726. Hydrated Calcium Silicates. Part I. Compound Formation at Ordinary Temperatures.

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Hydrous calcium silicates prepared at room temperature appear amorphous, but *X*-ray photographs show that compounds are formed having a considerable degree of crystalline character. Essentially the same product, calcium silicate hydrate (I), can be obtained by the action of water on tricalcium silicate, by double decomposition of calcium nitrate and sodium silicate, or by reaction of calcium hydroxide solution with silica gel, although crystallisation is more marked in the first case. The composition of this phase varies between approximately CaO,SiO_2,aq. and $3CaO,2SiO_2$,aq. without significant change in *X*-ray pattern. The phase relationships between solid and solution have been investigated and are sufficiently reproducible to suggest that the results represent a fair approximation to equilibrium conditions. A second phase, calcium silicate hydrate (II), with a composition in the neighbourhood of $2CaO,SiO_2$,aq. and an *X*-ray pattern differing only slightly from the above, has been obtained by decomposition of tricalcium silicate and probably exists in equilibrium with calcium hydroxide solutions containing over 1·13 g./l. of CaO. A tentative interpretation of the *X*-ray data of calcium silicate hydrate (I) suggests a layer structure, possibly showing some similarities to the clay minerals.

The system $CaO–SiO_2–H_2O$ is of considerable interest in pure and applied chemistry, and in geochemistry, if for no other reason than the abundance and accessibility of the materials involved. In particular, calcium silicates are the principal constituents of Portland cement and are the compounds chiefly responsible for the setting and hardening actions on mixing with water. Knowledge of the hydrated system is therefore essential to the understanding of these processes.

Earlier Investigations.—The study of the system at ordinary temperatures is made difficult by the indefinite nature of the substances involved, and although numerous investigations have been carried out, considerable doubt remains regarding the results. Previous studies have recently been reviewed by Steinour (*Chem. Reviews*, 1947, **40**, 391), and it is apparent that much of the recorded work is open to serious criticism and that very large discrepancies exist between the results of even the most recent investigations. Thus, Bessey (" Symposium on the Chemistry of Cements," Stockholm, 1938, p. 178), obtained evidence from phase-equilibrium data for the formation of two distinct phases, having compositions CaO,SiO_2,aq.—$3CaO,2SiO_2$,aq. and $2CaO,SiO_2$,aq. The latter was found to exist in equilibrium with saturated calcium hydroxide at 17°. Beitlich (*J. Amer. Chem. Soc.*, 1938, **60**, 1832), however, considered that only a single phase existed in equilibrium with aqueous solutions in this region and that its composition varied between $4CaO,5SiO_2$,aq. and $2CaO,SiO_2$,aq. Cirilli (*Ric. sci.*, 1939, **10**, 1042), on the basis of *X*-ray powder data, also rejected Bessey's view that $2CaO,SiO_2$,aq. existed as a distinct phase but considered the limits of composition of the other phase to be CaO,SiO_2,aq. and $3CaO,2SiO_2$,aq. Roller and Ervin (*J. Amer. Chem. Soc.*, 1940, **62**, 461) reached a similar conclusion but believed, as did Beitlich and also Flint and Wells (*J. Res. Nat. Bur. Stand.*, 1934, **12**, 751), that a further phase, poorer in lime than CaO,SiO_2,aq., could also be formed at room temperature.

Bessey, who alone among the previous investigators studied materials prepared by essentially different methods, considered that reproducibility in the phase data could be obtained. On the other hand, Steinour, while pointing out the possibilities of experimental errors in some of the investigations, also suggested tentatively that the differing lime : silica molar ratios of solid phases, supposedly in equilibrium with solutions of the same concentration, might be due to differences in their colloidal properties.

Degree of Crystalline Character.—Hydrated calcium silicates prepared at room temperature normally appear completely amorphous or gel-like under the microscope. A few optical investigations, discussed by Steinour (*loc. cit.*), indicated the formation of needles instead of or as well as the gel, but the conditions necessary for this are not clear and attempts by various workers to reproduce certain of these preparations have been unsuccessful. More recently, electron-microscope studies by Radczewski, Muller, and Eitel (*Naturwiss.*, 1939, **27**, 807), Sliepcevich, Gildart, and Katz (*Ind. Eng. Chem.*, 1943, **35**, 1178), and McMurdie (unpublished work quoted by Bogue, " The Chemistry of Portland Cement," Reinhold, 1947) have given indications that the gel itself may have a degree of crystalline character although, as Bogue points out, the results so far obtained by this method are inconclusive. More definite evidence of crystallinity has arisen from the *X*-ray powder studies by Chassevent (*Compt. rend.*, 1934, **199**, 673), Brandenberger (*Schweiz. Archiv*, 1937, **3**, 239), Forsen (" Symposium on the Chemistry of Cements," Stockholm, 1938, 389), Cirilli (*loc. cit.*), Stratling (*Zement*, 1940, **29**, 427, 441, 455, 475), McMurdie and Flint (*J. Res. Nat. Bur. Stand.*, 1943, **31**, 225), and Brocard (*Ann. Inst. Tec. Bat. Trav. Pub.*, 1948, No. 1, 1). While nearly all the patterns obtained show a general similarity, all, as will be shown, are incomplete and some include spacings due to other substances. No attempts to interpret the data have been recorded.

The Present Investigation.—This was undertaken because it appeared impossible to make any progress with further problems, such as the degrees of hydration and structures of the compounds, until the phase equilibria and *X*-ray data had been established with greater precision. A systematic study of hydrated calcium silicates prepared at room temperature by various methods was therefore carried out. This has made possible more conclusive identification of the compounds and knowledge of their limits of composition, and has yielded some indications regarding their structures.

Preparation of Hydrated Calcium Silicates.—Samples for phase equilibrium and *X*-ray investigation were prepared by decomposition of anhydrous tricalcium silicate, by reaction of calcium hydroxide solution with silica gel, and by double decomposition of calcium nitrate with sodium silicate. The products were white powders which appeared amorphous under the polarising microscope except for traces of calcium carbonate and, in the case of samples C6 and C7 (below), of calcium hydroxide. Analytical data are given in Table I. Following Roller and Ervin (*loc. cit.*), it was assumed that the carbon dioxide was present as calcium carbonate and the values given for % CaO and CaO/SiO_2 in Table I and elsewhere in this paper exclude CaO present in this form. In the case of samples made by double decomposition the small amounts of Na_2O present as impurity are included in the values given for CaO, since investigations by Kalousek (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 285) suggest that some replacement of lime in hydrated calcium silicates by soda can take place. The correction is in any case of little significance.

TABLE I.

Method of preparation.	Sample.	CaO, % (corr.).	SiO_2, %.	H_2O, %.	$CaCO_3$, %.	CaO/SiO_2 (corr.).
Tricalcium silicate and water	A1 *	39·8	30·5	22·2	7·5	1·40
	A2	40·5	30·8	23·9	4·8	1·41
	A3	45·9	30·0	23·4	0·66	1·64
	A4	47·6	26·9	23·8	1·7	1·90
	A5	45·1	24·8	29·5	0·59	1·94
Calcium hydroxide and silica gel	B1	32·9	38·2	26·0	2·9	0·92
Calcium nitrate and sodium silicate	C1	27·2	42·9	28·4	1·5	0·68
	C2	26·0	29·6	41·6	2·8	0·94
	C3	34·9	37·8	25·8	1·5	0·99
	C4	37·1	32·2	27·3	3·3	1·24
	C5	42·1	27·8	28·7	1·4	1·62
	C6	37·5	22·3	36·7	3·5	1·80
	C7	42·7	19·3	36·2	1·8	23·7

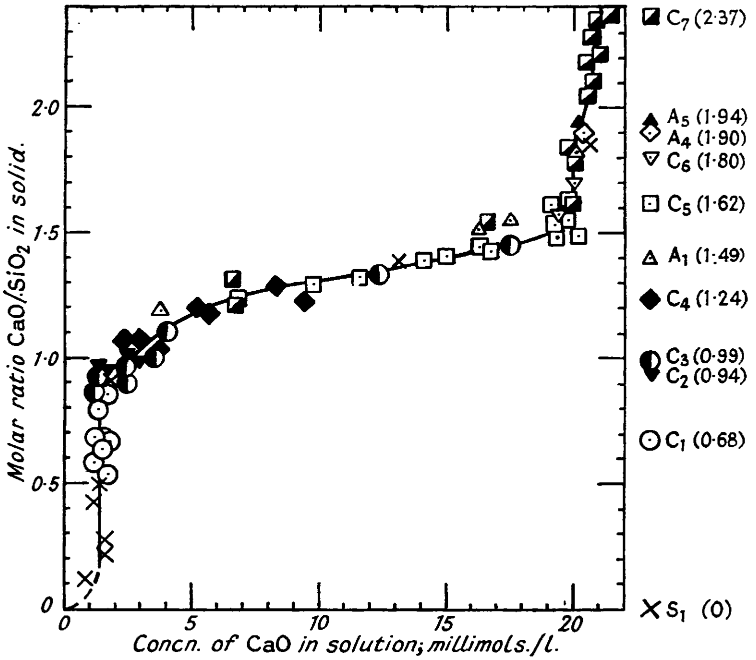
* Contained a trace of unchanged tricalcium silicate.
Na_2O was determined separately in two cases: C5, 0·33% and C7, 0·31%.

Investigation of Phase Equilibria.—Equilbria between the solid phases and aqueous solutions were investigated by shaking weighed amounts of the above preparations with water or calcium hydroxide solutions. In other experiments silica gel was shaken directly with calcium hydroxide solutions. From the initial and final concentrations of calcium hydroxide and silica in solution, the final lime : silica molar ratio of the solid phase was calculated in each case. The results of these experiments, expressed by plotting the lime : silica molar ratios of the solids against concentrations of lime in solution, are given in Fig. 1. Concentrations of silica in solution are given in Fig. 2.

Attainment of Equilibrium.—The existence of equilibrium in these experiments was demonstrated by the following tests: (i) Out of over 100 separate experiments all but a few gave results in fairly good agreement with each other, as shown in Fig. 1. In the few cases (not shown in Fig. 1) in which divergent results were obtained, repetition of the experiment with a longer period of shaking nearly always gave results in agreement with the remainder. (ii) Consistent results were obtained by the use of eleven different samples prepared by three distinct methods. (iii) Satisfactory agreement was obtained between experimental points obtained by the decalcification of lime-rich samples, such as C7, and points obtained by addition of lime to silica gel or lime-poor materials such as C3. (iv) In many cases pairs of points very near together in Fig. 1 represent the results of experiments which differed only in the period of shaking.

Fig. 1.

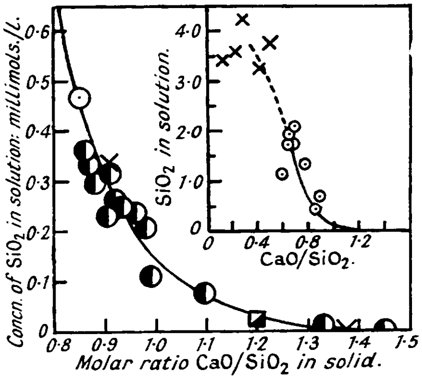
Equilibra between hydrous calcium silicates and solution.



On right of figure: key to samples used, showing initial values of CaO/SiO_2.

Fig. 2.

Silica concentrations in solution.



The symbols have the same significance as in Fig. 1. Inset: extension of figure on reduced scale.

Time needed to reach equilibrium. This was found to vary between a few days and several months, according to the nature of the initial material and the change in concentration of the solution which was involved. Small adjustments in the composition of the solid took place rapidly but large changes were often very slow. Different preparations varied markedly in this respect, the silica gel sample (S1) taking up 1·38 mols. of lime in 26 days, whereas with the hydrated calcium silicate preparation C3, continuous shaking for 68 and 80 days respectively was needed to obtain the points having CaO/SiO_2 values of 1·45 and 1·33.

Results of Phase-equilibrium Experiments.—It is probable from the above considerations that, in the case of solid phases having CaO/SiO_2 below about 1·5, the curve drawn in Fig. 1 approximates closely to equilibrium conditions. In the case of solids having CaO/SiO_2 greater than 1·5 it appears likely, for reasons discussed later, that only those points obtained by the use of samples A4 and A5, prepared from tricalcium silicate, represent true equilibrium. The true equilibrium curve cannot however differ greatly in this region from that shown in Fig. 1 since the concentration of lime in solution cannot exceed the solubility of calcium hydroxide. Owing mainly to the influence of particle size it is difficult to decide upon the value for this quantity which is most appropriate to the present case. Bassett (*J.*, 1934, 1270) obtained the value 0·0213M. for coarse particles at 18°, rising to 0·0236M. for very fine particles. The former value alone refers to a thermodynamically stable and reproducible condition, and is possibly to be preferred.

X-*Ray Investigation.*—Powder photographs were taken of all the samples listed in Table I and of 24 solids recovered from the phase-equilibrium experiments. In the latter, the moist solids were placed in cells having walls of mica : this prevented attack by atmospheric carbon dioxide or deposition of calcium hydroxide by evaporation of the solution, and avoided the danger of altering the composition of the solid by complete removal of the solution.

Preparations from tricalcium silicate, CaO/SiO_2 *below* 1·65. The *X*-ray pattern of sample A2 is given in Table II. Patterns identical with this were given by samples A1 and A3 with additional very weak lines, attributed to calcium carbonate, at 1·92 and 1·86 A. in the case of sample A1. The lines were broader than those given by normally crystalline substances under comparable experimental conditions and, as compared with zinc oxide, exposures of about ten times as long were needed to produce photographs of comparable intensity. The spacings were, however, sharp enough to allow measurement without difficulty to the degree of accuracy given in the table.

TABLE II.

Sample A2, obs.		Sample B1, obs.		Calculated.	
Spacing, A.	Intensity.*	Spacing. A.	Intensity.*	Spacing, A.	Indices.
10·0	s	11·5	s, d	—	—
5·3	vvw	5·3	w	—	—
3·03	vs	3·03	vs	3·02	110
2·80	ms	2·80	m	2·80	200
2·40	w	2·4	vw, d		
2·14	vw	2·1	w, d	—	—
2·04	w				
1·81	ms	1·80	ms	1·80	020
1·66	mw	1·66	mw	1·66	310
1·52	vw	1·52	vw	1·51	220
1·40	w	1·40	w	1·40	400
1·23	vvw	1·23	vvw	—	—
1·18	vvw	1·17	vvw	1·175	130
1·11	vw	1·11	vw	1·105	420
1·075	vvw	1·070	vvw	1·070	510

* vs = very strong; s = strong; ms = moderately strong; m = moderate; mw = moderately weak; w = weak; vw = very weak; d = diffuse.

Some early preparations made from tricalcium silicate contained traces of unchanged starting material. This could easily be recognised in the *X*-ray photographs not only by the positions of its stronger lines but also by the fact that, on account of the greater size of the crystalline particles, these lines had a much rougher appearance than the remainder.

Preparations made from silica gel or by double decomposition. The *X*-ray pattern of a sample (B1), made from silica gel, is also given in Table II. It was almost identical with that of sample A2, but several of the lines were more diffuse than the remainder, and the longest observed spacing was increased from 10·0 to 11·5 A. Patterns very similar to this were given by the samples prepared by double decomposition, and by solids recovered from phase-equilibrium experiments in which these had been used, provided that the lime : silica ratio of the sample when subjected to *X*-ray analysis lay between about 0·5 and 1·65. Slight variations were observed in the patterns of these samples. The longest spacing appeared to vary between about 11·0 and 12·5 A., and the 5·3 A. spacing varied in intensity from very, very weak to moderate. The reasons for these variations were not discovered; they did not appear to be related to differences in lime : silica ratio. In a very few cases of samples isolated from phase-equilibrium experiments additional very weak lines were observed. One sample having

CaO/SiO_2 = 1·05 showed lines at 8·25 and at 3·55 A., and two others having CaO/SiO_2 = 0·99 and 1·17 showed one at 3·69 A. The rare occurrence of these lines suggests the possibility that they may have been due to some unidentified impurity.

Silica-rich solids. When the lime/silica ratio fell below 0·4—0·5, the *X*-ray patterns became indistinct. Samples having CaO/SiO_2 = 0·27 and 0·21 showed only the strongest spacing of 3·03 A., together with a weak diffuse band of about the same or rather greater spacing, while one having CaO/SiO_2 = 0·11 showed only the band.

Lime-rich solids. Samples A4 and A5, prepared from tricalcium silicate, had CaO/SiO_2 = 1·90 and 1·94, respectively, and gave identical *X*-ray patterns (Table III) which differed slightly from those of the samples of lower lime : silica ratio. The most easily recognisable differences were the increased intensity of the 2·80 A. line relative to that of 3·05 A. and the presence of a relatively strong line of 1·55 A. in place of that of 1·66 A.

TABLE III.

Spacing, A.	Intensity.	Spacing, A.	Intensity.	Spacing, A.	Intensity.
10·0	s	2·00	m	1·225	vw
3·05	s	1·80	ms	1·165	vw
2·80	s	1·71	vvw	1·1	vvw/d
2·40	w	1·61	vvw	1·045	vvw
2·20	vw	1·55	w	1·025	vvw
2·10	vw	1·39	vw	1·000	vvw

Attempts to prepare a product identical with these by other methods were not successful. Samples C6 and C7, obtained by double decomposition and having CaO/SiO_2 = 1·80 and 2·37, respectively, gave *X*-ray photographs showing the spacings observed for lower lime : silica ratios together with those of calcium hydroxide. A similar result was obtained when sample C5 (CaO/SiO_2 = 1·62) was treated with saturated calcium hydroxide. The periods of shaking before filtration lay between 7 and 14 days in these experiments; it is possible that more prolonged treatment would have yielded different results.

DISCUSSION.

Reproducibility of Phase Data.—The results given in Fig. 1 show that, although reproducibility is probably not of the order to be expected in the case of fully crystalline substances, it is sufficiently good to suggest that a close approximation to true equilibrium can be attained. This view was held by Bessey (*loc. cit.*) and by Roller and Ervin (*loc. cit.*) and is in accordance with the considerable degree of crystalline character shown by the powder photographs. It is therefore probable that the wider discrepancies, at least, among the earlier data, are due, not to the differing particle sizes or other colloidal properties, but to experimental errors. Of the 15 investigations discussed by Steinour (*loc. cit.*), four, those of Jolibois and Chassevent (*Compt. rend.*, 1929, **188**, 452), Beitlich (*loc. cit.*), Tavasci (*Ann. Chim. appl.*, 1938, **23**, 413), and Nacken and Mosebach (*Z. anorg. Chem.*, 1935, **223**, 161) gave results in particularly bad agreement with each other and with all the remainder. In the last two investigations the data were obtained from experiments in which tricalcium silicate was shaken with water, and Steinour (*loc. cit.*) has suggested that equilibrium may not have been obtained. This view receives support from the difficulties encountered in the present investigation both of ensuring complete decomposition of this compound and of demonstrating its absence in the product except by *X*-ray photographs, which were not used by the above workers. Beitlich used a silica gel containing 20% of water; experiments in the present investigation showed a silica gel as dry as this to react extremely slowly, and it seems probable, as Roller and Ervin (*loc. cit.*) have suggested, that here also equilibrium was not obtained. The reason for the anomalous results of Chassevent is not clear.

X-*Ray Data.*—(i) *Lime/silica ratios* 1·0—1·5. Comparison of the spacings given in Table II with those of calcium carbonate, calcium hydroxide, and silica (Hanawalt, Rinn, and Frevel, *Ind. Eng. Chem. Anal.*, 1938, **10**, 457; A.S.T.M. index) shows that they cannot be accounted for by the presence of any or all of these substances. The strongest spacing observed is almost identical with that of calcium carbonate, but the strong calcium carbonate doublet 1·92 and 1·86 A. was only seen in a sample (A1) which contained 7·5% of calcium carbonate and was then so much weaker than the 3·05 A. spacing that the latter could not possibly have been due in more than a small degree to carbonate. The spacings are therefore those of a hydrated silicate, calcium silicate hydrate (I). The number and definition of the spacings shows that this phase has a considerable degree of crystalline character. The phase-equilibrium data (Fig. 1) indicate a maximum lime : silica molar ratio of about 1·5 and a minimum value which is less rather than greater than 1·0.

Comparison of the *X*-ray data of calcium silicate hydrate (I) with those of previous investigators shows good agreement with the results of Brandenberger (*loc. cit.*) and especially of Stratling (*loc. cit.*), although a greater number of spacings has been recorded than by either of these investigators. On the other hand, Chassevent's data (*loc. cit.*) appear to be compatible with a mixture of calcium silicate hydrate (I) and calcium carbonate. Cirilli's data (*loc. cit.*) and especially those of Brocard (*loc. cit.*) are in less satisfactory agreement with the remainder and it has not been found possible to account for this. Unpublished data by Bessey (private communication) agree closely with the results of the present investigation. The longest spacing of 10—12·5 A. has not previously been reported and, as will be shown, it is probable that its occurrence and characteristics afford an important clue to the structure of the compound.

The preparation studied by McMurdie and Flint (*loc. cit.*) was made by the prolonged (10-year) action of water on β-dicalcium silicate and had the composition $3CaO,2SiO_2,1{\cdot}5H_2O$. The dissimilarity of its *X*-ray pattern to those of samples made and examined in much shorter periods of time may possibly indicate a very slow ageing process. Flint, McMurdie, and Wells (*J. Res. Nat. Bur. Stand.*, 1938, **21**, 617), who described the preparation of this sample, also carried out a similar experiment using tricalcium silicate as starting material and state that *X*-ray photographs showed the product to be crystalline, but do not quote any data.

The independence of the powder diagram of calcium silicate hydrate (I) with regard to lime : silica ratio indicates that lime in excess of about 1·0 mol. is held in some manner sufficiently random not to influence the diffraction pattern. Certain workers, notably Bessey (*loc. cit.*) and Cirilli (*Ric. sci.*, 1939, **10**, 459), have considered that solid solution occurs between CaO,SiO_2,aq. and $3CaO,2SiO_2$,aq. If this is so, the solution must be of such a kind, as was envisaged by Lafuma (*Rev. mat. Const. Trav. pub.*, 1931, **1**, 45), as would not affect the *X*-ray spacings or intensities. The data are, however, equally consistent with the possibly not widely differing view that the excess lime is held by adsorption.

The differences between the powder patterns of the products obtained from tricalcium silicate and the remainder are of a kind which indicates differing degrees of crystallisation rather than distinct compounds. This, together with the phase-equilibrium results, supports Bessey's view (*loc. cit.*) that the same compound is obtained by the three different methods of preparation. The most nearly crystalline product is obtained by the decomposition of tricalcium silicate; this may be because formation of the hydrate occurs more slowly than in the other methods, or because the mechanism of the reaction is of a different character.

A fourth method of preparation, which may be possible at room temperatures but has so far been effected only under hydrothermal conditions, consists in the hydrolysis of sodium calcium silicates. Thilo (250th Anniv. Lecture, German Acad. Sci., Berlin, 1950) obtained a product of composition CaH_2SiO_4 by treatment of $CaNa_2SiO_4$ with water at 180°. *X*-Ray examination, by the author, of a sample kindly supplied by Professor Thilo gave a powder photograph identical with that of sample B1 of calcium silicate hydrate (I).

Solids of low lime/silica ratio. The existence of additional compounds, poorer in lime than calcium silicate hydrate (I), has been assumed by several investigators, formulæ $CaO,2SiO_2$,aq., $3CaO,4SiO_2$,aq., and $4CaO,5SiO_2$,aq. having been suggested (Steinour, *loc. cit.*). The *X*-ray data obtained in the present investigation do not provide any positive support for this view since a sample having CaO/SiO_2 as low as 0·41 showed all the spacing of calcium silicate hydrate (I) down to 1·66 A. and no others. It is possible that a compound poorer in lime may exist which is so similar to calcium silicate hydrate (I) as to have been indistinguishable from it by this means, but the simplest explanation of the observed data is that products having CaO/SiO_2 below about 1·0 consist of calcium silicate hydrate (I) mixed with gelatinous silica. Roller and Ervin (*loc. cit.*) based their evidence for the existence of $3CaO,4SiO_2$,aq. mainly on the presence of a break in their phase-equilibrium curve; this could not be confirmed in the present investigation, although the results do not entirely exclude the possibility of its existence. Flint and Wells (*loc. cit.*) based their conclusions on a study of the liquid phase in which they assumed all the silica to be present in the form of simple ions. It seems equally probable, however, that the variation in silica concentration (Fig. 2) corresponding to a constant calcium hydroxide concentration of about 0·0014M. is due, as Baylis (*J. Physical Chem.*, 1928, **32**, 1236) and Krasil'nikov and Kiselev (*J. Physical Chem. U.S.S.R.*, 1944, **18**, 527) have supposed, to the presence of varying amounts of silica in colloidal form. If this interpretation is correct, the concentration of silica in true solution at the invariant point is most probably that found in equilibrium with a solid having CaO/SiO_2 approaching unity, *i.e.*, in the order of 0·00025M.

Solids of high lime : silica ratio. The *X*-ray powder data given in Table III for the products obtained from tricalcium silicate and having $CaO/SiO_2 \approx 2$ strongly resemble those found for lower lime : silica ratios and, like the latter, do not contain any spacings which can be due wholly to calcium carbonate or hydroxide. In order to ascertain the minimum amount of calcium hydroxide detectable in admixture with the hydrated silicate, mixtures of calcium silicate hydrate (I) with calcium hydroxide were prepared in the dry state. *X*-Ray powder photographs of these preparations showed that the strongest spacing of calcium hydroxide could just be distinguished when 0·1 mol. of $Ca(OH)_2$ per mol. of SiO_2 was present, while a very strong calcium hydroxide pattern was observed if 0·3 or more mols. were present. The data given in Table III therefore indicate the existence of a compound, calcium silicate hydrate (II), which has a composition approximating to $2CaO,SiO_2$,aq., and a structure probably very similar to, although distinct from, that of calcium silicate hydrate (I). The existence of such a compound was first suggested by Bessey (*loc. cit.*) on the basis of the observation, confirmed in the present investigation, that the phase-equilibrium curve (Fig. 1) rises sharply from $CaO/SiO_2 = 1·5$ to 2·0 at a concentration appreciably below the solubility of calcium hydroxide. The present results show, however, that even when calcium silicate hydrate (II) has not been formed and free calcium hydroxide is present, the concentration of the latter may be depressed. The reason for this is not clear; since the materials used had been prepared by double decomposition it may have been due to the presence of traces of alkali in the solution.

The failure of several attempts by the present author to prepare calcium silicate hydrate (II) may account for Cirilli's observation (*Ric. sci.*, 1939, **10**, 1042) that a preparation having $CaO/SiO_2 = 1·67$ showed in its *X*-ray pattern a considerable proportion of calcium hydroxide. On the other hand, Forsen (*loc. cit.*), in general agreement with the present results, quoted powder data for a solid of composition $2CaO,SiO_2,4H_2O$, prepared from tricalcium silicate, which do not appear to show the presence of any calcium hydroxide but which could be interpreted as indicating either calcium silicate hydrate (I) or (II), mixed probably with some calcium carbonate.

Since the aqueous treatment used to produce the calcium silicate hydrate (II) samples in the present investigation was prolonged (5 months in the case of A5), it appears probable that this phase exists in equilibrium with calcium hydroxide solutions more concentrated than about 0·020M. and that the mixtures of calcium silicate hydrate (I) with excess of calcium hydroxide represent an unstable though somewhat persistent condition. It is, however, also possible that calcium silicate hydrate (II) is a metastable product peculiar to the decomposition of tricalcium silicate.

It has not yet been established whether any formation of solid solutions with phase (I) or other variation in composition of calcium silicate hydrate (II) is possible. There is, however, some evidence that its maximum value of CaO/SiO_2 cannot greatly exceed 2·0 and that it certainly lies well below 3·0. Numerous optical investigations, quoted by Steinour (*loc. cit.*) have shown that, whereas β-dicalcium silicate hydrates in a limited amount of water with the formation of barely enough calcium hydroxide to saturate the solution, yet tricalcium silicate yields under these conditions a hydrated silicate together with a considerable quantity of solid calcium hydroxide. Attempts to determine the latter quantitively have proved difficult, but values between 0·6 and 1·0 mol. of hydroxide per mol. of tricalcium silicate have usually been obtained (Steinour, *loc. cit.*). This suggests that the maximum lime : silica ratio of the hydrated product lies between 2·0 and 2·4.

The behaviour of β-dicalcium silicate in the above experiments strongly supports the view that a hydrated dicalcium silicate can be formed at room temperature. It cannot easily be accounted for if, as has sometimes been supposed, the hydrated compound does not have a lime : silica molar ratio exceeding 1·5.

A Tentative Interpretation of the X-*Ray Data of Calcium Silicate Hydrate* (I).—Although the present data do not permit of any complete interpretation, certain facts appear significant. The spacings given in Table I can be divided into those which are in all cases relatively sharp, and of consistent spacing and intensity, and those which vary in one or more of these respects. All those of the first category can be accounted for on the assumption that they are the $hk0$ spacings of a *c*-face centred unit cell having a and b axes of 5·60 and 3·60 A., respectively, the angle between these axes being 90°; moreover, all the $hk0$ spacings possible for such a cell, *i.e.*, those for which $(h + k)$ is even, are actually observed down to the shortest ones visible. Although the agreement may be fortuitous, it is sufficiently striking to suggest that the true unit cell spacings at least bear some simple relation to those postulated.

The facts that the remaining spacings are few in number, and sometimes more diffuse than the above, and that the longest observed spacing in particular can vary independently of the remainder, are reminiscent of the behaviour of the clay minerals (Hofmann, Endell, and Wilm, *Z. Krist.*, 1933, **86**, 340; Nagelschmidt, *ibid.*, 1936, **93**, 481), and could possibly admit of a somewhat similar explanation. It seems possible that calcium silicate hydrate (I) has a layer structure in which the individual layers, in the plane of the a and b axes, are relatively well crystallised, while the distances between them represented by the 10—12·5 A. spacing are less rigidly defined. Such a structure might also account for the ability of the lattice to accommodate varying amounts of lime without fundamental change. The postulated a and b axes, however, differ from those found in the clay minerals, and it is probable that on account of its greater ionic radius, calcium is unable to replace the magnesium or aluminium of the latter, without bringing about a considerable change in the structure of the silicate layer. Comparison of the postulated spacings with the unit cell of calcium hydroxide (hexagonal; $a = 3{\cdot}584$, $c = 4{\cdot}896$ A.; Bunn, Clark, and Clifford, *Proc. Roy. Soc.*, 1935, *A*, **151**, 141) suggests that distorted calcium hydroxide layers may be present in calcium silicate hydrate (I). The data are, however, inadequate for a definite conclusion.

Further investigations on the rôle of the water in calcium silicate hydrates, and on the influence of temperature on the phase equilibria, are in progress.

EXPERIMENTAL.

Considerable care must always be taken in the preparation and subsequent handling of hydrated calcium silicates to minimise contamination by atmospheric carbon dioxide. This can be achieved by suitable design of apparatus. The use of glass vessels has been found undesirable whenever prolonged treatment with aqueous solutions is required (Bessey, *loc. cit.*; Thorvaldson, *loc. cit.*, p. 218), and metal or other inert vessels are to be preferred.

Preparative Methods.—(i) *Decomposition of anhydrous tricalcium silicate.* 2—5-G. portions of tricalcium silicate (90% passed through a 170-mesh sieve) were shaken at 17° for 3—5 weeks with 250 ml. of carbon dioxide-free water in stainless-steel vessels of 350-ml. capacity, having caps lined with polyvinyl chloride. By use of a rubber bung fitted with a pipette and a soda-lime tube, 100 ml. of the solution were then removed and filtered, and portions titrated with acid. 100 Ml. of carbon dioxide-free water were added to replace the solution removed, and shaking was resumed. This procedure was repeated at 3—14-day intervals until the total amount of lime removed or in solution indicated that the lime : silica ratio of the solid had fallen to the desired value. A total period of shaking of at least 6 weeks was found necessary to effect complete decomposition of the tricalcium silicate as shown by subsequent *X*-ray analysis and behaviour in phase-equilibrium experiments. The solid was then filtered off by means of a Buchner funnel suitably fitted with a cover and inlet tube reaching into the reaction vessel to prevent atmospheric contamination, and washed with 50% acetone followed by pure acetone, ether, and finally carbon dioxide-free air until all the ether had been removed. The final concentration of calcium hydroxide in the solution was determined.

(ii) *Reaction of calcium hydroxide solution with silica gel.* The silica gel (S1) was supplied by The British Drug Houses Ltd., and had the following composition: SiO_2, 23·69; ignition loss, 75·80; Na_2O, 0·27; K_2O, 0·07; CaO + MgO, nil; Fe_2O_3, 0·01; Al_2O_3, 0·14; TiO_2, 0·015%. The same apparatus as above being used, 1·21 g. were shaken with 250 ml. of calcium hydroxide solution of initial concentration 1·245 g./l. (of CaO) for 45 days. The product was isolated as above.

(iii) *Double decomposition of calcium nitrate with sodium silicate.* Klasse and Kuhl (*Zement*, 1928, **17**, 2, 49) and Bessey (*loc. cit.*) showed that, provided sufficient calcium nitrate was added, the lime : silica ratio of the precipitate was dependent on the ratio of Na_2O to SiO_2 in the sodium silicate solution. 0·05—0·1 Mol. of the above silica gel was therefore dissolved in amounts of N- or 2N-sodium hydroxide indicated by Klasse and Kuhl's data and treated with 0·2—0·4 mol. of calcium nitrate. The lime : silica ratios of the products were usually in approximate agreement with those obtained by Klasse and Kuhl although anomalous results were sometimes obtained for reasons which have not been fully investigated.

The apparatus consisted of a 1-l. bolt-head flask fitted with tap-funnel, mercury-seal stirrer, inlet tube for carbon dioxide-free air and outlet tube reaching to the bottom of the flask which led to a Buchner funnel fitted with an air-tight cover. The silica gel (S1) was first placed in the flask and carbon dioxide-free air drawn through the apparatus for 30 minutes. Suction was discontinued, and the sodium hydroxide added from the tap-funnel, followed by a little carbon dioxide-free water to wash the latter. The silica gel was dissolved by stirring, aided if necessary by gentle warming. The flask was then cooled to room temperature, and the calcium nitrate, dissolved in 200 ml. of carbon dioxide-free water, was added. Stirring was continued for one hour, and the solid was then filtered off by reapplying suction to the Buchner flask. The precipitate was washed on the filter with 4—5 l. of calcium hydroxide solution which had itself been filtered directly into the tap-funnel to remove any carbonate present; this quantity was found sufficient to remove nitrate and all but a trace of sodium ions. The concentration of the washing solution varied from 0·1 g./l. (of CaO) in the case of precipitates of low lime : silica ratio to 1·10 g./l. when the predicted molar ratio was 1·5 or above. Washing was completed with 50% acetone, pure acetone, and carbon dioxide-free air, and the product was removed from the funnel and a portion analysed. The remainder was shaken for 7—14 days with calcium hydroxide solution of a concentration with which Bessey's data (*loc. cit.*) showed it to be in equilibrium, the same apparatus and method of isolation being used as for methods (i) and (ii). This treatment was carried out because the precipitate had been formed in a solution containing excess of calcium nitrate and sodium hydroxide. In view of the sensitivity of the composition of the solid to that of the solution it seemed advisable to bring it approximately into equilibrium with a pure calcium hydroxide solution before it was used in subsequent experiments.

Carbon dioxide was determined in the above preparations by Jones's method (*J. Soc. Chem. Ind.*, 1940, **51**, 29).

Investigation of Phase Equilibria.—100—300-Mg. portions of the initial solids were shaken continuously with 25 ml. of water or calcium hydroxide solutions in vessels of 40-ml. capacity at 17—20°. Some of the vessels were of brass, plated internally with silver, and others of polystyrene, the caps being lined in each case with polyvinyl chloride. No variations in the results could be traced to changes in the type of vessel or in temperature within the limits stated. After shaking, the solid was filtered off by using an apparatus designed to suck the liquid out of the vessel through a No. 4 sintered-glass filter into a receiving vessel, an inlet tube for carbon dioxide-free air being provided. Lime in the filtrate was determined by titration of 10-ml. portions with 0·1N-hydrochloric acid, a methyl-red–methylene-blue indicator being used. Silica, where significant, was determined colorimetrically as ammonium silicomolybdate on 1—10-ml. portions by means of a Hilger " Spekker " photoelectric colorimeter which was calibrated by using sodium silicate solutions of known concentration.

X-*Ray Apparatus.*—Copper-$K\alpha$ radiation was obtained, either sealed high vacuum or gas *X*-ray tubes being used with a nickel filter in contact with the film. Some photographs were taken by means of a 9-cm. powder camera, but the backgrounds were heavy in relation to the more diffuse lines, and much better results were obtained with 6-cm. cameras designed for single-crystal work, the specimen being mounted either on a glass fibre or in a mica cell. This had walls 0·0005 in. thick and 0·01 in. apart. It gave particularly clear backgrounds in the 3—10 A. region since no amorphous matter was present, and the characteristic spots and Laue streaks due to the mica could easily be distinguished, but was unsuitable for the investigation of spacings (using copper radiation) shorter than about 1·6 A. In all cases, exposures of 24—48 hours were necessary to bring out the weaker lines.

Spacings were usually determined by direct measurement on the film, and intensities estimated visually. In a few cases this was supplemented by using a Hilger non-recording microphotometer.

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