W. Gregory accidentally discovered what G. Tammann considers to be **sodium magnesium octometaphosphate**, $\text{Na}_2\text{Mg}_3\text{P}_8\text{O}_{24}$, in the preparation of phosphoric acid. In the extraction from bones by J. von Liebig's process, there is first a separation of magnesium metaphosphate, $\text{Mg}(\text{PO}_3)_2$, and then by repeated dilution and heating, the double octophosphate appears, which can be separated from the excess of phosphoric acid by treatment with cold water. G. Tammann obtained the double salt by melting a mol of a magnesium compound with a mol of tetrahydrated ammonium sodium hydrophosphate, and stirring the mass as it cools. The crystals are said to be rhombic dodecahedra, which, when dried at 100° , are free from water. According to W. Gregory, and R. Maddrell, the salt is insoluble in water or aq. phosphoric acid, soluble in conc. sulphuric acid, and slightly soluble in hydrochloric acid and aqua regia. G. Tammann said that the salt is insoluble in the two last-named menstrua; and that alkali sulphides have scarcely any action on the salt.

REFERENCES.

¹ R. Maddrell, *Mem. Chem. Soc.*, **3**, 273, 1848; *Phil. Mag.*, (3), **30**, 322, 1847; J. Stoklasa, *Zeit. anorg. Chem.*, **3**, 70, 1893; A. Glatzel, *Ueber Dimetaphosphorsäure und tetrametaphosphorsäure Salze*, Würzburg, 1880; T. Fleitmann, *Pogg. Ann.*, **78**, 259, 1849; H. Rose, *ib.*, **76**, 3, 1849; T. Fleitmann and W. Henneberg, *Liebig's Ann.*, **65**, 304, 1848; T. Graham, *Phil. Trans.*, **123**, 253, 1833; C. G. Lindbom, *Lund's Univ. Arsskr.*, **10**, 1874; *Ber.*, **8**, 122, 1875; G. Tammann, *Journ. prakt. Chem.*, (2), **45**, 423, 1892; W. Gregory, *Liebig's Ann.*, **65**, 97, 1848; L. Ouyvrad, *Compt. Rend.*, **106**, 1729, 1888; *Ann. Chim. Phys.*, (6), **16**, 311, 1889; G. F. Wach, *Schweigger's Journ.*, **59**, 297, 1830.