279. *The System Magnesium Oxide–Magnesium Chloride–Water.*

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Section 1. Equilibrium at 25°.

A KNOWLEDGE of the equilibria and other physicochemical properties of the system magnesium oxide–magnesium chloride–water is desirable owing to the extensive use of magnesium oxychloride or magnesian cement, prepared by mixing magnesium oxide with a concentrated solution of the chloride, together with certain inert " filling " and colouring materials.

Three not entirely successful attempts to study the problem on phase-rule lines have already been made, by Robinson and Waggaman at 25° (*J. Physical Chem.*, 1909, **13**, 673) and by Maeda and Yamane at 25° (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, **7**, 340) and at 50° (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, No. 50, 1926, **4**, 85). We now record a further attempt.

EXPERIMENTAL.

The procedure adopted was to mix the three components in suitable proportions and then to shake them in a thermostat at 25° until equilibrium had been established. The chief difficulties were the slowness with which equilibrium was attained, the establishment of metastable equilibria, and the bulky nature of the solid phases.

Systems involving basic salts are always sluggish in attaining equilibrium, but with this system the difficulty was much enhanced by the formation under certain conditions of either cements or gels. Preliminary experiments showed that, subject to certain precautions, equilibrium is established after constant shaking for 2 months at 25°. Small lumps of the cement, however, can be shaken with $MgCl_2$ aq. for many months without coming to equilibrium with it, and it is therefore necessary to break up any cement that may form before it hardens, and to grind it to a fine powder in an agate mortar before continuing the experiment. Gels disappear after long shaking, and this process may be hastened by breaking them up and adding more $MgCl_2$ aq.

Metastable equilibria may be avoided by inoculation with a trace of finely

powdered magnesian cement, which contains hydroxide and oxychloride : if this precaution be not taken, $Mg(OH)_2$, the stable solid phase in contact with solutions containing less than 10.9% $MgCl_2$, may coexist with solutions containing 15% or more of the chloride, even after 2 months' shaking.

The bulky nature of the solid phases, and particularly of the gel which may be formed as an intermediate product, necessitates the use of very small amounts of MgO, 0.5 g. to 30 c.c. of solution being found the max. possible. The use of relatively small amounts of oxide makes it difficult to establish the position of the triple point hydroxide–basic chloride–solution, for, unless the initial concn. of the solution lies in a very narrow range of concn., the small amount of oxide used is either completely converted into the oxychloride, or does not form it at all.

The MgO used contained about 0.3% of CaO : it was prepared by heating " magnesium carbonate (light) " to $850°$: MgO which has been heated to higher temperatures, or " burnt," is very slow in attaining equilibrium.

When equilibrium had been established, the mixtures were filtered through a sintered-glass plate (5—10μ). This operation lasted about 6 hours and was carried out in the thermostat. The solution and moist solid were analysed, Mg being determined as $Mg_2P_2O_7$, and Cl by Volhard's method. In the solution, Cl only was determined, since early experiments showed that Mg and Cl were always present in equivalent amount. All analyses quoted are the mean of two concordant determinations.

The results obtained are in Table I, being expressed as g. of MgO or $MgCl_2$

TABLE I.

| Solution. $MgCl_2$, %.	Moist solid. $MgCl_2$, %.	MgO, %.	Solid phase.*	Solution. $MgCl_2$, %.	Moist solid. $MgCl_2$, %.	MgO, %.	Solid phase.*
2·12	1·35	31·63		10·98	16·03	5·32	
2·65	1·72	30·26		14·41	15·56	5·77	
6·44	3·79	33·83		16·43	17·50	6·85	
8·61	5·51	25·27	A	17·36	18·06	4·98	
9·45	5·23	33·60		21·12	21·24	6·43	
10·36	6·72	29·79		21·38	21·06	7·29	B
10·52	5·20	38·09		24·21	23·63	8·75	
10·62	13·54	8·73	B†	26·59	25·87	8·35	
				26·86	25·14	7·72	
10·88	8·69	25·71	A & B	31·14	28·80	8·60	
10·90	11·44	19·70		33·69	31·07	7·30	
12·08	6·71	33·67	A†	34·77	33·52	2·71	
15·32	10·45	23·26		35·70	36·41	3·79	B & C
				35·72	40·10	2·19	
				35·72	—	—	C

* A = $Mg(OH)_2$; B = $3MgO,MgCl_2,11H_2O$; C = $MgCl_2,6H_2O$.

† Denotes metastable equilibrium.

per 100 g. of solution or moist solid, and are shown in Fig. 1 plotted on the usual triangular diagram (many points are omitted for the sake of clearness). Solutions, which contain no MgO, are represented by the line AB, the point A representing pure H_2O and the point B a solution saturated with $MgCl_2,6H_2O$. Dilute solutions are in equilibrium with $Mg(OH)_2$, and more conc. solutions with a basic or oxy-chloride represented by the point C. The concn. of $MgCl_2$ at the triple point hydroxide–oxychloride–solution, represented by the point

D, is $10 \cdot 89\%$. Robinson and Waggaman's figure for this concn.—about 16%—is undoubtedly erroneous owing to their having overlooked the possibility of metastable equilibria. Maeda and Yamane were unable to fix this point. The concn. of $MgCl_2$ at the triple point oxychloride–hexahydrate–solution is $35 \cdot 71\%$, which is identical with that of a solution saturated with the hexahydrate alone, for which we obtain a figure agreeing closely with the results of Biltz and Marcus (*Z. anorg. Chem.*, 1911, **71**, 168).

The compositions of the solid phases were obtained by extrapolation by Janecke's method (*ibid.*, 1906, **51**, 132), which is more convenient than the triangular diagram for this purpose. When, however, the solid phases are flocculent and the moist solid contains a large amount of solution, as is particularly the case with the oxychloride, all graphical methods are somewhat

FIG. 1.
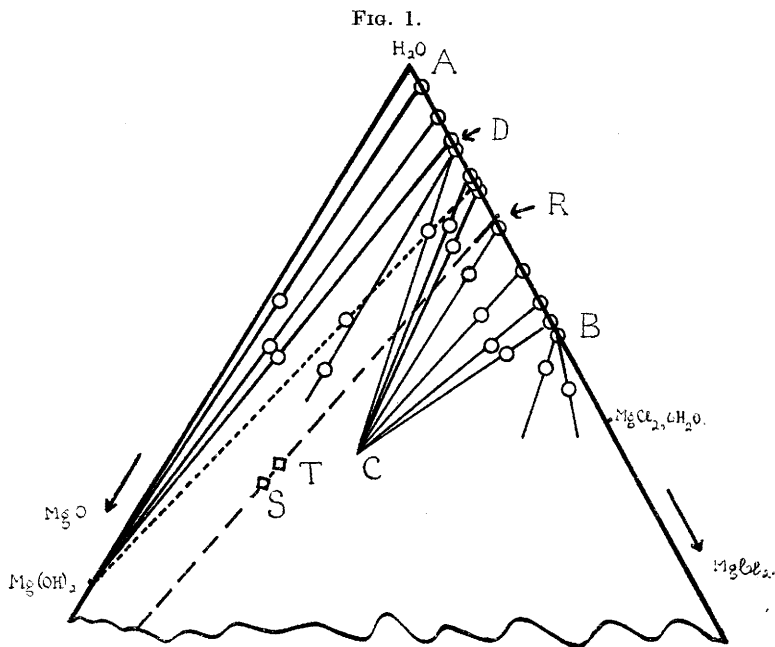
inaccurate. The solid phase coexisting with dilute solutions was found to be the hydroxide, $Mg(OH)_2$, in agreement with the conclusions of Maeda and Yamane, but not of Robinson and Waggaman, who state that it is " an indefinite solid solution of magnesia-chlorine and water." For the composition of the oxychloride, graphical extrapolation gave the ratios $MgO:MgCl_2 = 0 \cdot 77:0 \cdot 23$, and $MgO:H_2O = 0 \cdot 77:1 \cdot 27$, the nearest formulæ being $10MgO,3MgCl_2,35H_2O$ or $3MgO,MgCl_2,11H_2O$. While the more complex formula fits the ratios better, the accuracy of the graphical method hardly justifies selection of this, and the observations recorded later show that oxychloride tends to contain inclusions of the hydroxide. The simpler formula is therefore preferred. Maeda and Yamane and Robinson and Waggaman give $3MgO,MgCl_2,12H_2O$ and $3MgO,MgCl_2,10H_2O$ respectively.

PLATE I.
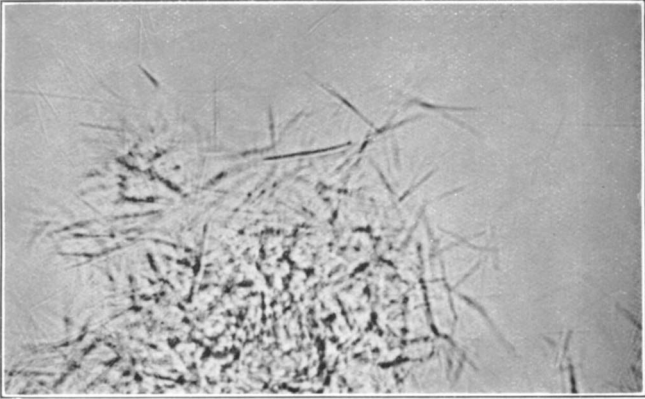
A × 600.
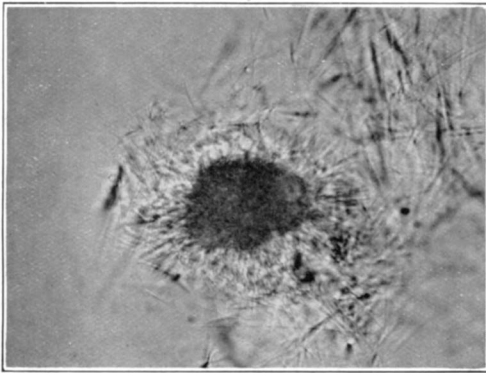
B × 600.

Section 2.   Gels.

Gels were discovered during work on equilibria described in Section 1 : their true nature, however, was not at once realised since they were either imperfectly formed or half synerised. Analyses of the gelatinous substances obtained and of the solutions in contact with them indicated that the composition of the solid phase varied widely; although it was usually close to that of the oxychloride, it also sometimes contained much hydroxide.

A series of experiments, undertaken to find the best conditions for the formation of these gelatinous substances, showed that perfect gels were easily obtainable by slight modifications of the procedure adopted in Section 1. A good method is to grind 0·5 g. of MgO to a fine powder with a trace of magnesian cement, and to shake this vigorously for 1 hr. in a machine with 25 c.c. of 12% $MgCl_2$ aq. On standing over-night, the entire mass sets to an unmistakable gel, resembling a stiff starch paste.

The gel has a structure visible under the microscope : a suspension of it in some of the solution used in making it is, however, more suitable for microscopic observations than the gel itself, which is too dense. The solution appears to act merely as a diluent, enabling minute portions of the gel to be isolated : the change that takes place on shaking gel with solution is very slow, and there is no reason to believe that any appreciable change takes place in the short time needed to make observations. Under these conditions the gel is seen (Plate I, A) to be a confused mass of small interlaced needles which are probably connected by twinning. The needles are about 20μ long but are too thin to be visible between crossed Nicols, though they are obviously crystalline. Analyses, the characteristic needle form, and the necessity in their preparation of inoculation with cement, which contains oxychloride, all lead to the conclusion that the needles are the oxychloride.

The top of the gel is sometimes covered with a scum of the apparently amorphous hydroxide; the gel, particularly when prepared from oxide which has not been finely ground, may also contain hedgehog-like masses (Plate I, B) composed of unpeptised oxide (probably converted into hydroxide) surrounded by a fringe of oxychloride needles. These are an unimportant constituent of the gel, since they may be almost entirely absent, but are probably an important constituent of the cement.

The gel, therefore, seems to owe its existence to innumerable minute crystalline needles of the oxychloride, which form a confused branched system as the result of twinning, and comprise 5—7% of the whole volume of the gel. The interstices are filled with $MgCl_2$ aq.

The conditions under which gels are formed depend on, and give valuable information about, the relative stabilities of magnesium oxide, hydroxide, and oxychloride, and their rates of interconversion. First, it is possible to form gels at 25° by the method described above if the concentration of $MgCl_2$ aq. is 9·7% or more, although oxychloride is only stable in contact with solutions containing 10·9% or more of $MgCl_2$. This fact approximately fixes the concn. of the solution at the triple point oxide–oxychloride–solution, as can be seen from Fig. 2, which is an enlarged diagrammatic representation of part of Fig. 1, the concn. of the oxide being grossly exaggerated.

Secondly, oxychloride is not formed spontaneously by the action of a solution containing less than 13% of $MgCl_2$ on either MgO or $Mg(OH)_2$, oxide being converted into the hydroxide which does not react further. If, however, hydroxide be treated with a solution containing 10·9—13% of $MgCl_2$ and inoculated with the oxychloride, it is very slowly converted into the oxychloride : relatively large, untwinned needles are produced and no gel is formed, in agreement with von Weimarn's hypothesis. If, on the other hand, oxide be treated similarly, it is rapidly changed to numerous, small, much-twinned needles of the oxychloride, to which the gel owes its existence.

Oxychloride is, however, formed spontaneously from MgO or $Mg(OH)_2$ and more conc. (15%) solutions of $MgCl_2$. This spontaneous formation occurs more readily in the sediment of MgO or $Mg(OH)_2$ that settles out on standing than it does in the well-stirred mixture; thus, $Mg(OH)_2$ was found in (metastable) equilibrium with a 15% solution after continuous stirring for 2 months, but if a similar mixture is kept without shaking, oxychloride will be formed within 24 hrs. Gels, therefore, can be produced without inoculation from more conc. solutions, but since spontaneous formation of oxychloride is

FIG. 2.
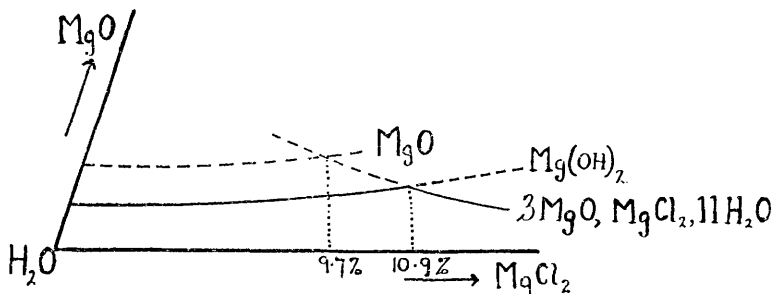
favoured by sedimentation, cements rather than gels are usually produced. With still more conc. solutions (20%), oxychloride is formed rapidly even in a well-stirred mixture.

Syneresis of gels made with dilute solutions containing 9·7—10·9% of $MgCl_2$ is due to the conversion of the oxychloride into $Mg(OH)_2$, a reaction which, like its reverse, is very slow. With gels made from more conc. solutions, syneresis is due to secondary recrystallisation; the larger crystals, being less soluble, grow at the expense of the smaller ones. This process is also rather slow.

Section 3.   *X-Ray Analysis* (with GEOFFREY GRIME).

The powder method of X-ray analysis has been used in order to confirm the conclusions reached in Section 1 and to obtain information as to the nature of magnesian cement. Previous measurements by Maeda (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, No. 73, 1926, 5, 95), using the same method, were inconclusive.

The following substances have been examined : (*a*) Natural magnesium hydroxide (brucite), (*b*) magnesium hydroxide and (*c*)

oxychloride (moist solids from phase-rule work), (d) hardened cement (aged 6 months), (e) freshly set cement (3 days old).

The specimens, after being powdered in a mortar when necessary, were mounted on a Ni rod at the centre of the cylindrical camera and exposed to Cu-Ka radiation. The information derived from the photographs is summarised in Table II, from which the following conclusions can be drawn.

TABLE II.

Indices, hk.l.	(a) Brucite. d, calc.	d, obs.	Int.	(b) Mg(OH)$_2$. d, obs.	Int.	(c) Oxychloride. d, obs.	Int.	(d) Cement (hardened). d, obs.	Int.	(e) Cement (fresh). d, obs.	Int.
						7·5	v.w.	7·5	v.w.		
00·1	4·78	4·78	v.s.	4·73	m.			4·77	m.	4·65	w.
						4·15	w.	4·11	m.	4·15	v.w.
								3·71	v.w.		
								2·53	v.w.	2·54	v.w.
						2·42	w.	2·43	m.		
00·1(2)	2·39	2·39	s.	2·39	m.			2·38	s.	2·37	s.
								2·28	v.w.		
								$2\cdot19_5$	v.w.		
						$1\cdot97_8$	v.w.	$1\cdot97_8$	m.	$1\cdot98_0$	v.w.
								$1\cdot92_7$	v.w.		
						$1\cdot85_1$	v.w.	$1\cdot84_2$	m.		
10·2	$1\cdot80_5$	$1\cdot80_5$	v.s.	$1\cdot80_8$	w.			$1\cdot80_2$	m.	$1\cdot80_5$	m.
								$1\cdot71_0$	v.w.		
11·0	$1\cdot57_5$	$1\cdot57_9$	v.w.	$1\cdot57_6$	v.w.			$1\cdot57_2$	m.	$1\cdot57_0$	s.
11·1	$1\cdot49_6$	$1\cdot49_7$	v.w.					$1\cdot49_0$	w.	$1\cdot48_9$	w.
10·0(2)	$1\cdot37_5$	$1\cdot37_2$	s.	$1\cdot37_4$	v.w.	$1\cdot37_7$	v.w.	$1\cdot37_1$	w.	$1\cdot38_0$	v.w.
⎧20·1	$1\cdot31_1$	$1\cdot31_5$	v.w.					$1\cdot31_2$	w.	$1\cdot30_9$	v.w.
⎩11·2	$1\cdot31_6$										
00·1(4)	$1\cdot19_6$	$1\cdot19_5$	v.w.								
10·1(2)	$1\cdot18_6$	$1\cdot18_8$	v.w.							$1\cdot18_8$	v.w.
11·3	$1\cdot12_6$	$1\cdot21_1$	v.w.								
10·4	$1\cdot09_6$	$1\cdot09_1$	v.w.							$1\cdot09_6$	v.w.
⎧20·3	$1\cdot03_6$					$1\cdot03_1$	v.w.			$1\cdot02_8$	v.w.
⎩12·0	$1\cdot03_1$										

Intensities: v.s., very strong; s., strong; m., medium; w., weak; v.w., very weak.

Indices: hk.l are the indices of the planes of the crystal.

d is the distance in Å.U. between the successive planes.

(Figures in brackets in col. 1 are the orders of reflexion when greater than 1.)

Brucite and the Mg(OH)$_2$ obtained as moist solid in Section 1 are identical, and have a unit cell of the hexagonal system of dimensions $a = 3\cdot15$ Å.U., $c = 4\cdot78$ Å.U., rather greater than those usually quoted (International Critical Tables, **1**, 344).

The unit cell of magnesium oxychloride cannot be determined from the available data.

Both hydroxide and oxychloride can be identified in each sample of cement, the hydroxide lines being by far the stronger, especially in the freshly set cement. The hardened specimen shows several faint lines not appearing in either hydroxide or oxychloride patterns. The oxychloride pattern given by this specimen is stronger than that from the pure material, and therefore the lines are probably those of the oxychloride. This conclusion is borne out by the fact that the lines do not appear in the freshly set cement where the oxychloride pattern is weak.

No MgO can be detected in either specimen of the cement.

Hardening of the cement appears to be associated with an increase in the quantity of the oxychloride detectable by X-rays. This may mean either that more oxychloride is actually formed, or that much of the oxychloride in the freshly set cement is present in a colloidal or microcrystalline form, and that this becomes crystalline on ageing.

Section 4. Magnesium Oxychloride Cement.

The cement is prepared by mixing MgO with conc. $MgCl_2$ aq. to a thick paste, which sets to form a cement in about 12 hrs. The most suitable conc. of solution is about 20%, this solution being represented in Fig. 1 by the point R. The relative amounts of oxide and solution used are so chosen that the resulting paste has a suitable consistency. We find that a typical pure magnesian cement contains about 43% MgO, 12% $MgCl_2$, and 45% H_2O, its composition being represented by the point S. In practice, some filling material is always used, with the result that a rather greater amount of solution is required to obtain a paste of suitable consistency, the composition of a typical filled cement being represented by the point T, the filling material being, of course, neglected in this representation.

From the diagram it follows that the cement at 25° is composed of three phases, magnesium hydroxide and oxychloride, and a solution containing 10·9% $MgCl_2$, the relative amounts of which are about 41, 49, and 10% for the pure cement and 37, 49, and 14% respectively for a filled cement. In so far as the nature of the crystalline phases is concerned, these conclusions are confirmed by X-ray analyses described in Section 3.

Thus, although the cement is a hard and apparently homogeneous substance, it must be porous, since 10—14% of its mass is a liquid. It is possible that equilibrium conditions in such a porous body, where surface forces come into play, may be slightly different from those found in Section 1.

Attempts to determine the structure of the cement from thin sections prepared by petrological methods were fruitless, but the observation made in Section 2, that MgO when incompletely converted into the oxychloride formed hedgehog-like masses, suggests that the structure of the cement can be regarded as a close-packed agglomeration of these hedgehogs; *i.e.*, it is composed of particles of hydroxide of various sizes from which radiate large numbers of fine, highly twinned needles of oxychloride which bind together the hydroxide particles, while the chloride solution is contained in the interstices.

The cement is in two respects unstable when exposed to the atmosphere. The $Mg(OH)_2$ it contains will in time be completely converted by a normal atmosphere into the carbonate : besides the normal carbonate, hydrated carbonates and hydrated basic carbonates are described in literature, one of which may be formed rather than the normal carbonate, but for these substances no thermodynamic data are available. An experiment described below makes it probable that a surface coating of some kind of carbonate is formed when the cement is exposed to the atmosphere, and that this coating is of value in protecting the cement from attack by moisture.

One of the phases of which the cement is composed is a 10·9% solution of $MgCl_2$. From vapour-pressure data (International Critical Tables, **3**, 367) it follows that this solution will absorb moisture when exposed to an atmosphere whose degree of humidity is greater than 93%. Absorption of moisture will cause decomp. of oxychloride, and ultimately the cement will be converted into the hydroxide and a dilute solution of the chloride. This actually happens if the cement is protected from the action of CO_2, for if a freshly mixed paste be placed in a desiccator over N-KOH, which provides a moist, CO_2-free atmosphere, it sets normally and then begins to deliquesce. Signs of this are evident after a day ; after a week the cement is surrounded by a pool of dilute chloride solution, and after a month its surface is converted

into a friable mass of hydroxide, which can readily be detached from the underlying unaltered cement. Again, a cement which has not been submitted to the action of CO_2 is converted by H_2O into a friable mass of the hydroxide, from which all chloride has been leached out. Cement which has been exposed to the air is far more resistant to moisture but is, nevertheless, slowly attacked on long exposure to a very moist atmosphere : in practice, the surface of the cement is often impregnated with some oil or wax to guard against this contingency.

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