STUDY OF THE SYSTEM CaO–SiO₂–H₂O AT 30 C AND OF THE REACTION OF WATER ON THE ANHYDROUS CALCIUM SILICATES

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ABSTRACT

A graph has been prepared representing the solubility of silica at 30 C in solutions containing increasing concentrations of lime up to saturation, the solutions being in "equilibrium" with solid phases composed of hydrated combinations of lime and silica. An electrometric and analytical study of both supersaturated and unsaturated solutions of silica at definite concentrations of lime, when correlated with these equilibrium solubility relationships, indicates the existence of definite compounds in the system $CaO-SiO_2-H_2O$ which may be the hydrated calcium salts of orthosilicic acid. Experimental values were obtained for the hydrolysis constants of these salts from which ionization constants for the four steps in the dissociation of orthosilicic acid were calculated. A study of the reaction of water upon the anhydrous calcium silicates ($CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, $\gamma-2CaO \cdot SiO_2$, $\beta-2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$) showed that the products formed depend upon the equilibrium relationships of the system $CaO-SiO_2-H_2O$. Of these compounds all but monocalcium silicate ($CaO \cdot SiO_2$) form solutions which precipitate hydrated calcium silicate on standing. Application of the same methods to a study of the reaction of water upon a portland cement indicated that hydrated calcium orthosilicate is formed during the hydration of portland cement. A study of the reaction between diatomaceous silica and lime solution and between silica gel and lime solution is also included.

CONTENTS

I. INTRODUCTION

An experimental study of the system lime-silica-water should possess considerable practical value not only for its direct bearing upon the problem of the setting of portland cement and hydraulic mortars but also for possible applications in fields of geology, soil equilibria, and water purification. In this report the relationship of the system to products formed by the reaction of portland cement with water will be especially considered.

Unfortunately it proved impossible to utilize petrographic methods in this study, owing to the apparently amorphous character of the solid phases formed by reactions between lime, silica, and water at room temperature. Hence the evidence obtained for the existence of definite compounds in the solid phases is indirect. Although it is realized that the state of combination of lime and silica in solution does not necessarily bear a direct relation to that in the solid phase, yet often changes which occur in the aqueous phase are of aid in interpreting changes which may take place in the solid phase. Accordingly, an investigation was made of the composition of lime-silica solutions to obtain as much indirect evidence as possible as to the probable composition of the solid phases with which these solutions might exist in equilibrium.

The term equilibrium will be used for the purpose of this paper to designate an apparently steady state between solid phase and solution, the composition of neither undergoing appreciable change in time periods of from several weeks to several months. It is recognized that this equilibrium may be displaced by the eventual crystallization of the solid phase, a process which, however, appears to proceed exceedingly slowly at room temperature.

The first part of this paper deals with the solubility relationships of lime and silica, and presents correlations between the compositions of hydrated solid phases and of solutions with which they may exist in equilibrium, and with the state of combination of lime and silica in these solutions as determined electrometrically.

The paper next considers the reaction of water upon compounds occurring in the binary system, lime-silica, in the light of the foregoing study. These compounds have the following molecular proportions:[1] $CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, $2CaO \cdot SiO_2$, and $3CaO \cdot SiO_2$. Tricalcium silicate ($3CaO \cdot SiO_2$) and dicalcium silicate in its beta modification ($\beta-2CaO \cdot SiO_2$) are the major constituents of portland cement,[2] in which the gamma form of dicalcium silicate ($\gamma-2CaO \cdot SiO_2$) also appears occasionally. It will be shown that the generalization of Le Chatelier[3] that hydraulic materials possess metastable solubilities, applies to the calcium silicates occurring in portland cement.

Finally the reactions of diatomaceous silica and of silica gel with lime in solution are compared and the relationship of the results to the system $CaO-SiO_2-H_2O$ is discussed briefly.

[1] A. L. Day, E. S. Shepherd, and F. E. Wright, The lime-silica series of minerals, Am. Jour. Sci., series 4 vol. 22, p. 265, 1906.

[2] G. A. Rankin, A study of the constitution of portland cement clinker, Jour. Ind. Eng. Chem., vol. 3, pp. 211–227, 1911; P. H. Bates, The constitution of portland cement, Concrete and Cement Age (Cement Mill Section) vol. 2, pp. 3–4, 1913; G. A. Rankin and F. E. Wright, The ternary system $CaO-Al_2O_3-SiO_2$, Am. Jour. Sci., series 4, vol. 39, pp. 1–79, 1915.

[3] H. Le Chatelier, Recherches Expérimentales sur la Constitution des Mortiers Hydrauliques, Thèse, Paris, 1887. English translation also prepared by J. L. Mack, New York, 1905.

II. PRELIMINARY STUDY OF THE SYSTEM CaO–SiO$_2$–H$_2$O AT 30 C

1. PREPARATION OF MATERIALS

Colloidal silica gel is probably the most reactive form of silica, but is difficult to prepare in the pure state. In this study, commercial granular silica gel, ground to pass a no. 200 sieve, and purified according to the method of Bennett,[4] was used. This method of purification involved boiling with concentrated nitric acid followed by repeated washing and subsequent electrolysis in distilled water with continuous removal of the solution at the electrodes. No nitric acid could be detected by qualitative tests in silica purified by the above method and used in this investigation. It had a nonvolatile residue of 0.02 percent, based on the weight of the ignited silica.

Distilled water for the solutions was freed from carbon dioxide by boiling and subsequently cooling in a stream of CO$_2$-free air. The preparation of calcium hydroxide solutions has been described previously.[5]

2. METHOD OF PROCEDURE

Preliminary experiments showed that silica gel dissolves slowly in dilute calcium hydroxide solutions at 30 C, but that increase of temperature had a marked effect upon its solubility and rate of solution. Thus, boiling an excess of purified silica gel with dilute solutions of calcium hydroxide for several days produced solutions generally containing 0.4 to 0.5 g SiO$_2$ and 0.02 to 0.05 g of CaO per liter. Although these solutions were perfectly clear on filtering at the boiling point, they gradually assumed a light-blue color on cooling to room temperature. Evidently this is due to a decreased solubility of silica at the lower temperature which results in the separation of a portion of the silica in the form of a colloidal sol. Such sols are very stable and may stand for months at room temperature with only very slight alteration in composition or appearance.

However, it was found that precipitation of the colloidal silica could be effected quite readily by the addition of a small quantity of saturated calcium hydroxide solution. The precipitated silica was then easily removed by filtration. Although the initial sol-containing solutions when examined under the ultra microscope were seen to contain myriads of particles in Brownian movement, no trace of such movement could be detected in the clear solutions after precipitation. It was assumed, therefore, that the latter were true solutions saturated with respect to silica at definite concentrations of calcium hydroxide.

To investigate further the solubility relationships of silica and lime, a large quantity of the sol-containing solution was prepared, care being taken to avoid contamination by carbon dioxide of the air. The composition of this solution corresponds to point A in figure 1.

This solution was then mixed in various proportions with a calcium hydroxide solution of the composition represented by point B, figure 1. Great care was taken to measure out the volume of these solutions accurately and to exclude CO$_2$ so that the initial compositions of the

[4] Personal communication from Prof. E. Emmet Reid.
[5] E. P. Flint and Lansing S. Wells, The activity coefficients of hydroxyl ion in solutions of calcium hydroxide at 30 C, B. S. Jour. Research, vol. 11 (RP584), pp. 163–171, 1933.

resultant mixtures, represented by points on the diagonal AB, might be accurately known.

The mixtures, in well-stoppered flasks, were placed directly in an air thermostat [6] maintained at $30 \pm 0.05°$ C. Rapid separation of a part of the lime and silica in the form of voluminous flocculent precipitates occurred as the solutions changed from unstable states to conditions more nearly approaching equilibrium. After 1 month the solutions were filtered from the precipitates and were analyzed for silica and lime, using 400 to 700 ml samples. Silica was determined by double dehydration, ignition to constant weight followed by volatilization with hydrofluoric acid and reignition to constant weight. Lime was precipitated as calcium oxalate and ignited to constant weight as the oxide. All evaporations and ignitions were made in platinum.

The proportions of lime to silica in the precipitates were obtained from the differences between the compositions of the solutions before and after precipitation. This method seemed preferable to direct analysis of the solid phases due to the difficulty of obtaining representative samples of these precipitated materials, part of which adhered quite firmly to the interiors of the flasks. It also avoids uncertainties involved in the washing of these bulky precipitates with alcohol and ether which may further precipitate lime and silica from the mother liquor retained after filtration and thus alter their composition. Control experiments showed that no appreciable quantity of lime was taken up by the glass in the time period used.

3. DISCUSSION OF RESULTS

The results are illustrated by figure 1, where the curve CDEFB represents the solubility of silica in solutions containing increasing concentrations of lime. The initial compositions of the unstable lime-silica solutions are represented by points on the diagonal AB. Broken lines from these points to points on the curve CDEFB connect the initial and final compositions. The figures accompanying these lines give the molar ratios of lime to silica in the precipitated material calculated from the differences between the initial and final compositions of the solutions.

The concentration of silica in the clear saturated solutions at first rises sharply from C to a maximum at D and then decreases as the concentration of lime increases. At the point E the direction of the solubility curve changes. From E the concentration of lime diminishes to a minimum at F where there is again a change in the direction of the solubility curve. Subsequently, as the concentration of lime increases from its minimum value at F to the value at B, the amount of silica in solution decreases to very low values.

Table 1 contains part of the data from which figure 1 was constructed.

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[6] For description see Lansing S. Wells, Reaction of Water on Calcium Aluminates, B.S. Jour. Research, vol. 1 (RP34), p. 954, 1928.

TABLE 1.—*Compositions of equilibrium solutions and molar ratios of lime to silica in precipitates which separated from unstable lime-silica solutions of initial compositions lying on AB in figure 1*

1	2	3	4	5	1	2	3	4	5
	Composition of solutions		Molar ratio of CaO/SiO$_2$			Composition of solutions		Molar ratio of CaO/SiO$_2$	
Number					Number				
	CaO	SiO$_2$	In solution	In precipitate		CaO	SiO$_2$	In solution	In precipitate
	g/l	*g/l*				*g/l*	*g/l*		
1	0.0273	0.1771	[a] 0.17	0.040	8	.0943	.2208	.48	.422
2	.0304	.1836	.18	.049	9	.1015	.2062	[c] .53	.537
3	.0380	.2340	.17		10	.0741	.1639	.46	.930
4	.0431	.2790	.17	.061	11	.0590	.1198	.53	.997
5	.0702	.3260	[b] .23	.103	12	.0482	.0760	[d] .68	1.03
6	.0852	.3068	.30	.217	13	.0493	.0465	1.14	1.07
7	.0954	.2610	.39	.293					

[a] C. fig. 1.   [b] D, fig. 1.   [c] E, fig. 1.   [d] F, fig. 1.
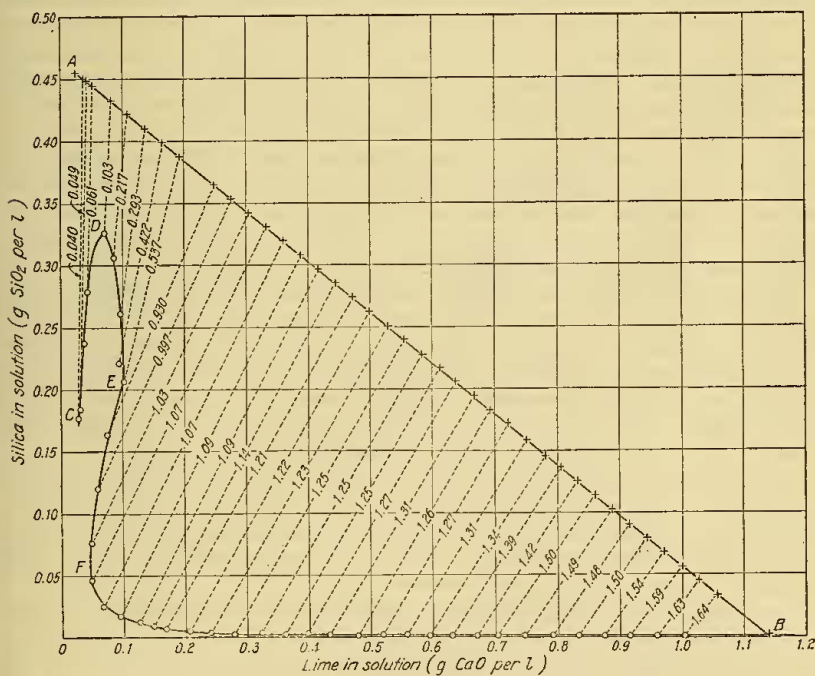
FIGURE 1.—*Showing the quantity of silica at 30 C in solutions of increasing lime concentration which are saturated with respect to hydrated solid phases containing lime and silica in the molar proportions shown.*

It will be shown later by an electrometric method that of the total lime in solution in the region of the curve CDEF a relatively small proportion is uncombined and that the molar ratios in column 4 very nearly represent the actual state of combination in solution. Thus, molar ratios between 0 and 0.5 may represent equilibria between hydrated silica and a calcium silicate containing lime and silica in the

molar proportion $1CaO:2SiO_2$. Molar ratios between 0.5 and 1 may represent equilibria between two calcium silicates of molar proportions $1CaO:2SiO_2$ and $1CaO:1SiO_2$. This possibility will be considered in detail in the following section.

The solid phases in equilibrium with solutions along the curve CD contain only a few hundredths of a mol of lime per mol of silica (table 1, column 5) and may consist, therefore, of hydrated silica with a small amount of adsorbed lime. Along the curve EF the molar ratio of lime to silica in the solid phases is unity within the experimental accuracy. In the intermediate region along DE the molar ratios vary between 0.2 and 0.5, but for reasons which will become apparent, it is believed that the true molar ratio in this region may be 0.5. To verify this supposition two additional compositions were prepared in the vicinity of solutions nos. 6 and 7 of table 1 and these precipitated materials of CaO/SiO_2 molar ratios of 0.39 and 0.48, respectively, in somewhat better agreement with the theory.

It should be noted here that the initial compositions along the diagonal AB were not all prepared at the same time nor from the same initial solutions, A and B, but were actually prepared from four different sets of initial solutions, the compositions of the mixtures being adjusted by addition of water so as to fall at regular intervals on the line AB. The consistency and duplicability of the results was such as to furnish good evidence that the curve CDEFB represents equilibrium conditions as defined in the introduction.

It was also found that when precipitation was carried out at boiling temperature and the precipitate allowed to stand in contact with the solution for several weeks that the composition of the final solution would be represented by a point on the curve CDEFB, thus giving further evidence that equilibrium had been established.

Tentatively, on the basis of the molar ratios of the solid phases, the segment CD of the curve may be assumed to represent the compositions of solutions saturated with respect to the solid phase, hydrated silica, at increasing concentrations of lime; DE may represent the compositions of solutions saturated with respect to a calcium silicate of the molar ratio $1CaO:2SiO_2$; EF may represent saturation with respect to a calcium silicate of the molar ratio $1CaO:1SiO_2$.

As previously mentioned, a difficulty presents itself in the variable molar ratios in the solid phases along DE. According to the phase rule only one solid phase may exist in equilibrium with these solutions under the prevailing conditions, whereas the molar ratios indicate that mixtures of two solid phases, hydrated silica and 1:2 calcium silicate, are present. The most probable explanation of this anomaly appears to be that two phases were precipitated together from the original sol-containing solution and that insufficient time was allowed for the system to approach a steady state which would have resulted in the transformation of the hydrated silica into calcium silicate. Experiments showed that re-solution of precipitates consisting of hydrated silica does not readily take place even at boiling temperature, hence it is to be expected that the reaction of solid hydrated silica with lime in solution to give solid calcium silicate would be a slow process. It is therefore believed that the curve DE represents the compositions of solutions saturated with respect to the 1:2 calcium silicate, although the steady state previously defined as equilibrium in the solid phase had not been attained.

The highest molar ratio of lime to silica in the solid phase indicated in figure 1 is 1.64. When a small volume of silica solution was mixed with a large volume of saturated lime solution, precipitates containing higher molar ratios of lime to silica were obtained. They were filtered off, washed with alcohol and ether, and analyzed. At lime concentrations of 1.052 and 1.159 g of CaO per liter, the molar ratios of lime to silica in the precipitates were 1.79 and 1.85, respectively. Thus it appears that the molar ratio $2CaO:1SiO_2$ is approached when the solid phase is in equilibrium with saturated lime solution.

These hydrated calcium silicate precipitates were found to set to a hard mass after drying between filter paper and in a desiccator. A similar observation has been made by Michaelis [7] and forms the basis of his "inner desiccation" theory for the hardening of portland cement. The mechanism of the formation of precipitates of entirely similar properties from metastable solutions of the anhydrous calcium silicates will be considered later in this paper. It will be shown there that Le Chatelier's theory of the metastable solubility of hydraulic materials is a necessary complement of Michaelis' theory of hydraulic hardening.

A number of previous investigators have prepared hydrated calcium silicates to which they have assigned formulas on the basis of analytical evidence. Le Chatelier,[8] from experiments on the reaction between hydrated silica and lime solution, concluded that the composition $CaO \cdot SiO_2 \cdot 2\ 1/2H_2O$ represents a definite compound and that higher molar ratios of lime to silica result from the adsorption of lime by this compound. Jordis and Kanter,[9] by similar means, obtained a product corresponding in composition to the formula $CaO \cdot SiO_2 \cdot H_2O$. Klassee [10] likewise prepared a hydrated calcium silicate having the molar ratio $CaO/SiO_2 = 1$ by the reaction: $Na_2SiO_3 + Ca\ (NO_3)_2 \rightarrow 2NaNO_3 + CaSiO_3$. He also obtained a hydrated silicate in which the molar proportion CaO/SiO_2 was equivalent to 3:2 by substituting sodium orthosilicate for sodium metasilicate. On shaking the resulting calcium silicate with saturated calcium hydroxide solution, the molar proportion of lime to silica increased to 1.8. From these experiments Klassee postulated the existence of hydrated 1:1, 3:2, and 2:1 calcium silicates.

Also, a number of crystalline hydrated calcium silicates containing lime and silica in the molar ratios, 1:2, 1:1, 3:2, and 2:1, occur in nature as rare minerals.[11]

III. CONSTITUTION OF CALCIUM SILICATE SOLUTIONS

1. THE COMBINATION OF LIME AND SILICA IN CALCIUM SILICATE SOLUTIONS

This portion of the investigation deals with a study of the equilibria existing in lime-silica solutions and the bearing of these equilibria upon the composition of solid phases which occur in the system CaO–SiO$_2$–H$_2$O. The assumption is made throughout that silica can exist in solution as a definite crystalloidal silicic acid capable of

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[7] W. Michaelis, Recognition of Hydraulic Cements, Frot. Ver. D.P.C.F., 1909.
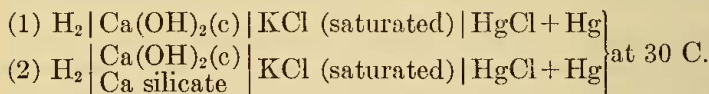[8] See footnote 3, p. 752.
[9] E. Jordis and E. H. Kanter, Contributions to the Knowledge of the Silicates, I, Z. anorg. Chem., vol. 35, p. 82, 1903.
[10] F. Klassee, Attempts to Prepare Calcium Hydrosilicates, Zement, vol. 17, p. 48, 1928.
[11] V. A. Vigfusson, The Hydrated Calcium Silicates, Am. Jour. Sci., vol. 21, pp. 67–78, 1931.

forming salts with calcium hydroxide. Justification for this view is furnished not only by the consistent interpretation which it gives to the observed data, but also by the work of previous investigators, including: (a) The construction of titration curves characteristic of a weak acid and the derivation of ionization constants therefrom,[12] (b) molecular weight determinations by freezing point lowering,[13] (c) preparation of organic derivatives of silicic acid such as ethyl orthosilicate,[14] (d) the crystallization of definite silicates from solution,[15] (e) measurements of conductivity of silicate solutions which indicate the presence of definite compounds therein,[16] (f) assignment of transference numbers to silicate ions,[17] and (g) diffusion experiments.[18]

As all lime-silica solutions prepared in this study were alkaline it was assumed that they contained mixtures of calcium hydroxide and calcium silicate formed by the partial or complete neutralization of silicic acid. The extent of combination between lime and silica in such silicate solutions was determined by electrometric measurements upon the cells:

(1) $H_2 \mid Ca(OH)_2(c) \mid KCl$ (saturated) $\mid HgCl + Hg$

(2) $H_2 \left| \begin{array}{c} Ca(OH)_2(c) \\ Ca\ silicate \end{array} \right| KCl$ (saturated) $\mid HgCl + Hg$ at 30 C.

The type of hydrogen electrodes and calomel half cell used and other details have been reported previously.[19]

The potentials of cells (1) and (2) should be identical when the concentration, $Ca(OH)_2(c)$, in the two cells is the same, assuming that the alteration of the potential of the liquid junction, $Ca(OH)_2$ (c) $\mid KCl$ (saturated), caused by the presence of calcium silicate, is negligible. With cell (1) the relationship between potential and calcium hydroxide concentration may be determined by direct measurements. Knowing this relationship the concentration of uncombined calcium hydroxide in calcium silicate solutions may readily be obtained from electrometric measurements. The difference between the total dissolved lime and that present as uncombined calcium hydroxide must represent lime combined as calcium silicate.

To determine the concentration of uncombined calcium hydroxide corresponding to a given electromotive force, measurements of the potentials of cell (1) were made for various concentrations of calcium hydroxide. Table 2 gives the data obtained. The pH values given in this and subsequent tables were calculated from a formula used in a previous electrometric study of solutions derived from the calcium

[12] A. F. Joseph and H. B. Oakley, The Action of Silica on Electrolytes, Jour. Chem. Soc., vol. 127, pp. 2813–2818, 1925; H.T.S. Britton, Electrometric Study of the Precipitation of Silicates, Jour. Chem. Soc., pp. 425–436, 1927; R. W. Harman, Aqueous Solutions of Sodium Silicates, VII, Jour. Phys. Chem., vol. 31, pp. 616–625, 1925; W. D. Treadwell and W. Wieland, The Hydrates of Silicic Acid, Helv. Chim. Acta, vol. 13, pp. 842–864, 1930.

[13] R. Willstätter, H. Kraut, and K. Lobinger, The Simplest Silicic Acids, Ber., 61B, pp. 2280–2293, 1928.

[14] A. W. Dearing and E. E. Reid, Alkyl Orthosilicates, Jour. Am. Chem. Soc., vol. 50, pp. 3058–3062, 1928.

[15] K. A. Vesterberg, $Na_2SiO_3 \cdot 9H_2O$, A Well-Defined Crystalline Sodium Silicate, Zs. anorg. Chem., vol. 88, 341–348, 1914; G. W. Morey, New Crystalline Silicates of Potassium and Sodium, Their Preparation and General Properties, Jour. Am. Chem. Soc., vol. 36, pp. 215–230, 1914.

[16] F. Kohlrausch, Solutions of Sodium Silicates, Zs. Physik. Chem., vol. 12, pp. 773–791, 1893; R. W. Harman, Aqueous Solutions of the Sodium Silicates, 1, Jour. Phys. Chem., vol. 29, pp. 1155–1168, 1925.

[17] R. W. Harman, Aqueous Solutions of the Sodium Silicates, II, Jour. Phys. Chem., vol. 30, pp. 359–368, 1926.

[18] P. B. Ganguly, Diffusion of Aqueous Sodium Silicate Solutions Across Semipermeable Membranes, Jour. Phys. Chem., vol. 31, pp. 407–416, 1927.

[19] See footnote 5, p. 753.

aluminates, $pH = \dfrac{emf \ (observed) - 0.2437}{0.06011}$, in order to preserve uniformity with that investigation.[20] This formula neglects liquid junction potentials and the values of pH are inserted merely for comparative purposes and to indicate the range covered.

TABLE 2.—*Electromotive force measurements upon the cell,* $H_2|Ca(OH)_2(c)|KCl$ *(saturated)*$|HgCl + Hg$ *at 30 C, and the* pH *of calcium hydroxide solutions calculated therefrom*

1	2	3	4	1	2	3	4
No.	$Ca(OH)_2$ concentration	emf	pH [a]	No.	$Ca(OH)_2$ concentration	emf	pH [a]
	$g\ CaO/l$	v			$g\ CaO/l$	v	
1	0.00083	0.78896	9.07	11	0.4002	0.95582	11.85
2	.00169	.81446	9.50	12	.4987	.96106	11.94
3	.00314	.83278	9.80	13	.5983	.96502	12.00
4	.00631	.85156	10.11	14	.6988	.9686	12.06
5	.0124	.87102	10.44	15	.8004	.9720	12.12
6	.0248	.88796	10.72	16	.8997	.9745	12.16
7	.0500	.90621	11.02	17	.9995	.97677	12.20
8	.1024	.92346	11.31	18	1.092	.9790	12.23
9	.2004	.93925	11.57	19	1.199	.9810	12.26
10	.2980	.94888	11.73				

[a] Calculated from relationship, $pH = \dfrac{emf(observed) - 0.2437}{0.06011}$.

In correlating data obtained by measurements upon cells of type (2) it was first assumed that lime and silica were combined in solution as monocalcium silicate (the calcium salt of metasilicic acid) and that only the calcium hydroxide in excess of this compound contributed to the potential of the cell. Figure 2 compares potential measurements made upon cell (1) with potential measurements made upon cell (2) for solutions derived from various sources and containing varying amounts of lime and silica and in which the lime present as calcium hydroxide is computed as that in excess of monocalcium silicate. A portion of the data for calcium silicate solutions contained in this figure will be presented in subsequent tables.

Inspection of figure 2 shows that if only a small amount of lime is present in excess of that required to form monocalcium silicate the emf of cell (2) is greater than that corresponding to the excess lime. Hence less lime must be combined with silica than is required by the molar ratio $1CaO:1SiO_2$. At higher concentrations of lime in excess of $CaO \cdot SiO_2$ the relationship is more closely fulfilled. With increasing concentration of calcium hydroxide the emf of cell (2) is less than that corresponding to lime in excess of monocalcium silicate, hence more lime must be combined with silica than corresponds to the ratio $1CaO:1SiO_2$.

A survey of the compositions of these calcium silicate solutions and of the emf data showed that: (1) Lime and silica in solution may be combined in a molar ratio of less than $1CaO:1SiO_2$, when the concentration of lime is low and that of silica relatively high; (2) the molar ratio of combined lime to silica may be greater than $1CaO:1SiO_2$ when the concentration of lime is high compared to the concentration

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[20] See footnote 6, p. 754.

of silica; (3) the molar ratio may equal $1CaO:1SiO_2$ in an intermediate region. It was shown in the previous section that the solid phases which precipitate from such solutions or are in equilibrium with them increase in lime content from a molar ratio of $0.04CaO:1SiO_2$ at the lowest lime concentration studied (0.0273 g CaO per l) to a molar ratio approaching $2CaO:1SiO_2$ when in contact with saturated lime solution.

Consideration of these facts led to the assumption that the calcium silicates present in the system $CaO-SiO_2-H_2O$ at 30 C are salts not of metasilicic acid but of orthosilicic acid (H_4SiO_4) of which four are possible: $Ca(H_3SiO_4)_2$, CaH_2SiO_4, $Ca_3(HSiO_4)_2$, and Ca_2SiO_4, in which the molar ratios of lime to silica are 1:2, 1:1, 3:2, and 2:1.
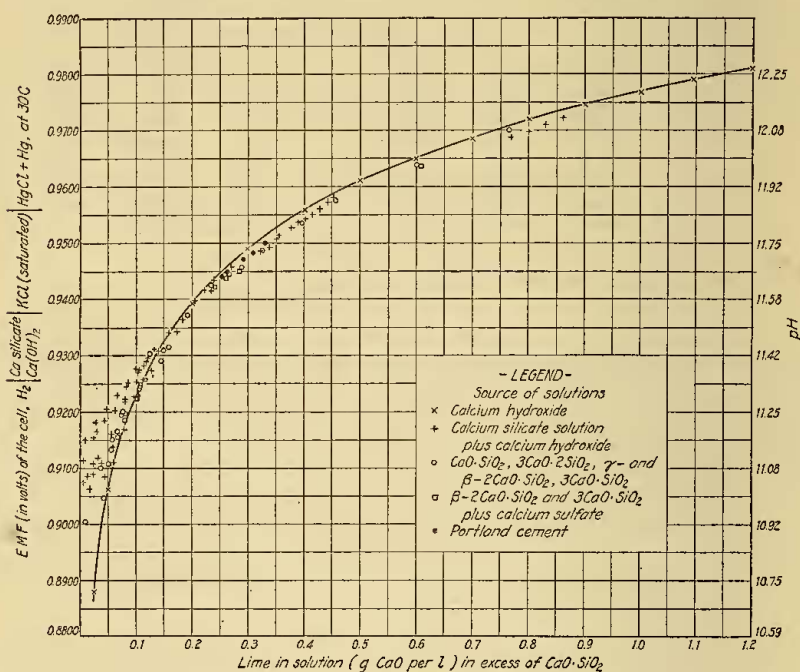
FIGURE 2.—*Correlation of electrometric measurements upon calcium hydroxide and calcium silicate solutions indicating that silica is not combined as monocalcium silicate at all concentrations of lime.*

2. EQUATIONS FOR THE SUCCESSIVE STAGES IN THE HYDROLYSIS OF CALCIUM ORTHOSILICATE

The hydrolyses of these calcium silicates and the corresponding mass action equilibrium expressions, assuming complete dissociation of calcium hydroxide and of the calcium silicates involved, are represented by the following equations:
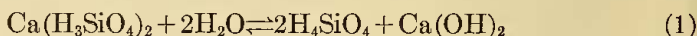
$$Ca(H_3SiO_4)_2 + 2H_2O \rightleftharpoons 2H_4SiO_4 + Ca(OH)_2 \qquad (1)$$

$$K_{h_4} = \frac{[H_4SiO_4][OH^-]}{[H_3SiO_4^-]} \qquad (1a)$$

$$2CaH_2SiO_4 + 2H_2O \rightleftharpoons Ca(H_3SiO_4)_2 + Ca(OH)_2 \qquad (2)$$

$$K_{h_3} = \frac{[\text{H}_3\text{SiO}_4^-][\text{OH}^-]}{[\text{H}_2\text{SiO}_4^=]} \tag{2a}$$

$$\text{Ca}_3(\text{HSiO}_4)_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CaH}_2\text{SiO}_4 + \text{Ca(OH)}_2 \tag{3}$$

$$K_{h_2} = \frac{[\text{H}_2\text{SiO}_4^=][\text{OH}^-]}{[\text{HSiO}_4^{\equiv}]} \tag{3a}$$

$$2\text{Ca}_2\text{SiO}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}_3(\text{HSiO}_4)_2 + \text{Ca(OH)}_2 \tag{4}$$
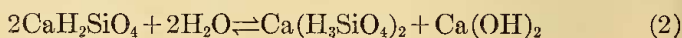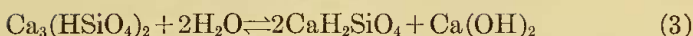
$$K_{h_1} = \frac{[\text{HSiO}_4^{\equiv}][\text{OH}^-]}{[\text{SiO}_4^{\equiv}]} \tag{4a}$$

K_{h_1}, K_{h_2}, K_{h_3}, and K_{h_4} are the equilibrium constants for the successive stages in the hydrolysis of calcium orthosilicate, Ca_2SiO_4.

Relationships between these hydrolysis constants and the ionization constants of orthosilicic acid will be developed later.
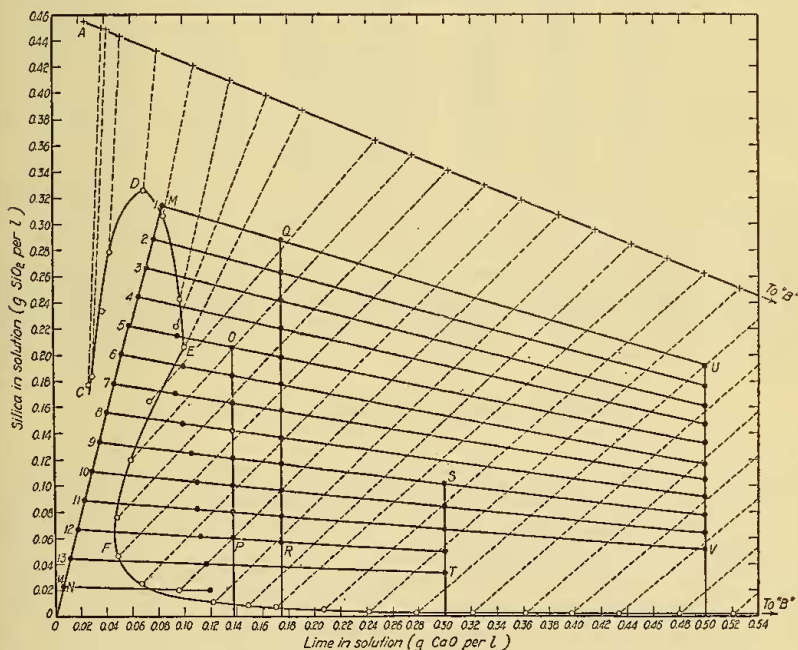
FIGURE 3.—*Showing the compositions of series of solutions prepared for investigation of the state of combination of lime and silica in solution at various lime concentrations and the relationships of these compositions to the diagram of figure 1.*

3. HYDROLYSIS OF Ca(H₃SO₄)₂

The validity of equation 1a, the mass action expression for the hydrolysis of the least basic calcium silicate, $\text{Ca}(\text{H}_3\text{SiO}_4)_2$, in its application to calcium silicate solutions was first investigated. For this purpose a series of dilutions of a silica solution, prepared according to the method described in the previous section, was made up. Their compositions are given in columns 2 and 3 of table 3 and are represented by points along the line MN of figure 3. Actually 2 series of dilutions of 2 different solutions were prepared, the first 4 composi-

tions of table 3 belonging to 1 group, and the remainder to another. The stable phase in contact with solutions of these compositions was found in the previous section to be probably hydrated silica.

TABLE 3.—*Data used in determining the hydrolysis constant K_{h_4} of the reaction:*
$Ca(H_3SiO_4)_2 + 2H_2O \rightleftharpoons 2H_4SiO_4 + Ca(OH)_2$

1	2	3	4	5	6	7	8	9
No.	Composition of solutions		emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO₂ in solution	SiO₂ in excess of Ca $(H_3SiO_4)_2$	$K_{h_4} \times 10^5$
	CaO	SiO₂						
	g/l	*g/l*	*v*	*g/l*			*g/l*	
1	0.0846	0.3136	0.82872	0.00267	9.73	0.280	0.1324	7.44
2	.0780	.2890	.82823	.00264	9.72	.279	.1219	7.44
3	.0720	.2668	.82802	.00261	9.72	.279	.1126	7.40
4	.0660	.2446	.82766	.00259	9.72	.278	.1064	6.86
5	.0584	.2226	.8241	.00229	9.66	.270	.0975	6.96
6	.0526	.2003	.8229	.00222	9.64	.269	.0876	6.78
7	.0467	.1781	.8219	.00215	9.62	.268	.0781	6.82
8	.0409	.1558	.8203	.00202	9.59	.266	.0682	6.27
9	.0350	.1336	.8202	.00201	9.59	.264	.0586	6.39
10	.0292	.1113	.8191	.00196	9.57	.262	.0488	6.51
11	.0234	.0890	.8189	.00195	9.57	.258	.0389	6.52
12	.0175	.0668	.8183	.00191	9.56	.250	.0293	6.81
13	.0116	.0445	.8147	.00171	9.50	.238	.0197	6.73
14	.0058	.0223	.8079	.00138	9.39	.213	.0099	6.68
Average								6.8×10^{-5}

The potentials of the cell of type (2) were measured immediately after preparation of the solutions and are recorded in column 4 of table 3. If equation (1) is applicable these measurements are given by the cell:

$$\text{H}_2 \left| \begin{array}{c} \text{Ca(OH)}_2 \\ \text{Ca(H}_3\text{SiO}_4)_2 \\ \text{H}_4\text{SiO}_4 \end{array} \right| \text{KCl (saturated)} \mid \text{HgCl} + \text{Hg},$$
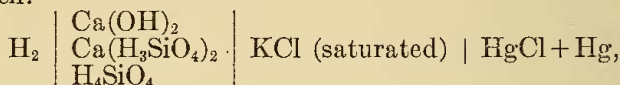
where the concentrations of lime and silica are varied.

The lime concentrations given in column 5 of table 3, corresponding to the measured potentials, were obtained from a large scale plot of emf against lime concentration prepared from data in table 2. By comparison of columns 2 and 5 (table 3) it is seen that only a small portion of the total lime present contributes to the potential of the cell. That which does nor contribute must be combined with silica and column 7 gives the molar ratio of this combined lime to the total silica. Evidently if equation (1) represents the equilibrium existing in these solutions this molar ratio should be intermediate between $CaO/SiO_2 = 0.5$, corresponding to the compound $Ca(H_3SiO_4)_2$, and $CaO/SiO_2 = 0$, corresponding to H_4SiO_4. It is seen that this condition is fulfilled by the data and it is evident that equations 2, 3, and 4 can not apply to this case.

Column 8 gives the concentration of silica calculated to be in excess of that required to form the compound $Ca(H_3SiO_4)_2$ with the total lime present. Data in columns 2, 5, and 8 permit calculation of the hydrolysis constant,

$$K_{h_4} = \frac{[\text{H}_4\text{SiO}_4][\text{OH}^-]}{[\text{H}_3\text{SiO}_4^-]} \tag{1a}$$

for the equation:

$$Ca(H_3SiO_4)_2 + 2H_2O \rightleftharpoons 2H_4SiO_4 + Ca(OH)_2 \tag{1}$$

Thus, for each mol of uncombined lime given in column 5, the solution must contain 2 mols of hydroxyl ion and 2 mols of H$_4$SiO$_4$ as expressed by the equation. The total silicic acid includes also the quantity calculated to be present in solution in excess of Ca(H$_3$SiO$_4$)$_2$. For each mol of combined lime, represented by the difference of the quantities in columns 2 and 5, the solution must contain 2 mols of H$_3$SiO$_4^-$. The concentrations [H$_4$SiO$_4$], [OH$^-$], [H$_3$SiO$_4^-$], may thus be readily obtained from the data and values of K_{h_4} calculated.

For example, the calculation of K_{h_4} for solution 1 of table 3 was performed as follows: $[OH^-] = \dfrac{0.00267}{\frac{1}{2} CaO}$; $[H_4SiO_4] = \dfrac{0.1324}{SiO_2} + \dfrac{0.00267}{\frac{1}{2} CaO}$; $[H_3SiO_4^-] = 2\left(\dfrac{0.0846 - 0.00267}{CaO}\right)$, where SiO$_2$ and CaO represent the molecular weights of silica and lime, respectively.

Then $K_{h_4} = \dfrac{\left(\dfrac{0.00267}{\frac{1}{2} CaO}\right)\left(\dfrac{0.1324}{SiO_2} + \dfrac{0.00267}{\frac{1}{2} CaO}\right)}{2\left(\dfrac{0.0846 - 0.00267}{CaO}\right)} = 7.44 \times 10^{-5}$, as given in column 9.

The absence of a general trend of increase or decrease in K_{h_4} as the solutions undergo an approximately 15-fold variation in concentration, and the constancy of these values within the experimental accuracy, justify the conclusion that equation 1 represents the equilibrium involved, i.e., the hydrolysis of a calcium silicate having the molar ratio CaO/SiO$_2$ = 0.5, to calcium hydroxide and silicic acid.

4. HYDROLYSIS OF CaH$_2$SiO$_4$

In order that the hydrolysis of CaH$_2$SiO$_4$ may proceed only to Ca(H$_3$SiO$_4$)$_2$ a sufficiently high concentration of calcium hydroxide must be present to repress the further hydrolysis to H$_4$SiO$_4$. To investigate the region where this condition occurs emf measurements were obtained for solutions whose compositions lie on the line OP of figure 3 as well as at lime concentrations intermediate between MN and OP, these compositions being prepared by adding calcium hydroxide to members of the MN series. The molar ratios of combined lime to total silica in the solutions was found to be approximately 0.5, indicating that they contained predominately Ca(H$_3$SiO$_4$)$_2$ with CaH$_2$SiO$_4$ and H$_4$SiO$_4$ probably also being present in smaller concentrations. Hence no satisfactory value of the hydrolysis constant of the equilibrium between CaH$_2$SiO$_4$ and Ca(H$_3$SiO$_4$)$_2$ could be obtained in this region.
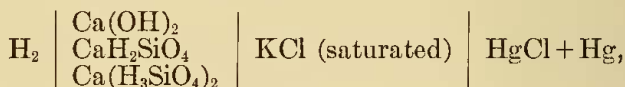
Therefore, a series of compositions (table 4) lying on the line QR of figure 3 was prepared at a somewhat higher lime concentration (0.1750 g CaO per l). Although these solutions were highly supersaturated with respect to hydrated calcium silicate all but the first three or four of table 4 remained stable for many hours with no trace of precipitation.

TABLE 4.—*Data used in determining the hydrolysis constant K_{h3} of the reaction*

$$2CaH_2SiO_4 + 2H_2O \rightleftarrows Ca(H_3SiO_4)_2 + Ca(OH)_2$$
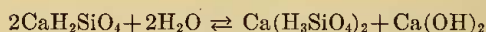
[Lime concentration=0.1750 g CaO per l in all solutions]

1	2	3	4	5	6	7	8
No.	Concentration of SiO_2	emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO_2 in solution	CaO in excess of CaH_2SiO_4	$K_{h3} \times 10^3$
	g/l	*v*	*g/l*			*g/l*	
1	0.2876	0.89582	0.0337	10.85	0.53	None	
2	.2634	.90024	.0406	10.92	.55	None	
3	.2418	.90598	.0497	11.02	.56	None	
4	.2205	.90947	.0557	11.08	.58	None	
5	.1985	.9112	.0608	11.10	.62	None	
6	.1776	.9150	.0708	11.17	.63	0.0091	7.3
7	.1571	.9182	.0804	11.22	.64	.0282	7.1
8	.1367	.9210	.0910	11.27	.66	.0473	7.1
9	.1166	.9231	.1006	11.30	.68	.0661	6.2
10	.0966	.9249	.1093	11.33	.73	.0848	4.6
11	.0788	.9275	.1218	11.38	.71	.1013	5.5
12	.0574	.9296	.1344	11.41	.76	.1110	4.5
Average							6.0×10^{-3}

If calcium hydroxide is present in sufficient concentration in these solutions to prevent the hydrolysis of CaH_2SiO_4 to H_4SiO_4 the potential measurements recorded in table 4 are given by the cell,

$$H_2 \left| \begin{array}{c} Ca(OH)_2 \\ CaH_2SiO_4 \\ Ca(H_3SiO_4)_2 \end{array} \right| KCl \text{ (saturated)} \left| HgCl + Hg, \right.$$

from which the hydrolysis constant,

$$K_{h3} = \frac{[H_3SiO_4^-][OH^-]}{[H_2SiO_4^=]}, \tag{2a}$$

of the reaction:

$$2CaH_2SiO_4 + 2H_2O \rightleftarrows Ca(H_3SiO_4)_2 + Ca(OH)_2, \tag{2}$$

may be calculated.

Column 6 of table 4 gives the molar ratios of combined lime to total silica and these values lie between 1, corresponding to the compound CaH_2SiO_4, and 0.5, corresponding to the compound $Ca(H_3SiO_4)_2$. It is evident that equation 2 only can apply to this equilibrium. Column 7 contains the lime in excess of that required by the silica to form the compound CaH_2SiO_4. No calculation of K_{h3} was attempted for those solutions which contained less total lime than corresponds to this compound. The method of calculating values of K_{h3} given in column 8 will be made clear by the following example:

Solution no. 6: $[OH^-] = \dfrac{0.0708}{1/2 \text{ CaO}}$; $[H_3SiO_4^-] = \dfrac{0.0708 - 0.0091}{1/2 \text{ CaO}}$;

$[H_2SiO_4^=] = \dfrac{0.1776}{SiO_2} - [H_3SiO_4^-]$; $K_{h3} = 7.3 \times 10^{-3}$.

The satisfactory agreement of the values of K_{h3} thus calculated justifies the application of equation 2 to this equilibrium.

5. HYDROLYSIS OF Ca$_3$(HSiO$_4$)$_2$

Figure 2 indicates that with a concentration of lime relatively high compared to the concentration of silica the molar ratio of combined lime to silica may exceed unity. If such combinations represent the neutralization of a definite silicic acid by calcium hydroxide then it is necessary to assume that the acid has more than two replaceable hydrogens.

To investigate solutions of higher proportion of combined lime to silica the series represented by the line ST in figure 3 was prepared. These solutions were highly supersaturated and unstable and, in the case of the first two, the equilibrium reading of potential was not obtained until after precipitation of hydrated calcium silicate had begun. The molar ratios of combined lime to silica of approximately unity given by these measurements indicated that CaH$_2$SiO$_4$ is present in these solutions probably together with lower concentrations of Ca(H$_3$SiO$_4$)$_2$ and Ca$_3$(HSiO$_4$)$_2$.

It had been noticed repeatedly that precipitation from unstable silicate solutions during measurement on the cell,

$$H_2 \left| \begin{array}{c} Ca(OH)_2 \\ Ca\ silicate \end{array} \right| KCl\ (saturated) \left| HgCl + Hg, \right.$$
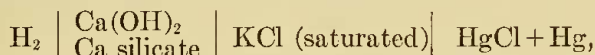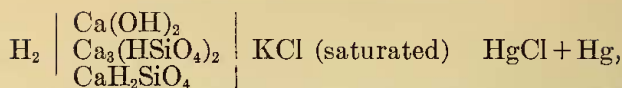
produced no apparent change in the emf when the concentration of lime was such that the amount of silica remaining in solution after precipitation was very small. This fact indicates that the amount of free calcium hydroxide in solution is unchanged by precipitation of calcium silicate and that the molar ratio of combined lime to silica in solution after precipitation is the same as that in the initial solution. As the calcium silicate solutions at the higher lime concentrations are very unstable it was necessary to make the assumption that the emf reading obtained, even after precipitation, represented conditions in the initial clear solution.

Table 5 gives data for solutions prepared at a concentration of 0.5 g CaO per l (UV, fig. 3). The molar ratio of combined CaO to SiO$_2$ (column 6) indicates that the values for emf (column 3) were produced by the cell,

TABLE 5.—*Data used in determining the hydrolysis constant* Kh$_2$ *of the reaction:*
Ca$_3$(HSiO$_4$)$_2$ + 2H$_2$O $\rightleftharpoons$ 2CaH$_2$SiO$_4$ + Ca(OH)$_2$

[Lime concentration = 0.5000 g CaO per l in all solutions]

1	2	3	4	5	6	7	8
No.	Concentration of SiO$_2$	emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO$_2$ in solution	CaO in excess of Ca$_3$(HSiO$_4$)$_2$	$K_{h_2} \times 10^2$
	g/l	*v*	*g/l*			*g/l*	
1	0.1915	0.94867	0.2950	11.73	1.12	0.2418	1.5
2	.1754	.94934	.3019	11.74	1.21	.2543	1.5
3	.1610	.95064	.3228	11.76	1.18	.2745	2.1
4	.1468	.95148	.3349	11.78	1.20	.2944	1.7
5	.1328	.95273	.3527	11.80	1.19	.3140	2.1
6	.1189	.95372	.3671	11.81	1.20	.3335	2.0
7	.1051	.95440	.3773	11.82	1.22	.3528	1.3
8	.0915	.95502	.3877	11.83	1.31	.3718	0.8
9	.0780	.95620	.4063	11.85	1.29	.3907	1.1
10	.0646	.95724	.4247	11.87	1.25	.4095	1.5
11	.0514	.95814	.4391	11.89	1.27	.4280	1.4
Average							1.5×10^{-2}

$$\text{H}_2 \ \left| \ \begin{array}{c} \text{Ca(OH)}_2 \\ \text{Ca}_3(\text{HSiO}_4)_2 \\ \text{CaH}_2\text{SiO}_4 \end{array} \ \right| \ \text{KCl (saturated)} \quad \text{HgCl} + \text{Hg,}$$

sufficient calcium hydroxide being present to repress further hydrolysis of CaH_2SiO_4.

The calculation of K_{h2} for the mass action expression,

$$K_{h2} = \frac{[\text{H}_2\text{SiO}_4^=]\,[\text{OH}^-]}{[\text{HSiO}_4^\equiv]}, \tag{3a}$$

of the equilibrium,

$$\text{Ca}_3(\text{HSiO}_4)_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CaH}_2\text{SiO}_4 + \text{Ca(OH)}_2, \tag{3}$$
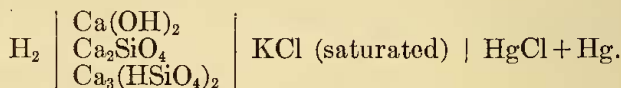
was performed by the same method as that used in calculating K_{h3}. Considering the experimental difficulties involved in obtaining data on calcium silicate solutions at the higher lime concentrations the values of K_{h2} (column 8) thus obtained are in satisfactory agreement. They support the assumption that the equilibrium is one between two salts of orthosilicic acid having the molar ratios CaO/SiO_2 of 3:2 and 1:1, respectively.

6. HYDROLYSIS OF Ca_2SiO_4

A series of four solutions was prepared to investigate the hydrolysis of Ca_2SiO_4 to the next lower calcium silicate, $\text{Ca}_3(\text{HSiO}_4)_2$. Table 6 summarizes the data. Column 7 shows that the molar ratio of combined lime to silica is intermediate between 2:1 and 3:2 in agreement with the equation,

$$2\text{Ca}_2\text{SiO}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}_3(\text{HSiO}_4)_2 + \text{Ca(OH)}_2 \tag{4}$$
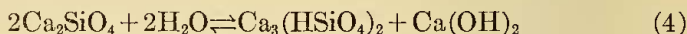
Evidently the electromotive forces recorded in column 4 represent measurements upon the cell,

$$\text{H}_2 \ \left| \ \begin{array}{c} \text{Ca(OH)}_2 \\ \text{Ca}_2\text{SiO}_4 \\ \text{Ca}_3(\text{HSiO}_4)_2 \end{array} \ \right| \ \text{KCl (saturated)} \ | \ \text{HgCl} + \text{Hg.}$$

Values of K_{h1} are recorded in column 9 and the agreement for the four solutions indicates that equation 4 represents the equilibrium involved.
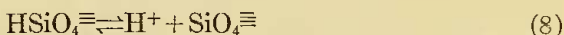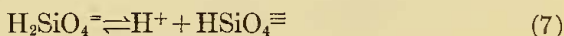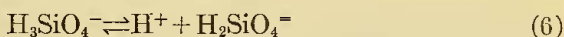
Theoretically K_{h1} should have a higher value than K_{h2} but it is seen that the value obtained is somewhat lower. The accuracy of the method is, however, not sufficiently great to differentiate between these two constants and it can only be said that they are of the same order of magnitude.

7. THE IONIZATION CONSTANTS OF ORTHOSILICIC ACID

Orthosilicic acid is assumed to ionize in four stages represented by the following equations;

TABLE 6.—*Data used in determining the hydrolysis constant K_{h1} of the reaction:*
$$2Ca_2SiO_4 + 2H_2O \rightleftharpoons Ca_3(HSiO_4)_2 + Ca(OH)_2$$

1	2	3	4	5	6	7	8	9
No.	Composition of solutions		emf of cell	CaO corresponding to emf	pH	Molar ratio of combined CaO to total SiO₂ in solution	CaO in excess of Ca₂SiO₄	K_{h_1}—10²
	CaO	SiO₂						
	g/l	*g/l*	*v*	*g/l*			*g/l*	
1	0.8500	0.0886	0.96864	0.6988	12.06	1.83	0.6846	1.3
2	.8750	.0812	.96986	.7353	12.08	1.84	.7233	1.2
3	.9000	.0739	.97107	.7717	12.10	1.86	.7620	1.1
4	.9250	.0665	.97226	.8100	12.12	1.85	.8008	1.2
Average								1.2×10^{-2}

$$H_4SiO_4 \rightleftharpoons H^+ + H_3SiO_4^- \tag{5}$$

$$H_3SiO_4^- \rightleftharpoons H^+ + H_2SiO_4^= \tag{6}$$

$$H_2SiO_4^= \rightleftharpoons H^+ + HSiO_4^\equiv \tag{7}$$

$$HSiO_4^\equiv \rightleftharpoons H^+ + SiO_4^\equiv \tag{8}$$

To equation 5 corresponds the mass action expression,

$$K_{a_1} = \frac{[H^+]\,[H_3SiO_4^-]}{[H_4SiO_4]}.$$

But from the equation 1a, $[H_3SiO_4^-] = \dfrac{[H_4SiO_4]\,[OH^-]}{K_{h_4}}$

and substitution of this quantity gives:

$$K_{a_1} = \frac{[H^+]\,[OH^-]}{K_{h_4}} = \frac{K_w}{K_{h_4}} \tag{5a}$$

Similarly:

$$K_{a_2} = \frac{[H^+]\,[H_2SiO_4^=]}{[H_3SiO_4^-]} = \frac{K_w}{K_{h_3}} \tag{6a}$$

$$K_{a_3} = \frac{[H^+]\,[HSiO_4^\equiv]}{H_2SiO_4^=} = \frac{K_w}{K_{h_2}} \tag{7a}$$

$$K_{a_4} = \frac{[H^+]\,[SiO_4^\equiv]}{[HSiO_4^\equiv]} = \frac{K_w}{K_{h_1}} \tag{8a}$$

Thus the four ionization constants of orthosilicic acid may be calculated from the hydrolysis constants of its salts and the ionization constant of water.

Using the value, $K_w = 1.47 \times 10^{-14}$, for the ionization constant of water at 30 C [21] and the average values of the hydrolysis constants of

[21] H. S. Harned, The Ionization Constant of Water and the Dissociation of Water in Potassium Chloride Solutions from Electromotive Forces of Cells Without Liquid Junction, Jour. Am. Chem. Soc., vol. 55, pp. 2194–2206, 1933.

the four calcium salts of orthosilicic acid: $K_{h_4} = 6.8 \times 10^{-5}$, $K_{h_3} = 6.0 \times 10^{-3}$, $K_{h_2} = 1.5 \times 10^{-2}$, and $K_{h_1} = 1.2 \times 10^{-2}$, the following values of the constants for the first, second, third, and fourth stages in the ionization of orthosilicic acid were obtained: $K_{a_1} = 2.2 \times 10^{-10}$, $K_{a_2} = 2.0 \times 10^{-12}$, $K_{a_3} = 1 \times 10^{-12}$, and $K_{a_4} = 1 \times 10^{-12}$.

Harman [22] measured the hydrolysis of sodium metasilicate in aqueous solution by electrometric determinations of hydroxyl ion concentration and obtained 1.6×10^{-10} and 5.1×10^{-17} for the primary and secondary ionization constants of silicic acid. By electrometric titration of sodium silicate solution with hydrochloric acid he obtained $K_{a_1} = 2.2 \times 10^{-10}$. Electrometric methods for determing the degree of hydrolysis of sodium silicates were applied by Bogue [23] who derived for K_{a_1} the values 4.8 to 18.3×10^{-10} and for K_{a_2}, 5.2 to 16.7×10^{-12}. Hägg [24] by a similar procedure estimated that $K_{a_1} = 10^{-9}$, $K_{a_2} = 10^{-13}$.

Britton [25] prepared titration curves by neutralizing sodium silicate solutions with hydrochloric acid and concluded from their form that the mode of ionization of silicic acid cannot be expressed in terms of ionization constants. However, Joseph and Oakley [26] prepared a similar curve and asserted it to be typical of the combination of a strong base with a weak dibasic acid. From inflections of their curve they derived the values $K_{a1} = 10^{-10}$ and $K_{a2} = 10^{-12}$. Treadwell and Wieland [27] also constructed titration curves and obtained $K_{a1} = 10^{-9.7}$, $K_{a2} = 10^{-12}$.

Despite the absence of good agreement, the results of these investigators indicate that the primary and secondary ionization constants of silicic acid are of the magnitude, $K_{a1} = 10^{-10}$ and $K_{a2} = 10^{-12}$, thus checking roughly the values obtained in this study.

In figure 4 are titration curves prepared from electrometric measurements upon solutions having compositions on the lines MN, OP, QR, ST, and UV in figure 3. The curves of figure 4 show the change in emf as solutions of initial compositions lying on the line MN (fig. 3) are titrated with calcium hydroxide solution. The curve for calcium hydroxide solutions constructed from data in table 2 is also plotted in figure 4. A comparison of the emf of the cell containing calcium hydroxide at any definite concentration to that of the cell containing also calcium silicate in solution at the same total lime concentration illustrates graphically the marked effect of the dissolved silica in lowering the emf and pH.

8. DISCUSSION OF RESULTS WITH REFERENCE TO SOLUBILITY RELATIONSHIPS IN THE SYSTEM CaO–SiO₂–H₂O

It has been shown in the preceding sections that the constitution of solutions in the region of the curve CDE (fig. 1) is governed by the equilibrium, $Ca(H_3SiO_4)_2 + 2H_2O \rightleftharpoons 2H_4SiO_4 + 2Ca(OH)_2$. The value

[22] R. W. Harman, Aqueous Solutions of Sodium Silicates, VII, Jour. Phys. Chem., vol. 31, pp. 616–625, 1925.

[23] R. H. Bogue, The Hydrolysis of the Silicates of Sodium, Jour. Am. Chem. Soc., vol. 42, pp. 2575–2582, 1920.

[24] G. Hägg, The Hydrolysis of the Sodium Silicates, Zs. anorg. allgem. Chem., vol. 155, pp. 21–41, 1926.

[25] H. T. S. Britton, Electrometric Study of the Precipitation of Silicates, Jour. Chem. Soc., pp.425–436, 1927.

[26] A. F. Joseph and H. B. Oakley, The Action of Silica on Electrolytes, Jour. Chem. Soc., vol. 127, pp. 2813–2818, 1925

[27] W. D. Treadwell and W Wieland, The Hydrates of Silicic Acid, Helv. Chim. Acta, vol. 13, pp. 842–864, 1930.

of the hydrolysis constant of this reaction was determined by setting up the proper relationship between total silica, total lime, and uncombined calcium hydroxide in the solutions studied. Using the value of this constant and the concentrations of total lime and silica in any solution for which the above equilibrium is valid, the hydroxyl ion concentration may be computed from the following easily derived equation:

$$[OH^-] = -1/2([SiO_2]-2[CaO]+K_{h4})+1/2\sqrt{([SiO_2]-2[CaO]+K_{h4})^2+8[CaO]K_{h4}}$$

in which $[SiO_2]$ and $[CaO]$ are molar concentrations of silica and lime, respectively, and $K_{h4} = 6.8 \times 10^{-5}$. The amount of lime combined as calcium disilicate may then be computed as well as the concentrations of silicate ion and silicic acid. Such calculations are presented in table 7 for compositions on the curve CDE and it is shown there that the concentration of $H_3SiO_4^-$ reaches a maximum value between D and
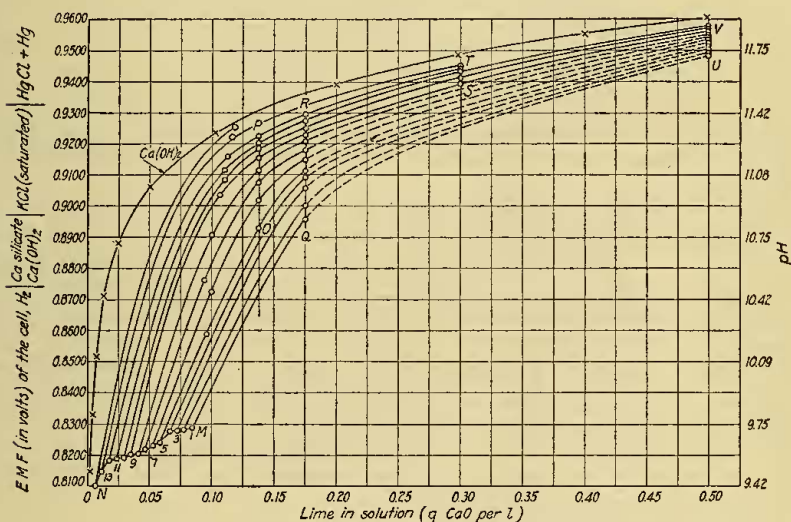

FIGURE 4.—*Electrometric titration curves showing the effect of adding calcium hydroxide to lime-silica solutions.*

E (fig. 1) while that of H_4SiO_4 has its maximum value to the left of D and thereafter decreases sharply. No calculations are presented for the concentrations of the various constituents at E or along the curve EF where an overlapping of two steps in the hydrolysis undoubtedly occurs.

TABLE 7.—*Molar concentrations of OH⁻, $H_3SiO_4^-$, and H_4SiO_4 in solutions on curve CDE, figure 1, which are governed by the equilibrium:* $Ca(H_3SiO_4)_2 + 2H_2O \rightleftharpoons 2H_4SiO_4 + Ca(OH)_2$

No.	$[OH^-]$ $\times 10^5$	$[H_3SiO_4^-]$ $\times 10^3$	$[H_4SiO_4]$ $\times 10^3$	No.	$[OH^-]$ $\times 10^5$	$[H_3SiO_4^-]$ $\times 10^3$	$[H_4SiO_4]$ $\times 10^3$
1	3.2	0.94	2.01 (C)	5	5.6	2.49	2.98 (D)
2	3.6	1.05	2.01	6	9.2	2.95	2.16
3	3.5	1.32	2.58	7	19.2	3.21	1.14
4	3.3	1.50	3.14	8	32.4	3.04	0.64 (E)

It does not necessarily follow, of course, that the composition of the solid phases, whose solubility is represented by the curve CDE, is governed by the equilibrium, $Ca(OH)_2 + 2H_4SiO_4 \rightleftharpoons Ca(H_3SiO_4)_2 + 2H_2O$, yet the available evidence indicates that such is the case, for it has already been pointed out (p. 756) on the basis of the molar ratios in the solid phases that the curve CD appears to represent the compositions of solutions saturated with respect to hydrated silica and DE with respect to a calcium disilicate, $CaO \cdot 2SiO_2$. Along EF where the equilibrium, $Ca(OH)_2 + Ca(H_3SiO_4)_2 \rightleftharpoons 2CaH_2SiO_4 + 2H_2O$, is involved, the molar ratios indicate that the solid phase is a monocalcium silicate, $CaO \cdot SiO_2$. To indicate their possible derivation from orthosilicic acid these compounds may be assigned the formulas, $Ca(H_3SiO_4)_2$, and CaH_2SiO_4, respectively, each possessing an unknown degree of hydration.

In a ternary system at constant temperature and pressure one solid phase in contact with solution makes the system univariant. This condition, although not experimentally realized along DE, should occur along the curves CD and EF and also DE at equilibrium. The lime concentration along these curves may be varied within certain limits, without changing the state of the system. At point D the system should be invariant with two solid phases, hydrated silica and hydrated $Ca(H_3SiO_4)_2$, present; likewise E should be a second invariant point where hydrated $Ca(H_3SiO_4)_2$ and hydrated CaH_2SiO_4 are present.

Beyond F the gradual increase in CaO/SiO_2 molar ratios of the solid phases cannot definitely be accounted for. It will be noted from figure 1 that when a concentration of approximately 0.7 g CaO per liter is reached the composition of the solid phase corresponds to a calcium silicate of the molar ratio $3CaO:2SiO_2$. Finally, as shown previously, the molar ratio approaches $2CaO:1SiO_2$ when the solid phase is in contact with saturated lime solution. This evidence, together with the fact that a well-defined crystalline dicalcium silicate hydrate has been prepared in this laboratory by reaction between lime, silica, and water at 150 C, appears sufficient to postulate the existence of a hydrated calcium silicate to which the formula $Ca_2SiO_4 \cdot nH_2O$ may be assigned.

That the compound, hydrated $Ca(H_3SiO_4)_2$, may have solubilities lying on or to the right of an extension of DE was indicated by the great stability of solutions prepared in this region, which showed no precipitation even after several months. Such solutions would be supersaturated with reference to the solubility curve EF but would be stable in the absence of appreciable quantity of solid hydrated CaH_2SiO_4. An attempt was made to work out such a curve by analyzing solutions resulting after spontaneous precipitation from mixtures on the lines OP and QR, figure 3. The resultant compositions fell to the right of an extension of DE but could not well be represented by a curve. Apparently equilibrium is not readily attained by precipitation from the slightly supersaturated solutions.

IV. REACTION OF WATER ON THE ANHYDROUS CALCIUM SILICATES

1. METHOD OF PROCEDURE

Binary compounds of lime and silica are the chief constituents of portland cement and their reaction with water plays an important part in setting. The study described herein will deal with the mechanism of this reaction and with the relationship of the products to equilibrium conditions in the system CaO–SiO_2–H_2O. It will also attempt to show that the hydraulic properties of the anhydrous calcium silicates are intimately related to their capacity to form solutions supersaturated with respect to the hydrated calcium silicates.

The following anhydrous compounds were prepared from chemically pure calcium carbonate and silica by methods already described:[28]

Monocalcium silicate — $CaO \cdot SiO_2$
Tricalcium disilicate — $3CaO \cdot 2SiO_2$
γ–Dicalcium silicate — γ–$CaO \cdot SiO_2$
β–Dicalcium silicate — β–$2CaO \cdot SiO_2$
Tricalcium silicate — $3CaO \cdot SiO_2$

Chemical analyses and petrographic examination of the products showed their lime-silica ratios to be correct and the purity to be that desired. Free lime, measured by the ammonium acetate titration method,[29] was present in the tricalcium silicate to the extent of 0.3 percent, but was absent in the other preparations. The materials were ground and passed through a no. 200 sieve.

The experiments described in this section are analogous to those reported in a study of the reaction of water on calcium aluminates.[30] The procedure followed was to shake the finely ground compounds with distilled CO_2-free water for a definite period of time and to stop the reaction by rapidly filtering the solution from the residue. A proportion of 20 grams solid per liter of water was used throughout. Immediately after filtering samples of the clear filtrates were taken for chemical analysis of their lime and silica contents and the remainder set aside in well-stoppered flasks for further observation. In most cases the extent of combination between lime and silica in solution was also determined by the electrometric method already described.

2. REACTION OF WATER ON MONOCALCIUM SILICATE (CaO·SiO₂)

The compositions of solutions derived from monocalcium silicate are shown in figure 5 for increasing periods of contact of the solid with the solution.

The guide lines marked $1CaO:1SiO_2$, $2CaO:1SiO_2$, and $3CaO:1SiO_2$ in this figure indicate the compositions of solutions which would contain lime and silica in these ratios. The displacement of the curve for solutions derived from monocalcium silicate to the right of the $1CaO:1SiO_2$ guide line shows that the solutions contain an amount of

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[28] B. S. Technologic Papers Nos. 43 and 78.
[29] W. Lerch and R. H. Bogue, Revised Procedure for the Determination of Uncombined Lime in Portland Cement, Ind. & Eng. Chem., anal. ed., vol. 2, p. 296, 1930.
[30] See footnote 6, p. 754.

lime slightly greater than that corresponding to the molar ratio of the anhydrous compound.

The monocalcium silicate forms apparently stable solutions which may stand for months without appreciable change in composition, differing in this respect, as will be shown later, from the more basic anhydrous calcium silicates, all of which form metastable solutions capable of spontaneous precipitation. As the more basic compounds are hydraulic while monocalcium silicate is nonhydraulic,[31] it appears that the property of metastable solubility is closely connected with the capacity of calcium silicates to set and harden.

However, figure 9, which indicates the relationship of solutions derived from the calcium silicates to equilibrium conditions in the system CaO–SiO_2–H_2O, shows that solutions derived from anhydrous
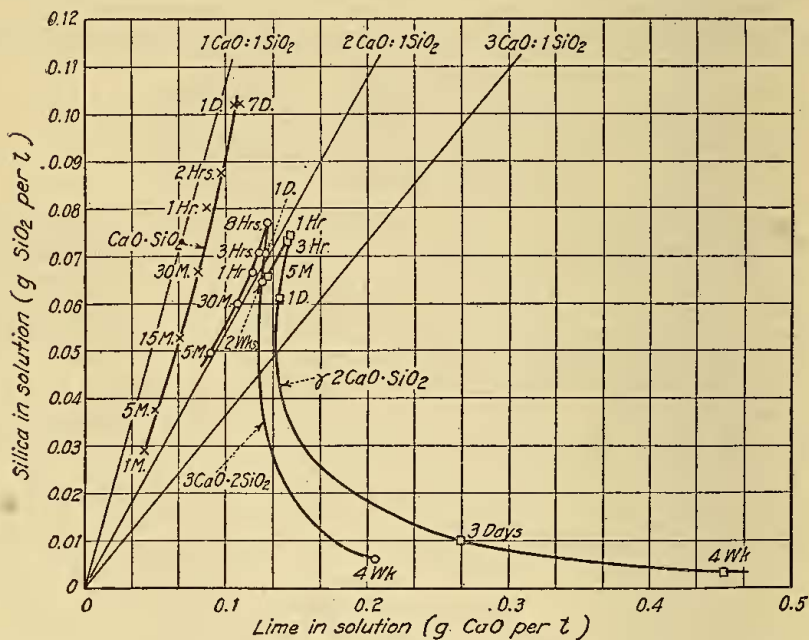

FIGURE 5.—*Showing the compositions of solutions derived from $CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, and γ–$2CaO \cdot SiO_2$ after increasing time of contact with water.*

monocalcium silicate lie in a region of supersaturation with respect to hydrated monocalcium silicate. But in the absence of this phase such solutions are relatively stable. When hydration of the anhydrous compound starts, or if solutions are placed in contact with solid hydrated monocalcium silicate, precipitation should occur until points on the lower solubility curve EF are reached.

It was actually found that solutions which had remained in contact with solid anhydrous $CaO \cdot SiO_2$ for periods of a month or more had compositions closer to the curve EF, indicating possibly that hydration of the anhydrous compound had begun. This behavior differs from that of the more basic lime silicates which contribute lime greatly in excess of the ratio $1CaO : 1SiO_2$ to solution by continued

[31] A. A. Klein and A. J. Phillips, The Hydration of Portland Cement, B.S. Technologic Paper No. 43.

hydrolysis, eventually, in the case of the 3:1 and 2:1 calcium silicates, producing a solution saturated with calcium hydroxide if a sufficient quantity of the silicate were present originally.

Electrometric measurements, which showed that the molar ratio of combined lime to silica in this region was approximately 0.5, indicated that $Ca(H_3SiO_4)_2$ is the principal product of the hydrolysis of monocalcium silicate. Thus it appears that anhydrous monocalcium silicate cannot be said to have a true solubility but rather one that is incongruent.

3. REACTION OF WATER ON TRICALCIUM DISILICATE (3CaO·2SiO$_2$)

Tricalcium disilicate is only obtained by crystallization from a melt of the proper composition[32] and hence cannot be a constituent of portland cement. Its reaction with water, however, illustrates the development of the property of metastable solubility with increase in the basicity of the calcium silicates.

Figures 5 and 9 show that the amount of dissolved silica derived from tricalcium disilicate first increases to a maximum with time of contact of the anhydrous solid with the solution, then drops off sharply with a subsequent gradual increase in the concentration of lime. Initially the reaction appears to involve mainly the formation of supersaturated solutions, followed by precipitation at a rate exceeding that of solution. Thereafter the lime concentration in solution increases through the momentary solution of the anhydrous compound followed by precipitation of hydrated calcium silicate of lower lime-silica molar ratio. The final solid product of this reaction would be hydrated tricalcium disilicate. Electrometric measurements of the compositions shown in figure 5 derived from tricalcium disilicate showed that at these concentrations lime is combined with silica in molar ratios of $0.8 - 0.9$, indicating that these solutions contain mixtures of CaH_2SiO_4 and $Ca(H_3SiO_4)_2$.

It appears then that tricalcium disilicate differs from monocalcium silicate in its ability to form supersaturated solutions capable of spontaneous decomposition. This property, according to Le Chatelier,[33] is characteristic of hydraulic materials and thus these experiments indicate that the 3:2 calcium silicate should be feebly hydraulic.

4. REACTION OF WATER ON GAMMA-DICALCIUM SILICATE (γ–2CaO·SiO$_2$)

Dicalcium silicate occurs in cement predominantly in the unstable beta form.[34] The gamma modification is the stable form at ordinary temperatures and is known to be comparatively unreactive. Thus Newberry and Smith[35] found that γ–2CaO·SiO$_2$ was not appreciably hydrolyzed after long contact with water and only slightly hydrated. Klein and Phillips[36] likewise concluded that the compound is nonhydraulic. Lerch and Bogue,[37] however, showed that its reaction

[32] G. A. Rankin and F. E. Wright, The Ternary System CaO–Al$_2$O$_3$–SiO$_2$, Am. Jour. Sci. Series 4, vol. 39, p. 6, 1915.
[33] See footnote 3, p. 752.
[34] See footnote 2, p. 752.
[35] S. B. Newberry and M. M. Smith, Studies on the Constitution of Hydraulic Cements, Cement & Eng News, vol. 13, p. 66, 1902.
[36] See footnote 31, p. 772.
[37] W. Lerch and R. H. Bogue, Studies on the Hydrolysis of Compounds Which May Occur in Portland Cement, Jour. Phys. Chem., vol. 31, pp. 1627–1646, 1927.

with water, though slow, does not differ in type from that of $\beta-2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ and that it hydrolyzes even in saturated lime solution.

Figure 5 shows that the reaction of $\gamma-2CaO \cdot SiO_2$ with water is very similar to that of $3CaO \cdot 2SiO_2$ but somewhat more rapid. Both form metastable solutions capable of spontaneous precipitation. The relationship of the compositions of solutions derived from this compound to equilibrium conditions is indicated in figure 9. Initially the $\gamma-2CaO \cdot SiO_2$ is hydrolyzed, giving solutions containing principally CaH_2SiO_4 as indicated by electrometric measurements. As $\gamma-2CaO \cdot SiO_2$ can hydrolyze even in saturated lime solution, it is to be expected that the final product in equilibrium with the solution would be hydrated Ca_2SiO_4 and hydrated $Ca_3(HSiO_4)_2$ when the amount of lime in the silicate initially present is large compared with that required to saturate the solution.

It thus appears that there has been an increase in hydraulic characteristics in passing from tricalcium disilicate to $\gamma-$dicalcium silicate.

5. REACTION OF WATER ON BETA-DICALCIUM SILICATE ($\beta-2CaO \cdot SiO_2$)

Experiments of Klein and Philllips [38] led them to believe that $\beta-$dicalcium silicate hydrates very slowly without the liberation of lime by hydrolysis. However, the conclusion is at variance with the results of other investigators [39] who found that this compound undergoes both hydrolysis and hydration, when placed in contact with water. According to Bates and Klein [40] $\beta-2CaO \cdot SiO_2$ sets slowly but after 28 days attains sufficient strength to be almost upon an equality with tricalcium silicate.

The reaction of this compound with water is illustrated in figure 6. The rate of reaction is much greater than that of $\gamma-2CaO \cdot SiO_2$ and the solutions formed were more highly supersaturated with respect to the hydrated products, as the comparison of their compositions with equilibrium conditions afforded by figure 9 indicates. Precipitation from the solutions containing the highest concentrations of silica started within a half hour. The course of precipitation from the unstable to the corresponding equilibrium states and the molar ratios of lime to silica in the precipitates are indicated in figure 6. The precipitates were similar in appearance to those formed by precipitation from mixtures having compositions represented by points on the line AB in figure 9.

The molar ratios of combined lime to silica in solution given by electrometric measurements showed that the dicalcium silicate gives solutions containing CaH_2SiO_4 with increasing amounts of $Ca_3(HSiO_4)_2$ being formed as the lime concentration increases. The final insoluble product of the reaction when a saturated lime solution had been formed should have a composition approaching the molar ratio $2CaO:1SiO_2$ of hydrated calcium orthosilicate, when the quantity of anhydrous silicate originally present is sufficiently large. On the other hand, with insufficient anhydrous calcium silicate initially present to form a saturated lime solution, the molar ratio of lime to

[38] See footnote 31, p. 772.
[39] Lerch and Bogue, see footnote 34; T. Thorvaldson and V. Vigfusson, Action of Water on Tricalcium Silicate and Beta-Dicalcium Silicate, Trans. Roy. Soc. Can. series 3, vol. 22, pp. 423–431, 1928.
[40] P. H. Bates and A. A. Klein, Properties of the Calcium Silicates and Calcium Aluminate Occurring in Normal Portland Cement, B.S. Technologic Paper No. 78, 1917.

silica in the hydrated product would correspond to some other equilibrium relationship along the curve *BFEDC* of figure 9.
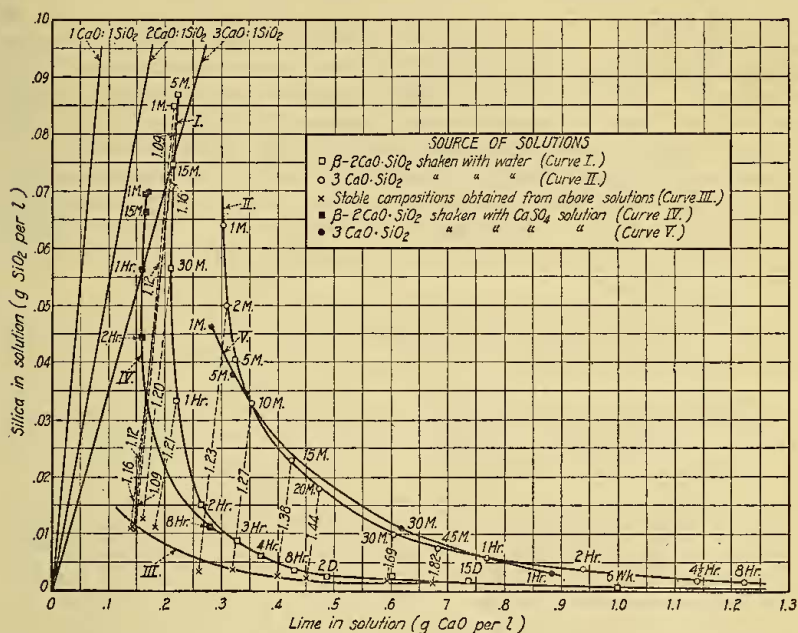

FIGURE 6.—*Showing the compositions of solutions derived from β–2CaO·SiO₂ and 3CaO·SiO₂ after increasing time of contact with water and with calcium sulphate solution.*

6. REACTION OF WATER UPON TRICALCIUM SILICATE (3CaO·SiO₂)

Le Chatelier [41] believed that the fundamental reaction in the hydration of portland cement is one between tricalcium silicate and water as follows: $3CaO \cdot SiO_2 + H_2O \rightarrow CaO \cdot SiO_2 \cdot 2\ 1/2H_2O + Ca(OH)_2$. Newberry and Smith [42] found that tricalcium silicate, in the presence of excess water, gives a residue of approximately the composition $3CaO \cdot 2SiO_2 \cdot 3H_2O$. Lerch and Bogue, and Thorvaldson and Vigfusson have studied the rate of reaction [43] between tricalcium silicate and water by determination of the lime liberated to solution at progressive time intervals. The two latter authors believed that hydrated 3:2 calcium silicate and hydrated monocalcium silicate were possible products of the reaction with water of both tricalcium silicate and β–dicalcium silicate.

Klein and Phillips [44] reported that tricalcium silicate hydrates readily with the formation of hydrated silicate and lime, and Bates and Klein [45] state that this compound has all the important properties of portland cement, especially those of "rate of setting" and strength developed.

[41] See footnote 3, p. 752.   [43] See footnote 39, p. 774.   [45] See footnote 40, p. 774.
[42] See footnote 35, p. 773.   [44] See footnote 31, p. 772.

The reaction of water with tricalcium silicate, illustrated in figure 6, is one of great rapidity, as might be expected in the case of such a highly basic compound. As before, lines connecting points on the upper and lower curves indicate the course of precipitation from the metastable to the corresponding equilibrium states and the figures accompanying these lines are the molar ratios of lime to silica in the precipitates. These values are slightly higher than those obtained by precipitation from mixtures having initial compositions lying on the line AB in figure 9 but the latter are probably more accurate due to the greater difference between the initial and final compositions of the solutions which makes possible greater accuracy in calculating the compositions of the precipitates by difference. The precipitates which separated from the metastable solutions were similar to those previously obtained.

Although a saturated lime solution resulted after 4½ hours' contact with the silicate, hydrolysis continued further and a supersaturated solution containing 1.226 g CaO per l and 0.0023 g SiO_2 per l was produced after 8 hours. It is probable that supersaturation of calcium hydroxide as well as supersaturation of the silicates plays an important part in the setting of portland cement. This phenomenon of the formation of solutions supersaturated with respect to calcium hydroxide has previously been noted by Lerch and Bogue.[46]

The reaction of tricalcium silicate is differentiated from that of the less basic calcium silicates by its much greater rate and the instability of the solutions formed as figure 9 indicates. The principal products of hydrolysis in the presence of saturated or supersaturated lime solution would be hydrated calcium orthosilicate, $Ca_2SiO_4 \cdot nH_2O$, and solid calcium hydroxide. Work in this laboratory has also shown that well-defined crystalline dicalcium silicate are formed by reaction between tricalcium silicate and water at 150 C and crystalline calcium hydroxide.

Figure 7 compares the rate of liberation of lime to solution by the different calcium silicates and illustrates clearly the rapidity of the reaction in the case of tricalcium silicate and the tendency of this compound to form supersaturated lime solutions. The curve for the hydrolysis of beta-di-calcium silicate is interesting in that the lime concentration in solution initially decreases with time of contact of the anhydrous solid. This is undoubtedly due to the precipitation of hydrated calcium silicate in this region removing more lime from solution than is being supplied by hydrolysis and solution of the anhydrous silicate.

The curves for the less basic silicates show the much slower rate of reaction of these compounds. It is seen that the reactivity of the calcium silicates increases in the following order: $CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, $\gamma-2CaO \cdot SiO_2$, $\beta-2CaO \cdot SiO_2$, and $3CaO \cdot SiO_2$.

7. REACTION OF WATER ON PORTLAND CEMENT

The application of the foregoing methods to the reaction of water upon a commercial portland cement of the following composition was then investigated.

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[46] See footnote 37, p. 773.

Oxide composition	Percent	Compound composition [47]	Percent
SiO_2_ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _	21. 58	$3CaO \cdot SiO_2$_ _ _ _ _ _ _ _ _ _ _ _ _ _ _	67
Fe_2O_3_ _ _ _ _ _ _ _ _ _ _ _ _ _ _	2. 81	$2CaO \cdot SiO_2$_ _ _ _ _ _ _ _ _ _ _ _ _ _ _	11
Al_2O_3_ _ _ _ _ _ _ _ _ _ _ _ _ _ _	4. 15	$3CaO \cdot Al_2O_3$_ _ _ _ _ _ _ _ _ _ _ _ _ _	6
CaO_ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _	66. 22	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$_ _ _ _ _ _ _ _ _	8
MgO_ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _	2. 27	$CaSO_4$_ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _	3
SO_3_ _ _ _ _ _ _ _ _ _ _ _ _ _ _	1. 93		
Ignition loss, 1.18%; insoluble, 0.08%; free lime, 0.4%.			

[47] R. H. Bogue, Calculation of Compounds in Portland Cement, Ind. & Eng. Chem., anal. ed., vol. 1, p. 192, 1929.
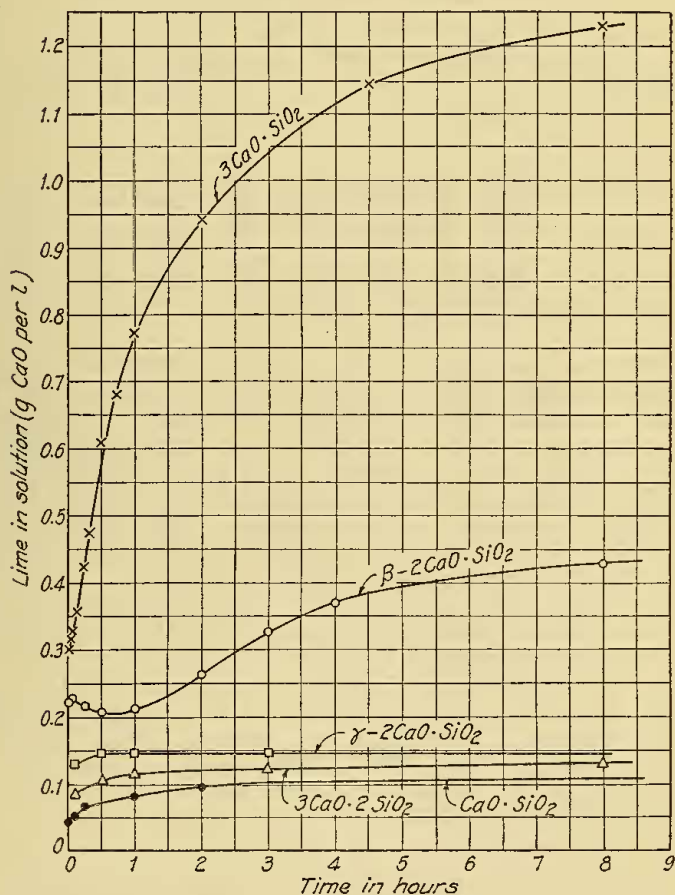

FIGURE 7.—*Showing the relative rates of liberation of lime to solution by the anhydrous calcium silicates.*

This cement was chosen because of its high tricalcium silicate content and freedom from alkalies.

Proceeding as in the study of the calcium silicates, shaking 20 grams of cement with a liter of water, gave the results contained in table 8. Columns 2, 3, 4, and 5 of this table give the compositions of the solutions for increasing time of contact between the cement and water

(column 1).   Column 9 of this table shows that the lime concentration increased in 8 hours to give a solution highly supersaturated with respect to $Ca(OH)_2$.   The sulphate of the cement was dissolved almost completely during the earlier periods but its concentration subsequently decreased.   The alumina concentration was low at all time periods.   Finally, the solutions contained concentrations of silica in metastable condition comparable to those supplied by tricalcium and β–dicalcium silicate at corresponding lime concentrations.

TABLE 8.—*Compositions and* pH *of solutions derived from a portland cement*

1	2	3	4	5	6	7	8	9	10
Time of contact	Composition of solutions				Emf of cell	CaO corresponding to emf	pH	CaO in excess of $CaSO_4+$ $CaO\cdot$ Al_2O_3	Molar ratio of combined CaO/SiO_2 in solution
	CaO	SO_3	Al_2O_3	SiO_2					
	g/l	*g/l*	*g/l*	*g/l*	*v*	*g/l*		*g/l*	
1 min	0.5168	0.3423	0.0064	0.0234	0.9440	0.2464	11.65	0.2729	1.21
3 min	.5236	.3414	.0050	.0208	.9447	.2544	11.66	.2881	1.38
5 min	.5586	.3509	.0052	.0198	.9471	.2808	11.70	.3099	1.57
10 min	.5634	.3358	.0022	.0216	.9483	.2942	11.72	.3269	1.62
30 min	.5744	.3214	.0020	.0202	.9502	.3154	11.75	.3482	1.74
1 hr	.6284	.3317	.0028	.0154	.9537	.3654	11.81	.3946	
2 hr	.7624	.3095	.0008	.0102	.9617	.5257	11.94	.5452	
8 hr	1.6125	.1538	.0025	.0020	.9850		12.33	1.5035	

To determine the amount of lime combined with silica in these solutions it was assumed that the sulphate was present as calcium sulphate and alumina as monocalcium aluminate.[48]   The dissolved alumina is so low that even if it were not so combined in the presence of calcium sulphate the calculation would not be seriously in error. Electrometric measurements were made of the quantity of uncombined calcium hydroxide in these solutions.   The lime in solution in excess of that required to form calcium sulphate and monocalcium aluminate and not present as free calcium hydroxide was calculated as combined with silica (column 10).   The good agreement between these molar ratios of combined lime to silica and previous determinations at corresponding lime concentrations indicates that the particular part of the reaction between portland cement and water involving anhydrous calcium silicates is not essentially different from the reactions of the individual constituents, $3CaO\cdot SiO_2$ and β–$2CaO\cdot SiO_2$, with water.   The solutions derived from the cement were also metastable and gave hydrated precipitates similar to those obtained from other unstable lime-silica solutions.

To determine whether or not the presence of calcium sulphate had any appreciable effect upon the rate of hydrolysis of β–$2CaO\cdot SiO_2$ and $3CaO\cdot SiO_2$, these compounds were shaken with a solution of approximately the same calcium sulphate content as that formed during the earlier periods in the reaction between water and the portland cement.   From figure 6, where lime in excess of calcium sulphate is plotted against silica in solution, it is seen that the calcium sulphate, at the concentration present, retards the reaction but little.

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[48] See footnote 6, p. 754.

The sulphate concentration of the original solution was practically unchanged after contact with the calcium silicate, differing in this respect from the reaction of water on the portland cement which contained both aluminates and silicates. Values were obtained for the molar ratios of combined lime to total silica in solution upon the assumption that the total lime less the sum of that present as free calcium hydroxide and combined as calcium sulphate represented lime combined with silica. The good agreement of the molar ratios with those previously obtained at corresponding lime concentrations and the fact that decomposition of these solutions, which were supersaturated in silica, did not appreciably alter the sulphate concentration indicates the correctness of the assumption that calcium sulphate is present uncombined in solution.

Insofar as the calcium silicates are concerned, therefore, the reaction of portland cement with water appears to involve the formation of supersaturated solutions of calcium silicate and subsequently of calcium hydroxide and spontaneous precipitation from such solutions. The results indicate that hydrated calcium orthosilicate, $Ca_2SiO_4 \cdot nH_2O$, together with solid calcium hydroxide are products of the reaction of portland cement with water under usual conditions, the hydrolysis of the former compound being reduced by the supersaturated solution of calcium hydroxide which is formed. Such a process, involving the formation of supersaturated solutions from the anhydrous compounds and the spontaneous precipitation of much less soluble products therefrom, is in agreement with the mechanism of hydraulic reactions first proposed by Le Chatelier.[49] The subsequent setting and hardening may then occur through the withdrawal of water from the hydrated products according to the mechanism suggested by Michaelis.[50]

If, in these experiments, the calcium silicates had been treated with a quantity of water similar to that used in the technical cement mix it is believed that the resultant products would not be essentially altered since only a relatively small quantity of the anhydrous calcium silicate is required to form the solution supersaturated with respect to calcium hydroxide with which the final hydrated silicate may exist in equilibrium. It may be definitely concluded from the results of this investigation that the calcium silicates occurring in cement are not hydrolyzed completely to silicic acid and calcium hydroxide in the presence of a relatively small quantity of water, as has sometimes been stated. Such extensive hydrolysis can occur only when the lime concentration has been reduced to a few hundredths of a gram of CaO per liter, a condition not likely to occur in the setting of portland cement. Instead, hydrated calcium orthosilicate and calcium hydroxide appear to be the most probable products of the reaction under usual conditions.

The influence of alkalies, which are nearly always present in cement, and of sulphate in higher concentrations than those studied in this paper as well as the nature of products, other than hydrated calcium silicate and calcium hydroxide, which may be formed during the reaction of portland cement with water, are not considered in this study.

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[49] See footnote 3, p. 752.   [50] See footnote 7, p. 757.

V. REACTIONS OF DIATOMACEOUS SILICA AND OF SILICA GEL WITH LIME SOLUTION

A reactive naturally occurring form of silica is diatomaceous silica. The pozzolanic properties of this material are apparently due to its capacity to fix lime in chemical combination in the presence of water giving hydrated calcium silicate which is capable of setting and hardening. The reaction is essentially the reverse of that which occurs between the anhydrous calcium silicates and water but the composition of the final products should also be governed by the equilibrium relationships in the system $CaO-SiO_2-H_2O$ as shown in figure 9. It was decided to include some phases of an investigation of the reaction between diatomaceous silica and lime solution in this study, which chronologically had been completed before the present investigation was started.

The only report of the previous study was that briefly described in B.S. Technical News Bulletins nos. 141 and 142 (January and February 1929, respectively). It is believed that some of the unpublished results are now clarified by the present information on the system $CaO-SiO_2-H_2O$.

The method was similar in principle to that developed at the Building Research Station of Great Britain [51] for evaluating the pozzolanic activity of a material in that it involved the measurement of the rate of change in concentration of calcium hydroxide in solutions in contact with the pozzolana. The present procedure was to place weighed quantities (1.0 g) of the diatomaceous silicas and measured volumes (250 ml) of saturated lime solution (1.15 g CaO per l) in flasks which were then stoppered tightly and shaken at frequent intervals. After definite periods of time the solutions were filtered from the solid residues and their lime concentrations determined by titration with standard hydrochloric acid. Fifteen commercial diatomaceous silicas and 3 other forms of finely divided silica were studied, 8 initial mixtures of each being made up and allowed to stand for various lengths of time.

It was found that the reaction of all the diatomaceous silicas was very similar: First a rapid decrease in lime content of solutions occurred, followed by a more gradual reduction in the lime concentration until a rather definite final value of $0.07-0.09$ g CaO per liter was reached. This limiting concentration was apparently not greatly altered by 4 years' contact between the solid phase and solution.

The other forms of silica included a microcrystalline mineral silica, an amorphous silica, and ground quartz (100 percent through a no. 200 sieve). These reduced the lime concentration of the solution after 4 years to 0.3880, 0.4630, and 0.6750 g CaO per liter, respectively.

To determine whether the decrease in lime concentration was attended by a simultaneous increase in the concentration of silica in solution, the series illustrated in figure 8, curve A, was prepared. This series consisted of 11 mixtures of a diatomaceous silica and lime solution which were allowed to stand for various lengths of time, filtered, and analyzed for both lime and silica. The rate of removal of lime from solution by this diatomaceous silica is typical of the group

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[51] A. D. Cowper and F. L. Brady, Pozzolanas, Building Research Bulletin No. 2 (Great Britain); Reports of the Building Research Board (of Great Britain) for the years 1926 to 1928, inclusive.

studied.   Inspection of the figure shows that with the lime concentration reduced to approximately 0.1 g CaO per liter a very sharp increase in silica concentration occurred.   Subsequently the lime concentration did not decrease greatly.   The point corresponding to the highest silica concentration represents a solution obtained after 4 years' contact with the diatomaceous earth.

Estimations were also made of the extent of combination of lime and silica in the residue by analyzing the portion soluble in 10 percent HCl at various stages of the reaction.   It was found that the molar ratios of lime to silica in the soluble portion were approximately the
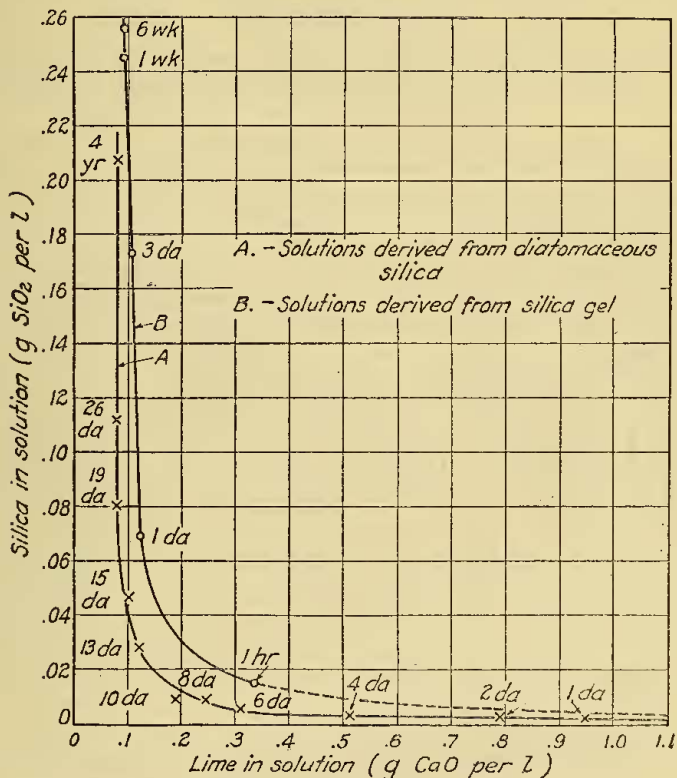

FIGURE 8.—*Showing the compositions of solutions resulting after increasing time of contact between (A) a diatomaceous silica and lime solution, and (B) silica gel and lime solution.*

same as those shown in figure 9 at corresponding lime concentrations. Thus it appears that initially small amounts of the more basic calcium silicates are formed but as the lime concentration decreases the molar ratio of combined lime to silica in the solid phase also decreases.   As the reaction proceeds, more and more lime is taken up in chemical combination by the silica until the solid phase approaches equilibrium with the solution.

Curve B, figure 8, compares the reaction of the silica gel used in this study with that of the diatomaceous silica.   The same proportion of silica to lime solution of corresponding initial concentration was

used in these experiments. It is seen that the silica gel is by far the more active, giving solutions containing appreciably higher concentrations of silica in much shorter periods of time. In the region of the equilibrium curve DE, figure 9, the rate of solution is strongly inhibited and the maximum solubility of silica, corresponding to point D was not attained. However, it is of interest that the compositions of the solutions follow the curve DE as the concentration of silica increases.

The lesser reactivity of the diatomaceous silica may be due to the presence of impurities and a coarser structure than that of the silica gel.

VI. SUMMARY

The study herein described has sought information relative to the possible existence of definite hydrated compounds in the system
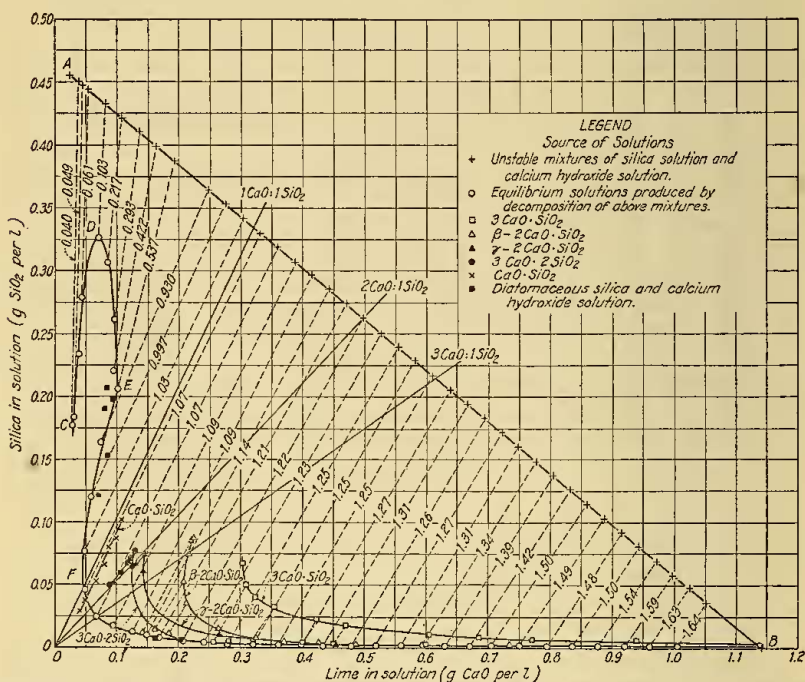

Figure 9.—*Comparison of solution and solid phase relationships in the system* $CaO-SiO_2-H_2O$ *with compositions of solutions resulting after increasing periods of contact between the anhydrous calcium silicates and water.*

$CaO-SiO_2-H_2O$ and their possible relationship to products formed by the reaction of water upon anhydrous calcium silicates. It did not include determinations of the extent of hydration of such compounds but attempted only to show that they are salts formed by the neutralization of a definite silicic acid by calcium hydroxide.

The sequence of procedure in this investigation was the following:

(1) The solubility relationships of lime and silica in solutions of increasing concentrations of lime up to saturation were investigated as well as the compositions of solid phases which could exist in

equilibrium with such solutions. These solid phases were amorphous or microcrystalline and could not be identified by petrographic methods.

(2) Electrometric measurements of the extent of combination of lime and silica in solution permitted the CaO/SiO$_2$ molar ratios found therein to be assigned to definite calcium silicates derived from orthosilicic acid and having the following formulas: Ca(H$_3$SiO$_4$)$_2$, CaH$_2$SiO$_4$, Ca$_3$(HSiO$_4$)$_2$, and Ca$_2$SiO$_4$. It proved to be possible to express the hydrolytic equilibria of these compounds in terms of the law of mass action and hydrolysis constants were calculated from the data for the four successive stages in the hydrolysis of calcium orthosilicate, Ca$_2$SiO$_4$. From these values, knowing the ionization constant of water at 30 C, the four ionization constants of orthosilicic acid were calculated to be the following: $K_{a_1} = 2.2 \times 10^{-10}$, $K_{a_2} = 2.0 \times 10^{-12}$, $K_{a_3} = 1 \times 10^{-12}$, $K_{a_4} = 1 \times 10^{-12}$.

(3) A correlation of the results obtained under (1) and (2) above, indicated that the solid phases in this system may be hydrated calcium salts of orthosilicic acid. Their solubilities are represented graphically and the application of the phase rule to the diagram is considered.

(4) The reaction between water and the anhydrous calcium silicates was then investigated. It was demonstrated that the solutions of compounds having the lime-silica molar ratios, 3:2, 2:1, and 3:1 are metastable and precipitate hydrated calcium silicate on standing. These results further support the postulate of Le Chatelier that the formation of supersaturated solutions is a characteristic phenomenon in the reactions of hydraulic materials with water. Metastable solubility curves of these compounds were constructed (fig. 9) to show their relationship to equilibrium conditions. Monocalcium silicate differs from the more basic calcium silicates in that it forms stable solutions and hence is nonhydraulic.

Similar methods were then applied to a study of the reaction of water upon a portland cement. It was found that probable solid products of this reaction are hydrated calcium orthosilicate, Ca$_2$SiO$_4 \cdot n$H$_2$O, and calcium hydroxide. The presence of calcium sulphate in the concentration used appears to have a practically negligible effect upon the rate of reaction between water and the calcium silicates.

(5) An investigation was also made of the reaction between diatomaceous silica and lime solution, and between silica gel and lime solution, which are in some respects the reverse of the reaction of water upon anhydrous calcium silicates.

WASHINGTON, March 22, 1934.