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The System of Lime, Alumina, and Water from 50° to 250° C

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The system $CaO-Al_2O_3-H_2O$ has been investigated over the range 50° to 250° C. At equilibrium, only two stable ternary compounds exist in the system, namely, $3CaO\cdot Al_2O_3\cdot 6H_2O$ up to 215° C and $4CaO\cdot 3Al_2O_3\cdot 3H_2O$ from 215° to 250° C. Hexagonal hydrated calcium aluminates occur as metastable phases with decreasing stability with increasing temperature until at temperatures over 100° C they exist only momentarily. There are only two stable alumina hydrates, namely, gibbsite ($Al_2O_3\cdot 3H_2O$) up to 150° C, and boehmite ($Al_2O_3\cdot H_2O$) thereafter. A stable phase throughout the temperature range is $Ca(OH)_2$. The equilibria curves of these solid phases maintain the same general relationships to each other throughout. As the temperature increases to 250° C, the solubility fields are compressed into the water apex of the diagram.

1. Introduction

Numerous investigations of the system $CaO-Al_2O_3-H_2O$ have been reported in the literature [1, 2, 3, 4, 5],[1] and present knowledge of the system has been ably summarized by Steinour [6]. The importance and applications of studies of this system have been stressed by these authors.

Although calcium hydroaluminates have been prepared hydrothermally [7, 8, 9, 10], the ternary system as such has not been studied at elevated temperatures and pressures. The present paper is a study of this system from 50° to 250° C and from 1- to approximately 39-atm pressure. The system, in turn, will be compared with that previously studied at 21° C and 90° C [5].

At higher temperatures, such difficulties as the low solubility of the compounds and interference of carbon dioxide, become magnified, and superimposed on these difficulties are those inherent in hydrothermal investigations.

The system was investigated at one intermediate temperature, namely, 50° C, and then at 120°, 150°, 200°, and 250° C. Thus it is possible to describe the system over the range 21° to 250° C. This probably includes the entire range over which useful information may be obtained because the solubilities of the various compounds in this system become immeasurably small above 250° C.

A study of this system at elevated temperatures may provide some information about the mechanism of the reactions that occur in the steam curing of portland cement. It should also have a bearing on reactions that take place if high-alumina cements (which are composed largely of anhydrous calcium aluminates) are heated to elevated temperatures and pressures. The system from 21° to 250° C may also have applications in the fields of geology, soil equilibria, water purification, and in the formation of boiler scale.

2. Apparatus and Procedure

In the investigation at 50° C, the apparatus and techniques were essentially the same as those used by Wells, Clarke, and McMurdie [5], who studied this system at 21° and 90° C. The method is described in detail by these authors.

In the present investigation polyethylene bottles of ½-liter capacity were used. They were filled with lime water of varying concentrations, and 1 g of an appropriate solid phase was added to each. The bottles were then tightly stoppered and stored in an electric oven maintained at 50° C for periods up to 200 days.

They were shaken manually at least once a day, and from time to time, portions of each were filtered. Aliquots of these filtrates were analyzed gravimetrically for lime and alumina. The alumina was determined by the method of Blum [11], and the lime was precipitated as the oxalate and ignited to the oxide.

The corresponding solid phases in the precipitate were identified by the petrographic microscope, and, in case of any doubt as to their identities, By X-ray diffraction patterns also.

It is not known to what extent the solubilities of the compounds in this system are affected by pressure, but it is assumed that the effect is small. The investigation was carried out with sealed bombs in which both the vapor and liquid coexisted at equilibrium. Because the amount of dissolved material was generally small. the pressures corresponding to the various temperatures are approximately the equilibrium vapor pressures of water at those temperatures. The system is throughout considered to be condensed.

The metastable equilibria in this system at 50° C were determined by an approach from supersaturation. In this case also, the method of Wells, Clarke, and McMurdie was used [5]. Briefly, a series of initially metastable solutions was prepared from the filtrate of high-alumina cement shaken with water, and from calcium hydroxide solutions. Precipitation of metastable solid phases began immediately upon mixing the alumina-cement filtrate and the lime water in all cases except those of lowest alumina concentrations. There were precipitates in all cases at the end of 3 days, however. Again, aliquots of filtrates of these metastable solutions were analyzed gravimetrically and the solid phases identified petrographically and with X-ray diffraction patterns.

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[1] Figures in brackets indicate the literature references at the end of this paper.

For the investigations above 100° C, three stainless-steel pressure bombs were used. There bombs are described in detail in a previous publication [12]. Briefly, these bombs consisted of two vessels, each of ½- to 1-liter capacity, separated by a stainless-steel disk containing a Munroe filter crucible. The liquid and solid phases were placed in one of these vessels, which was then covered by the center disk, and the other vessel, and the whole was bolted together.

The filter crucible was coated with platinum sponge made by reducing an alcoholic paste of ammonium chloroplatinate. It was held in place in the center disk by means of a threaded nut, with an annealed silver washer placed on the top and the bottom of the flange of the filter crucible. Copper gaskets made the seals between the center disk and the two vessels.

When assembled, the bombs were placed in electric ovens maintained at the desired temperature for periods of time up to 7 days. Tests made at 120° C indicated that equilibrium had been attained in this time.

The bombs were shaken manually at least once a day, and at the end of 5 or 7 days were removed from the ovens. Filtration was accomplished by inverting the bombs and plunging into cold running water the vessel that did not contain the solid and liquid phases. The lowering of the pressure in this vessel resulting from vapor condensation caused the liquid in the other vessel to be pushed through the filter crucible by its own vapor pressure.

The bombs were then removed from the cold water, further cooled, and disassembled. Aliquots of the filtrate were analyzed gravimetrically for lime and alumina as before.

The calcium oxide used in this investigation was prepared by heating calcium carbonate of reagent quality overnight in an electric furnace at 950° C. The calcium hydroxide solutions were prepared with the addition of distilled water to this calcium oxide and stored in a large tightly stoppered bottle. Whenever some of the solution was withdrawn from the stock bottle for use in a series of experiments, it was filtered and analyzed gravimetrically for CaO.

The gibbsite ($Al_2O_3{\cdot}3H_2O$) used in these experiments was homogeneous when examined under the microscope. It contained 0.02 percent of total alkalies as Na_2O, as determined by the flame photometer.

Boehmite ($Al_2O_3{\cdot}H_2O$) was prepared from this gibbsite by heating it in a pressure bomb with excess water for 5 days at 250° C. It appeared homogeneous when examined by the microscope, and its X-ray powder pattern was identical with published patterns of artificial boehmite (see table 1).

TABLE 1. *X-ray pattern of synthetic boehmite: interplanar spacing, d, and relative intensity, I*

[S, strong; M, medium; W, weak; VW, very weak]

d	*I*	*d*	*I*
7.21	S	27.63	W
7.77	VW	30.28	VW
14.08	M	32.05	W
19.18	M	32.52	VW
22.90	VW	33.85	VW
24.48	M	35.98	W
24.61	M	36.08	W
25.82	VW		

The isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ was prepared as follows: An aqueous slurry prepared from CaO and gibbsite, with CaO in slight excess of the stoichiometric ratio, was placed in a platinum dish in a pressure bomb containing excess water. The bomb was heated at 170° C for 5 days. The resulting compound was filtered from the excess water, and washed with water to remove the calcium hydroxide, after which it was washed by alcohol and ether. This product appeared homogeneous when examined under the microscope and had an index of 1.605. In all such preparations, there were small amounts of birefringent inclusions. A gravimetric analysis of one preparation gave a formula of $3.0\ CaO{\cdot}1.0\ Al_2O_3{\cdot}6.2\ H_2O$.

The hydrated calcium aluminate, $4CaO{\cdot}3Al_2O_3{\cdot}3H_2O$, was prepared by heating a lime-alumina clinker with a 4 to 3 molar ratio of CaO to Al_2O_3 with water for 7 days at 278° C. The resulting product was found to be homogeneous when examined microscopically. It consisted of rectangular plates having low birefringence with indices very close to 1.627.

Several difficulties and sources of error were encountered. At temperatures under 150° C, the filtrations in the pressure bombs were slow, taking approximately 10 minutes. It is estimated that the temperature of the vessel containing the solid and liquid phases changed 15 deg in this time, when taken from an oven at 150° C. In an effort to minimize this temperature change, the portion of the bomb that was not being cooled was covered with an asbestos glove during the filtration. The magnitude of the error is not known, because it depends in each case on how rapidly the liquid phase changes composition with temperature.

Above 150° C the filtrations were much more rapid, because of the greater pressure differential. In these cases, however, the spongy platinum on the Munroe-filter crucibles became perforated, allowing some solid to get into the filtrate. To overcome this difficulty, additional layers of spongy platinum had to be put on the filters. At 200° C and above, the liquid phase would go around the annealed silver gaskets above and below the flanges of the filter crucible, and this, too, would permit solid to get into the filtrate. Asbestos paper and Garlock gaskets were tried with no success. This problem was eventually solved by extending the layer of spongy platinum to cover the joints between the filter crucible and the silver gaskets.

It was found that distilled water alone, even at 120° C, attacked the bombs. With lime solutions the attack was more severe until a protective coating had been built up on the inner surface of the bombs. Then, at 120° C, the iron in the filtrate was reduced to about 1 part per million and the soluble chromate to a few parts per million.

When it became necessary to change the solid phase in the bombs, great care was taken to remove every trace of the preceding solid phase.

The attack on the bomb became increasingly severe as the temperature increased. At the same time, above 120° C, the solubilities of the compounds were decreasing. Accordingly, a platinum lining was fabricated for one of the bombs, and the system at 200° and 250° C was worked out by using this bomb.

The chromium extracted from the bombs was apparently all in the oxidized state as chromate and so did not interfere with the gravimetric determinations of lime and alumina. Most of the iron extracted from the bombs appeared to be in the form of insoluble flakes.

The necessity of excluding carbon dioxide from these determinations has been frequently pointed out by other investigators. The present authors, however, found that even when the most elaborate precautions were taken, it was impossible to exclude carbon dioxide completely. After each determination a trace of calcite was evident in the solid phases.

The constancy of oven temperature was about 1 percent at 120° C and 2 percent at 200° C.

3. Review of the System CaO-Al_2O_3-H_2O at 21° and 90° C

The investigation by Wells, Clarke, and McMurdie [5] has been mentioned earlier. They found that gibbsite is the only stable alumina hydrate in this system at both 21° and 90° C. Amorphous hydrated alumina exists metastably with respect to this gibbsite at 21° C, but no attempt was made to work out its solubility curve. Phase-equilibria diagrams are presented for this system at these two temperatures (see figs. 1 and 2). From these two diagrams, which, for convenience, are reproduced here (see figs. 1 and 2), one sees that at 21° C gibbsite is the stable hydrate of alumina from 0 to 0.33 g/liter of CaO and that it exists metastably to a concentration of about 0.7 g/liter of CaO. The maximum alumina hydrate in stable solution is about 0.02 g/liter at 0.33 g/liter of CaO, and the maximum alumina hydrate in metastable solution is about 0.06 g/liter at 0.7 g/liter of CaO. At 90° C, the stable gibbsite curve has rotated counterclockwise about the origin, and so lies above and has a steeper slope than the corresponding curve at 21° C. Gibbsite is seen to be the stable alumina hydrate from 0 to 0.33 g/liter of CaO and to have a much shorter metastable prolongation thereafter. The maximum ascertained stable solubility of alumina hydrate at 90° may be seen to be about 0.11 g/liter at 0.33 g/liter of CaO. The maximum stable solubility of the gibbsite at each of these temperatures corresponds to an invariant point with isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

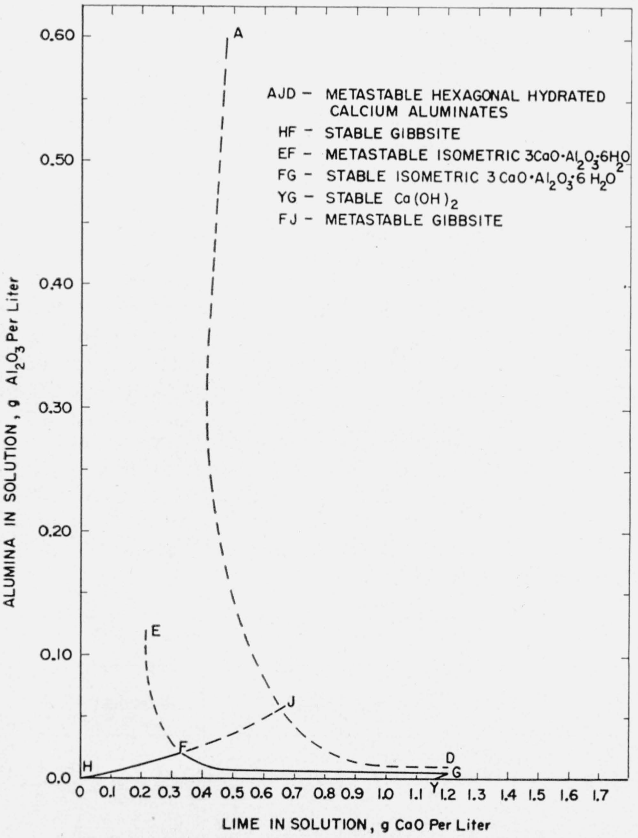

FIGURE 1. *The system* CaO-Al_2O_3-H_2O *at 21° C.*

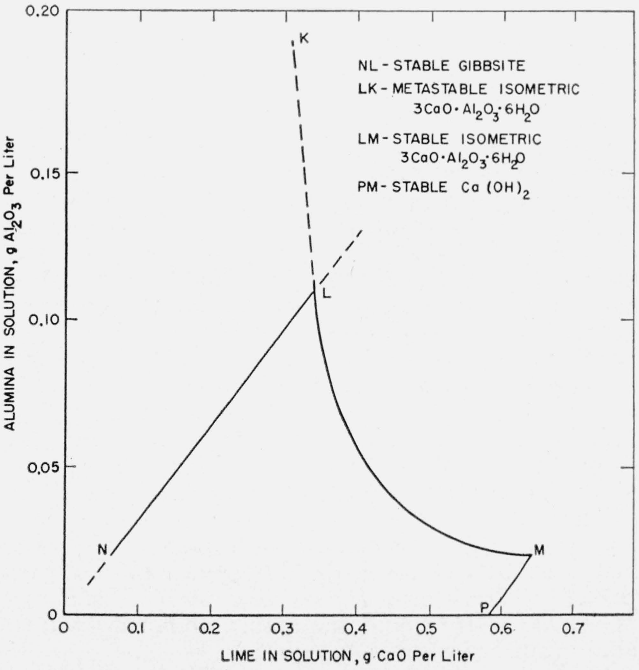

FIGURE 2. *The system* CaO-Al_2O_3-H_2O *at 90° C.*

One might suppose from the equilibria diagrams at these two temperatures (as the authors suggest) that there exists a family of stable equilibria curves for gibbsite at various intermediate temperatures, starting at the origin and being more or less straight lines with increasing slope as the temperature increases. It might also be supposed that since the gibbsite-isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ invariant points at these two temperatures lie directly above each other, the corresponding invariant points of the intermediate family of curves would lie on the straight line joining them.

Referring to figures 1 and 2, one sees that the authors found that the solubility of $Ca(OH)_2$ in water alone to be 1.17 g/liter at 21° C and about 0.58 g/liter at 90° C. The stable equilibria curves of $Ca(OH)_2$ were taken to be the straight line joining the points representing its solubility in water alone to the points where it coexists at equilibrium with isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$. In going from 21° to 90° C, this equilibrium curve lengthened and moved toward the origin. As it is known that the solubility of $Ca(OH)_2$ decreases with increasing temperature [13], it is assumed that at temperatures between 21° and 90° C there exists in this system a family of stable $Ca(OH)_2$ equilibria curves, lengthening and moving toward the origin as the temperature increases.

Wells, Clarke, and McMurdie [5] found three ternary compounds in this system at 21° C, namely, stable isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ and two metastable hexagonal calcium aluminate hydrates, $2CaO{\cdot}Al_2O_38H_2O$ and $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$.

To establish the metastable solubility curve of the hexagonal hydrates by approach from supersaturation, they prepared large quantities of metastable solutions by shaking alkali-free calcium-aluminate cements with distilled water. These mixtures were filtered, analyzed, and mixed with known amounts of lime water. They were put in stoppered bottles, stored at 21° C, and examined microscopically and aliquots analyzed from time to time. The same metastable equilibria as defined by final compositions of these solutions was approached also from undersaturation by mixing $2CaO{\cdot}Al_2O_3{\cdot}8H_2O$ and $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ with known varying concentrations of lime water. In this fashion these authors [5] were able to establish a metastable curve for the hexagonal phases lying above and to the right of the stable isometric hydrate curve. This curve is reproduced in fig. 1. From the molar CaO to Al_2O_3 ratios of the resulting solutions and the solid phases, these authors concluded that their metastable hexagonal hydrates curve actually corresponds to two intersecting metastable equilibria curves, one for $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ and one for $2CaO{\cdot}Al_2O_3{\cdot}8H_2O$. From these molar ratios, the shift in refractive index, and from X-ray diffraction data, they also concluded that so-called hexagonal tricalcium aluminate hydrate is actually a mixture of $4CaO{\cdot}Al_2O_313H_2O$ and $2CaO{\cdot}Al_2O_38H_2O$ intercrystallized in equimolecular proportions. This problem was not investigated further and for simplicity only the one metastable hexagonal calcium aluminate hydrate curve is reproduced here.

These same authors permitted a series of these metastable solutions containing hexagonal phases to stand at 21° C until the hexagonal phases were partially transformed to the stable isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$, and the stable isometric hydrate equilibrium curve was approached.

The only stable ternary compound in this system at 21° C was found to be the isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$. Its equilibrium curve was established by approach from undersaturation by letting the isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ stand in contact with lime solutions of varying concentrations. The isometric hydrate was found to dissolve congruently (went into solution parallel to the $3CaO{:}Al_2O_3$ composition line) at all concentrations up to the stable invariant point between $Ca(OH)_2$ and isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$, which in this case lies very close to the point representing the solubility of $Ca(OH)_2$ in water at 21° C (fig. 1).

It was assumed that the hexagonal phases would be so extremely metastable at 90° C and would have such a transitory existence before converting to the stable isometric hydrate that their equilibria relationships were not investigated by these authors.

In the present investigation, however, the undiluted filtrate of a high-alumina cement, representing a metastable solution of approximately 1.2 g/liter of CaO and 1.9 g/liter of Al_2O_3, was allowed to stand at 90° C. Precipitation of solid phases began almost immediately. At the end of 1 hour, these solid phases were metastable hexagonal aluminate hydrates only. At 4 hours, there were approximately equal amounts of isometric and hexagonal phases, and, at the end of 22 hours, although the isometric phases greatly predominated, the hexagonal phases were still present. Accordingly, a series of preparations of metastable solutions, whose Al_2O_3 contents varied from 0.1 to 0.6 g/liter, were held at 90° C for 1 hour and filtered. The solid phases were examined microscopically and the filtrates analyzed gravimetrically for lime and alumina. In all cases there was isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ as well as the hexagonal hydrates in the solid phases, though the isometric hydrate was of relatively small particle size. The initial and final compositions are shown in table 2 and figure 3. The curve so defined is considered to represent a metastable region rather than to define a metastable equilibrium. The metastable hexagonal hydrate equilibrium curve would lie above this curve and to the right of it. Experiments were performed that indicated that the solutions would have to be analyzed after only 5 minutes in order to define this curve. As one cannot expect to obtain consistent data in so short a time, this was not done. Wells, Clarke, and McMurdie found a metastable, extension of their stable isometric curve to the left and above the stable gibbsite-isometric $3CaO{\cdot}Al_2O_3{\cdot}3H_2O$ invariant. This metastable extension would presumably intersect the metastable hexagonal calcium aluminate hydrate curve at some point, as was the case at 21° C.

TABLE 2. *Metastable hexagonal phases at 90° C*

Experiment	Initial CaO	Initial Al_2O_3	Time	Final Al_2O_3	Final CaO	Final solid phases
	g/liter	*g/liter*	*Hours*	*g/liter*	*g/liter*	
1	1.20	0.60	1	0.640	0.585	Hexagonal phases predominate over isometric, with Al_2O_3 gel, in all cases.
2	1.20	.40	1	.252	.440	
3	1.20	.30	1	.118	.488	
4	1.20	.20	1	.055	.626	
5	1.20	.10	1	.026	.834	

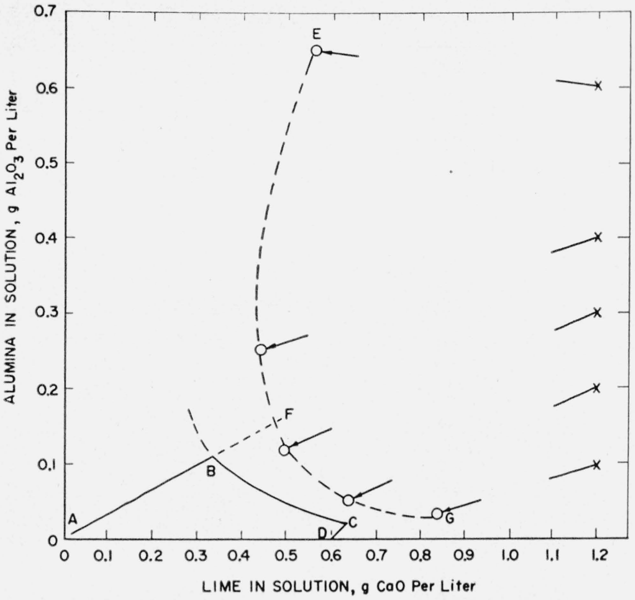

FIGURE 3. *Metastable hexagonal calcium aluminate hydrates in the system* CaO-Al_2O_3-H_2O *at 90° after one hour.*

Composition of initial metastable solutions are indicated by an X; compositions of these solutions at the end of one hour by an O. The dashed line, EFG, defines the region of metastability of the hexagonal calcium aluminate hydrates. The stable solubility fields in the system CaO-Al_2O_3-H_2O at 90° C are indicated by the area ABCD.

Presumably there exists also in this system at 21° C a metastable amorphous hydrated alumina solubility curve lying above the stable solubility curve of gibbsite. There should be an invariant between this curve and the metastable part of the isometric hydrate curve, as well as an invariant between the metastable alumina hydrate and the metastable hexagonal hydrate curve. This was not investigated by the present authors. If one takes Bessey's curve [3] for the solubility of Al_2O_3Aq and superimpose it on the diagram of the system at 21° C (fig. 1), the invariant with the metastable isometric would be at about 0.17 g/liter of Al_2O_3 and 0.20 g/liter of CaO, and the invariant with the metastable hexagonal phases would be at about 0.32 g/liter of Al_2O_3 and 0.4 g/liter at CaO. Unfortunately, Bessey gave no details about how he prepared and determined the solubility of Al_2O_3Aq, and, indeed, the practical difficulties of doing so are very great. More will be said about this in another portion of this paper.

The equilibrium curve for isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in this system at 90° C, as found by Wells, Clarke, McMurdie [5] is also reproduced here for convenience (see fig. 2). Referring to it one sees that this curve has the same shape as that at 21° C, lies above it, and has a shorter metastable extension. This curve was established by a perfectly analogous procedure, and again it was found that the isometric hydrate dissolves congruently in lime water of all concentrations up to that of the $Ca(OH)_2$-isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ invariant. As the above authors point out, it is reasonable to expect that a family of such curves exist between these two curves corresponding to temperatures between 21° and 90° C. The system was accordingly investigated at 50° C.

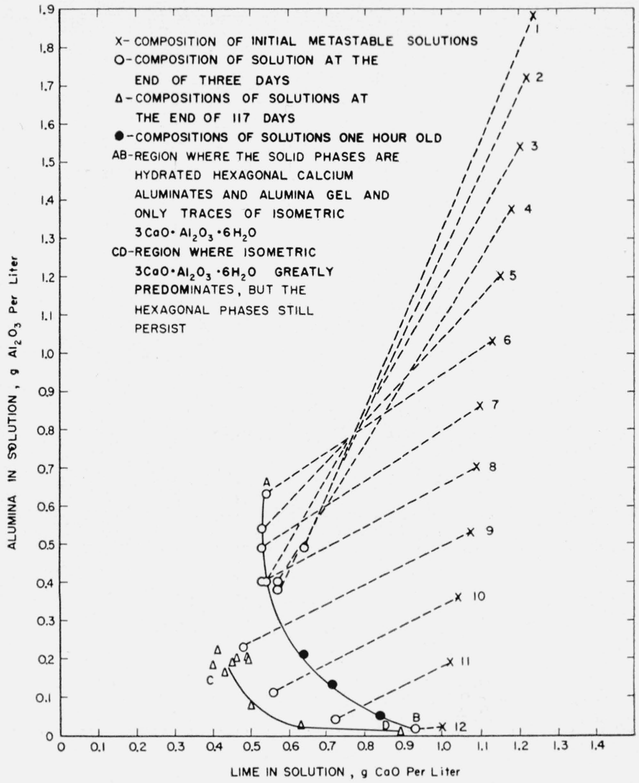

FIGURE 4. *Metastable hexagonal calcium aluminate hydrates in the system* CaO-Al_2O_3-H_2O *at 50° C.*

4. Discussion

4.1. The System CaO-Al_2O_3-H_2O at 50° C

The role of the hexagonal phases in the system CaO-Al_2O_3-H_2O at 50° C was investigated, using techniques similar to those used in the investigation at 21° C mentioned earlier.

A series of initially metastable solutions were prepared from the filtrate of high-alumina cement shaken with water plus additions of $Ca(OH)_2$ solutions. Precipitation began immediately upon mixing the alumina cement filtrate and the lime water in all cases except those of lowest alumina concentration. There was precipitation in all cases at the end of 3 days, however. Points representing these initial compositions are shown in figure 4. Referring to this figure, one sees that those initial mixes of highest alumina content were least stable. At the end of 3 days these mixtures had precipitated hexagonal phases and approached a relatively small area representing the alumina hydrate hexagonal calcium aluminate hydrate invariant point. Data on the solubility of the hexagonal calcium aluminate hydrates in the system CaO-Al_2O_3-H_2O at 50° C are presented in table 3. A total of 70 points was determined, but in the interests of simplicity, only the initial and final data are presented.

The behavior of composition 12, figure 4, is of special interest. The first precipitate, at the end

TABLE 3. *Solubility of the hexagonal calcium aluminate hydrates in the system* CaO-Al_2O_3-H_2O *at 50° C*

	Time	Initial Al_2O_3	Initial CaO	Final Al_2O_3	Final CaO	Final solid phases
		g/liter	*g/liter*	*g/liter*	*g/liter*	
1	3 days	1.88	1.24	0.487	0.635	Al_2O_3 gel, hexagonal, and isometric with hexagonal phases predominating.
2	do	1.72	1.22	.377	.566	Do.
3	do	1.54	1.20	.404	.545	Do.
4	do	1.37	1.18	.402	.568	Do.
5	do	1.20	1.15	.542	.539	Do.
6	do	1.03	1.13	.630	.545	Do.
7	do	.86	1.11	.488	.532	Do.
8	do	.70	1.09	.397	.527	Do.
9	1 hour	.30	1.20	.208	.639	Al_2O_3 gel and hexagonal phases.
10	do	.20	1.20	.132	.710	Do.
11	do	.10	1.20	.050	.836	Do.
12	3 days	.019	1.00	.013	.930	Do.
13	117 days	1.54	1.20	.200	.490	Hexagonal and isometric with hexagonal phases predominating.
14	do	1.37	1.18	.200	.462	Do.
15	do	1.20	1.15	.193	.494	Do.
16	do	1.03	1.13	.161	.430	Do.
17	do	.86	1.11	.189	.445	Do.
18	do	.70	1.09	.217	.414	Do.
19	do	.53	1.07	.185	.400	Hexagonal and isometric with isometric phases predominating.
20	do	.36	1.04	.076	.495	Do.
21	do	.188	1.02	.022	.630	Do.
22	do	.019	1.00	.002	.894	Hexagonal and isometric with hexagonal phases predominating.

of 3 days, was a mixture of isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and the hexagonal phases. When measured again at 10 days, however, the proportions of these two phases were reversed, with the hexagonal phases predominating. When the resulting composition of mixture 12 was measured at 35 days, hexagonal phases greatly predominated over the isometric phase, and after 90 days, the isometric phase had disappeared completely. At 117 days, $Ca(OH)_2$ crystals were observed, together with the hexagonal calcium aluminate hydrates, and the composition of the liquid in contact with these solid phases defined a point below the stable isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ curve.

It has been speculated by others [3, 15] that at high calcium hydroxide concentrations, the hexagonal rather than the isometric calcium aluminate hydrates are stable. As the behavior of the mixture represented by composition 12 tended to support this view, two new preparations, whose initial compositions lay between those of compositions 11 and 12 in figure 13, were prepared. These new preparations, however, precipitated both isometric and hexagonal phases. One of them defined a point on the metastable hexagonal hydrate equilibrium curve and the other a point between the hexagonal hydrate curve and the stable isometric curve at 0.95 g/liter of CaO. The distance between the two curves at this point is equivalent to only 0.05 g/liter of Al_2O_3. If one assumes that this point represents a hexagonal hydrate-isometric hydrate invariant point, and that composition 12 at the end of 117 days represents a hexagonal hydrate-$Ca(OH)_2$ invariant point, it might be concluded that the metastable curve of the hexagonal phases extends downward, intersecting both the stable isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and the stable $Ca(OH)_2$ equilibria curves. The authors feel that the evidence is entirely too slight to warrant this assumption. Moreover, the triangular area that would be thus defined is considerably smaller than the area of experimental uncertainty, so that the problem could not be resolved.

The path of precipitation of compositions 1 to 5, inclusive, (fig. 4) was extremely steep downward, and there was little difficulty in identifying Al_2O_3 gel in the solid phases. There was also in these compositions at the end of 3 days very small amounts of the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$, though the hexagonal phases greatly predominated. Between 3 and 10 days, the hexagonal phases continued to predominate greatly, and the cluster of points representing the compositions of the solutions coalesced and moved vertically downward as Al_2O_3 gel precipitated. For simplicity, only the initial paths of precipitation are shown in figure 4. At the end of 90 days, the hexagonal phases still predominated in all compositions except number 1.

The compositions of preparations 6 to 11 all alter in a path downward and parallel to each other but not exactly parallel to either the $3CaO:Al_2O_3$ or the $4CaO:Al_2O_3$ composition lines. The compositions of preparations 6 to 8 defined the cluster of points representing the Al_2O_3Aq-hexagonal calcium aluminate hydrate invariant (the point approached by the points representing the compositions of preparations 1 to 6) and had only traces of the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in them at the end of 3 days. Preparations whose compositions are indicated by 9 to 11 at the end of 3 days had a large proportion of isometric phase in the solid phases and no hydrated alumina detectable either with the petrographic microscope or X-ray patterns. The metastable curve of the hexagonal phases at 50° C (see fig. 4) was drawn through all points representing the compositions at the end of 3 days, except in the case of compositions 9 through 11. In these cases it is drawn through the points representing the compositions at the end of 1 hour of preparations, originally at approximately the same place as preparations 9, 10, and 11, and not shown in figure 4. The solid phases in compositions 9, 10, 11, even at 22 hours, had a large proportion of isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$, and this proportion increased with increasing time until at 90 days, although the hexagonal phases still existed, their proportion was very small.

The X-ray diffraction patterns of the hexagonal phases obtained in this investigation agree fairly well with those published by Wells, Clarke, and McMurdie [5], as seen in table 4. It could not be decided whether they more nearly represented those of $4CaO \cdot Al_2O_3 \cdot 13H_2O$ or $2CaO \cdot Al_2O_3 \cdot 8H_2O$, the patterns of which are themselves very similar.

Although the conversion of the hexagonal phases to the isometric phase is more rapid at 50° C than at 21° C, it is too slow to try to define the position of the stable isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ curve from supersaturation. The closest approach to this curve is shown in figure 4, at the end of 117 days.

The stable equilibrium curve of isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in this system at 50° C was established by approach from undersaturation, using the same technique as was used in the investigation at 21° and 90° C. Stoppered polyethylene bottles were used instead of glass. Quantities of solid isometric hydrate in the proportion of 2 g/liter of solid were mixed with different lime solutions of known concentrations.

TABLE 4. *X-ray patterns of the hexagonal phases interplanar spacings, d; relative intensities, I*

[S, strong; M, medium; W, weak]

This investigation at 50° C		Investigation of Wells, Clarke, and McMurdie [5] at 21° C for $2CaO \cdot Al_2O_3\ 8H_2O$	
d	*I*	*d*	*I*
7.557	S	10.6	S
5.15	S	5.3	S
3.767	S	3.55	M
2.864	S	2.87	S
2.576	W	2.69	W
		2.54	W
2.482	M	2.48	M
2.144	W	2.11	W
2.039	M	1.955	W
1.680	S	1.835	W
1.664	M		
		1.667	M
		1.591	W
1.596	W	1.443	M

It was observed that, as in the case of the investigation at 21° C, the isometric hydrate went into solution congruently in all concentrations of lime water up to that corresponding to the $Ca(OH)_2$-isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ invariant point.

Limitations of sample caused some of the determinations to be ended much sooner than corresponding ones that established the position of the gibbsite equilibrium curve at 50° C. However, the isometric hydrate approached equilibrium much faster at 50° C than does gibbsite.

In shape, the isometric hydrate curve is completely analogous to those at 21° and 90° C and lies between them. It is one of a family of such curves predicted by Wells, Clarke, and McMurdie [5]. The isometric calcium aluminate hydrate equilibrium curve at 50° C is presented in figure 5 and the corresponding data in table 5. It may be observed that the solubility of the isometric tricalcium aluminate hydrate, both in water and in lime solutions, is higher than at 21° C. The invariant point, C, with $Ca(OH)_2$ is taken as the average of the cluster of points in that area, where $Ca(OH)_2$ and the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ coexist at equilibrium. This invariant point is located at 0.961 g/liter of CaO and 0.005 g/liter of Al_2O_3.

TABLE 5. *Solubility of isometric* $3CaO \cdot Al_2O_3 \cdot 6H_2O$ *in the system* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 50° C*

Experiment	Concentration of lime solution	Time	Final Al_2O_3	Final CaO	Final solid phases
	g/liter	*Days*	*g/liter*	*g/liter*	
1	0	14	0.133	0.223	Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.
2	0.10	15	.089	.317	Do.
3	.10	40	.055	.254	Do.
4	.10	170	.095	.233	Do.
5	.20	15	.060	.386	Do.
6	.20	40	.036	.232	Do.
7	.30	14	.021	.332	Do.
8	.30	18	.019	.325	Do.
9	.30	38	.013	.319	Do.
10	.40	14	.007	.408	Do.
11	.40	18	.006	.404	Do.
12	.40	38	.007	.416	Do.
13	.50	15	.007	.552	Do.
14	.50	30	.008	.559	Do.
15	.60	14	.010	.678	Do.
16	.60	30	.007	.671	Do.
17	.70	14	.003	.747	Isometric; some birefringent occlusions.
18	.70	30	.005	.737	Do.
19	.80	15	.006	.805	Do.
20	.80	40	.004	.717	Do.
21	.90	16	.002	.887	Isometric with birefringent occlusions.
22	1.00	8	.003	.968	Isometric+$Ca(OH)_2$.
23	1.00	36	.003	.956	Do.
24	1.10	54	.005	.930	Do.
25	1.10	100	.007	.980	Do.
26	([a])	49	.002	.924	Do.
27	([a])	100	.006	.947	Do.
Experiments in which which both isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and gibbsite were the initial solid phases					
28	0	49	0.130	0.301	
29	0	100	.153	.258	
30	0	220	.182	.271	

[a] Saturation.

It is probable that Al_2O_3 gel has a metastable existence in the system at 50° C, lying above the stable gibbsite ($Al_2O_3 \cdot 3H_2O$) curve and intersecting and the metastable prolongation of the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ curve and the metastable hexagonal calcium aluminate hydrate curve.

In an attempt to determine the solubility of alumina gel, a quantity of it was prepared by double decomposition between $AlCl_3$ and NH_4OH. The resulting gelatinous hydrated alumina had occluded

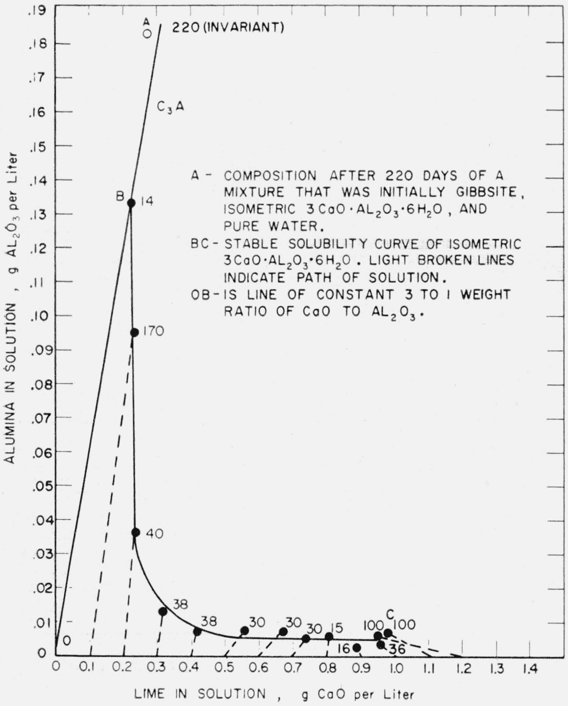

FIGURE 5. *Solubility of isometric* $3CaO \cdot Al_2O_3 \cdot 6H_2O$ *in the system* CaO-Al_2O_3-H_2O *at 50° C.*

much of the NH_4Cl formed by this reaction. An attempt was made to remove this occluded NH_4Cl by ordinary dialysis. At the end of 5 days, however, the gelatinous hydrated alumina still had retained enough electrolyte to suppress its solubility to 0.001 g/liter, or less. Moreover, X-ray diffraction patterns of the gel indicated that at the end of 3 days the hydrated alumina had already gone over to the gibbsite structure. Accordingly, attempts to measure the solubility of alumina gel were abandoned.

The solubility of alumina hydrate in this system at 50° C was found to be somewhat higher than that at 21° C. Again, gibbsite was found to be the stable hydrated phase of alumina, and its equilibrium curve and invariant point with isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ had the relation to those at 21° and 90° C that were earlier predicted.

Referring to figure 6 and table 6, one sees that the gibbsite apparently absorbs lime even at concentrations of lime less than that at the isometric hydrate-gibbsite invariant point. This is caused mainly by the fact that in the long periods of time involved carbon dioxide from the air was able to leak through the rubber stoppers and thus reduce the lime concentration by formation of calcite. The amount of calcite increased with increasing time, and the solubility of the gibbsite was essentially congruent until it had been formed. The fact that examination of the final solid phases showed nothing but gibbsite (other than a small amount of calcite) indicates that the reduction in lime concentration was not caused by chemical reaction between lime water and gibbsite.

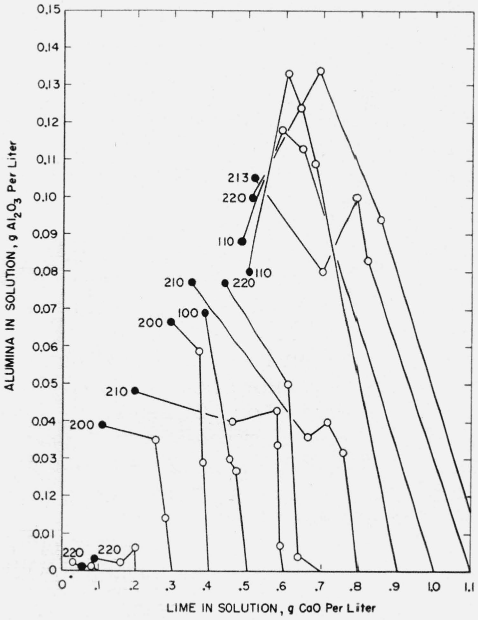

FIGURE 6. *Solubility of gibbsite in the system* CaO-Al_2O_3-H_2O *at 50° C.*

Closed circles indicate the composition of liquids in contact with gibbsite at the termination of the experiments. The corresponding ages in days are indicated by the accompanying numbers.

At concentrations of lime greater than that at the invariant point, however, once the gibbsite had reached its maximum metastable solubility, the reduction in lime concentration was much greater. The variation in the composition of the liquid phase occurred consistently in one path, and the final solid phases were gibbsite and hexagonal calcium aluminate hydrates. Accordingly, this is interpreted to mean that the gibbsite in supersaturated solution reacted with the lime water and points representing the composition of the liquid phase moved from the metastable hexagonal calcium aluminate hydrate-gibbsite invariant point toward the stable isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$-gibbsite invariant point. The behavior at 50° C is thus analogous to the behavior observed at 21° C.

The maximum metastable solubility of gibbsite at 50° C is seen by reference to figure 6 to be 0.13 g/liter as Al_2O_3, and is therefore considerably greater than that observed at 21° C.

The stable and metastable solubility curves of gibbsite are defined by the heavy black dots in figure 6; those taken at longest periods of time from the initial mixture of gibbsite and lime solutions. In most cases, these times were over 200 days. It is recognized that in no case was final equilibrium attained. This was due mainly to limitations of sample. The extreme sluggishness of approach to equilibrium at this temperature was somewhat unexpected.

Taking these final points as the best or nearest approach to equilibrium, it was thought that the

TABLE 6. *Solubility of gibbiste in the system* CaO-Al_2O_3-H_2O *at 50° C*

Experiment	Concentration of lime solution	Time	Final Al_2O_3	Final CaO	Final solid phases
	g/liter	*Days*	*g/liter*	*g/liter*	
1	0.10	45	[a] 0.001	0.077	Gibbsite.
2	.10	100	.002	.031	Do.
3	.10	220	.001	.053	Do.
4	.20	30	.006	.197	Do.
5	.20	48	[a] .002	.171	Do.
6	.20	220	.003	.088	Do.
7	.30	45	.014	.276	Do.
8	.30	100	.035	.250	Do.
9	.30	200	.039	.106	Do.
10	.40	48	.029	.379	Do.
11	.40	100	.059	.368	Do.
12	.40	200	.067	.286	Do.
13	.50	30	.030	.447	Do.
14	.50	50	.027	.467	Do.
15	.50	100	.069	.385	Do.
16	.60	14	.007	.587	Do.
17	.60	39	.034	.580	Do.
18	.60	56	.043	.584	Do.
19	.60	110	.040	.460	Do.
20	.60	210	.047	.197	Do.
21	.70	50	[a] .004	.641	Gibbsite+C_2Aaq.
22	.70	100	.050	.609	Do.
23	.70	200	.077	.436	Do.
24	.80	20	.032	.761	Gibbsite.
25	.80	39	.040	.712	Do.
26	.80	56	.036	.660	Do.
27	.80	110	[a] .02	.60	Do.
28	.80	210	.077	.352	Do.
29	.90	20	.109	.678	Do.
30	.90	39	.124	.642	Do.
31	.90	55	.133	.606	Do.
32	.90	110	.080	.500	Do.
33	1.00	20	.082	.675	Do.
34	1.00	39	.113	.641	Do.
35	1.00	55	.118	.590	Do.
36	1.00	110	.088	.48	Do.
37	1.10	45	.083	.820	Do.
38	1.10	55	.100	.787	Do.
39	1.10	110	[a] .08	.70	Do.
40	1.10	213	.105	.520	Do.
41	([b])	48	.094	.846	Do.
42	([b])	100	.134	.696	Do.
43	([b])	220	.100	.507	Do.

[a] The value of the Al_2O_3 is uncertain because a very small sample was taken for analysis.

[b] Saturation.

equilibrium curve could best be represented by a straight line. Accordingly, a straight line was fitted to these data by the method of least squares.

The invariant point of gibbsite-isometric hydrate was taken as the intersection of the stable gibbsite and stable isometric hydrate equilibria curves.

An attempt was made to find this invariant point directly by adding gibbsite and isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ to water and analyzing the resulting solutions from time to time. However, the stable invariant point was not approached closely even after 220 days, and attempts to define it in this fashion were abandoned.

The over-all diagram of the system at 50° C is presented in figure 7. It is analogous to the corresponding diagram of the system at 21° C (fig. 1).

The metastable invariant point between the metastable hexagonal phases and the metastable prolongation of the stable gibbsite solubility curve was found to be at 0.13 g/liter of Al2O3 and 0.63 g/liter of CaO. Referring to figure 7, one sees that this metastable invariant has the relationship to the corresponding invariant at 21° C that might be expected.

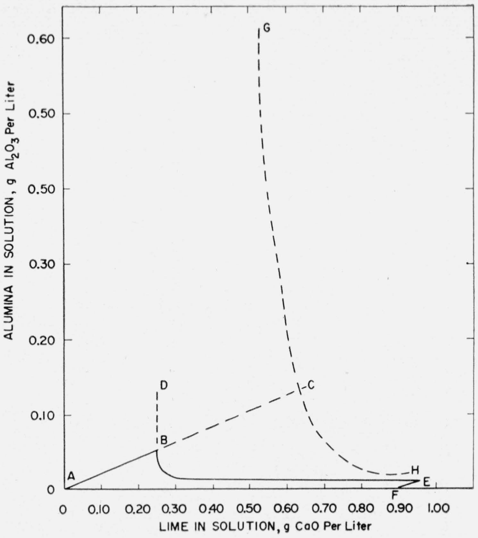

FIGURE 7. *The system* CaO-Al_2O_3-H_2O *at 50° C.*

The solid line AB indicates the stable gibbsite equilibrium curve; BE, the stable isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ curve; EF, stable $Ca(OH)_2$; the dashed line BC, metastable gibbsite; DB, metastable isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$; GCH, metastable hexagonal calcium aluminate hydrates.

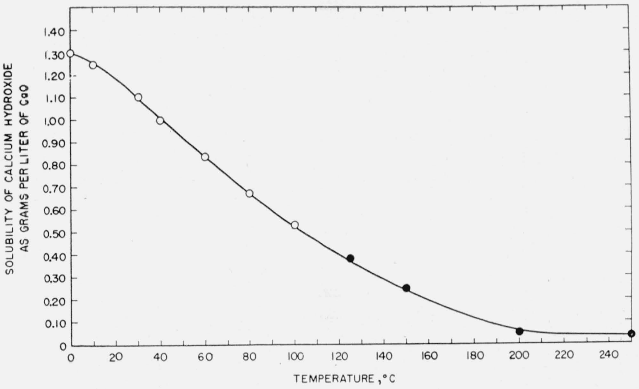

FIGURE 8. *The solubility of* $Ca(OH)_2$ *at various temperatures.*

The data of Bassett [13] is indicated by open circles; that of this investigation by closed circles.

The solubility of $Ca(OH)_2$ in this system at 50° C was taken from a graph of Basset's data [13], reproduced here in figure 8. It is seen, as was predicted, that the solubility curve of $Ca(OH)_2$ has lengthened and moved toward the origin, and is intermediate between that at 21° and that at 90° C.

4.2. The System CaO-Al_2O_3-H_2O at 120° C

In investigating the solubility of alumina hydrate in this system at 120° C, it was found that gibbsite again was the stable phase, that its solubility curve was again a straight line, and that it dissolved congruently in all concentrations of lime water up to the invariant point with isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

TABLE 7. *Solubility of gibbsite in the system* CaO-Al_2O_3-H_2O *at 120° C*

Experiment	Concentration of lime solution	Time	Final CaO	Final Al_2O_3	Final solid phases	Remarks
	g/liter	*Days*	*g/liter*	*g/liter*		
1	0.10	5	0.085	0.070	Gibbsite	
2	.20	5	.195	.176	do	
3	.30	13	.337	.323	do	
4	.40	5	.320	.294	do	Index raised.
5	.50	5	.336	.293	do	Do.
6	.60	5	.315	.308	Gibbsite, isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$	Index of gibbsite raised.
7	.70	5	.323	.316	Gibbsite	Do.
8	.80	5	.320	.320	do	Do.
9	.90	5	.347	.266	do	Do.
10	1.00	5	.296	.293	do	Index raised.
11	1.10	5	.332	.338	Gibbsite, isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.	
12	[a] 1.17	5	.330	.300	do	

[a] Saturation.

Thereafter it lowered the concentrations of the lime of the initial solutions by reacting chemically to form isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$. The final compositions of the solutions were those of the stable isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$-gibbsite invariant, which was found to lie directly above this invariant at lower temperatures. In the system at 120°, however, there was virtually no metastable prolongation of the gibbsite equilibrium curve, and, of course, no Invariant between this metastable curve and that of the hexagonal phases (see table 7 and fig. 9).

The pressure at 120° C, the equilibrium vapor pressure of water at this temperature, has approximately doubled, but the system, as discussed earlier, is still to be considered as a condensed system. The equilibrium curve of gibbsite at 120° C is then comparable to those at lower temperatures. It is a member of the same family of curves starting near the origin and having increasing slope with increasing temperature. The sudden pressure change, however, is accompanied by a change in the rate at which the slope of these curves have been increasing with temperature (see fig. 10 and table 8).

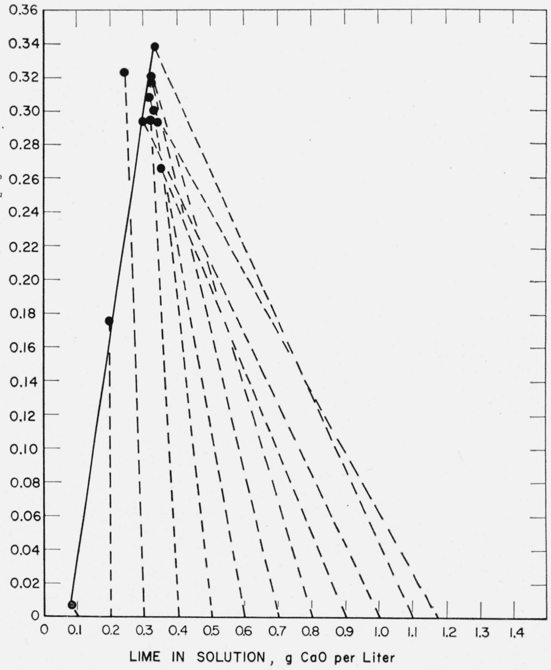

FIGURE 9. *Solubility of gibbsite in the system* CaO-Al_2-O_3-H_2O *at 120° C.*

Equilibrium approached from under-saturation. Dotted lines indicate change in composition of the liquids in contact with solid gibbsite.

TABLE 8. *Slope of the gibbsite equilibria curves as a function of temperature*

Temperature	Average slope [1]
°C	
21	0.054
50	.184
90	.336
120	.909

[1] Average slope is the average ratio of Al_2O_3 to CaO for all experimental points at lesser lime concentrations than that corresponding to the gibbsite-isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ invariant point.

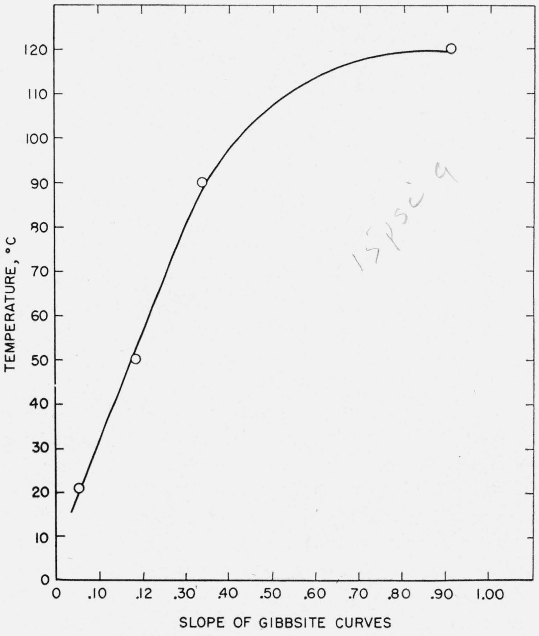

FIGURE 10. *Slope of the gibbsite equilibria curves in the system* CaO-Al_2O_3-H_2O *as a function of temperature.*

Values for the solubility of $Ca(OH)_2$ in water at 125°, 150°, 200°, and 250° C (see table 9) were determined with the apparatus and technique used in the phase equilibria investigations. A solution of $Ca(OH)_2$ saturated at room temperature was placed in one vessel of the pressure bomb, which was heated to the desired temperature for 5 days. It was then removed from the oven and filtration accomplished as described earlier. The liquid in each case was in equilibrium with large, well-developed crystals of $Ca(OH)_2$. It was analyzed for CaO by the usual gravimetric determination of oxalate and ignition to the oxide. These values of the solubility of $Ca(OH)_2$ in water were added to those obtained by Bassett [13], and a composite graph was constructed (fig. 8). The solubility of $Ca(OH)_2$ in water at 120° C was taken from this graph.

TABLE 9. *Solubility of calcium hydroxide in water at various temperatures*

Experiment	Temperature	Time	Solubility	Remarks
	°C	*Days*	*g/liter as* CaO	
1	30	9	0.87	
2	30	10	.90	
3	30	11	.91	
4	30	14	.93	
5	30	16	.96	
6	30	18	.97	
7	30	21	.99	
8	30	23	1.00	
9	30	25	1.03	Constant thereafter.
10	125	5	0.380	
11	150	2	.266	Equilibrium with small crystals.
12	150	10	.270	Do.
13	150	2	.240	Equilibrium with large crystals.
14	150	5	.247	Do.
15	200	5	.047	
16	200	7	.05	
17	200	5	.05	
18	250	7	.037	

The invariant point of calcium hydroxide and isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ was determined in the course of an investigation of the solubility of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in this system at 120° C. It was found to lie at 0.42 g/liter of CaO and 0.042 g/liter of Al_2O_3. Accordingly, a straight line between this invariant point and the point on the CaO concentration axis representing the solubility of CaO in water alone is taken to represent the stable equilibrium curve of $Ca(OH)_2$ in the ternary system at 120°. It is evident that this line is also a member of the family of $Ca(OH)_2$ equilibria lines that lengthen and approach the origin as the temperature increases.

Possible metastable existence of the hexagonal calcium aluminate hydrates phases was not investigated, but none was found in any of the experiments made. The equilibrium curve of isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ was established by an approach from undersaturation, by heating isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ with lime water of varying strengths for 5 to 7 days.

The equilibrium curve of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in the system at 120° C is shown in figure 11 and the corresponding data in table 10. It may be seen that the equilibrium line is a nearly vertical straight line, having no horizontal section as had the corresponding equilibria curves at lower temperatures. The isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ still dissolves congruently, however, at all lime concentrations under that of the invariant with $Ca(OH)_2$.

TABLE 10. *Solubility of isometric* $3CaO\text{-}Al_2O_3\text{-}6H_2O$ *in the system* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 120° C*

Experiment	Time	Concentration of lime solution	Final CaO	Final Al_2O_3	Final solid phases
	Days	*g/liter*	*g/liter*	*g/liter*	
1	5	0.00	0.300	0.170	Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$
2	5	.10	.327	.132	Do.
3	5	.10	.335	.132	Do.
4	5	.20	.359	.115	Do.
5	5	.30	.432	.070	Isometric+$Ca(OH)_2$.
6	5	.40	.408	.050	Do.
7	5	.60	.428	.054	Do.
8	5	.70	.450	.040	Do.
9	5	.80	.415	.052	Do.
10	5	.90	.408	.038	Do.
11	5	1.10	.433	.038	Do.
12	5	[1] 1.204	.402	.043	Do.
Invariant, initial phases being gibbsite and isometric.					
13	6	0.00	0.273	0.252	Gibbsite + isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$. Gibbsite, with index raised.

[1] Saturated.

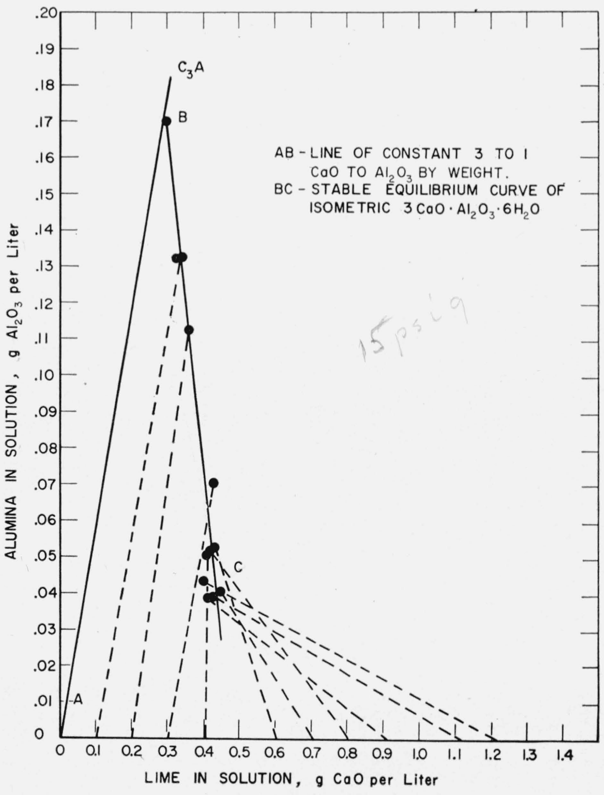

FIGURE 11. *Solubility of isometric* $3CaO \cdot Al_2O_3 \cdot 6H_2O$ *in the system* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 120° C.*

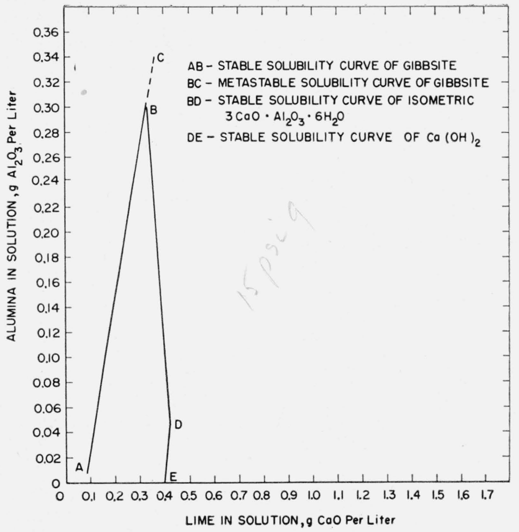

Figure 12. *The system* $CaO-Al_2O_3-H_2O$ *at 120° C.*

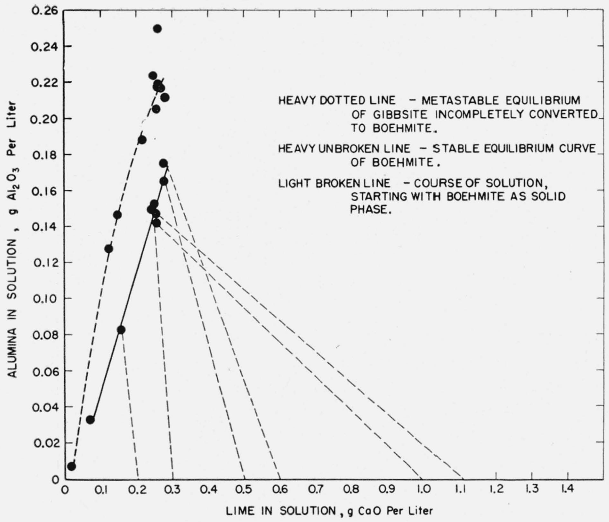

Figure 13. *Solubility of alumina hydrates in the system* $CaO-Al_2O_3-H_2O$ *at 150° C.*

The over-all system at 120° C is presented in figure 12. The solubility of alumina has reached a maximum, and the solubility fields are compressed toward the alumina-concentration axis. It may be observed that the metastable prolongation of the alumina hydrate curve still persists at this temperature, to a maximum of 0.34 g/liter of Al_2O_3.

4.3. The System $CaO-Al_2O_3-H_2O$ at 150° C

At 150° C it was found that gibbsite ($Al_2O_3 \cdot 3H_2O$) was no longer the stable alumina hydrate, but converted to boehmite ($Al_2O_3 \cdot H_2O$). The transformation was sufficiently slow at this temperature, because it is very close to the gibbsite-boehmite transition temperature in water alone as reported in the literature [14], that it was possible to work out a metastable solubility curve for gibbsite at 150° C (see fig. 13 and table 11).

When gibbsite was the initial solid phase, the final solid phase at the end of 5 days was not gibbsite, but a mixture of gibbsite and boehmite. The "metastable equilibrium curve" of gibbsite in figure 13 is then an arbitrarily chosen one, the one which represents the particular degree of conversion to boehmite that obtains at the end of 5 days. It is intended that this curve represents only a region of metastability.

The stable boehmite curve was established in the same manner as before, using boehmite as the initial solid phase and placing it in varying concentrations of lime water (see fig. 13 and table 12).

Again the points representing the composition of the liquids in equilibrium with boehmite define a straight line starting near the origin. It may be noted that the slope of this line is less than that of the gibbsite at 120° C.

The positions, lengths, and slopes of the various equilibria curves at 150° C no longer show a direct proportionality to the temperature. The pressures are increasing, and the solubilities are decreasing at an accelerated rate. It was found that the departure

Table 11. *Solubility of gibbsite in the system* $CaO-Al_2O_3-H_2O$ *at 150° C*

Experiment	Concentration of lime solution	Time	Final CaO	Final Al_2O_3	Final solid phases	Remarks
	g/liter	*Days*	*g/liter*	*g/liter*		
1	0.05	7	0.020	0.008	Boehmite [1]	Some gibbsite, index of boehmite is lowered.
2	.10	5	.127	.128	do	Do.
3	.20	5	.248	.200	do [2]	Do.
4	.20	5	.276	.212	do	Do.
5	.30	5	.153	.147	do	Do.
6	.40	5	.217	.189	do	Index varies between boehmite and gibbsite.
7	.50	5	.247	.224	Boehmite+isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.	Some gibbsite.
8	.60	5	.259	.219	do	Do.
9	.70	5	.255	.250	do	Do.
10	.80	5	.258	.218	do	Do.
11	.90	5	.262	.205	do	Do.
12	[3] 1.11	5	.273	.217	do	Do.

[1] Boehmite predominated in all cases, but gibbsite was incompletely converted.
[2] Filtration imperfect.
[3] Saturation.

from the behavior below 120° C could be correlated with pressure, but as pressure is not an independent variable here but a function of temperature, only the effect of temperature on solubility will be discussed.

It may be observed from figure 13 that the boehmite-isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ invariant point has shifted from 0.33 g/liter of CaO to 0.25 g/liter in going from 120° to 150° C. No metastable prolongation of the boehmite equilibrium curve was found beyond this invariant point. When mixes of boehmite with lime water of concentrations greater than 0.25 g/liter were held at 150° C for 5 days, the final compositions of the liquids fell in a small area, the average of which was taken as the invariant point. This indicated that the boehmite behaved in the same manner as the gibbsite, combining with CaO of the solution to form the isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$. The solid phases in equilibrium at this invariant point were again identified both petrographically and by X-ray diffraction patterns.

The solubility of CaO in water at 150° C was taken from the graph mentioned earlier. The $Ca(OH)_2$ equilibrium curve in this system at 150° C has again lengthened and moved to the left, continuing the trend previously established.

The equilibrium curve of the isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ in the system at 150° C is shown in figure 14, and the corresponding data are presented in table 13. It is analogous in all respects to the corresponding curve at 120° C, but it is shorter and closer to the alumina concentration axis.

The over-all system at 150° C is shown in figure 15. The solubility fields have been compressed

TABLE 12. *Solubility of boehmite in the system* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 150° C*

Experiment	Concentration of lime solution	Time	Final CaO	Final Al_2O_3	Final solid phases
	g/liter	*Days*	*g/liter*	*g/liter*	
1	0.10	7	0.072	0.034	Boehmite.
2	.20	7	.160	.084	Do.
3	.30	7	.240	.150	Do.
4	.40	7	.250	.153	Boehmite+isometric $3CaO.Al_2O_3{\cdot}6H_2O$.
5	.50	7	.277	.166	Do.
6	.60	7	.281	.176	Do.
7	.70	7	[1].210	.116	Do.
8	1.00	5	.259	.142	Do.
9	[2]1.112	5	.261	.147	Do.

[1] Filtration imperfect.
[2] Saturation.

TABLE 13. *Solubility of isometric* $3CaO.Al_2O_3.6H_2O$ *in the system* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 150° C*

Experiment	Concentration of lime solution	Time	Final CaO	Final Al_2O_3	Final solid phases
	g/liter	*Days*	*g/liter*	*g/liter*	
1	0.00	7	0.256	0.208	Isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$.
2	.00	6	.235	.204	Do.
3	.10	7	.270	.130	Do.
4	.20	7	.300	.090	Do.
5	.30	7	.290	.070	Do.
6	.60	7	.340	.046	Isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ $+Ca(OH)_2$.
7	.70	7	.342	.050	Do.
8	.80	7	.345	.054	Do.
9	.90	7	.324	.060	Do.
10	1.00	7	.342	.061	Isometric $3CaA{\cdot}Al_2O_3{\cdot}6H_2O$ $+Ca(OH)_2$.
11	Satin	7	.331	.042	Do.
12[1]	0.00	5	.267	.154	
13[2]	.00	5	.256	.194	
14[1]	.00	5	.226	.200	

[1] Isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ and gibbsite initially.
[2] Isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ and boehmite initially.

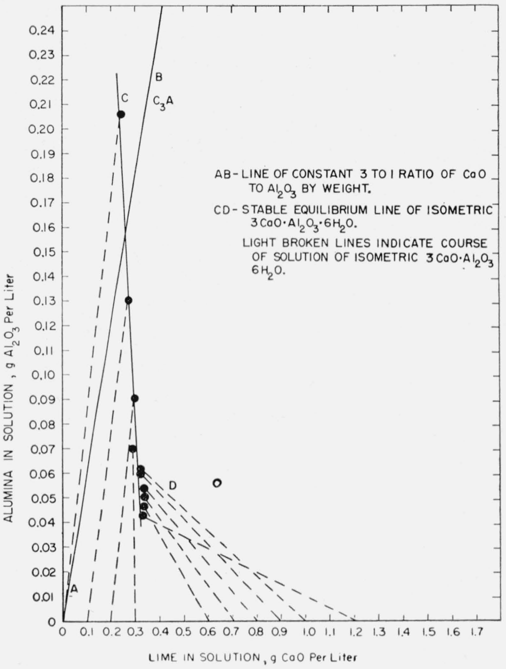

FIGURE 14. *Solubility of isometric* $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ *in the system* $CaO\text{-}Al_2O_3\text{-}H_2C$ *at 150° C.*

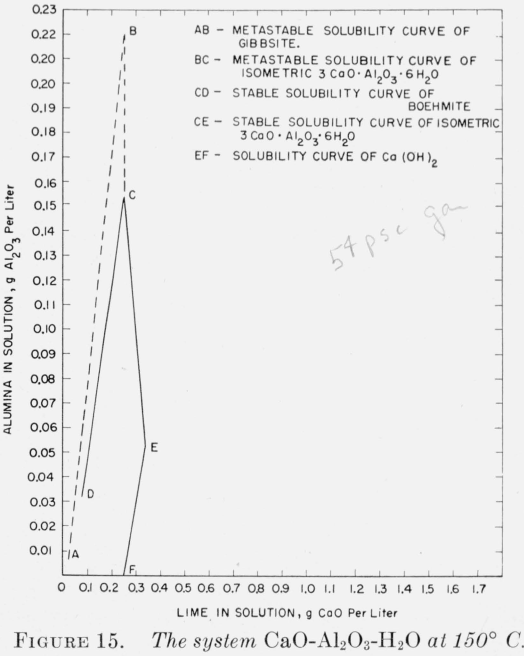

FIGURE 15. *The system* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 150° C.*

toward the water apex. The maximum stable solubility of alumina has become 0.15 g/liter, and nowhere does the solubility of $Ca(OH)_2$ exceed 0.33 g/liter. The metastable prolongation of the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ equilibrium curve, which meets the metastable gibbsite curve, was not determined experimentally. Indeed, as this portion of the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ curve lies above the $3CaO:Al_2O_3$ composition line, and the $3CaO \cdot Al_2O_3 \cdot 6H_2O$ dissolves congruently, it could not be directly determined. Although it might be established indirectly, its length is too short to justify the work involved.

4.4. The System CaO-Al_2O_3-H_2O at 200° C

At 200° C, when gibbsite is the initial phase and is placed in varying concentrations of lime water, it converts completely to boehmite. After 5 days, and perhaps much earlier, gibbsite does not exist even metastably in the system at 200° C.

At this temperature, attack on the bomb is very severe, and boehmite absorbs CaO from the lime solutions. When boehmite was placed in contact with lime solutions up to 0.10 g/liter, it absorbed as much as 5 percent by weight of CaO from the solution, causing marked reduction in lime concentrations and making it impossible to work out the boehmite equilibrium curve in the same fashion as before. What was actually obtained was a small cluster of points in the area between 0 and 0.03 g/liter of CaO and 0 and 0.007 g/liter of Al_2O_3.

When gibbsite or boehmite were held in contact with saturated lime water for 5 days, however, the composition of the final solutions was the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O_3$-boehmite invariant at 0.085 g/liter of Al_2O_3 and 0.11 g/liter of CaO. Accordingly, a straight line from the average value of the cluster of points near the origin to this invariant was taken to represent the stable equilibrium curve of boehmite, even though, because of experimental difficulties, intermediate points could not be obtained (see table 14 and fig. 16). This line is shorter than the corresponding one at 150° C, and its maximum is somewhat lower, but the alope has again increased.

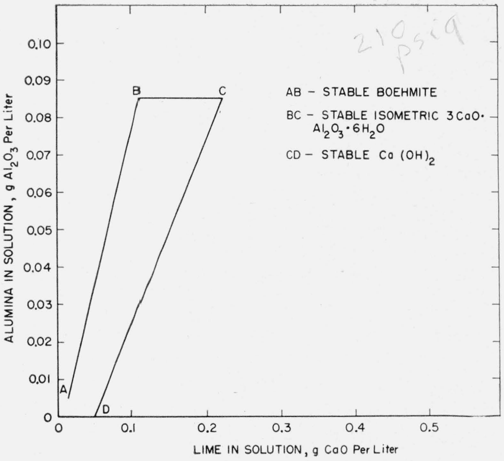

FIGURE 16. *The system* CaO-Al_2O_3-H_2O *at 200° C.*

The solubility of $Ca(OH)_2$ in the system at 200° C was found to be of the order of 0.05 g/liter as CaO, and mixtures of isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and saturated lime water gave equilibrium mixtures of the two solid phases in contact with a solution whose composition was 0.085 g/liter of Al_2O_3 0.22 g/liter of CaO. The point thus defined is the $Ca(OH)_2$- isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ invariant point. A straight line joining this point with the point representing the solubility of $Ca(OH)_2$ in water alone is, as before, taken to be the stable equilibrium curve of $Ca(OH)_2$ in the system at 200° C. It follows the trend of and belongs to the family of curves for $Ca(OH)_2$ at lower temperatures.

The phase diagram for the system CaO-Al_2O_3-H_2O at 200° C is presented in figure 16 and the corresponding data in table 14. The equilibrium curve of the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ is analogous to that at 150° C, but again has shortened and moved toward the alumina concentration axis.

TABLE 14. *Equilibrium compositions in the system* CaO-Al_2O_3-H_2O *at 200° C*

Experiment	Initial solid phase	Initial CaO	Time	Final Al_2O_3	Final CaO	Final solid phases
		g/liter	*Days*	*g/liter*	*g/liter*	
1	Boehmite	0.025	7	0.001	0.022	Boehmite.
2	Gibbsite	.025	7	.001	.003	Do.
3	Boehmite	.050	7	.004	.023	Do.
4	do	.200	7	.002	.018	Do.
5	Gibbsite	.200	7	.002	.020	Do.
6	Gibbsite+isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.	0.00	7	.064	.093	Boehmite+isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.
7	Boehmite	1.20	5	.051	.100	Do.
8	do	1.20	5	.090	.112	Do.
9	do	1.20	5			
10	Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$	1.20	7	.091	.200	Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$+$Ca(OH)_2$.
11	do	1.20	7	.080	.225	Do.
12	do	1.20	7	.080	.258	Do.
13	do	1.20	7	.091	.200	Do.
14	Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$	0.00	7	.148	.175	Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.
15		1.20	5		.047	$Ca(OH)_2$
16		1.20	7		.050	Do.
17		1.20	5		.050	Do.

419 psi

When the compound $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ is added to saturated lime water at 200° C, the isometric hydrate and boehmite are found to be the final phases, and when the isometric hydrate is the initial phase it is also the final solid phase. There is some difficulty, however, in that the proportion of birefringent inclusions of the isometric hydrate, never absent, increases with temperature, until at 200° C, the occlusions are definitely prominent. A series of determinations was made between 200° C and 250° C, at 10-deg intervals to locate more accurately the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$-$4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ transition temperature. The temperature at which microscopically detectable amounts of the 4:3:3 hydroaluminate were first evident was found to be between 210° and 220° C. At times under 4 days, however, the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ persisted metastably up to 250° C.

Above 120° C, a maximum solubility of the alumina hydrate has been reached, and the invariants between the alumina hydrate and the stable ternary compound descend with temperature after 120° C. The lengths of the isometric hydrate equilibria curves continue to decrease and are defined by straight lines as the solubility fields compress with increasing temperature to the H_2O apex.

4.5. The System CaO-Al_2O_3-H_2O at 250° C

When the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ is used as the initial solid phase at 250° C, it is quantitatively converted to the 4:3:3 hydroaluminate at initial concentrations of lime water from 0.1 g/liter to saturation. A photomicrograph of this compound is shown in figure 17. The $Ca(OH)_2$-$4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ invariant at this temperature was determined by heating $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ with saturated lime water. Similar experiments, starting with boehmite as the initial solid phase, established the $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$-boehmite invariant. The $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$-$Ca(OH)_2$ invariant is at 0.02 g/liter of Al_2O_3 and 0.065 g/liter of CaO; that of $4CaO \cdot 3Al_2O_3 3H_2O$-boehmite, at 0.034 g/liter of Al_2O_3 and 0.063 g/liter of CaO (see table 15). These two invariants are so close together and so close to a point representing the solubility of $Ca(OH)_2$ in water alone that the phase diagram at 250° C was constructed simply by connecting these points by straight lines (see fig. 18).

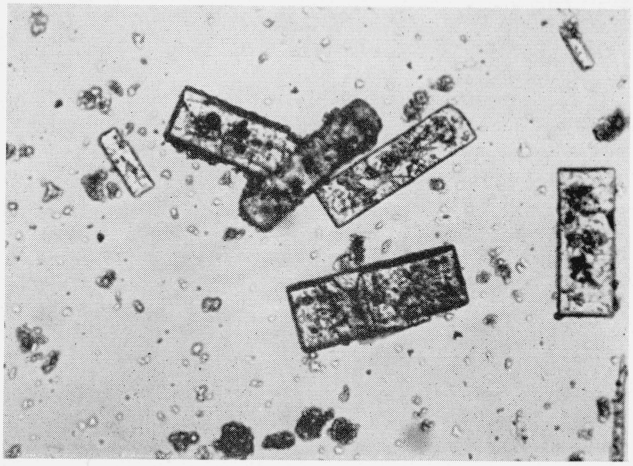

FIGURE 17. *Synthetic* $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$.

Magnification, X 180.

560 psig

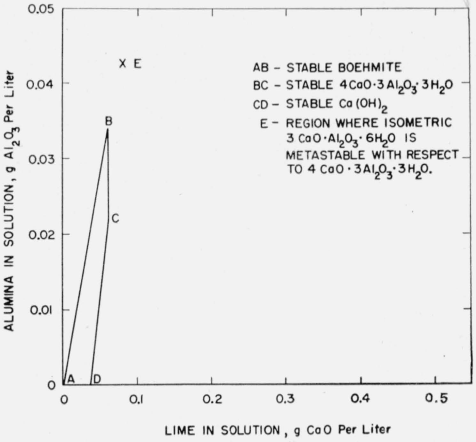

FIGURE 18. *The system* $CaO \cdot Al_2O_3$-H_2O *at 250° C.*

The region where the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ exists metastably with respect to $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ is indicated in this figure by a cross, E.

The entire solubility fields have been compressed severely into the water apex. It may be seen that the diagram at 250° C is similar to that at 200° C, differing mainly in that the solubility of the alumina hydrate at 250° C is much smaller.

TABLE 15. *Equilibrium compositions in the system* CaO-Al_2O_3-H_2O *at 250° C*

Experiment	Initial solid phase	Initial CaO	Time	Final CaO	Final Al_2O_3	Final solid phase
		g/liter	*Days*	*g/liter*	*g/liter*	
1		1.20	5	0.037	--------	$Ca(OH)_2$.
2	Boehmite	1.20	4	.078	0.045	Boehmite+$4CaO \cdot 3Al_2O_3 \cdot 3H_2O$.[1]
3	do	1.20	5	.039	.022	Do.
4	do	1.20	6	.072	.036	Do.
5	$4CaO \cdot 3Al_2O_3 \cdot 3H_2O$	1.20	5	.065	.018	$Ca(OH)_2$+$CaO \cdot 3Al_2O_3 \cdot 3H_2O$.
6	do	0.10	5	.057	.025	Do.

[1] Contains trace of isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

4.6. The System $CaO\text{-}Al_2O_3\text{-}H_2O$ Over the Range 21° to 250° C

The metastable equilibria of hydrated amorphous alumina, which presumably exist only at lower temperature in the system, have not been worked out. Its invariant with metastable hexagonal phases at 21° and 50° C has been determined, and a straight line between this point and the origin probably represents the Al_2O_3Aq solubility curve fairly well. The experimental difficulties in obtaining these solubility curves have been discussed earlier.

Gibbsite is the only stable alumina hydrate in the system, up to and including 150° C. At temperatures up to 100° C, its solubility is directly proportional to the temperature (see fig. 10), the slope of the equilibrium curve increasing 0.04 g/liter of Al_2O_3 for every 10-deg C increase in the temperature.

Gibbsite persists in the system at 150° C, but it is metastable with respect to boehmite, and at 200° C, gibbsite does not exist in the system, and boehmite is the stable alumina phase.

It is seen from figure 20 that the equilibria curves for alumina are a family of straight lines from the vicinity of the origin. Above 120° C these curves shorten and have greater slopes. At some temperature above 250° C the solubility of Al_2O_3 would presumably become negligibly small.

The maximum Al_2O_3 concentration values, which are those of the alumina hydrate-isometric hydrate invariant point versus temperature, may be seen in figure 10. It may be observed that the corresponding concentration of CaO remains almost constant throughout. (0.30 ±0.05 g/liter.) There is a sharp maximum at 120° C of 0.30 g/liter of Al_2O_3. This is presumably the maximum Al_2O_3 that can exist in stable solution in this system at any temperature.

The solubility of $Ca(OH)_2$ in water alone decreases rapidly as the temperature increases (see fig. 9). In the temperature range investigated in varies from 1.15 g/liter at 21° C to 0.037 g/liter as CaO at 250° C. At all temperarures, the $Ca(OH)_2$ equilibria curves slope slightly to the right (with the possible exception of that at 21° C, where the $Ca(OH)_2$ equilibrium curve is so short as to be very difficult to define). The slope of the $Ca(CH)_2$ equilibrium curve, like that of alumina hydrate, is directly proportional to the temperature up to 120°, where it goes through a sharp maximum. From figure 20 it can be seen that the $Ca(OH)_2$ equilibria curves are a family, lengthening and moving to the left as the temperature increases. A line through the extremities of these curves represents the maximum solubility of $Ca(OH)_2$ in the system as a function of temperature.

The equilibria curves of the isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ in this system at various temperatures are of two types (fig. 20). Those at 120° C and below have sharp curves, from a nearby vertical to a nearly horizontal direction. Above 150° C the curves are straight lines, with negative slopes, moving to the left and becoming shorter as the temperature increases. The effect of the rapidly diminishing solubility of $Ca(OH)_2$ with increasing temperature on the slope and position of these curves has already been mentioned.

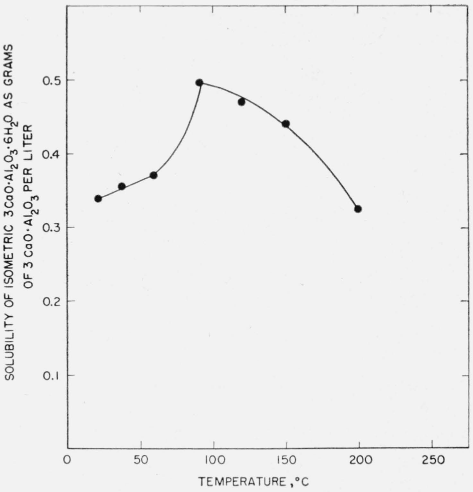

FIGURE 19. *Solubility of isometric* $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ *in water at various temperatures.*

TABLE 16. *Solubility of isometric* $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ *in water as a function of temperature*

Temperature	Final composition of solution		$CaO+Al_2O_3$	Weight ratio CaO/Al_2O_3
	CaO	Al_2O_3		
°C	*g/liter*	*g/liter*	*g/liter*	
21	0.208	0.131	0.339	1.59
50	.223	.133	.356	1.68
60 [1]	.246	.123	.369	2.00
90	.306	.190	.496	1.61
120	.300	.170	.470	1.76
150	.235	.204	.439	1.51
200	.175	.148	.323	1.19

[1] For 17 days.

Table 16 gives values of the solubility of the isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ in water at various temperatures, and these values are plotted in figure 19. One observes that the solubility increases rapidly with the temperature to the neighborhood of the boiling point of water and thereafter falls off rapidly. It follows that the maximum stable solubility of isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ is 0.49 g/liter as $3CaO{\cdot}Al_2O_3$, corresponding to 0.685 g/liter as $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$. There is a great deal of variation in the literature values of the solubility of isometric hydrate near room temperature. These are discussed in detail in the investigation of Wells, Clarke, and McMurdie, [5], whose value is plotted in figure 19.

An over-all picture of the system $CaO\text{-}Al_2O_3\text{-}H_2O$ from 21° to 250° C is seen in figure 20. It is assumed that at temperatures above 250°C, the solubility fields will become immeasurably small and vanish into the water apex of the diagram.

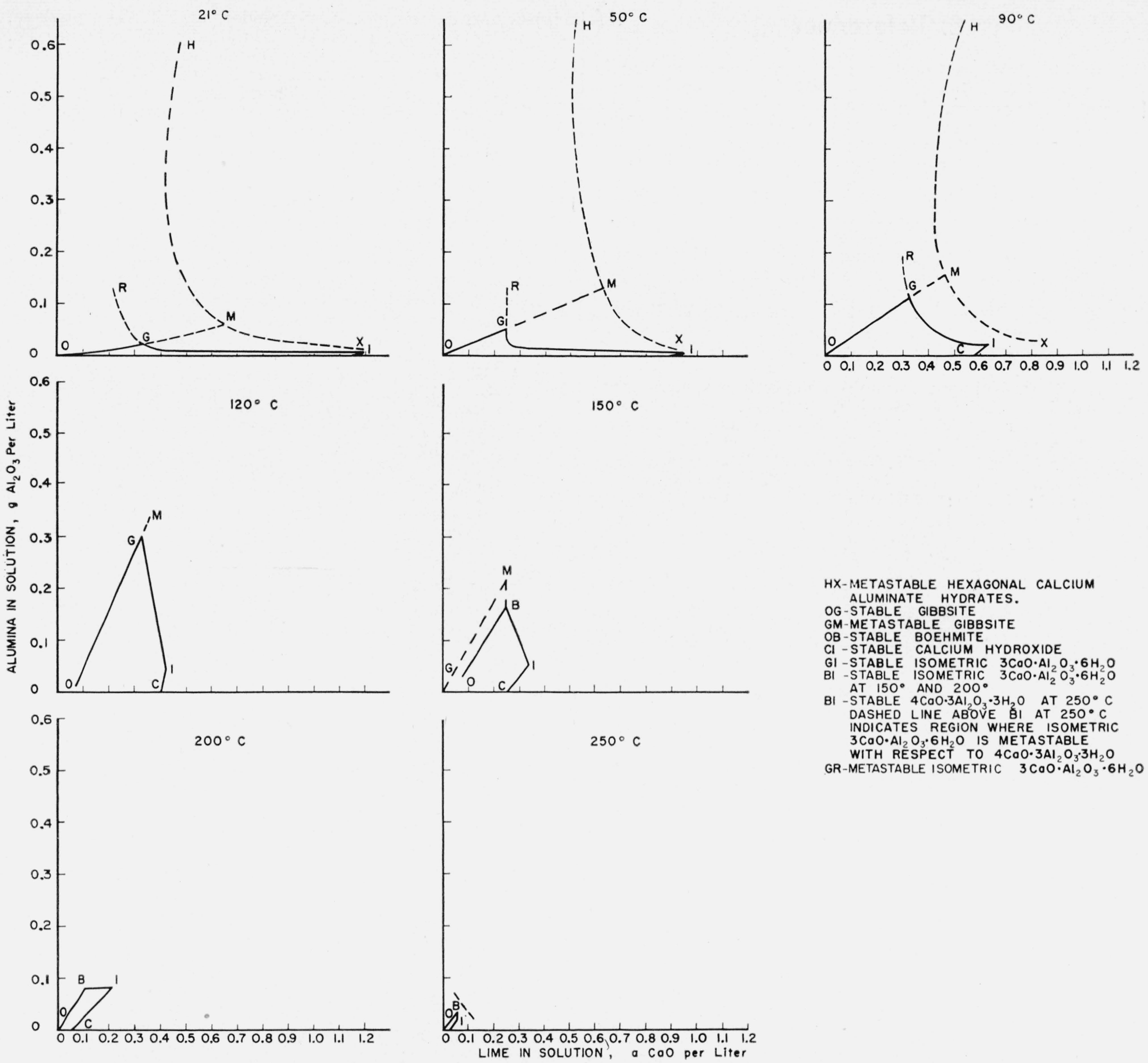

FIGURE 20. *The system* CaO-Al_2O_3-H_2O *at various temperatures.*

5. Summary

The system CaO-Al_2O_3-H_2O has been investigated over the range 50° to 250° C.

It was found that gibbsite was the stable alumina hydrate under 150° C, and that above this temperature boehmite was the stable alumina phase. Isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ is the only stable ternary compound in the system up to and including approximately 215° C, and the metastable hexagonal calcium aluminate hydrates persist up to and including 90° C. At 250° C, the stable ternary compound is $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$.

With increasing temperature, the $Ca(OH)_2$ equilibria curves lengthen and move toward the origin in a rectangular plot, the isometric $3CaO \cdot Al_2O_3 \cdot 6H_2O$ curves become shorter and more vertical, and move toward the origin; the alumina curves rotate counterclockwise about the origin to a maximum at 120° C and thereafter shorten and rotate clockwise. The over-all effect is to compress all the equilibria curves against the Al_2O_3-concentration axis and into the water apex of the diagram.

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