U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1539

Part of Journal of Research of the National Bureau of Standards, Volume 30, May 1943

STUDY OF THE SYSTEM $CaO-Al_2O_3-H_2O$ AT TEMPERATURES OF 21° AND 90° C

By Lansing S. Wells, W. F. Clarke, and H. F. McMurdie

ABSTRACT

A study has been made of the system $CaO-Al_2O_3-H_2O$ at temperatures of 21° and 90° C. Diagrams have been constructed showing the solubility relations of the various phases at these temperatures. The solid phases were investigated by petrographical and X-ray diffraction methods. By means of X-ray diffraction patterns, it was found that the so-called hexagonal tricalcium aluminate hydrate is in reality a mixture of hexagonal $2CaO.Al_2O_3.8H_2O$ and hexagonal $4CaO.Al_2O_3.13H_2O$ intercrystallized in equimolecular proportions. On standing at room temperature, dry dicalcium aluminate hydrate is slowly converted into the tetracalcium aluminate hydrate and hydrated alumina. Loss of water of hydration in the tetracalcium aluminate hydrate results in a decrease in the unit cell along the *c* axis. Although the hexagonal di- and tetracalcium aluminate hydrates exist only as metastable phases in the system between 21° and 90° C, their approximate solubility relationships were ascertained at 21° C. As the temperature increases, the hexagonal aluminates become less stable. The only stable phases that occur in the system $CaO-Al_2O_3-H_2O$ at atmospheric pressure over the temperature range of 21° to 90° C are gibbsite ($Al_2O_3.3H_2O$), the isometric tricalcium aluminate hexahydrate ($3CaO.Al_2O_3.6H_2O$), and $Ca(OH)_2$. The solubility curves of these three stable phases in the system $CaO-Al_2O_3-H_2O$ were determined at 21° and 90° C. Over this temperature range, gibbsite is the stable phase up to a concentration of 0.33 g of CaO per liter; at concentrations greater than this, $3CaO.Al_2O_3.6H_2O$ is the stable phase until those points are reached at which $Ca(OH)_2$ also appears as a solid phase. The series of invariant points for gibbsite and the isometric phase occur at a concentration of 0.33 g of CaO per liter, but with the concentration of Al_2O_3 increasing from 0.02 g of Al_2O_3 per liter at 21° C to 0.11 g of Al_2O_3 per liter at 90° C.

CONTENTS

I. INTRODUCTION

The extensiveness of the literature pertaining to the hydrated calcium aluminates shows the scientific interest and technological importance which have been attached to these compounds. An experimental study of the system $CaO-Al_2O_3-H_2O$ should possess considerable practical value not only for its direct bearing on the setting of high-alumina cements (which are composed largely of anhydrous calcium aluminates) and portland cements, but also for possible applications in the fields of geology, soil equilibria, water purification, and the extraction of purified hydrated alumina from crude bauxite.

The study of the system $CaO-Al_2O_3-H_2O$ presents many difficulties, including:

1. The existence of numerous highly hydrated compounds, the determination of the degree of hydration of which is often a problem in itself.
2. The relatively low solubility of these compounds.
3. The fact that most of the compounds are metastable, yet, once formed, persist over long periods of time.
4. The close similarity in crystal habit and optical properties of the compounds occurring as thin hexagonal (or pseudohexagonal) plates.
5. The necessity for the rigid exclusion of carbon dioxide of the air.

II. GENERAL PROCEDURE

Only by approaching equilibrium in a number of different ways can any conclusive results be obtained in a system of the type of $CaO-Al_2O_3-H_2O$ in which a number of metastable phases occur.

In order to study the phases that precipitate from supersaturation at 21° C, the first step was to prepare rather large quantities of metastable monocalcium aluminate solutions by shaking, for an hour or so, either anhydrous calcium aluminates less basic than tricalcium aluminate or alkali-free calcium aluminate cements with distilled water in the proportion of 50 g of solid to 1 liter of water. The mixtures then were filtered rapidly through a Büchner funnel. Samples of the clear filtrates were taken at once for chemical analysis. By this procedure, as was shown in a previous publication [1],[1] metastable solutions which contained up to 2.4 g of Al_2O_3 and 1.4 g of CaO per liter were obtained.

These clear, filtered solutions were then mixed in various proportions with solutions of calcium hydroxide of known concentration in the preparation of several series of reaction mixtures containing at least 2 liters of solution. Since precipitation of minute cyrstals started, in many instances, almost immediately upon the addition of the

---

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

calcium hydroxide solutions to the metastable calcium aluminate solutions, it was impossible to secure samples of the mixtures at this stage. But, inasmuch as care had been taken to measure out the volumes of the component solutions and to exclude CO_2, the initial compositions of the resultant mixtures were known accurately. The mixtures were set aside, for further observations, in tightly stoppered flasks in a room maintained at 21°±1° C. This same general procedure was followed in a previous study of the system CaO-SiO_2-H_2O [2].

A separation of solid phases occurred rapidly at first, and then more slowly, as the solutions changed from unstable states to conditions more nearly approaching equilibrium. The mixtures were shaken from time to time to facilitate an approach to equilibrium. Small samples of the precipitated material were removed at intervals for microscopical examination to follow any change in the solid phases which might be occurring. By this procedure it became evident that a phase which first appeared, in turn, often disappeared with the formation of a new phase as equilibrium was approached. Obviously, the problem was to establish the boundaries of the fields where the various metastable and stable phases precipitated from solution.

Having approached equilibrium by precipitation from supersaturation at 21° C, the next step was to determine whether the same equilibrium conditions could be attained from undersaturation. In these cases the solid phases were placed in calcium hydroxide solutions of varied concentrations, and the changes in both the aqueous and solid phases were followed.

Attempts also were made to reach equilibrium by lowering the temperature of the mixtures from higher temperatures to 21° C.

In all of these studies it was essential that the identity of the solid materials be established not only by chemical analysis, but also, whenever possible, by their optical properties. But, inasmuch as many of the products could not be identified definitely by optical means, it was necessary to obtain X-ray diffraction patterns.

The same procedures, except as noted otherwise, were used in studying the system at 90° C as at 21° C.

In the chemical analyses, the filtered solutions were made acid with hydrochloric acid, and the aluminum was precipitated as the hydroxide, redissolved, reprecipitated, and ignited to the oxide, according to Blum's method [3]. The calcium was precipitated as the oxalate, ignited to constant weight in a platinum crucible over a Meker burner, and weighed as the oxide. The solid phases, unless otherwise stated, were washed with alcohol and ether and then dried over calcium chloride in a desiccator and analyzed chemically for lime, alumina, and water (loss on ignition). It was often preferable to make the analyses for alumina and lime on samples other than those used for the determination of loss on ignition, because heat converted a portion of the alumina to a form difficultly soluble in acids. Blank determinations for alumina and lime were made for the reagents used and the proper corrections were applied.

Although these were the general procedures followed in this investigation, it will be necessary, as the occasion arises, to give more specific details.

III. STUDIES OF THE SYSTEM CaO-Al_2O_3-H_2O AT 21° C

1. HEXAGONAL HYDRATED CALCIUM ALUMINATES IN THE SYSTEM AT 21° C

Consideration will now be given to the studies of the metastable hexagonal hydrated calcium aluminates,[2] leaving those pertaining to the stable isometric form and hydrated alumina for later discussion. The results of the studies are being presented in several arbitrarily chosen parts. The first deals primarily with the molar ratio, CaO/Al_2O_3, in the hexagonal hydrated calcium aluminates; the second with the water content of the products; the third with their optical properties; the fourth with their structure as revealed by X-ray data; and the fifth with a brief discussion of some conclusions which seem warranted. The real significance of the hexagonal hydrated calcium aluminates in the system CaO-Al_2O_3-H_2O can be appreciated only after the investigations of the other phases have been presented.

(a) MOLAR RATIO, CaO/Al_2O_3, IN THE HEXAGONAL CALCIUM ALUMINATES

Table 1 gives data pertaining to the hexagonal hydrated calcium aluminates obtained by approaching equilibrium from supersaturation. Column 5 shows the time that elapsed between the preparation of the initial unstable solutions and the subsequent filtration occasioned by the appearance of microscopically detectable quantities of solid phases other than the hexagonal hydrated calcium aluminates. The time ranged from 1 to 309 days. In 22 of 48 preparations, this was less than 10 days. The molar ratios, CaO/Al_2O_3, in the precipitates, as given in column 9, were calculated from the differences between the compositions of the unstable solutions before precipitation (columns 2 and 3) and after precipitation (columns 6 and 7). The molar ratios—CaO/Al_2O_3 (column 10) and H_2O/Al_2O_3 (column 11)—were computed from direct analyses of the solid phases that had been dried over $CaCl_2$. The indices of refraction of these solid phases (columns 12 and 13) were determined at the time the analyses were made.

In figure 1 the compositions of the initial solutions are represented by closed circles. Broken lines from these points to open circles connect the initial and final compositions. The numbers accompanying these lines give the molar ratios, CaO/Al_2O_3, in the precipitated hexagonal hydrated calcium aluminates as calculated from the differences in composition between the initial and final solutions (see table 1, column 9).

A curve, *ABD*, has been drawn primarily to facilitate the discussion of the solubility relations of these hexagonal hydrated calcium aluminates. Because the hexagonal aluminates were formed from supersaturation, it was felt that this curve should be passed through those points that indicated the more extensive precipitation rather than through the average of the points. *D* pertains to a composition

---

[2] In this paper the plate form will be designated as the hexagonal form, since the crystals appeared as thin hexagonal plates. In general, the crystals were too small to obtain satisfactory interference figures with a petrographic microscope to determine whether the crystals were uniaxial, and hence actually hexagonal. The tendency to form hexagonal (or pseudohexagonal) plates was so marked that, in those instances in which the interference figures revealed that the crystals were biaxial negative, the hexagonal configuration of the plates still persisted.

TABLE 1.—*Solubility relations pertaining to the hexagonal hydrated calcium aluminates as ascertained by an approach from a state of supersaturation at a constant temperature of 21°C, together with the refractive indices of the hexagonal aluminates thus formed.*

Experiment	Composition of initial solutions			Time to approach metastable equilibrium [a]	Composition of resulting solutions			Composition of hexagonal aluminates			Indices of refraction of hexagonal aluminates	
	Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3		Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3	Molar ratio, CaO/Al_2O_3 (calculated)	Molar ratio, CaO/Al_2O_3 (analysis)	Molar ratio, H_2O/Al_2O_3 (analysis)	ω	ϵ
1	2	3	4	5	6	7	8	9	10	11	12	13
	g/liter	*g/liter*		*Days*	*g/liter*	*g/liter*						
1	1.003	0.998	1.81	5	0.512	0.440	1.56	2.07	1.99	5.62	1.535	1.523
2	0.793	.764	1.75	5	.505	.445	1.60	2.01	1.99	5.90	1.534	1.524
3	.620	.600	1.76	1	.465	.435	1.70	2.04	------	------	------	------
4	1.036	1.186	2.08	3	.367	.432	2.10	2.07	2.05	6.54	1.532	1.520
5	0.797	0.935	2.13	4	.364	.438	2.19	2.09	2.03	5.93	1.534	1.524
6	.587	.714	2.21	9	.345	.432	2.28	2.12	2.12	6.15	1.534	1.523
7	.798	1.052	2.40	3	.285	.449	2.86	2.14	2.09	5.93	1.535	1.525
8	.589	0.809	2.50	9	.267	.434	2.95	2.12	2.13	6.05	1.534	1.521
9	.556	.775	2.53	130	.286	.463	2.94	2.10	2.18	6.31	------	------
10	.472	.708	2.73	138	.244	.436	3.25	2.17	------	------	1.535	1.520
11	.795	1.108	2.53	3	.262	.457	3.17	2.22	2.16	6.07	1.537	1.520
12	.592	0.868	2.66	9	.238	.451	3.44	2.14	2.10	6.47	1.533	1.520
13	.400	.663	3.01	142	.221	.439	3.61	2.27	2.22	7.00	1.532	1.517
14	.433	.697	2.99	57	.216	.438	3.69	2.20	2.18	6.16	1.530	1.520
15	.504	.813	2.93	1	.208	.458	4.00	2.20	------	------	------	------
16	.576	.946	2.98	70	.201	.481	4.35	2.25	2.17	5.97	1.533	1.521
17	.400	.731	3.33	133	.201	.470	4.25	2.39	2.29	7.02	1.528	1.516
18	.762	1.196	2.85	70	.195	.466	4.34	2.34	2.33	7.03	1.535	1.515
19	.577	0.984	3.10	70	.185	.496	4.87	2.26	2.21	6.17	1.538	1.522
20	.400	.766	3.48	133	.188	.485	4.70	2.41	2.34	7.37	1.535	1.514
21	.708	1.174	3.02	57	.171	.488	5.22	2.32	2.21	6.33	1.535	1.510
22	.318	0.702	4.02	36	.154	.495	5.86	2.29	------	------	1.535	1.512
23	.575	1.045	3.30	69	.167	.530	5.77	2.40	2.29	6.22	1.534	1.523
24	.400	0.828	3.77	142	.169	.509	5.49	2.51	2.40	7.34	1.536	1.517
25	.609	1.164	3.48	309	.149	.506	6.17	2.60	2.43	6.63	------	------
26	.400	0.886	4.03	133	.154	.528	6.19	2.64	2.42	7.59	1.533	1.516
27	.501	1.103	4.00	142	.130	.508	7.10	2.91	2.62	8.05	------	------
28	.400	0.950	4.32	123	.146	.542	6.74	2.92	2.77	8.51	1.533	1.514
29	.557	1.210	3.95	70	.127	.523	7.48	2.91	2.63	8.00	1.537	1.515
30	.400	1.001	4.55	70	.116	.550	8.67	2.93	------	------	------	------
31	.454	1.150	4.79	7	.113	.595	9.59	2.96	2.97	8.25	1.535	1.518
32	.181	0.704	7.08	56	.112	.586	10.4	3.12	------	------	1.530	1.510
33	.440	1.161	4.80	17	.096	.587	11.1	3.03	3.01	8.88	1.535	1.517
34	.394	1.168	5.39	17	.100	.614	11.2	3.43	3.45	10.98	1.538	1.515
35	.388	1.154	5.41	7	.104	.620	10.8	3.42	------	9.98	1.538	1.519
36	.286	0.993	6.32	48	.078	.614	14.3	3.32	3.54	11.25	1.540	1.517
37	.394	1.237	5.70	121	.090	.631	12.7	3.62	3.67	12.00	1.542	1.520
38	.241	0.939	7.08	56	.091	.658	13.1	3.40	3.73	12.25	------	------
39	.348	1.175	6.14	8	.083	.639	16.9	3.68	3.69	11.57	1.530	1.511
40	.337	1.215	6.56	7	.067	.644	17.5	3.75	------	------	1.540	1.521
41	.302	1.183	7.12	6	.070	.687	17.8	3.85	3.82	11.98	1.530	1.511
42	.256	1.190	8.44	6	.042	.732	31.7	3.89	3.81	12.07	1.533	1.512
43	.219	1.227	10.2	8	.028	.813	52.7	3.94	3.94	12.60	1.541	1.523
44	.174	1.204	12.6	8	.025	.870	63.3	4.07	3.97	13.04	1.547	1.512
45	.164	1.239	13.7	8	.019	.914	87.6	3.99	------	------	1.545	1.521
46	.109	1.239	20.7	8	.012	1.032	156.0	3.88	3.68	10.83	1.550	1.520
47	.094	1.221	23.6	39	.012	1.047	159.0	3.96	3.97	12.01	1.550	1.520
48	.055	1.244	41.1	8	.006	1.132	342.0	4.16	3.97	13.00	------	------

[a] Time which elapsed between the preparation of the initial unstable solutions and the subsequent filtration occasioned by the appearance of microscopically detectable quantities of solid phases other than metastable hexagonal hydrated calcium aluminates.

at a concentration of lime somewhat greater than that of a solution in equilibrium with coarsely crystalline $Ca(OH)_2$ as indicated by *C* (equivalent to 1.15 g of CaO per liter).

In general, the increase in lime in solution is accompanied by a decrease in alumina, and a more or less gradual increase from 2 to 4 in the molar ratio, CaO/Al_2O_3, in the solid phases. It is evident that there are no extensive sections along the curve *ABD* where the molar ratios, CaO/Al_2O_3, of the solid phases are exactly 2.0, 3.0, or 4.0, such as would characterize a series of separate and distinct solubility curves of a hydrated dicalcium, tricalcium, or tetracalcium aluminate.

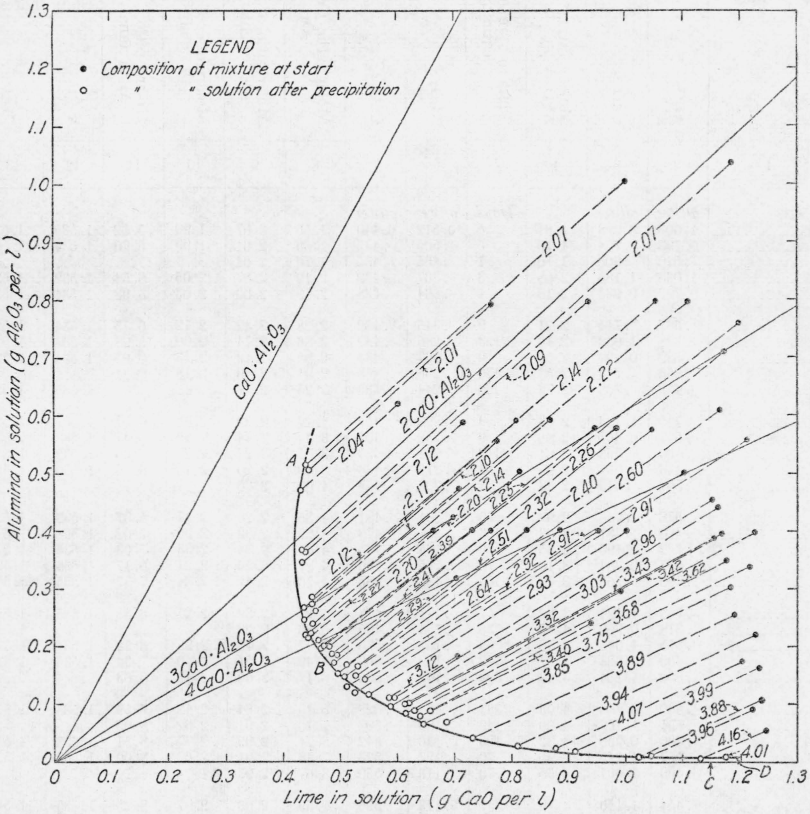

FIGURE 1.—*Quantity of alumina in solutions of increasing lime concentrations that are saturated with respect to metastable hexagonal calcium aluminate hydrates containing lime and alumina in the molar proportions shown; temperature, 21° C.*

It is significant, however, that all the initial solutions having molar ratios, CaO/Al_2O_3, less than 2 gave rise to precipitates having molar ratios that approximated 2. Furthermore, although there was no instance in which the composition of the initial solution was exactly on the $2CaO.Al_2O_3$-composition line, yet, from experiment 4 of table 1, it can be seen that the molar ratios, CaO/Al_2O_3, of the unstable initial solution, of the precipitated solid phase, and of the resulting solution were all very close to 2.

Initial solutions having molar ratios greater than 2.1 produced precipitates having molar ratios less than the respective original solutions. Those initial solutions whose compositions were either on or very close to the $3CaO.Al_2O_3$-composition line (experiments 13, 14, 15, 16, and 21 of table 1) yielded solid phases whose molar ratios, CaO/Al_2O_3, were much less than 3 (ranging from 2.20 to 2.32). There may be considered to be a small section on the curve *ABD*, where the molar ratios, CaO/Al_2O_3, of the solid phases precipitated were approximately 3, but the molar ratios of the initial solutions from which these solid phases precipitated were, in general, greater than 4.

There is a somewhat longer section along the lower two-thirds of the curve from *B* to *D*, where the molar ratios, CaO/Al_2O_3, of the solid phases are close to 4, but the initial solutions from which these phases precipitated were much more basic than a tetracalcium aluminate solution.

Two explanations may be postulated for the rather gradual increase from 2 to 4 in the molar ratios, CaO/Al_2O_3, of the precipitates resulting as the molar ratios of the initial solutions increase beyond 2.1: (a) That the solubility data pertain to overlapping solubility curves of a series of separate hydrated calcium aluminates of simple molar ratios, which were not at equilibrium at the time of filtering; or (b) that the curve represents the solubility of a solid-solution series of hydrated aluminates varying continuously in molar ratio, CaO/Al_2O_3, from 2 to 4. The fact that these haxagonal phases are metastable makes it impossible to determine which of these explanations is correct, merely from these experiments, where the solid phases were precipitated from supersaturation.

The next step was to approach equilibrium from a state of undersaturation, by placing separately crystalline hydrated dicalcium and tetracalcium aluminates in calcium hydroxide solutions of increasing concentrations. Three series of mixtures were prepared, containing, in each case, 2 g of the hydrated calcium aluminate per liter of solution. In series *A* the dicalcium aluminate, which had been dried over $CaCl_2$, had the molar composition $2.12CaO.Al_2O_3.6.39H_2O$. The dicalcium aluminate of series *B* was not dried over $CaCl_2$, but was used within a few hours after its preparation. It was merely washed with alcohol and ether. This hydrate had the molar composition $2.07CaO.Al_2O_3.8.23H_2O$. Both of these preparations had slightly more lime than theoretically required for dicalcium aluminate. The hydrated tetracalcium aluminate used in the third series, *C*, was somewhat deficient in lime, since its formula computed from the analysis was $3.93CaO.Al_2O_3.11.72H_2O$. This product had been dried over $CaCl_2$ prior to analysis. The individual mixtures of the three series were shaken from time to time and filtered, as before, at the first appearance of a solid phase other than hexagonal aluminates.

Table 2 contains data relative to these solubility experiments. Column 2 gives the concentration of the calcium hydroxide solutions (expressed as grams of CaO per liter) to which the crystalline hydrated calcium aluminates were added.

The manner in which the hydrated aluminates dissolved in the calcium hydroxide solutions of increasing concentrations is shown in figure 2. The points representing the compositions of the resulting solutions fall fairly well along the curve *ABD*, as transferred from figure 1, wherein equilibrium had been approached by precipitation from the unstable supersaturated aluminate solutions. The numbers accompanying the points refer to the numbers of the experiments of table 2.

The behavior of the two preparations of the hydrated dicalcium aluminates (series *A* and *B*) was notably different from that of the hydrated tetracalcium aluminate (series *C*).

The composition of the solution obtained when the $2.12CaO.Al_2O_3.6.39H_2O$ product was added to water (experiment 1) lies on the $2CaO.Al_2O_3$-composition line, slightly below the point at which the curve ABD intersects this line. This suggests that the hydrated dicalcium aluminate may at first dissolve congruently. But, inasmuch as the $2.12CaO.Al_2O_3.6.39H_2O$ product contained some aluminate more basic than dicalcium aluminate, there was an enrichment of the more basic aluminate in the remaining material, evidenced by an increase in molar ratio, CaO/Al_2O_3, of the solid from 2.12 to 2.34. Furthermore, the $2.07CaO.Al_2O_3.8.23H_2O$ preparation, when placed in a solution of calcium hydroxide containing 0.1 g of CaO per liter, appeared to dissolve along a path parallel to the $2CaO.Al_2O_3$—composition line (experiment 8). Likewise, the path of the $2.12CaO.Al_2O_3.6.39H_2O$ preparation was approximately parallel to this line, starting from the point of 0.2 g of CaO per liter (experiment 2). At higher concentrations of calcium hydroxide, lime was removed from solution by both of the preparations of hydrated dicalcium aluminate, and the molar ratio, CaO/Al_2O_3, of the resulting solid phases consequently increased.

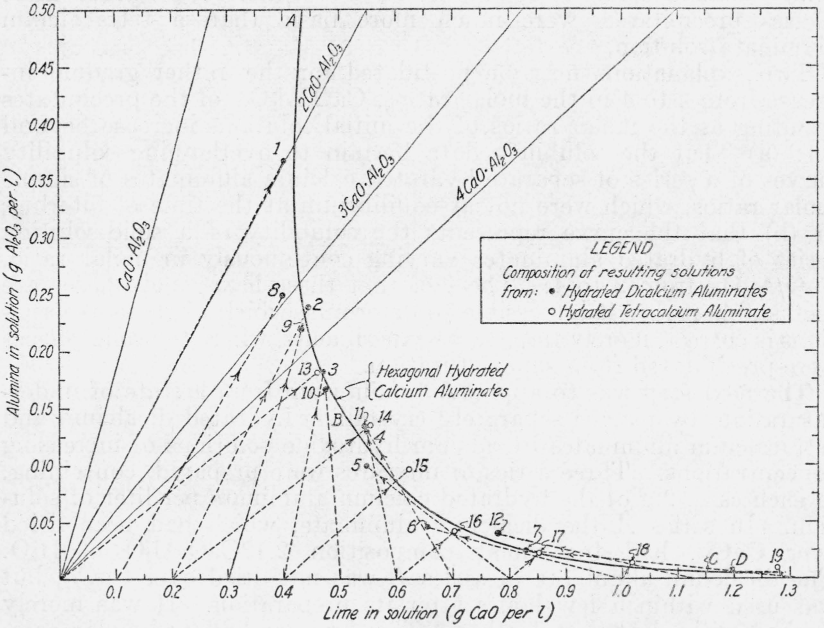

FIGURE 2.—*Composition of the solutions obtained by placing hexagonal hydrated dicalcium and tetracalcium aluminates, respectively, in solutions of calcium hydroxide of increasing concentrations; maintained at a temperature of 21° C.*

TABLE 2.—*Solubility relations pertaining to the hexagonal hydrated calcium aluminates obtained from mixtures of hydrated di- and tetracalcium aluminates, respectively, with calcium hydroxide solutions of increasing concentrations.*

Experiment	Concentration of $Ca(OH)_2$ solutions	Composition of initial mixtures			Time to approach metastable equilibrium [a]	Composition of resulting sloutions			Composition of hexagonal aluminates		
		Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3		Al_2O_3	CaO	Molar ratio, CaO/Al_2O_3	Molar ratio, CaO/Al_2O_3 (calculated)	Molar ratio, CaO/Al_2O_3 (analysis)	Molar ratio, H_2O/Al_2O_3 (analysis)
1	2	3	4	5	6	7	8	9	10	11	12
Series *A*—Dicalcium aluminate (2 g of 2.12 $CaO.Al_2O_3.6.39\ H_2O$ per liter of solution)											
	g of CaO/ *liter*	*g/liter*	*g/liter*		*Days*	*g/liter*	*g/liter*				
1	0	0.607	0.708	2.12	1.3	0.369	0.402	1.98	2.34	2.47	7.40
2	.200	.607	.908	2.72	134	.238	.438	3.34	2.31	-------	-------
3	.400	.607	1.108	3.32	87	.183	.469	4.66	2.74	2.64	8.72
4	.600	.607	1.308	3.92	55	.131	.549	7.62	2.90	3.03	9.19
5	.800	.607	1.508	4.52	23	.099	.549	10.1	3.43	3.51	10.40
6	1.000	.607	1.708	5.12	23	.046	.654	25.9	3.42	3.63	10.92
7	1.310	.607	2.018	6.04	23	.025	.826	60.0	3.77	3.74	11.67
Series *B*—Dicalcium aluminate (2 g of 2.07 $CaO.Al_2O_3.8.23\ H_2O$ per liter of solution)											
8	0.100	0.557	0.734	2.40	8	0.248	0.397	2.91	1.98	1.87	[b] 8.15
9	.300	.557	.934	3.05	4	.219	.429	2.99	2.72	2.65	[b] 9.81
10	.500	.557	1.134	3.70	3	.166	.474	5.19	3.07	2.96	[b] 10.49
11	.700	.557	1.334	4.35	8	.134	.547	7.42	3.38	3.22	[b] 11.00
12	1.123	.557	1.757	5.71	3	.041	.778	23.9	3.57	3.66	[b] 12.03
Series *C*—Tetracalcium aluminate (2 g of 3.93 $CaO.Al_2O_3.11.72H_2O$ per liter of solution)											
13	0	0.382	0.826	3.93	16	0.182	0.460	4.59	3.33	3.32	10.03
14	.200	.382	1.026	4.88	16	.137	.555	7.36	3.49	3.37	10.41
15	.400	.382	1.226	5.83	16	.097	.623	11.7	3.85	3.78	11.62
16	.600	.382	1.426	6.79	16	.042	.704	30.5	3.86	3.84	12.06
17	.800	.382	1.626	7.74	16	.023	.852	67.2	3.92	3.91	11.95
18	1.000	.382	1.826	8.69	16	.015	1.018	123	4.00	3.87	11.84
19	1.290	.382	2.116	10.1	16	.009	1.279	259	4.08	3.89	11.97

[a] Time which elapsed between preparation of mixtures and subsequent filtration occasioned by appearance of microscopically detectable quantities of solid phases other than metastable hexagonal hydrated calcium aluminates.

[b] Not dried over $CaCl_2$ prior to determining molar ratio, H_2O/Al_2O_3, as in case of series *A* and *C*.

On the other hand, the hydrated tetracalcium aluminate does not appear to dissolve congruently when placed in water (experiment 13), since the composition of the resulting solution does not lie on the $4CaO.Al_2O_3$-composition line. The molar ratio, CaO/Al_2O_3, of the solid material was reduced to 3.33. The hydrated tetracalcium aluminate placed in the calcium hydroxide solution containing 0.2 g of CaO per liter also gave up appreciable lime to the solution in excess of that of the proportion of 4 CaO to 1 Al_2O_3, and, consequently, the molar ratio, CaO/Al_2O_3, of the solid was reduced, this time to 3.49. At the higher concentrations of calcium hydroxide the hydrated tetracalcium aluminate dissolved with little or no change in molar composition.

Summarizing the results of the solubility experiments obtained at this stage, several conclusions can be drawn. The molar ratio, CaO/Al_2O_3, of the solid phases when equilibrium was approached from undersaturation corresponded fairly well with those obtained along the various segments of the curve ABD where equilibrium had been approached from supersaturation. Thus, solid phases having a molar ratio, CaO/Al_2O_3, of 4, or approximately 4, were obtained at the higher concentrations of lime along ABD not only by an approach to equilibrium from supersaturation (table 1 and fig. 1) but also by two approaches from undersaturation (table 2 and fig. 2), namely, when the hydrated tetracalcium aluminate had been placed in the more concentrated solutions of calcium hydroxide and when the hydrated dicalcium aluminates had removed considerable lime from such solutions. The molar ratio, CaO/Al_2O_3, of the solid material was about 2 only at the lower concentrations of lime, but in this case the hydrated tetracalcium aluminates did not yield such a product. The significance of these solubility experiments will become clearer after consideration has been given to the findings of the X-ray studies.

(b) MOLAR RATIO, H_2O/Al_2O_3, IN THE HEXAGONAL CALCIUM ALUMINATES

One has but to review the literature on the hexegonal hydrated calcium aluminates to realize that there is a difference of opinion as to their exact water content.

The difficulties involved in determining the water content of the plate forms become apparent merely from a consideration of the nature of these crystalline compounds. In the first place, these aluminates are made up of very thin layers of hexagonal (or pseudohexagonal) plates and are highly hydrated. Furthermore, a portion of the water is readily lost even at relatively high humidities [13]. One is always in doubt, therefore, whether the water so lost may have been (1) absorbed water, because thin crystals of this character have such large surfaces, (2) water between the laminas of the crystals, or (3) water of crystallization. The presence of either absorbed water or water between the laminas of the crystals as a possible source of error in the determination of the refractive indices of the plate forms has been pointed out in a previous publication [1] and, more recently, has been mentioned by other investigators. Obviously, the drying of these crystals should have as its objective the removal of the absorbed water and water between the laminas as completely as possible without the loss of any of the water of crystallization. Assarsson [4, 5, 6, 7] washed his samples with a little water, then with alcohol (or acetone), and finally with ether, and omitted further drying prior to analysis. Others have used various methods of drying. As stated previously, the hydrates in the present investigation were, for the most part, washed with alcohol and ether, and then were dried at room temperature in a desiccator containing $CaCl_2$.

This method may be open to criticism (as may also many other methods of drying) in that there is no assurance that some of the water of crystallization may not have been lost. Accordingly, in some instances, which will be mentioned subsequently, the samples were not dried over $CaCl_2$.

The molar ratios, H_2O/Al_2O_3, in the hexagonal hydrated calcium aluminates, as determined from loss on ignition, are given in column 11 of table 1 and column 12 of table 2. It can be seen from these tables that, in general, the molar ratio, H_2O/Al_2O_3, increased with an increase in the molar ratio, CaO/Al_2O_3.

Figure 3 shows the molar ratios, H_2O/Al_2O_3, plotted against the molar ratios, CaO/Al_2O_3, not only for these hexagonal hydrated calcium aluminates dried over $CaCl_2$ (differentiated by closed circles), but also for similar ratios calculated from data of other investigators, including Assarsson [4, 5, 7], Mylius [8], Thorvaldson, Grace, and Vigfusson [9], Koyanagi [10], Salmoni [11], Lafuma [12], Bessey [13], Kühl, Thilo, and Chi Yü [14], Pulfrich and Linck [15], MacIntire and Shaw [16], and Travers and Sehnoutka [17].

The hydrates prepared by Assarsson (open circles) likewise show that an increase in molar ratio, CaO/Al_2O_3, is attended by an increase in molar ratio, H_2O/Al_2O_3. But, almost invariably, his products, which were not dried, contained more water than those dried over $CaCl_2$ in this laboratory.

With few exceptions the points representing the compositions of all of the preparations are contained in a field bounded by the following limits:

$$\begin{tikzcd} 2CaO.Al_2O_3.9H_2O \arrow[r, dash] \arrow[d, dash] & 4CaO.Al_2O_3.14H_2O \arrow[d, dash] \\ 2CaO.Al_2O_3.5H_2O \arrow[r, dash] & 4CaO.Al_2O_3.12H_2O \end{tikzcd}$$

(c) OPTICAL PROPERTIES OF THE HEXAGONAL CALCIUM ALUMINATES

Microscopical examination of samples of the materials from the mixtures of calcium aluminate and calcium hydroxide solutions showed the presence of flat hexagonal plates or spherulites consisting of radiating aggregates of these crystals. Usually the individual plates were so small that satisfactory interference figures could not be obtained to determine whether the crystals were uniaxial or biaxial. Consequently, the refractive indices given in columns 12 and 13 of table 1 are recorded as those of ω and ϵ, respectively.

There are no very marked differences in the refractive indices of these hexagonal hydrated calcium aluminates, especially those of ϵ. The ω indices of the dicalcium aluminates were, however, lower than those of the tetracalcium aluminates. Inasmuch as the refractive indices of certain of these products, differing considerably in chemical composition, are nearly identical, the differentiation of the plate forms by microscopical means was difficult.

Table 3 gives data obtained by various investigators on the plate forms of the hydrated calcium aluminates for which the molar ratios, CaO/Al_2O_3, were fairly close to 2, 3, and 4. The methods of washing and drying the products differed markedly, and the moles of H_2O per mole of $2CaO.Al_2O_3$ and of $3CaO.Al_2O_3$ ranged from 5 to 11.3 and from 7 to 12.5, respectively. Where refractive indices have been reported, the values of ω and ϵ are recorded, and in these cases the optical character has been stated to be uniaxial negative. In most instances, the water content of the dicalcium aluminates listed in table 3 was higher, and the refractive indices were lower than for the dicalcium aluminates given in table 1.

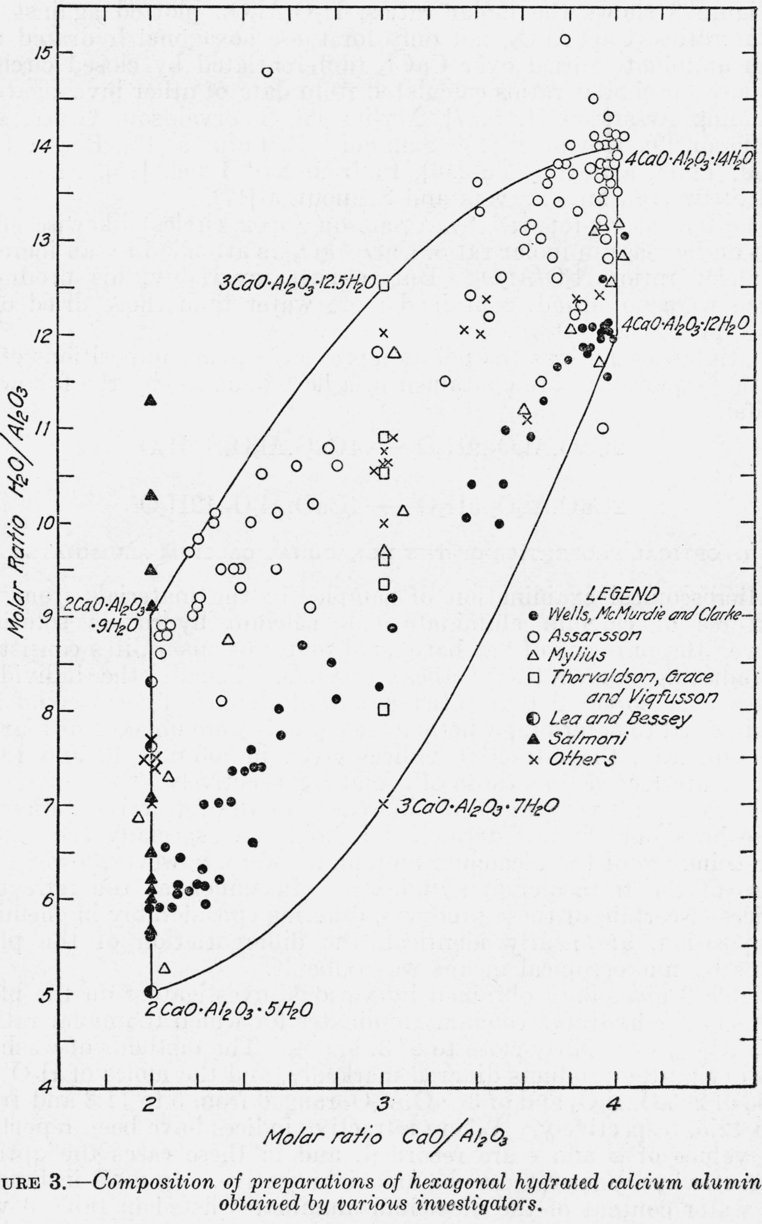

FIGURE 3.—*Composition of preparations of hexagonal hydrated calcium aluminates obtained by various investigators.*

TABLE 3.—*Water content and optical properties of hydrated calcium aluminates (plate forms) as given by various investigators.*

Moles of H_2O	Refractive Indices		Optical character	Observers	Method of preparation	Method of drying
	ω^a	ϵ^a				
				$2CaO.Al_2O_3.XH_2O$		
7.0				Allen and Rogers [22] (1900)	Al-metal+solution $Ca(OH)_2$	Over $CaCl_2$.
7.0				Lafuma [12] (1925)	Partial hydrolysis $4CaO.Al_2O_3.12H_2O$ in water.	Do.
8.2				Koyanagi [23] (1930)	Precipitation from calcium aluminate solution.	Not stated.
8.4	1.519	1.506	Uniaxial negative	Assarsson [5] (1931)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Washed with alcohol and ether. Drying not stated.
7.6	1.520	1.512	do	Koyanagi [10] (1932)	Calcium aluminate cement+$Ca(OH)_2$ solution.	Not stated.
6.8	1.522	1.502	do	Mylius [8] (1933)	Hydrated alumina gel+$Ca(OH)_2$ solution.	Washed with water, dried 24 hr. in vacuum over $CaCl_2$.
7.3	1.522	1.502	do	do	Potassium aluminate solution+$Ca(OH)_2$ solution.	Washed with water and ether, dried 24 hr. in vacuum over $CaCl_2$.
5.3				do	do	In vacuum over P_2O_5.
8.7				Salmoni [11] (1934)	Direct hydration at 0° C of a clinker of the composition $2CaO.Al_2O_3$.	Washed with water, alcohol or acetone, and ether at 0° C.
7.1				do	do	Over $CaCl_2$ for 24 hr.
5.7				do	do	Over P_2O_5 at 20° C.
6.5				do	do	Over $CaCl_2$ at 20° C.
6.0				do	do	Over H_2SO_4, 76 percent, at 20° C.
6.1				do	do	Over H_2SO_4, 72 percent, at 20° C.
6.2				do	do	Over H_2SO_4, 63 percent, at 20° C.
9.1				do	do	Saturated solution of Na_2SO_4 at 20° C.
9.5				do	do	Saturated solution of KCl at 20° C.
10.3				do	do	Saturated solution of $Pb(NO_3)_2$ at 20° C.
11.3				do	do	Saturated solution of KIO_3 at 20° C.
8.7	1.519	1.506	Uniaxial negative	Assarsson [7] (1936)	Precipitation from calcium aluminate solution.	Washed with alcohol and ether, drying not stated.
9.0	1.519	1.506	do	do	Salmoni's method	Do.
9.0	1.523	1.510	do	Nacken [24] (1937)	Not stated	Not stated.
8.3	1.520	1.505	do	Bessey [13] (1938)	Not stated	At vapor pressure equivalent to 13.5 mm Hg at 17° C.
7.6	1.521	1.512	do	do	do	At vapor pressure equivalent to 2.8 mm Hg at 17° C.
5.0	1.540	1.530	do	do	do	Over CaO at 17° C.

See footnote at end of table.

TABLE 3.—*Water content and optical properties of hydrated calcium aluminates (plate forms) as given by various investigators*—Continued

Moles of H_2O	Refractive Indices		Optical character	Observers	Method of preparation	Method of drying
	ω^a	ϵ^a				
				$3CaO.Al_2O_3.XH_2O$		
12.0				Candlot [18] (1890)	Direct hydration $3CaO.Al_2O_3$	
10.0				Gallo [20] (1908)	Calcium aluminate solution $Ca(OH)_2$ solution.	Between sheets of filter paper.
	1.520	1.504	Uniaxial negative	Klein and Phillips [19] (1914)	Direct hydration $3CaO.Al_2O_3$	Not stated.
10.5				do	do	Over concentrated H_2SO_4, 24 hr.
9.0				do	do	Over concentrated H_2SSO_4, 48 hr. in vacuum.
7.0	1.538	1.523	Uniaxial negative	Pulfrich and Linck [15] (1924)	do	In air at room temperature.
10.0				MacIntire and Shaw [16] (1925)	Hydrated alumina gel+$Ca(OH)_2$ solution.	Do.
12.5	1.527	1.505	Uniaxial negative	Thorvaldson, Grace, and Vigfusson [9] (1929).	Direct hydration $3CaO.Al_2O_3$ in cold	Over saturated solution of $Pb(NO_3)_2$ (18.1 mm Hg).
10.9	1.530	1.510	do	do	do	Over saturated solution of KCl (16.1 mm Hg).
8.0	1.538	1.520	do	do	do	Over CaO to constant weight.
12.5	1.529	1.505	do	Assarsson [5] (1931)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Washed, alcohol (or actone) and ether. Drying not stated.
10.7	1.539	1.524	do	Koyanagi [21] (1931)	do	Washed, alcohol and ether, dried in vacuum desiccator.
11.8	1.528	1.508	do	Mylius [8] (1933)	Potassium aluminate solution+$Ca(OH)_2$ in excess KOH.	Washed, alcohol and ether, dried 2 hr. with vacuum, 24 hr. without vacuum over $CaCl_2$.
10.1				do	Potassium aluminate solution+$Ca(OH)_2$ solution.	Washed with water, alcohol, and ether and dried to constant weight over $CaCl_2$.
9.7				do	do	Over P_2O_5, without vacuum, 71 days.

$4CaO.Al_2O_3.XH_2O$

12				Le Chatelier [25] (1887)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Not stated.
12				Lafuma [12] (1925)	Calcium aluminate solution+$Ca(OH)_2$	Over NaCl.
12.0	1.532	1.505	Uniaxial negative	Wells [1] (1928)	Calcium aluminate solution+saturated $Ca(OH)_2$ solution.	Over $CaCl_2$.°
12.+	1.533	1.514	Optically negative	Assarsson [4] (1930)	Al metal+saturated $Ca(OH)_2$ solution	Washed with alcohol and ether. Drying not stated.
13.5	(γ)1.538	(α)1.510	Biaxial negative ($2V=14°$)	Assarsson [5] (1931)	Calcium aluminate solution+saturated $Ca(OH)_2$ solution.	Do.
13.0	1.533	1.522	Uniaxial negative	Mylius [8] (1933)	Potassium aluminate solution+$Ca(OH)_2$ solution.	Washed alcohol and ether. Dried in air.
12.0	1.549	1.533	do	do	By drying 13.0 hydrate over $CaCl_2$	Over $CaCl_2$ in vacuum.
14.0	(γ)1.535	(α)1.520	Biaxial negative (alpha form) $2V=10°$.	Assarsson [7] (1936)	Calcium aluminate solution+$Ca(OH)_2$ solution.	Washed alcohol and ether. Drying not stated.
14.0	(γ)1.535	(α)1.507	Biaxial negative (beta form) $2V=14°$.	do	do	Do.
12.0	(γ)1.549	(α)1.527	Biaxial negative (dehydrated alpha).	do	By dehydrating the alpha form (14.0 hydrate).	Do.
12.0	(γ)1.542 (β)1.538	(α)1.522	Biaxial negative $2V$ (calculated from $2E$)=38°. $2V$(calculated from indices)=25°.	Wells, Clarke, and McMurdie	Calcium aluminate solution+CaO	Over $CaCl_2$.
12.0	(γ)1.557 (β)1.553	(α)1.535	Biaxial negative $2V$ (calculated from $2E$)=24°±2°.	Tilley, Megaw, and Hay [26] (1934)	Hydrocalumite, a mineral from Scawt Hill, Co. Antrim, Ireland.	

---

[a] In those cases in which the crystals are biaxial negative, the indices of refraction are differentiated parenthetically as (γ) and (α) instead of ω and ε, respectively, which pertain to the uniaxial crystals. In two instances the β index is also included.

The water content of the hydrated tetracalcium aluminates has been reported as varying only from about 12 to $14H_2O$. Furthermore, the optical character of these aluminates had been given variously as uniaxial and biaxial negative.[3] In addition to those of other investigators, data are given in table 3 for a biaxial form [4] which has been prepared in this laboratory. The properties of the mineral hydrocalumite are also included.

The refractive indices of all of the artificially prepared tetracalcium aluminate hydrates having 12.0 moles of H_2O are lower than those of the mineral hydrocalumite found in altered intrusive contact-rocks in Ireland and described by Tilley, Megaw, and Hey [26]. Bessey [13] suggests that the high refractive indices may be explained on the basis that the mineral contained 1.8 percent of carbon dioxide, probably held in solid solution, since he prepared a tetracalcium carbonato-aluminate of the formula

$$4CaO.Al_2O_3.CO_2.11H_2O \text{ (or } 3CaO.Al_2O_3.CaCO_3.11H_2O),$$

which had indices of refraction of $\omega=1.552 \pm 0.003$ and $\epsilon=1.532 \pm 0.003$. He is of the opinion that a small amount of this compound, by this solid-solution formation, may influence the structure of the tetracalcium aluminate hydrate and thus have a bearing on the indices observed by others. Bessey does not state whether the carbonato-aluminate is uniaxial or biaxial in optical character.

(d) X-RAY DIFFRACTION PATTERNS OF THE HEXAGONAL CALCIUM ALUMINATES

In order to study further the relationships of the various hexagonal forms of the hydrated calcium aluminates, X-ray powder patterns were made by means of copper radiation. The cylindrical cameras had a radius of about 52 cm. The radiation was filtered with nickel foil, and the camera radius was calibrated with NaCl.

Patterns were first made on eight freshly prepared samples, whose compositions ranged from about $2CaO.Al_2O_3.8H_2O$ to about $4CaO.Al_2O_3.13H_2O$,[5] as shown in table 4.

The indexed interplanar spacings and relative intensities of the lines of sample 1 ($2.04CaO.Al_2O_3.7.92H_2O$) are given in table 5. The lines appear to be those of a compound having an hexagonal unit cell in which $a=8.8$ A and $c=10.6$ A.

---

[3] In those cases in which the crystals are biaxial negative, the indices of refraction are differentiated parenthetically in table 3 as (γ) and (α) instead of ω and ϵ, respectively, which pertain to the uniaxial crystals. In two instances the β index is also included.

[4] This particular preparation of tetracalcium aluminate hydrate was obtained by adding to a highly supersaturated monocalcium aluminate solution a quantity of freshly ignited CaO in excess of that required to combine with the alumina for the formation of a tetracalcium aluminate, and, in addition, to somewhat more than saturate the solution with regard to $Ca(OH)_2$. The resulting $Ca(OH)_2$ formed as a solid phase was then dissolved by replacing portions of the saturated solution of the mixture by water until the concentration of calcium hydroxide in solution was decreased to a value slightly under that at saturation. The crystals of the aluminate were then allowed to develop for slightly over 3 years. After filtering, the crystals were washed with alcohol and ether and dried in a desiccator containing $CaCl_2$. Analysis of this preparation gave the composition 41.3 percent of CaO, 19.1 percent of Al_2O_3, 39.6 percent of H_2O, corresponding to the ratios: $3.93CaO:1.00Al_2O_3:11.72H_2O$. Microscopical examination revealed the presence of a few percent of the isometric tricalcium aluminate, $3CaO.Al_2O_3.6H_2O$, as well-formed rhombic dodecahedrons. From subsequent discussion it will become evident why it is difficult to grow well-formed crystals of the hexagonal forms free of the isometric modification. Optical examination by H. Insley, National Bureau of Standards, of this hydrated tetracalcium aluminate showed the presence of platy crystals of hexagonal outline, with the acute bisectrix perpendicular to the plane of the plates. The indices of refraction (with indices of the reference liquids checked on the refractometer at the time of measuring) were: $\gamma=1.542\pm0.003$, $\beta=1.538\pm0.003$, and $\alpha=1.522+0.003$; $2E$ (measured) was $60°\pm5°$; with $2V$ (calculated from $2E$) $=38°$ and $2V$ (calculated from indices) $=25°$.

[5] The indices of refraction of the products having compositions close to $2CaO.Al_2O_3.8H_2O$ were: $\omega=1.519 \pm0.003$, $\epsilon=1.509\pm0.003$; values agreeing fairly well with those reported by other investigators and listed in table 3. Satisfactory optical properties were not obtained with the other freshly prepared samples, given in table 4, because they were very finely divided.

Table 4.—*Composition of freshly prepared samples of hexagonal hydrated calcium aluminates, before and after drying over* $CaCl_2$

Experiment	Molar ratio, CaO/Al_2O_3	Molar ratio, H_2O/Al_2O_3 (freshly prepared)	Molar ratio, H_2O/Al_2O_3 (after drying)
1	2.04	7.92	5.85
2	2.11	7.96	5.41
3	2.16	8.10	--------
4	2.30	8.44	6.12
5	2.40	9.05	7.92
6	3.15	10.91	9.09
7	3.73	13.68	11.60
8	3.88	12.60	11.23

Table 5.—*Interplanar spacings and estimated relative intensities of hexagonal* $2CaO.Al_2O_3.8H_2O$

[*VS*, very strong; *M*, medium; *S*, strong; *W*, weak]

hkl	*d*	Estimated Intensity	*hkl*	*d*	Estimated Intensity
001	10.6	*VS*	310	2.11	*W*
002	5.3	*S*	214	1.955	*W*
201	3.55	*M*	304	1.835	*W*
120	2.87	*S*	410	1.667	*M*
004	2.69	*W*	412	1.591	*W*
122	2.54	*W*	420	1.443	*M*
301	2.48	*M*			

In table 6 are similar data for example 8, of a composition near $4CaO.Al_2O_3.13H_2O$. Here the lines appear to result from an hexagonal cell in which $a=8.8$ *A* and $c=8.2$A. In these two compounds ($2CaO.Al_2O_3.8H_2O$ and $4CaO.Al_2O_3.13H_2O$) the length of the *a* axis is very nearly the same.

In both samples the strong intensities of the 001 lines and the plate habit lead to the probability that the hexagonal calcium aluminates are built up of hexagonal $Ca(OH)_2$ and $Al(OH)_3$ layers with H_2O between them, as suggested by Brandenberger [27].

If, for the purpose of discussion, the formulas are written in the form of hydroxides, $2CaO.Al_2O_3.8H_2O$ becomes $2Ca(OH)_2.2Al(OH)_3.3H_2O$, whereas $4CaO.Al_2O_3.13H_2O$ becomes $4Ca(OH)_2.2Al(OH)_3.6H_2O$. Dividing this last formula by two, it becomes $2Ca(OH)_2.Al(OH)_3.3H_2O$. The densities of the compounds in this series have been reported as ranging from about 2.0 to 2.1 [9, 13]. These densities and the unit-cell sizes would give two "molecules" to a unit cell. Thus, for the dicalcium aluminate hydrate, the cell content is $4Ca(OH)_2.4Al(OH)_3.6H_2O$, and for the tetracalcium aluminate hydrate, the cell content is $4Ca(OH)_2.2Al(OH)_3.6H_2O$. It is evident, therefore, that the difference between the content of one unit cell and the other is $2Al(OH)_3$, and, since the difference in length of the two cells is 2.4 A, it may be assumed that one layer (containing $2Al(OH)_3$) has the thickness of 2.4 A.

The X-ray powder patterns of the samples with compositions intermediate between the above compounds gave lines of both cells. The relative intensities of the 001 lines (at 10.6 and 8.2 A) were in the proper relation to the compositions to indicate the presence, in all cases, of appropriate proportions of the two compounds—$2CaO.Al_2O_3$.

$8H_2O$ and $4CaO.Al_2O_3.13H_2O$. Thus, sample 6, of table 4, with a molar ratio, CaO/Al_2O_3, of 3.15 gave a pattern in which the two 001 lines were of almost equal intensity. Consequently, it appears that the so-called hexagonal tricalcium aluminate hydrate, which has been assumed to be a definite compound by many investigators, is in reality not a separate compound but a mixture of the hexagonal hydrated dicalcium and tetracalcium aluminates in equal molecular proportions.

TABLE 6.—*Interplanar spacings and estimated relative intensities of hexagonal* $4CaO.Al_2O_3.13H_2O$

[*VS*, very strong; *VW*, very weak; *M*, medium; *W*, weak]

hkl	*d*	Estimated intensity	*hkl*	*d*	Estimated intensity
001	8.2	*VS*	004	2.06	*W*
002	4.1	*M*	104	2.000	*W*
111	3.9	*M*	222	1.951	*VW*
210	2.9	*M*	320	1.766	*W*
211	2.73	*W*	410	1.670	*M*
103	2.64	*VW*	411	1.637	*W*
300	2.55	*VW*	403	1.554	*VW*
301	2.45	*M*	501	1.500	*VW*
212	2.37	*W*	323	1.475	*VW*
113	2.31	*VW*	420	1.440	*W*
203	2.24	*M*			

It should be recalled that the hexagonal hydrated calcium aluminates, as a group, exhibit a similarity in optical properties. The indices of refraction of the various samples, in general, increased as the molar ratio, CaO/Al_2O_3, increased. Despite the fact that the X-ray patterns indicate the presence of two crystalline compounds in cases in which the molar ratio, CaO/Al_2O_3, is intermediate between 2 and 4, nevertheless, the products appeared microscopically to consist of only one compound. It is believed, therefore, that the hydrated dicalcium and tetracalcium aluminates, being of very similar structure parallel to the *a* axis, can intercrystallize and give masses which are made up of layers of the one compound so intimately mixed with layers of the other that the average indices of refraction are obtained.

It has been remarked in the literature that all these hexagonal hydrated calcium aluminates have a "family resemblance" in respect to their X-ray powder patterns. In most cases the methods used for obtaining the patterns were such that they did not record lines of interplanar spacings greater than 3 A. Since the lines with large spacings were not obtained, the strongest lines appearing were *hko* lines, and, since the spacings of such lines are functions only of the length of the *a* axis, they are in the same position in the dicalcium and tetracalcium aluminates and mixtures thereof.

A second series of patterns was made on samples of hydrated calcium aluminates of molar ratios of lime to alumina almost identical with those reported above. In this case, however, the samples had been stored in stoppered vials for 2 to 3 years. The losses on ignition of the samples were practically unchanged from those obtained when freshly prepared, but the indices of refraction had increased, especially for those products of low molar ratios of lime to alumina. After storage, the materials all had indices of refraction typical of hydrated tetracalcium aluminate, and the X-ray diffraction patterns, in all cases, were those of hexagonal tetracalcium aluminate hydrate.

Therefore, on standing, $2CaO.Al_2O_3.8H_2O$ breaks down according to the equation:

$$2Ca(OH)_2.2Al(OH)_3.3H_2O \rightarrow 2Ca(OH)_2.Al(OH)_3.3H_2O + Al(OH)_3.$$

Thus, the one extra layer of $Al(OH)_3$ separates out of the crystal, and, since no extra lines are present in the pattern, the $Al(OH)_3$ may be assumed to be amorphous.

A portion of each of the eight samples that had been examined when freshly prepared (table 4) were stored in open dishes over $CaCl_2$ in a desiccator for 3 weeks, and the losses on ignition were then redetermined. The water content in the $2CaO.Al_2O_3.8H_2O$ compound had dropped to about 6 moles. In the composition $4CaO.Al_2O_3.13H_2O$ the content of H_2O after dry storage was 11.23 moles. Preparations of intermediate compositions had lost water proportionately.

X-ray diffraction patterns were made on these dried samples. The sample with composition $4CaO.Al_2O_3.11.23H_2O$ had a pattern very similar to that of the freshly prepared compound with about 13 moles of H_2O. There was, however, a slight but definite decrease in the size of the unit cell along the c axis. The dried material had a c axis of about 8.1 A in length. All samples of lower molar ratios, CaO/Al_2O_3, had broken down almost completely to the tetracalcium aluminate hydrate, just as had those stored for several years, in closed vials.

Although the X-ray diffraction patterns showed that the dicalcium aluminate hydrate dissociated into the tetracalcium aluminate hydrate and amorphous hydrated alumina on storage in the dry state, it is not known from this investigation whether this conversion occurs in contact with the calcium aluminate solutions. Bessey states, in his discussion of an article by Büssem [28], that $2CaO.Al_2O_3.8H_2O$ in contact with its saturated solution in water is converted to the tetracalcium compound without recrystallization or change in crystal form, but with liberation of hydrated alumina. He also states that, in contact with solutions of higher lime concentration, the dicalcium aluminate hydrate is converted to the similar tricalcium or tetracalcium compound, again without disturbance of the existing crystals. Bessey, however, does not give the direct experimental evidence on which he based his assertions. The X-ray data of the present investigation have shown no evidence for the existence of a hexagonal hydrated tricalcium aluminate. The conversion of the dicalcium aluminate into the tetracalcium aluminate when kept in contact with solutions of higher lime concentrations, is, however, confirmed.

The relation of these compounds to the natural mineral hydrocalumite ($4CaO.Al_2O_3.12H_2O$) [26] is not clear. This mineral is monoclinic and appears to be made up-of alternate layers, just as seems to be the case in these hexagonal compounds. The cell characteristics $a = 9.6$ A, $b = 11.4$ A, $c = 16.84$ A, $\beta = 69°$ are not similar to the hexagonal compounds considered here.

(e) DISCUSSION OF THE HEXAGONAL CALCIUM ALUMINATES

From the X-ray studies of the relations of the hexagonal hydrated calcium aluminates, it is now evident that of the two explanations formerly postulated for the more or less gradual increase in the molar ratio, CaO/Al_2O_3, in the aluminates along the curve *ABD* of figure 1, the first, namely, that the solubility data pertain to overlapping solubility curves of separate hydrated aluminates ($2CaO.Al_2O_3.8H_2O$ and $4CaO.Al_2O_3.13H_2O$), is more valid than the second—that involving a solid-solution series. If this "curve" is now reexamined, it will be noted that there is a limited section where the molar ratio, CaO/Al_2O_3, is perhaps close enough to 2 to warrant the conclusion that this applies primarily to the dicalcium aluminate hydrate. Likewise, at the higher lime concentrations there is a section which might be ascribed as pertaining mainly to the solubility of the hexagonal tetracalcium aluminate hydrate. The portion between these two sections may logically correspond to that region where the two aluminates markedly intercrystallize because of the close similarity of their crystal structures. That no evidence of the existence of a hexagonal hydrated tricalcium aluminate was obtained in this study lends weight to this argument.

If these explanations are correct, there should be a metastable invariant point (since both hexagonal aluminates, as will be shown later, are metastable with regard to the isometric aluminate $3CaO.Al_2O_3.6H_2O$) where the solution is saturated with respect to both the dicalcium and tetracalcium aluminates. But, in view of the extreme difficulty in obtaining equilibrum, it may not be found possible to trace the metastable curves individually with sufficient accuracy to establish this point. Notwithstanding, it is believed that the metastable invariant point, $2CaO.Al_2O_3.8H_2O$, $4CaO.Al_2O_3.13H_2O$, and solution, lies somewhere between 0.5 and 0.6 g of CaO and 0.10 and 0.15 g of Al_2O_3 per liter. At concentrations of lime greater than that at the invariant point, the solutions in metastable equilibrium with dicalcium aluminate appear to be supersaturated with respect to the tetracalcium aluminate, and, consequently, the mixture is predominantly composed of the tetracalcium aluminate, whereas at the lower concentrations of lime the reverse seems to hold. There should also be a second metastable invariant point for $4CaO.Al_2O_3.13H_2O$, $Ca(OH)_2$, and a solution containing about 1.15 g of CaO per liter and somewhere between 0.005 and 0.01 g of Al_2O_3 per liter.

The point of intersection of the curve *ABD* with the $2CaO.Al_2O_3$-composition line gives a value slightly higher than that suggested by Bessey [13] for the solubility of $2CaO.Al_2O_3.8H_2O$, as well as that found in this study where equilibrium was approached from undersaturation.

The relation of the biaxial form (or forms) of the tetracalcium aluminate to the uniaxial hexaginal modification in the system $CaO\text{-}Al_2O_3\text{-}H_2O$ at 21° C warrants further study.

2. TRANSITION OF THE HEXAGONAL HYDRATED CALCIUM ALUMINATES INTO THE ISOMETRIC TRICALCIUM ALUMINATE HEXAHYDRATE, $3CaO.Al_2O_3.6H_2O$, IN THE SYSTEM AT 21° C

Attention will now be directed to the changes which took place when the mixtures of calcium aluminate-calcium hydroxide solutions were not filtered at the first appearance of phases other than the metastable hexagonal hydrated calcium aluminates. The first of these changes to be considered will be the transition of the hexagonal forms into the isometric tricalcium aluminate hexahydrate, $3CaO.Al_2O_3.6H_2O$. This crystalline hydrated aluminate can be recognized readily with a microscope by its refractive index, which is close to 1.605. Well-formed icositetrahedrons or rhombic dodecahedrons having this index were observed in 1928 by one of the present authors in a previous study of the reaction of water on the calcium aluminates [1]. However, as the crystals were associated with other phases, they were not recognized as being the compound $3CaO.Al_2O_3.6H_2O$ that had been noted by Allen and Rogers [22] as early as 1900. After the careful investigation of Thorvaldson and Grace [29], there was no doubt concerning the identity of the crystals previously observed.

By following the changes in the crystalline phases, it was noticed that the isometric crystals grew at the expense of the hexagonal forms. After appreciable quantities of the isometric crystals had been formed, several of the mixtures were filtered, and the solid phases and resulting solutions were analyzed to ascertain the region in the diagram where the changes were taking place.

Figure 4 shows this region, together with the curve *ABD* (pertaining to the hexagonal hydrated aluminates) which has been transferred from figure 1. The closed circles give the compositions of the initial unstable calcium aluminate solutions, and the open circles containing crosses, the compositions of the resulting solutions following partial transformation of the hexagonal phases into the isometric $3CaO.Al_2O_3.6H_2O$. Although the numbers accompanying the lines connecting these points give the molar ratios, CaO/Al_2O_3, in the solid phases thus formed, the connecting lines do not reveal the actual paths of precipitation except in those instances in which these ratios remain as 3. Thus, it can be seen from figure 1 that for the hexagonal aluminates this ratio was approximately 3 along that section of the curve *ABD* where the concentration of lime ranged from about 0.5 to about 0.6 g CaO per liter. From figure 4, it is apparent that, as the formation of the isometric aluminate carried the precipitation beyond that section of the curve *ABD*, the precipitation continued along paths closely parallel to the $3CaO.Al_2O_3$-composition line.

The molar ratio, CaO/Al_2O_3, of the hexagonal aluminates was less than 3 along that section of the curve *ABD* of figure 1 where the concentration of lime was less than 0.5 g of CaO per liter. As the isometric was formed in this region, this molar ratio of the solid phases increased to about 3 (fig. 4). Such an increase could take place only by a removal of lime from solution. This, coupled with the fact that the hexagonal phases are metastable with respect to the isometric phase, resulted in the solutions moving away from the curve *ABD*, but at slopes different from those of the connecting lines of figure 1.

On the other hand, the conversion of the hexagonal aluminates having molar ratios greater than 3 (at lime concentrations greater than 0.6 g of CaO per liter along *ABD* of fig. 1) into the isometric $3CaO.Al_2O_3.6H_2O$ must, at first, have liberated lime to the solutions. But, since the solubility of the hexagonal aluminates decreases in this region as the concentration of lime in solution increases, the tendency would be for the solutions to change in composition along this section of the curve *ABD*. Figure 4 shows that in three instances (those wherein the molar ration, CaO/Al_2O_3, of the solid phases were 3.24, 3.34, and 3.58) the compositions did remain on this curve. In four other instances, where the conversion of the hexagonal aluminate to the isometric was more complete, the continued formation of the more stable $3CaO.Al_2O_3.6H_2O$ eventually carried the precipitation beyond the curve *ABD*.

Because appreciable quantities of the hexagonal forms of the hydrated calcium aluminates still persisted in the solid phase of the reaction mixtures which had been filtered, the remaining unfiltered mixtures were set aside to permit the further transformation into the isometric modification to proceed more nearly to completion. The object in view was to construct a solubility curve for the isometric hydrate. In the meantime, a considerable quantity of $3CaO.Al_2O_3.6H_2O$ was prepared and placed in calcium hydroxide solutions of increasing concentrations to approach equilibria in this manner. Consideration will now be given to the results of these experiments.

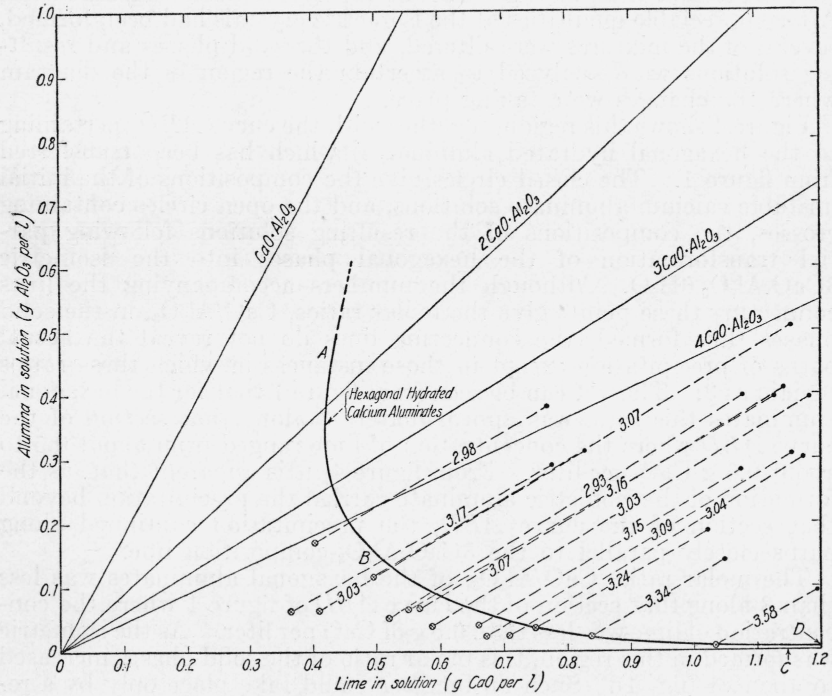

FIGURE 4.—*Composition of the calcium aluminate solutions resulting from partial transformation of the metastable hexagonal hydrated calcium aluminates into the stable isometric tricalcium aluminate hexahydrate* $3CaO.Al_2O_3.6H_2O$ *at 21° C.*

3. ISOMETRIC TRICALCIUM ALUMINATE HEXAHYDRATE, $3CaO.Al_2O_3.6H_2O$, IN THE SYSTEM AT 21° C.

The isometric hexahydrate $3CaO.Al_2O_3.6H_2O$ was prepared, in a platinum dish, by direct hydration of anhydrous tricalcium aluminate with saturated steam at 177° C (equivalent to a pressure of 150 lb/in.^{2}) following the general procedure described by Thorvaldson and Grace [29]. Despite the fact that the preparation was steamed twice, it still contained a small quantity of the hexagonal phase, estimated microscopically to be 1 percent or less. The index of refraction of the isometric hydrate was very close to 1.605.

Two series of reaction mixtures that contained, in each instance, 1 g of the isometric hydrate per liter of a clear solution of calcium hydroxide were then prepared. The concentration of the calcium hydroxide solutions ranged from the equivalent of 0.0 to 1.296 g of CaO per liter. The mixtures, which were placed in tightly stoppered flasks, were shaken from time to time to facilitate approach to equilibrium. One series was maintained continuously at a temperature of 21° C, and the second was first heated on a steam bath for several hours and then slowly cooled for several hours to the same constant temperature. At intervals of 1 to 3 months, depending upon the changes occuring, aliquots of the filtrates from separate reaction mixtures were taken, until successive analyses indicated that equilibrium had been attained, as evidenced by no successive change in the concentration of dissolved alumina or lime greater than that which could be ascribed to the limits of the accuracy of the analytical procedure.

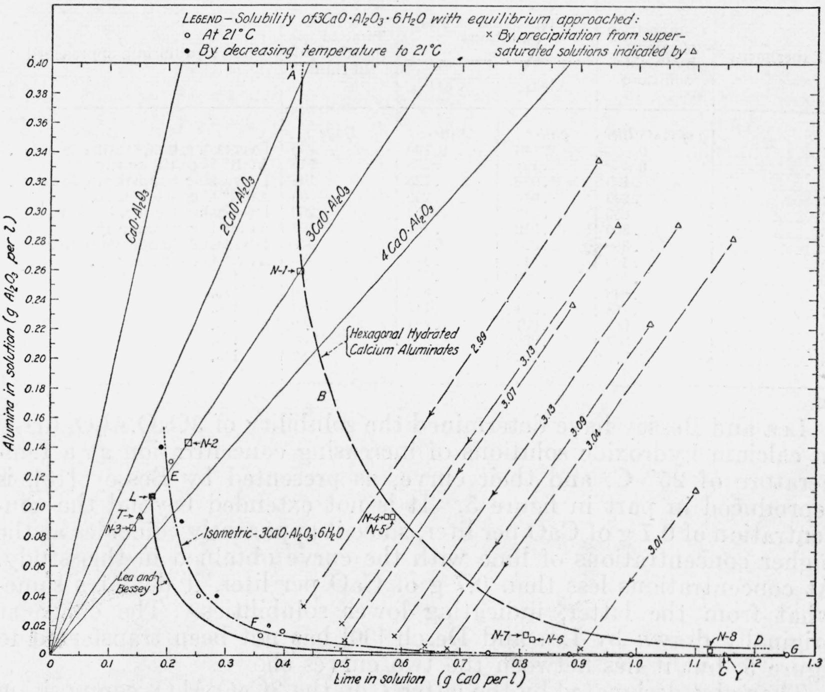

FIGURE 5.—*Solubility relationships of isometric tricalcium aluminate hexahydrate,* $3CaO.Al_2O_3.6H_2O$, *in the system* CaO-Al_2O_3-H_2O *at 21° C.*

Data pertaining to these solubility determinations are given in table 7. In figure 5 the quantity of alumina in solution is plotted against the lime in solution, and a curve, EFG, is drawn through these points. The open circles pertain to the solubility values obtained at a constant temperature of 21° C, and the closed circles to those where equilibrium was approached from a higher temperature. The figure also shows a portion of the curve ABD representing the solubility of the hexagonal hydrated calcium aluminates, as transferred from figure 1. In addition, there are shown seven instances (indicated by crosses) where the solubility curve of $3CaO.Al_2O_3.6H_2O$ was approached from supersaturation. Although the inversions of the hexagonal forms into the isometric had proceeded further than in the examples shown in figure 4, nevertheless, they were still incomplete in several instances, despite the fact that these particular mixtures had stood for over a year.

TABLE 7.—*Solubility of isometric tricalcium aluminate hexahydrate,* $3CaO.Al_2O_3.6H_2O$, *at 21° C*

[Obtained from mixtures containing 1 g of $3CaO.Al_2O_3.6H_2O$ per liter of both water and aqueous solutions of calcium hydroxide]

Experiment	Composition of calcium hydroxide solutions	Composition of final solutions		Time to approach equilibrium	Equilibrium approached
		Al_2O_3	CaO		
	g of CaO*/liter*	*g/liter*	*g/liter*	*Days*	
1	0	0.140	0.190	236	Decreasing temperature to 21° C.
2	0	.131	.208	516	At 21° C continuously.
3	.100	.090	.223	108	Decreasing temperature to 21° C.
4	.200	.040	.255	509	At 21° C continuously.
5	.259	.040	.285	260	Decreasing temperature to 21° C.
6	.350	.013	.361	509	At 21° C continuously.
7	.389	.020	.375	478	Decreasing temperature to 21° C.
8	.400	.017	.398	89	At 21° C continuously.
9	.518	.009	.504	89	Do.
10	.648	.002	.632	89	Do.
11	.758	.001	.747	89	Do.
12	.907	.001	.884	89	Do.
13	1.037	.0008	.990	89	Do.
14	1.296	.0003	1.256	89	Do.

Lea and Bessey have determined the solubility of $3CaO.Al_2O_3.6H_2O$ in calcium hydroxide solutions of increasing concentration at a temperature of 25° C, and their curve, as presented by Bessey [13], is reproduced in part in figure 5. It is not extended beyond the concentration of 0.7 g of CaO per liter, since it apparantly coincides at the higher concentrations of lime with the curve obtained in this study. At concentrations less than 0.7 g of CaO per liter, it deviates somewhat from the latter, indicating lower solubilities. The curve as originally drawn by Lea and Desch [30] has not been transferred to figure 5, but it lies between the two curves shown.

The point designated by the letter *L* on the $3CaO.Al_2O_3$-composition line locates the solubility of the compound $3CaO.Al_2O_3.6H_2O$ as given by Bessey, as well as the ascribed invariant point $3CaO.Al_2O_3.6H_2O$-Al_2O_3.aq.

Small quantities of an additional phase (very likely hydrated alumina) were found in the mixtures which had less than 0.3 g of CaO per liter (table 7, experiments 1 to 5, inclusive). The mean refractive index ranged from about 1.56 to 1.58, which is distinctly less than 1.605, the index of $3CaO.Al_2O_3.6H_2O$. At concentrations of lime greater than 0.35 g of CaO per liter, this material was absent. The reason for its presence from *E* to *F* and absence from *F* to *G* along the curve *EFG* of figure 5 will become more evident following the discussions of the role of hydrated alumina in the system CaO-Al_2O_3-H_2O.

Thorvaldson, Grace, and Vigfusson [9] found that the compound $3CaO.Al_2O_3.6H_2O$ dissolved to the extent of 0.246 and 0.268 g of anhydrous tricalcium aluminate per liter of water at temperatures of

21° and 40° C, respectively. The solubility at 21° C is equivalent to 0.153 g of CaO and 0.093 g of Al_2O_3 per liter, and this value is plotted herein as a closed triangle symbolized by the letter *T* in figure 5. This point falls on the $3CaO.Al_2O_3$-composition line.

Nacksen and Mosebach [31] have reported the solubility of the isometric hexahydrate as being 0.6774 g of $CaO.Al_2O_3$ per liter at a temperature of 23° C; a value over twice that of any of those mentioned. Their value, which is the average of several separate determinations, is plotted in figure 5 and is represented by the symbol *N–1*. Note that it falls on the curve showing the solubility of the hexagonal hydrated calcium aluminates.

In their determinations, Nacken and Mosebach shook anhydrous tricalcium aluminate (actually 2.93 $CaO.Al_2O_3$) with water for periods as long as 2 months. It is well known that when tricalcium aluminate is hydrated with water hexagonal crystals are formed which, more or less rapidly, depending on the temperature, change to the isometric form. Nacken and Mosebach commented on the silky appearance (usually characteristic of the platy hexagonal crystals) of their mixtures during the first few days of shaking and showed that the dissolved CaO plus Al_2O_3 was greater than 0.6774 g per liter, the average value obtained by shaking for about 2 months. In one instance it reached a value of 0.7792 g per liter. These higher solubility values lie in the region above that of the hexagonal solubility curve. Hence, it would appear that, when the anhydrous tricalcium aluminate first reacted with water, solutions were formed which were unstable with respect to the hexagonal phases. This was followed by a further precipitation of a portion of the CaO and Al_2O_3 as hexagonal material.

Despite the fact that further shaking resulted in a transformation of the bulk of the hydrated material to the isometric hexahydrate, Nacken and Mosebach found that the composition of the solutions remained at the point *N–1* (fig. 5). It should be recalled that the investigations carried out in this laboratory have demonstrated that the approach to equilibrium from supersaturation in regard to the phase $3CaO.Al_2O_3.6H_2O$ is a very slow process.

In a later publication, Nacken and Mosebach [32] carried out two solubility determinations of $3CaO.Al_2O_3.6H_2O$, starting, in these cases, with the hexahydrate itself rather than with the anhydrous tricalcium aluminate. The values they obtained are indicated by the symbols *N–2* and *N–3* in figure 5 and pertain to their experiments 8 and 9, respectively. These solubility values are of the order of magnitude of those obtained by others, in marked contrast to the higher solubility (*N–1*) when the hexagonal crystals are formed as an intermediate phase. Notwithstanding, Nacken and Moseback considered that their higher solubility value (*N–1*) was correct.

They also carried out some experiments pertaining to the composition of solutions resulting from the reaction between CaO plus $3CaO.Al_2O_3$ plus water. Points *N–4* and *N–5* of figure 5 represent the compositions of the solutions they obtained by shaking duplicate mixtures containing 0.31 g of CaO plus 2.705 g of $3CaO.Al_2O_3$ in 1 liter of H_2O; and *N–6* and *N–7* are check solubilities obtained with the additions of 0.81 g of CaO to the same quantities of tricalcium aluminate and water. They noted in their experiments the initial formation of the hexagonal phase and its tendency to revert to the isometric phase.

Again, as with *N–1*, the points *N–4* and *N–5* lie close to the metastable solubility curve of the hexagonal hydrates. Points *N–6* and *N–7* are between the solubility curves of the hexagonal and isometric phases. When Nacken and Mosebach added larger quantities of CaO to their mixtures, they observed that the solubility further decreased (*N–8*). When sufficient CaO had been added to give appreciable quantities of $Ca(OH)_2$ as a solid phase (slightly above C), they found but traces of alumina in solution; in agreement with the findings of Bessey [13] and those of the present investigation.

Although Lerch and Bogue [52] did not give the actual solubility of hydrated tricalcium aluminate in a solution saturated with respect to $Ca(OH)_2$, they, nevertheless, showed that there was no indication of the hydrated tricalcium aluminate forming the hydrated tetracalcium aluminate. This again demonstrates that hydrated tricalcium aluminate, and not hydrated tetracalcium aluminate, is the stable phase in a solution saturated with respect to $Ca(OH)_2$.

Since the solubility of $3CaO.Al_2O_3.6H_2O$ is very low in calcium hydroxide solutions approaching saturation with respect to $Ca(OH)_2$, there is no reason to believe that the solubility of coarsely crystalline $Ca(OH)_2$ in such solutions would be detectably different from that in water. No actual determination was made of the solubility of $3CaO.Al_2O_3.6H_2O$ at a concentration of 1.15 g of CaO per liter (*C*, the solubility of coarsely crystalline $Ca(OH)_2$ in water at 21° C), but it appears from experiments 13 and 14 of table 7 that with such a solution the quantity of alumina in solution should be close to 0.0005 g per liter. Accordingly, *Y* of figure 5 is ascribed as the invariant point at 21° C for $3CaO.Al_2O_3.6H_2O$, coarsely crystalline $Ca(OH)_2$, and a solution containing 0.0005 g of Al_2O_3 and 1.15 g of CaO per liter, and finally the very short line *YC* represents the stable solubility curve of $Ca(OH)_2$ in the system.

4. HYDRATED ALUMINA AS A SOLID PHASE IN THE SYSTEM AT 21° C

Thought will now be given to those regions, in the system $CaO\text{-}Al_2O_3\text{-}H_2O$ at 21° C, where hydrated alumina exists as one of the principal phases. This in turn will be followed by a consideration of the changes that occur as the amorphous hydrated alumina initially produced gradually ages and is converted into crystalline gibbsite, $Al_2O_3.3H_2O$.

Mixtures of calcium aluminate-calcium hydroxide solutions were prepared in a manner similar to that already described in the investigation of the system where the hexagonal hydrated calcium aluminates separated as primary phases. Microscopical examinations of the solid phases were made at intervals to follow any changes which might be taking place.

Some of the regions in which hydrated alumina was formed as a solid phase are shown in figure 6. The compositions of the original mixtures are indicated by closed circles, and crosses show the compositions of the solutions after precipitation of a portion of the alumina as a solid phase. Open circles enclosing crosses signify that crystalline hexagonal hydrated aluminates also are present. The figures accompanying the lines connecting the compositions of the original mixtures and those of the solutions subsequently produced give the molar ratios, CaO/Al_2O_3, in the materials precipitated. The connecting lines do not necessarily reveal the actual course of precipitation. In fact, it is known in many cases that the paths of precipitation are far different from those indicated by these lines. This applies particularly to the metastable solutions that yielded hexagonal aluminates associated with hydrated alumina. For example, it was observed that from those original mixtures in which the molar ratio, CaO/Al_2O_3, was approximately 2, hexagonal hydrates usually crystallized prior to the appearance of hydrated alumina as a solid phase. Therefore, it seems possible, from figure 1, that the course of precipitation from such solutions must at first have been along a path more or less parallel to the $2CaO.Al_2O_3$-composition line down to some point on the solubility curve of the hexagonal hydrated calcium aluminates, as the hexagonal hydrates crystallized from solution. From this point the path shifted when hydrated alumina separated from solution as a solid phase. But, inasmuch as the hexagonal hydrates were present as solid phases, the path of precipitation proceeded downward along the solubility curve of the hexagonal hydrated calcium aluminates.

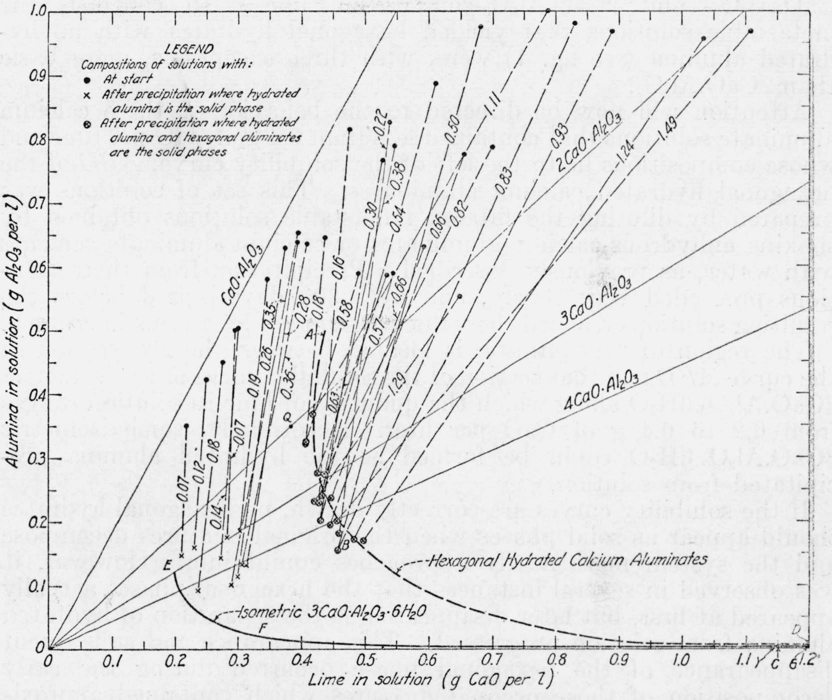

FIGURE 6.—*Some of the regions in the system CaO-Al_2O_3-H_2O at 21° C. in which hydrated alumina is formed as a solid phase.*

However, in most instances in which the molar ratio of CaO/Al_2O_3 was less than 2, it was not possible to follow the actual paths of precipitation, because the hydrated alumina made its appearance either simultaneously with that of the hexagonal hydrates, or so soon thereafter that it was not feasible to filter the mixtures rapidly enough to ascertain the separate paths of precipitation. It is significant, nevertheless, that the compositions of most of the solutions resulting from the precipitation of both hydrated alumina and the hexagonal hydrates lie fairly well along the solubility curve of the hexagonal hydrated calcium aluminates.

Figure 6 shows that the metastable solutions that decomposed with separation of both hydrated alumina and hexagonal hydrated aluminates contained more than 0.4 g of CaO per liter; i. e., they are located to the right of the solubility curve *ABD* of the hexagonal hydrated calcium aluminates. Furthermore, with two exceptions the compositions of these highly metastable solutions lie between the $CaO.Al_2O_3$- and $2CaO.Al_2O_3$-composition lines. In contrast, the metastable solutions that yielded hexagonal hydrates with no hydrated alumina (see fig. 1) were, with three exceptions, more basic than $2CaO.Al_2O_3$.

Attention will now be directed to the behavior of these calcium aluminate solutions that contained less than 0.4 g of CaO per liter and whose compositions lie to the left of the solubility curve, *ABD* of the hexagonal hydrated calcium aluminates. This set of solutions was prepared by diluting the filtered metastable solutions obtained by shaking anhydrous calcium aluminates or calcium aluminate cements with water, as previously described. Precipitation from those solutions proceeded very slowly, and over 300 days lapsed before the resulting solutions reached the values designated by crosses in figure 6.

The region of precipitation is located between the *AB* section of the curve *ABD* and that section of the solubility curve of the isometric $3CaO.Al_2O_3.6H_2O$ along which the quantity of lime in solution ranges from 0.2 to 0.4 g of CaO per liter. Accordingly, some isometric $3CaO.Al_2O_3.6H_2O$ could be formed as the hydrated alumina precipitated from solution.

If the solubility curves are correctly drawn, no hexagonal hydrates should appear as solid phases when the original mixtures decompose and the system more nearly approaches equilibrium. However, it was observed in several instances that the hexagonal phases actually appeared at first, but later disappeared as the separation of hydrated alumina from solution progressed. This appearance and subsequent disappearance of the hexagonal phase occurred during the early decomposition of those original mixtures which contained approximately 0.4 g of CaO and 0.65 g of Al_2O_3 per liter. Hence, it is thought that the solubility curve of the hexagonal hydrated calcium aluminates should be shifted slightly to the left, and that the curve probably does not bend around so much as indicated. This shifting of the curve is likewise suggested not only by the somewhat lower solubility value of hydrated dicalcium aluminate when equilibrium was approached from undersaturation (see experiment 1 of fig. 2), but also by the still lower solubility value of $2CaO.Al_2O_3.8H_2O$ given by Bessey [13] and indicated by the letter *Q* on the $2CaO.Al_2O_3$-composition line of figure 6.

It should be emphasized again that the hexagonal phases are formed only as intermediate phases in the more gradual approach to real equilibrium. The difficulty of locating accurately the metastable solubility curves of the hexagonal hydrated calcium aluminates should be evident by now, not only because of the separation of hydrated alumina as a solid phase, but also on account of the previously mentioned transformation of the hexagonal phases into the more stable isometric hydrate $3CaO.Al_2O_3.6H_3O$.

After the hexagonal phases disappeared the course of precipitation apparently moved away from the curve of the hexagonal hydrated calcium aluminates and approached that of the isometric $3CaO.Al_2O_3.6H_2O$. This was accompanied by a slight decrease of lime in solution.

The indices of refraction of the hydrated alumina when first formed although variable, averaged about 1.50, and later increased as the hydrated alumina aged. The hydrated alumina separated from solution as both flakes and pellets, and upon aging the refractive indices of the outside surfaces of both the flakes and pellets increased more rapidly than the interior. Consequently, it was rather difficult to determine the exact indices of refraction. All that can be said is that the refractive indices of the outside shells increased to as much as from 1.56 to 1.58, and that the refractive indices of the interiors of flakes and pellets were definitely less than these values.

It was observed also that the more pronounced increases in indices of refraction in the shells were associated with higher contents of lime in the precipitated materials. This suggested the idea that possibly some of the lime in solution had reacted with the hydrated alumnia which had separated from solution and had formed small amounts of the isometric $3CaO.Al_2O_3.6H_2O$ within the shell of the flakes and pellets. The reaction, however, appeared not to have proceeded far enough to have raised the indices to 1,605, the value for $3CaO.Al_2O_3.6H_2O$. The indicated limited formation of $3CaO.Al_2O_3.6H_2O$ can account only in part for the increase in refractive index of the hydrated alumina upon aging. It does not explain the increases where very small quantities of lime were present in the precipitated products. This must be attributed to a change taking place in the hydrated alumina itself.

In a previous study of the products formed in the reaction of water with calcium aluminates and calcium aluminate cements [1], it was pointed out that the refractive indices of the hydrated alumina obtained ranged from about 1.48 to 1.57. Attention was called to the fact that the index 1.57 agreed fairly well with the mean refractive index of gibbsite, $\alpha=1.566$, $\gamma=1.587$, $\beta=1.556$ [33]. It was also mentioned that Fricke and Wever [34] and Böhm and Niclassen [35], by means of X-ray diffraction patterns, had shown that aged hydrated alumina was crystalline.

Assarsson [36] later found that the hydrated alumina which separated from the calcium aluminate solutions likewise had similar variable indices of refraction and that the index of refraction of the outer layers of the concentric shells of the spherulites was higher than that of the inner. He demonstrated by means of X-ray analysis that the hydrated alumina upon aging exhibited the detectable crystal structure of gibbsite, the complete structure of which was worked out by Megaw [37]. Assarsson came to the conclusion that gibbsite was the final product of the aging, even though some of his samples of hydrated alumina contained between 3 and 4 moles of H_2O rather than the prescribed 3 moles for gibbsite, $Al_2O_3.3H_2O$. The extra water he ascribed to absorbed water rather than to constitutional water of crystallization.

Likewise, X-ray diffraction patterns of samples of aged hydrated alumina were found in the present investigation to contain the lines characteristic of gibbsite. The intensity of the lines increased as the hydrated alumina aged. It was noted also that the moles of water were in many instances somewhat greater than 3. In addition, the molar ratio, H_2O/Al_2O_3, increased with that of the CaO/Al_2O_3 in the products. Whether the simultaneous increase in molar ratio, H_2O/Al_2O_3, is in part caused by the formation of small quantities of $3CaO.Al_2O_3.6H_2O$ in the shell of the pellets and flakes of hydrated alumina is not known. If $3CaO.Al_2O_3.6H_2O$ was thus formed, it was not present in sufficient quantities to give rise to lines characteristic of this compound in the X-ray diffraction patterns studied.

X-ray diffraction patterns were also obtained of precipitates that had aged a long time before filtering and which contained both hydrated alumina and the hexagonal aluminate. Again, the presence of gibbsite was indicated.

Dilute monocalcium aluminate solutions having less than 0.15 g of CaO per liter remained clear for months and showed but little tendency to liberate hydrated alumina as a solid phase. No attempt was made to see to what extent they might have decomposed had they been "seeded" with gibbsite.

From these studies it can be concluded that hydrated alumina is one of the solid phases formed, and that on aging it is converted to crystalline gibbsite. Furthermore, the aging at 21° C is a very slow process, and, accordingly, a very long time must elapse before true equilibrium is attained. It is evident from the scattered points of figure 6 that equilibrium had not been reached even though the mixtures has stood for over 300 days. Therefore, it was decided to investigate the solubility of gibbsite at increasing concentrations of lime by starting with well-crystallized gibbsite, rather than by continuing the very slow approach to equilibrium from supersaturation.

5. GIBBSITE, $Al_2O_3.3H_2O$, IN THE SYSTEM AT 21° C

The synthetically prepared $Al_2O_3.H_2O$ used in this study was thoroughly washed with water to remove small quantities of alkali salts. The loss on ignition after drying at a temperature of 110° C was 34.50 percent (theoretical H_2O, 34.65 percent). The indices of refraction of the dried material were: $\alpha=1.573\pm0.003$; β, not determined; $\gamma=1.592$ 0.003; and are slightly higher than the values $\alpha=1.566$, $\beta=1.566$, $\gamma=1.587$, as listed by Larsen and Berman [33] for gibbsite. There was a trace of undetermined material with a mean index of refraction somewhat greater than 1.62, but less than 1.63. An X-ray diffraction pattern gave the lines characteristic of gibbsite.

A series of reaction mixtures, containing in each case 2.000 g of gibbsite per liter of solution of calcium hydroxide, was prepared and placed in tightly stoppered flasks. The concentration of the calcium hydroxide solutions ranged from the equivalent of 0.050 g to that of 1.300 g of CaO per liter. The mixtures were maintained at a temperature of 21° C and were shaken from time to time to facilitate an approach to equilibrium. At various intervals of time, aliquots of the solutions were taken for analysis. The compositions of the solutions are given in table 8.

The solubility determinations up to and including those where the initial concentration of lime was 0.300 g of CaO per liter (experiments 1 to 17, inclusive) indicate that no solid phase other than gibbsite is present. In no instance was more than 0.01 g of CaO removed from solution. At a concentration of 0.350 g of CaO per liter, slightly more lime was removed from solution at the later periods. In experiment 20 this amounted to 0.019 g of CaO. When the gibbsite was placed in the more concentrated calcium hydroxide solutions (experiments 21 to 46, inclusive), greater quantities of lime were removed from solution. In experiment 46, at the end of 810 days, the concentration of lime had been reduced from 1.300 to 0.320 g of CaO per liter.

TABLE 8.—*Solubility of gibbsite,* $Al_2O_3.3H_2O$, *at 21° C*

[Obtained from mixtures containing 2 g of gibbsite per liter of aqueous solution of calcium hydroxide.]

Experiment	Composition of calcium hydroxide solution	Time to approach equilibrium	Composition of resulting solution		Molar ratio, CaO/Al_2O_3, in solid phase
	g of CaO/*liter*	*Days*	*g of* Al_2O_3/*liter*	*g of* CaO/*liter*	
1	0.050	86	0.005	0.047	0.004
2	.050	249	.004	.047	.004
3	.050	810	.005	.046	.006
4	.100	14	.002	.092	.010
5	.100	249	.008	.094	.009
6	.100	439	.007	.100	.0
7	.150	60	.007	.144	.008
8	.150	249	.005	.143	.010
9	.200	14	.005	.192	.010
10	.200	249	.010	.193	.010
11	.200	439	.011	.195	.010
12	.250	87	.008	.243	.010
13	.250	219	.017	.243	.010
14	.250	439	.015	.240	.030
15	.300	60	.009	.290	.010
16	.300	93	.016	.291	.010
17	.300	249	.014	.291	.010
18	.350	87	.017	.344	.008
19	.350	219	.018	.336	.02
20	.350	439	.019	.331	.03
21	.450	87	.016	.435	.02
22	.450	189	.025	.413	.05
23	.450	249	.027	.395	.08
24	.450	439	.017	.326	.17
25	.500	60	.014	.484	.008
26	.500	93	.022	.455	.06
27	.500	189	.032	.436	.09
28	.500	441	.023	.377	.17
29	.605	133	.034	.552	.08
30	.605	244	.040	.536	.10
31	.605	353	.040	.500	.15
32	.706	133	.041	.645	.12
33	.706	244	.054	.616	.13
34	.706	353	.047	.603	.15
35	.900	14	.008	.842	.08
36	.900	60	.031	.804	.14
37	.900	93	.037	.739	.23
38	.900	189	.057	.649	.36
39	.900	334	.047	.594	.44
40	.900	441	.040	.542	.51
41	1.300	14	.008	1.219	.11
42	1.300	60	.019	0.998	.43
43	1.300	189	.031	.654	.92
44	1.300	334	.042	.544	1.09
45	1.300	441	.037	.477	1.18
46	1.300	810	.018	.320	1.48

Equilibrium appears to have been attained in the mixtures that initially contained 0.350 g or less of CaO per liter (experiments 1 to 20, inclusive). Where the concentrations were greater than 0.350 g of CaO per liter, the dissolved alumina at first increased as the lime was removed from solution, reached a maximum, and then decreased.

The course of these changes is shown in figure 7, where the alumina in solution is plotted against the lime in solution. The numbers accompanying the indicated compositions refer to the time, in days, that had lapsed since the mixtures were prepared. A smooth curve (*HFJ*) has been drawn through the points pertaining to the maximum solubility values of alumina.

The solubility curve *EFG* of the isometric $3CaO.Al_2O_3.6H_2O$ and a portion of that of the hexagonal hydrated calcium aluminates have been replotted to fit the enlarged scale used in figure 7 for grams of Al_2O_3 per liter.

The curve HFJ intersects *EFG* where the alumina in solution is 0.02 g of Al_2O_3 per liter and the lime in solution approximately 0.33 g of CaO per liter. This point of intersection, *F*, should represent, therefore, the invariant point $3CaO.Al_2O_3.6H_2O$-$Al_2O_3.3H_2O$ (gibbsite). Consequently, gibbsite is the stable phase in the system CaO-Al_2O_3-H_2O at 21° C up to a concentration of lime of 0.33 g of CaO per liter (*HF*), and the isometric $3CaO.Al_2O_3$. $6H_2O$ is the stable phase beyond 0.33 g of CaO per liter (*FG*). Thus, it becomes apparent why gibbsite dissolves in calcium hydroxide solutions up to concentrations of 0.33 g of CaO per liter without removing lime from solution, and also why hydrated alumina was observed as a solid phase in the solubility determinations of $3CaO.Al_2O_3.6H_2O$ along the metastable segment *EF* of the curve *EFG*.

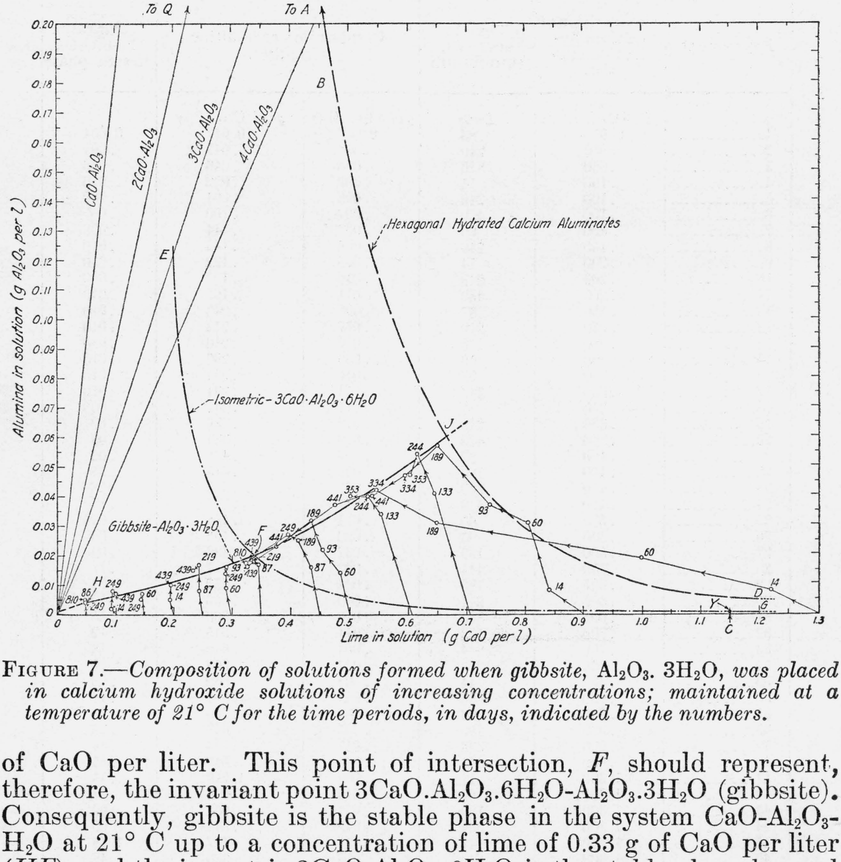

FIGURE 7.—*Composition of solutions formed when gibbsite,* Al_2O_3. $3H_2O$, *was placed in calcium hydroxide solutions of increasing concentrations; maintained at a temperature of 21° C for the time periods, in days, indicated by the numbers.*

Since *F* is the invariant point $3CaO.Al_2O_3.6H_2O$-$Al_2O_3.3H_2O$, then in mixtures of gibbsite and calcium hydroxide solutions more concentrated than 0.33 g of CaO per liter, the CaO would eventually be reduced to this value, and the alumina in solution would reach a value of 0.02 g of Al_2O_3 per liter. Three of the mixtures appear to have arrived very closely to *F*. They are indicated by experiments 20, 24, and 46 of table 8, where the initial concentrations of calcium hydroxide solutions were 0.350, 0.450, and 1.300 g of CaO per liter, respectively. Although the other mixtures had not attained final equilibrium, they appear from figure 7 to be approaching *F*. The mechanism of this approach to the invariant point *F* from mixtures containing more than 0.33 g of CaO per liter seems to be as follows: First, the gibbsite rather slowly dissolves in the solutions of calcium hydroxide, but, inasmuch as $3CaO.Al_2O_3.6H_2O$ is the stable phase rather than gibbsite, some of the lime in solution reacts with either the dissolved alumina or solid gibbsite with the ultimate production of some $3CaO.Al_2O_3.6H_2O$. Consequently, the reactions are taking place at an ever-decreasing concentration of lime. Eventually, however, the composition of the solution reaches some point along the metastable segment *FJ* of the curve *HFJ*, since the rate of solution of gibbsite exceeds the rate of formation of $3CaO.Al_2O_3.6H_2O$. Having reached *FJ*, the path proceeds downward along *FJ* to *F* as this process of formation of $3CaO.Al_2O_3.6H_2O$ and dissolving of gibbsite continues.

Attention will now be directed to the paths followed by two of the reaction mixtures. Experiments 35 to 40, inclusive, pertain to the mixtures starting with a concentration of calcium hydroxide of 0.900 g of CaO per liter. Figure 7 shows that at the end of 60 days the composition of the solution was very close to the metastable solubility curve of the hexagonal hydrated aluminates. Small amounts of hexagonal plates were observed microscopically. The maximum solubility of alumina was reached at the end of 189 days (experiment 38), and the composition is near the point *J*. The path then proceeded downward along *FJ* toward *F*, but, even at the end of 441 days, less than half of the distance to *F* had been covered. During these changes the hexagonal phase disappeared, and the refractive index of the outer shells of the gibbsite crystals increased to about 1.60 because of the formation of some $3CaO.Al_2O_3.6H_2O$.

The mixture prepared with a supersaturated calcium hydroxide solution containing 1.300 g of CaO per liter yielded solutions at the end of 14 and 60 days in the field where the hexagonal phase (probably hydrated tetracalcium aluminate) is formed as a mestastable phase, and hexagonal crystals were observed microscopically. At 189 days the reactions had proceeded to where the composition of the solution was no longer in this region, and the hexagonal phase disappeared. The composition of the solution had not yet reached the metastable section *FJ*, as in the case of the mixtures initially containing 0.900 g of CaO per liter. At the end of 334 days the composition of the solution was on the section *FJ* at a point close to that attained at the end of 441 days by the mixture prepared with calcium hydroxide having 0.900 g of CaO per liter. The path then proceeded along *FJ*, but, in this case, reached the invariant point *F*, but only after a lapse of 810 days. These experiments show the long time required to reach equilibrium, even under rather favorable conditions.

This study of the system $CaO-Al_2O_3-H_2O$ at 21°C may be considered as not entirely complete in that it does not deal with the solubility curves of the hydrates of alumina other than gibbsite, $Al_2O_3.3H_2O$. For example, there are the mineral diaspore ($Al_2O_3.H_2O$); its reported isomer [34, 35, 38, 39, 40, 41, 42, 43, 48], often called "böhmite"; and possibly an isomer of gibbsite $Al_2O_3.3H_2O$ [38, 44, 45, 46, 47, 48, 49], sometimes referred to as bayerite. There seems to be some doubt, however, as to the existence of this last trihydrate. Notwithstanding that there is some difference of opinion among various investigators as to the order of stability of these hydrates of alumina in alkaline solutions, there are considerable data showing that gibbsite is one of the more stable hydrates, if not the most stable, at room temperature. Therefore, gibbsite is perhaps the most important hydrate of alumina in relation to the behavior of cements.

Lea and Bessey [13, 30] are of the opinion that a stable solubility curve for $Al_2O_3.aq$ at 25°C coincides with the $3CaO.Al_2O_3$-composition line from *O* to *E* (fig. 6). The point *E*, or a point very close to *E*, is, according to Lea and Bessey, the invariant point $3CaO.Al_2O_3.6H_2O-Al_2O_3.aq$. They also suggest that the solubility curve for $Al_2O_3.aq$ then proceeds from *E* to *Q* (see figure 6 for location of *Q*), and that *Q* is the metastable invariant point $2CaO.Al_2O_3.8H_2O-Al_2O_3.aq$. Jones [51] points out, however, that the stable section for the solubility of $Al_2O_3.aq$, as given by Lea and Bessey, pertains to the gel form, and the solubility curve with respect to crystalline $Al_2O_3.3H_2O$ must fall below this. Our studies have demonstrated that Jones is correct, and it has been shown that *HF* (fig. 7) is the stable solubility curve for $Al_2O_3.3H_2O$ (gibbsite) and that the stable invariant point between $3CaO.Al_2O_3.6H_2O$ and gibbsite is at *F*.

IV. STUDIES OF THE SYSTEM $CaO-Al_2O_3-H_2O$ AT 90° C

1. HEXAGONAL HYDRATED CALCIUM ALUMINATES IN THE SYSTEM AT 90° C

In the investigation of the system $CaO-Al_2O_3-H_2O$ at 21°C, it was shown that the hexagonal phases were metastable. The hexagonal phases become less stable with rising temperature, and are so unstable at 90°C that no attempt was made to study their solubility relationships.

2. ISOMETRIC TRICALCIUM ALUMINATE HEXAHYDRATE, $3CaO.Al_2O_3.6H_2O$, IN THE SYSTEM AT 90° C

Despite the fact that the hexagonal phases are so unstable at 90°C that it was not feasible to determine their solubilities, nevertheless, once they are formed, they persist in small amounts for some time, even in the presence of the $3CaO.Al_2O_3.6H_2O$, into which they are eventually converted. For this reason, it seemed preferable to investigate the solubility of the isometric aluminate by placing this solid phase in solutions of calcium hydroxide and heating the mixtures to 90°C rather than to attempt to approach equilibrium from supersaturation by mixing together metastable calcium aluminate solutions and calcium hydroxide solutions heated to 90°C.

The mixtures, which contained 2 g of $3CaO.Al_2O_3.6H_2O$ per liter of calcium hydroxide solutions of varied concentrations, were placed on a steam bath in well-stoppered flasks provided with soda-lime adsorption tubes. Aliquots of the aqueous phase were taken at intervals for analysis. Equilibrium appeared to be attained much sooner at a temperature of 90° C than at 21° C, and table 9 gives the quantities of alumina and lime in the aqueous phase at the end of 4 to 5 days. Because the calcium hydroxide solutions attacked the glass of the containers somewhat at 90° C, the small quantities of silica were removed prior to the determination of alumina.

In experiments 5 and 6 the concentrations of the calcium hydroxide solutions were decreased from the equivalent of 0.856 g and 1.112 g of CaO per liter to 0.628 g and 0.638 g of CaO per liter, respectively, and finely divided crystalline $Ca(OH)_2$ was found mixed with $3CaO.Al_2O_3.6H_2O$.

TABLE 9.—*Solubility of isometric tricalcium hexahydrate*, $3CaO.Al_2O_3.6H_2O$, *at 90° C.*

[Initial mixtures: 2 g of $3CaO.Al_2O_3.6H_2O$ per liter of calcium hydroxide solution]

Experiment	Composition of calcium hydroxide solutions	Composition of final solutions		Remarks
		Al_2O_3	CaO	
	g of CaO */liter*	*g/liter*	*g/liter*	
1	0	0.190	0.306	
2	.250	.089	.335	
3	.390	.073	.381	
4	.500	.029	.509	
5	.856	.013	.628	Finely crystalline $Ca(OH)_2$ present.
6	1.112	.017	.638	Finely crystalline $Ca(OH)_2$ present.

In figure 8 the solubility values of $3CaO.Al_2O_3.6H_2O$ are plotted as grams of Al_2O_3 per liter versus grams of CaO per liter, and a curve, *KLM*, has been drawn to approximate the points representing these compositions. A comparison of figure 8 with figure 5 shows that $3CaO.Al_2O_3.6H_2O$ is more soluble at 90° than at 21° C. At 21° C, however, the curve extends to higher lime concentrations than at 90° C because the solubility of $Ca(OH)_2$ decreases with an increase in temperature.

M represents the invariant point for $3CaO.Al_2O_3.6H_2O$, $Ca(OH)_2$, and a solution containing 0.015 g of Al_2O_3 and 0.63 g of CaO per liter (the average of the compositions of the final solutions of experiments 5 and 6 of table 9). This concentration of CaO is about 0.04 g per liter greater than that indicated by *P*, which pertains to the solubility of coarsely crystalline $Ca(OH)_2$ in water at 90° C, as given by Bassett [50]. Connecting *P* with *M* gives the line *PM*, which represents the solubility of $Ca(OH)_2$ in the system at 90° C.

3. GIBBSITE, $Al_2O_3.3H_2O$, IN THE SYSTEM AT 90° C

The role of gibbsite in the system CaO-Al_2O_3-H_2O at 90° C was investigated in a manner similar to that employed in the study of the solubility relationships of $3CaO.Al_2O_3.6H_2O$ at this temperature. The mixtures in these experiments contained 2 g of gibbsite per liter of calcium hydroxide solutions of known but varied concentrations.

The data of experiments 1, 2, and 3 of table 10 show that the solubility of the gibbsite increases as the concentration of the calcium hydroxide increases. In experiments 4 to 8, inclusive, in which the initial concentration of lime in solution was more than 0.3 g of CaO per liter, there was a definite removal of lime from solution. This was manifested also by a change in the solid phases: First, by an increase in the refractive index of the outside layer of the gibbsite particles (experiment 4); followed by the appearance of increasing quantities of $3CaO.Al_2O_3.6H_2O$, which became better crystallized as the concentration of the calcium hydroxide of the original mixtures increased (experiments 5 to 8, inclusive).

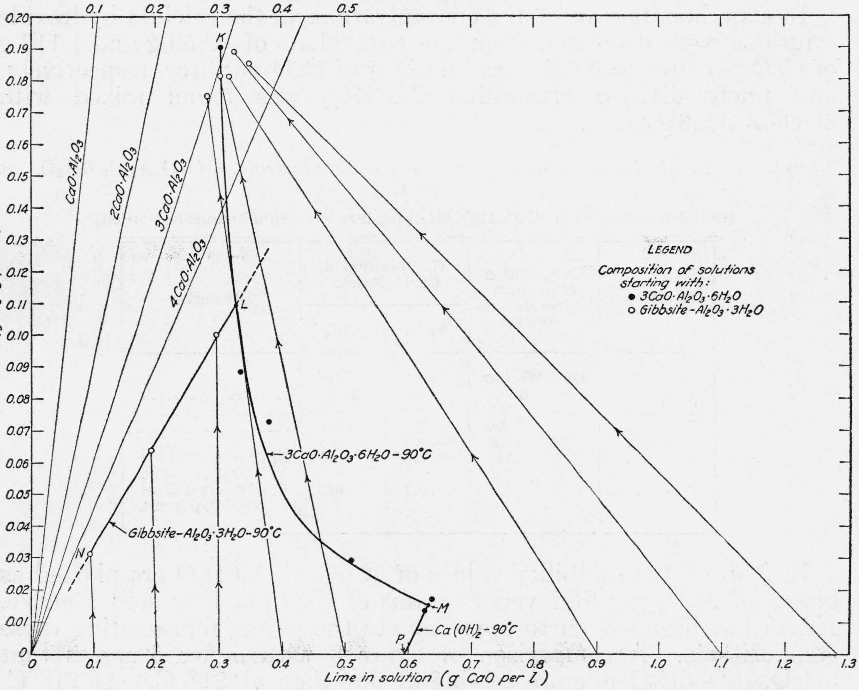

FIGURE 8.—*Composition of solutions formed when isometric* $3CaO.Al_2O_3.6H_2O$ *and gibbsite,* $Al_2O_3.3H_2O$, *were placed, separately, in calcium hydroxide solutions of increasing concentrations; maintained at a temperature of 90° C.*

These reactions were attended by a marked increase in the quantity of alumina in solution, from experiment 3, where the initial concentration of the calcium hydroxide was equivalent to 0.300 g of CaO per liter, to experiments 4 to 8, inclusive, where the concentrations of the calcium hydroxide were higher than this. Furthermore, the quantities of alumina in solution in experiments 4 to 8, inclusive, were almost identical, and the lime in solution had been reduced to concentrations of about 0.3 g of CaO per liter in these same mixtures. The compositions of these resulting solutions were approximately the same as that attained when $3CaO.Al_2O_3.6H_2O$ was dissolved in water at 90° C (see table 9, experiment 1).

TABLE 10.—*Solubility of gibbsite,* $Al_2O_3.3H_2O$, *at 90° C*

[Initial mixtures: 2 g of gibbsite per liter of calcium hydroxide solution.]

Experiment	Composition of calcium hydroxide solutions	Composition of final solutions		Remarks
		Al_2O_3	CaO	
	g of CaO*/liter*	*g/liter*	*g/liter*	
1	0.100	0.031	0.092	Indices of refraction unchanged.
2	.200	.063	.189	Do.
3	.300	.099	.294	Do.
4	.400	.175	.283	Indices of refraction raised
5	.500	.178	.298	Small amount of $3CaO.Al_2O_3.6H_2O$.
6	.900	.178	.319	Considerable $3CaO.Al_2O_3.6H_2O$.
7	1.101	.189	.327	Do.
8	1.284	.178	.353	Do.

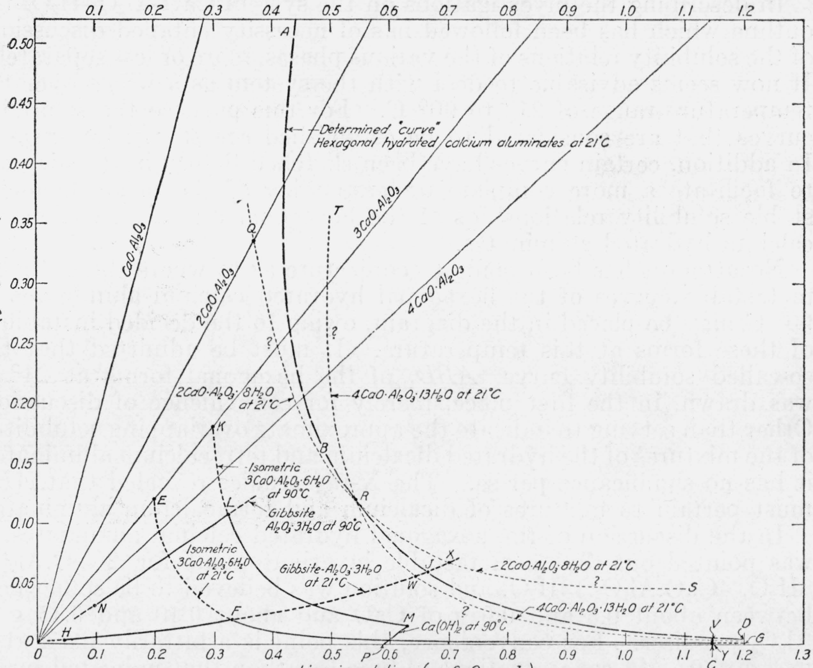

FIGURE 9.—*System* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at temperatures of 21° and 90° C.*

The curves and points are as follows:

ABD, Metastable solubility "curve" for mixtures of the hexagonal hydrates $2CaO.Al_2O_3.8H_2O$ and $4CaO.Al_2O_3.13H_2O$ at 21° C; *QRS*, suggested metastable solubility curve for hexagonal hydrate $2CaO.Al_2O_3.8H_2O$ at 21° C; *Q*, approximate solubility of hexagonal hydrate $2CaO.Al_2O_3.8H_2O$, apparently congruent, in water at 21° C, (Bessey [13]); *TRV*, suggested metastable solubility curve for hexagonal hydrate $4CaO.Al_2O_3.13H_2O$ at 21° C; *R*, suggested metastable invariant point $2CaO.Al_2O_3.8H_2O\text{-}4CaO.Al_2O_3.13H_2O$ at 21° C; *C*, solubility of coarsely crystalline $Ca(OH)_2$ in water at 21° C; *V*, approximate metastable invariant point $4CaO.Al_2O_3.13H_2O\text{-}Ca(OH)_2$ at 21° C; *EFG*, solubility curve of isometric hydrate $3CaO.Al_2O_3.6H_2O$ at 21° C, with *EF* metastable with respect to gibbsite; and *FG* the stable section. (See also, Bessey [13]); *Y*, stable invariant point $3CaO.Al_2O_3.6H_2O\text{-}Ca(OH)_2$ at 21° C, *YC*, solubility curve of $Ca(OH)_2$ at 21° C, *HFJ*, solubility curve of gibbsite, $Al_2O_3.3H_2O$ at 21° C, with *HF* the stable section; and *FJ* metastable with respect to $3CaO.Al_2O_3.6H_2O$; *F*, stable invariant point $3CaO.Al_2O_3.6H_2O\text{-}Al_2O_3.3H_2O$ (gibbsite) at 21° C; *W*, suggested metastable invariant point $4CaO.Al_2O_3.13H_2O\text{-}Al_2O_3.3H_2O$ (gibbsite) at 21° C; *X*, possible metastable invariant point $2CaO.Al_2O_3.8H_2O\text{-}Al_2O_3.3H_2O$ (gibbsite) at 21° C; *KLM*, solubility curve of isometric hydrate $3CaO.Al_2O_3.6H_2O$ at 90° C; *M*, stable invariant point $3CaO.Al_2O_3.6H_2O\text{-}Ca(OH)_2$ at 90° C; *NL*, solubility of $Al_2O_3.3H_2O$ (gibbsite) at 90° C; *L*, stable invariant point $3CaO.Al_2O_3.6H_2O\text{-}Al_2O_3.3H_2O$ at 90° C; *P*, solubility of coarsely crystalline $Ca(OH)_2$ in water at 90° C, (Basset [50]); *PM*, solubility curve of $Ca(OH)_2$ at 90° C.

This status of gibbsite in the system $CaO\text{-}Al_2O_3\text{-}H_2O$ at 90° C is illustrated in figure 8, which also shows the solubility relations of the $3CaO.Al_2O_3.6H_2O$ at this temperature. The straight line drawn through the compositions of the solutions resulting from dissolving of gibbsite in calcium hydroxide in concentrations equivalent to 0.100, 0.200, and 0.300 g of CaO per liter (table 10, experiments 1 to 3, inclusive), when extended, cuts the solubility curve *KLM* of $3CaO.Al_2O_3.6H_2O$ at *L*. Consequently, *L* must be the invariant point for $3CaO.Al_2O_3.6H_2O$, gibbsite ($Al_2O_3.3H_2O$), and the solution which has the approximate composition of 0.11 g of Al_2O_3 and 0.33 g of CaO per liter.

V. DISCUSSION OF THE SYSTEM $CaO\text{-}Al_2O_3\text{-}H_2O$ OVER THE TEMPERATURE RANGE 21° TO 90° C

In describing the investigations on the system $CaO\text{-}Al_2O_3\text{-}H_2O$, the outline which has been followed has of necessity entailed discussions of the solubility relations of the various phases, more or less separately. It now seems advisable to deal with the system as a whole over the temperature range of 21° to 90° C. For this purpose the solubility curves that are considered to be established are shown in figure 9. In addition, certain curves have been sketched lightly in the diagram to facilitate a more complete understanding of the probable metastable solubility relationships of the hexagonal dicalcium and tetracalcium hydrated aluminates.

No attempt has been made to conjecture as to where the probable metastable curves of the hexagonal hydrated calcium aluminates at 90° C may be placed in the diagram, owing to the decided instability of these forms at this temperature. It must be admitted that the so-called solubility curve, *ABD*, of the hexagonal forms at 21° C was drawn, in the first place, merely for convenience of discussion. Other than serving to indicate the approximate overlapping solubilities of the mixtures of the hydrated dicalcium and tetracalcium aluminates, it has no significance per se. The X-ray studies revealed that *ABD* must pertain to mixtures of dicalcium and tetracalcium aluminates.

In the discussion of the hexagonal hydrated calcium aluminates, it was pointed out that a metastable invariant point for $2CaO.Al_2O_3.8H_2O$, $4CaO.Al_2O_3.13H_2O$, and solution was believed to lie somewhere between about 0.5 and 0.6 g of CaO and about 0.10 and 0.15 g of Al_2O_3 per liter. For convenience, this point is arbitrarily fixed at *R* in figure 9. At concentrations of lime less than that indicated by *R*, the mixture of solid phases is composed predominantly of the dicalcium compound, whereas at the higher line comcentrations the tetracalcium aluminate constitutes the greater proportion of the solid phases.

If consideration now be given to the relations of the metastable hexagonal hydrated aluminates in regard to the other phases in the system, it is evident that there can be no stable equilibrium curves for these two aluminates, since they exist only as metastable phases. If attempts were to be made to secure sufficient data with the hope of establishing a metastable curve of the hydrated dicalcium aluminate free of the hydrated tetracalcium aluminate, it is clear that hydrated alumina, or the isometric hydrate, or both, very probably would make their appearance and defeat the object in view. Similar difficulties would be encountered with the hydrated tetracalcium aluminate.

Inasmuch as the actual determinations of these separate metastable solubility curves hold but little promise of success, it may not be amiss to sketch diagrammatically (fig. 9) how it is thought these metastable curves may be located with respect to one another, as well as to the experimental curve *ABD*.

The point *Q* in figure 9 indicates the solubility of $2CaO.Al_2O_3.8H_2O$ in water, as reported by Bessey [13]. This is somewhat lower than the point of intersection of the curve *ABD* with the $2CaO.Al_2O_3$.-composition line, as might be expected, since *ABD* was constructed from the data of solutions resulting from an approach from supersaturation.

Connecting *Q* and *R*, as shown in figure 9, gives a curve which will be ascribed as a section of a diagrammatic metastable curve for $2CaO.Al_2O_3.8H_2O$ at 21°C where this aluminate is more stable than the hydrated tetracalcium aluminate. Beyond *R* the curve should proceed along some path (*RS*) where this aluminate is less stable than the tetracalcium aluminate. Accordingly, at each concentration of lime in this region the concentration of alumina in a solution saturated with respect to the dicalcium aluminate will be greater than the quantity of alumina in a solution saturated with respect to the tetracalcium aluminate. By analogy, a suggested metastable solubility curve (TRV) for $4CaO.Al_2O_3.13H_2O$ is diagrammatically represented as shown. The point *V* is a suggested metastable invariant point for $4CaO.Al_2O_3.13H_2O$-$Ca(OH)_2$.

As demonstrated previously, *EFG* represents the solubility of $3CaO.Al_2O_3.6H_2O$ and *HFJ*, that of gibbsite, $Al_2O_3.3H_2O$, at 21°C. The point *F* is the stable invariant point for these two solid phases. Since *FJ* represents the metastable solubility of gibbsite, *W* becomes a metastable invariant point, $4CaO.Al_2O_3.13H_2O$-$Al_2O_3.3H_2O$; and on extending *FJ* to *X*, a second metastable invariant point, $2CaO.Al_2O_3.8H_2O$-$Al_2O_3.3H_2O$, is reached. It should be borne in mind that these two metastable invariant points are not established because the actual locations of the metastable curves, as stated previously, have not been determined.

It can be seen from the diagram that, if the concentration of lime is maintained in excess of 0.33 g of CaO per liter at a temperature of 21°C, gibbsite must eventually disappear as a solid phase and be converted into the isometric $3CaO.Al_2O_3.6H_2O$, which is the only stable phase in the region extending from a concentration of lime beyond 0.33 g of CaO per liter up to 1.15 g of CaO per liter. The solubility curve of $3CaO.Al_2O_3.6H_2O$ has been extended slightly beyond C (for solutions supersaturated with respect to coarsely crystalline $Ca(OH)_2$ can easily be prepared); but, at true equilibrium, crystalline $Ca(OH)_2$ would also appear as a solid phase, and the concentration of lime in solution would be reduced to 1.15 g of CaO per liter. The alumina in solution at this invariant point, Y, is but 0.0005 g per liter. The very short line *YC* represents the solubility of $Ca(OH)_2$ at 21°C.

To represent properly the effect of temperature on the solubility relationships of the various phases in the system CaO-Al_2O_3-H_2O, one perhaps should resort to a space model. However, as the system is rather simple at 90°C, it was felt that a clear presentation could be made merely by projecting the solubility curves of the isometric tricalcium aluminate hexahydrate, gibbsite, and $Ca(OH)_2$ onto the diagram at 21°C. Accordingly, in figure 9, *KLM* shows the role of the isometric aluminate, *NL* that of the gibbsite, and *PM* that of $Ca(OH)_2$ at 90°C.

The solubility of both the isometric hydrated aluminate and gibbsite increase with an increase in temperature from 21° to 90° C. The increases in solubility are such that the invariant point at 90° C (*L*), $3CaO.Al_2O_3.6H_2O$, $Al_2O_3.3H_2O$ (gibbsite), and solution occurs at practically the same lime concentration as at 21° C (*F*), namely, 0.33 g of CaO per liter.

It follows that, at temperatures between 21° and 90° C, there is a family of curves for $3CaO.Al_2O_3.6H_2O$ and $Al_2O_3.3H_2O$ (gibbsite), with each pair intersecting at invariant points of constant lime concentration (0.33 g of CaO per liter), but of increasing concentration of alumina (from 0.02 g of Al_2O_3 to 0.11 g of Al_2O_3 per liter) with increase in temperature.

Hence, at temperatures between 21° and 90° C, gibbsite is the stable solid phase up to a concentration of lime in the aqueous phase of 0.33 g of CaO per liter. At concentrations of lime greater than this, $3CaO.Al_2O_3.6H_2O$ becomes the stable phase, but the limit of concentration at any given temperature is ultimately restricted by the solubility of $Ca(OH)_2$ at that temperature. Consequently, there is a series of invariant points between 21° and 90° C for $3CaO.Al_2O_3.6H_2O$, $Ca(OH)_2$, and solutions whose compositions vary continuously from *Y* (1.15 g of CaO and 0.0005 g of Al_2O_3 per liter) to *M* (0.63 g of CaO and 0.015 g of Al_2O_3 per liter). For solubility values of $Ca(OH)_2$ in water between 21° and 90° C, one should consult Bassett [50].

Even though this investigation covers most of the salient factors pertaining to the system CaO-Al_2O_3-H_2O between temperatures of 21° and 90° C, nevertheless, the possible role of certain hydrates other than those encountered in this study of the system should be considered.

Travers and Sehnoutka [17], and later, Mylius [8] have described a tricalcium aluminate 18-hydrate, $3CaO.Al_2O_3.18H_2O$, occurring as fine needles, orthohombic and biaxial negative. This hydrate has been prepared only by precipitation from potassium aluminate solutions and has never been perceived either upon the addition of solutions of calcium hydroxide to calcium aluminate solutions or in the hydration of calcium aluminates. Accordingly, it appears that this compound is formed only in the presence of potassium (or sodium) ions or others than those of the hydrated calcium aluminates, and consequently is unstable in the system CaO-Al_2O_3-H_2O.

In addition, there is the so-called pentacalcium hydrate, $5CaO.Al_2O_3.34H_2O$, which has been reported only by Assarsson [6, 7, 36], who acknowledged, however, in his discussion of a paper by Bessey [13], that it seems to be impossible to prepare such an aluminate without any trace of sulfate. For this reason, it may be presumed that this hydrate is unstable in the ternary system CaO-Al_2O_3-H_2O, but may exist in the quaternary system CaO-Al_2O_3-$CaSO_4$-H_2O as a metastable phase. For further information on this latter point one should consult the extensive investigation by Jones [51] on this quaternary system at 25° C.

Although the studies of Assarsson [6, 7, 36] seem to indicate the existence of a monocalcium aluminate hydrate of the formula $CaO.Al_2O_3.10H_2O$, this compound has been prepared by precipitation from monocalcium aluminate solutions only at relatively low temperatures. It does not seem to be stable at a temperature so high as 21° C and was not observed in the present investigation.

Therefore, the foregoing considerations indicate that the three hydrated aluminates, $3CaO.Al_2O_3.18H_2O$, $5CaO.Al_2O_3.34H_2O$, and $CaO.Al_2O_3.10H_2O$, are no factors of moment in the ternary system CaO-Al_2O_3-H_2O from 21° to 90° C, and, if they exist at all in this system, they must be very unstable.

As mentioned earlier, the relation of the biaxial form of the tetracalcium aluminate hydrate to the hexagonal modification in the system CaO-Al_2O_3-H_2O warrants further study, as do those hydrates of alumina other than gibbsite.

VI. SUMMARY

The foregoing investigation included a study of the system CaO-Al_2O_3-H_2O at 21° and 90° C.

The solid phases were investigated by petrographical and X-ray diffraction methods. By means of X-ray diffraction patterns, it was found that the so-called hexagonal tricalcium aluminate hydrate is in reality a mixture of hexagonal $2CaO.Al_2O_3.8H_2O$ and hexagonal $4CaO.Al_2O_3.13H_2O$ intercrystallized in equimolecular proportions. On standing, the dicalcium aluminate hydrate is slowly converted into the tetracalcium aluminate hydrate and hydrated alumina. Loss of water of hydration in the tetracalcium aluminate hydrate results in a decrease in the unit cell along the *c* axis.

Although the di- and tetracalcium aluminate hydrates exist only as metastable phases in the system CaO-Al_2O_3-H_2O between 21° and 90° C, a study was made of their solubility relationships at 21° C. There appears to be a metastable invariant point for these two phases and a solution containing between 0.5 and 0.6 g of CaO per liter and 0.10 and 0.15 g of Al_2O_3 per liter. As the temperature increases the hexagonal aluminates become less stable.

The only stable solid phases that were found in the system CaO-Al_2O_3-H_2O over the temperature range of 21° to 90° C were: gibbsite, $Al_2O_3.3H_2O$; the isometric tricalcium aluminate hexahydrate, $3CaO.Al_2O_3.6H_2O$; and $Ca(OH)_2$. The solubility curves of these phases in the system CaO-Al_2O_3-H_2O were determined at 21° C and at 90° C. Over this range of temperature, gibbsite is the stable phase up to a concentration of 0.33 g of CaO per liter; at concentrations greater than this, the isometric hexahydrate is the only stable phase, until those points are reached at which $Ca(OH)_2$ also appears as a solid phase. The series of invariant points for gibbsite and the isometric phase occurs at a concentration of CaO of 0.33 g per liter, but with the concentration of Al_2O_3 increasing from 0.02 g per liter at 21° C to 0.11 g per liter at 90° C.

In carrying out the work in connection with this paper the authors had the valuable assistance of H. Insley in the microscopical examinations.

VII. REFERENCES

[1] Lansing S. Wells, *Reaction of water on calcium aluminates*, BS J. Research **1**, 951–1009 (1928) RP34.

[2] E. P. Flint and Lansing S. Wells, *Study of the system* $CaO\text{-}SiO_2\text{-}H_2O$ *at 30° C and of the reaction of water on the anhydrous calcium silicates*, BS J. Research **12**, 751–83 (1934) RP687.

[3] W. Blum, *Determination of aluminum as oxide*, Bul. BS **13**, 515–34 (1916–17) S286.

[4] Gunnar Assarsson, *The action of limewater on metallic aluminum*, Z. anorg. allgem. Chem. **191**, 333–39 (1930).

[5] Gunnar Assarsson, *The crystallization of the calcium aluminate solutions at 20° C*, Z. anorg. allgem. Chem. **200**, 385–408 (1931).

[6] Gunnar Assarsson, *The reaction between alumina cement and water*, Sveriges Geologiska Undersökn, Årsbok 1933, **27**, [C] No. 379, 22–60.

[7] Gunnar Assarsson, *The conditions of formation of the hydrated compounds in the system* $CaO\text{-}Al_2O_3\text{-}H_2O$ (solutions) *and the hydration of the anhydrous calcium aluminates*, Sveriges Geologiska Undersökn, Årsbok 1936, **30**, [C] No. 399, 5–202.

[8] C. R. W. Mylius, *On the calcium aluminate hydrates and their double salts*, Acta Acad. Aboensis, Math. et Phys. **7**, 3–147 (1933).

[9] T. Thorvaldson, N. S. Grace, and V. A. Vigfusson, *The hydration of the aluminates of calcium. II. The hydration products of tricalcium aluminate*, Can. J. Research **1**, 201–13 (1929).

[10] K. Koyanagi, *The action of lime hydrate upon the hydration of fused alumina cement*, Chichibu Cement A.-G. Assn. of Jap. Portland Cement Engrs. Review of Twenty-first General Meeting, Tokio, Oct. 1932, p. 8–11.

[11] R. Salmoni, *The hydrates of dicalcium aluminate*, Gazz. chim. ital. **64**, 719–34 (1934).

[12] H. Lafuma, *The aluminates of calcium and the chemistry of cement. Researches on the aluminates of calcium and on their combinations with the chloride and the sulfate of calcium.* (Extracts from the doctorate thesis of the author), Ciment **30**, 174–89 (1925). Also, Dissertation, Univ. of Paris, 1925.

[13] G. E. Bessey, *The calcium aluminate and silicate hydrates*, Proc. Symposium on Chem. of Cements, Stockholm, 1938, p. 178–230.

[14] H. Kühl, F. Thilo, and A. Chi Yü, *The dispersion relationships of monocalcium aluminate in water solutions*, Mitt. Zementtech. Inst. tech. Hochschule Berlin, **48**, 3–22 (1934).

[15] H. Pulfrich and G. Linck, *Contribution to the knowledge of the hydration processes in the setting of portland cement and of clinker*, Kolloid-Z. **34**, 117–22 (1924).

[16] W. H. MacIntire and W. M. Shaw, *The ternary systems* $CaO\text{-}Fe_2O_3\text{-}CaSO_4$ *and* $CaO\text{-}Al_2O_3\text{-}CaSO_4$ *as explaining the retention of sulfates by heavily limed soils*, Soil Sci. **19**, 125–51 (1925).

[17] A. Travers and J. Sehnoutka, *Study of the calcium aluminate hydrates*, Ann. chim. [X] **13**, 253–335 (1930).

[18] H. Candlot, *On the properties of the hydraulic products. The role of calcium chloride and of calcium sulfate in the setting and the hardening of mortar*, Bul. soc. encour. ind. nat. 89th yr. [4] **5**, 685–716 (1890).

[19] A. A. Klein and A. J. Phillips, *Hydration of portland cement*, Tech. Pap. BS **5**, 3–71 (1914–15) T43.

[20] G. Gallo, *Study of pozzolana mortars*, Gazz. chim. ital., **38**, pt. 2, 156–204 (1908).

[21] K. Koyanagi, *The hydration of calcium aluminate in portland cement*, Zement **20**, 968–73: 1016–1021 (1931).

[22] E. T. Allen and H. F. Rogers, *The action of caustic hydroxides on aluminum*, Am. Chem. J. **24**, 304–18 (1900).

[23] K. Koyanagi, *Why does not fused alumina cement tolerate portland cement?* Zement **19**, 866–69 (1930).

[24] R. Nacken, *The problem of the hardening of cement*, Zement **26**, 701–704; 715–19 (1937).

[25] H. LeChatelier, *Experimental researches on the constitution of the hydraulic mortars*, Thesis, Paris, 1887. Also, English translation by J. L. Mack. (McGraw Publishing Co., New York, N. Y., 1905).

[26] C. E. Tilley, H. D. Megaw, and M. H. Hey, *Hydrocalumite* ($4CaO.Al_2O_3.12H_2O$). *A new mineral from Scawt Hill, Co. Antrim*, Mineralog. Mag. **23,** 607–15 (1934).

[27] E. Brandenberger, *Crystal structure studies on the calcium aluminates*, Schweiz. mineral. petrog. Mitt. **13,** 569–70 (1933).

[28] W. Büssem, *X-rays and cement chemistry*, Proc. Symposium on Chem. of Cements, Stockholm, 1938, p. 141–77.

[29] T. Thorvaldson and N. S. Grace, *The hydration of the aluminates of calcium*, Can. J. Research **1,** 36–47 (1929).

[30] F. M. Lea and C. H. Desch, *The Chemistry of Cement and Concrete*, p. 153 (Longmans, Green & Co., New York, N. Y., and Edward Arnold & Co., London; 1935).

[31] R. Nacken and R. Mosebach, *Investigations on the system* CaO–Al_2O_3–H_2O, Z. anorg. allgem. Chem. **225,** 289–301 (1935).

[32] R. Nacken and R. Mosebach, *Investigations on the three component system* CaO-Al_2O_3-H_2O. pt. II. Z. anorg. allgem. Chem. 227, 328–36 (1936).

[33] E. S. Larsen and H Berman, *The microscopic determination of the nonopaque minerals*, U. S. Geol. Survey Bul. 848, [ed. 2], 1–266 (1934).

[34] R. Fricke and F. Wever, *Roentgenspectrographic studies of aged hydroxides of metals*, Z. anorg. allgem. Chem. **136,** 321–24 (1924).

[35] J. Böhm and H. Niclassen, *On amorphous precipitates and crystallized sols*, Z. anorg. allgem. Chem. **132,** 1–9 (1924).

[36] Gunnar Assarsson, *Studies on calcium aluminates IV. On the properties of the aluminum hydroxide crystallizing from calcium aluminate solutions*, Z. anorg. allgem. Chem. **222,** 321–36 (1935).

[37] Helen D. Megaw, *The crystal structure of hydrargillite*, $Al(OH)_3$, Z. Krist, **87,** 185–204 (1934).

[38] J. Böhm, *On aluminum and iron hydroxides I. On amorphous precipitates and crystallized sols*, Z. anorg. allgem. Chem. **149,** 203–16 (1925).

[39] J. de Lapparent, *The hydrated alumina of the bauxites*, Compt. rend. **184,** 1661–62 (1927).

[40] H. B. Weiser and W. O. Milligan, *X-ray studies of the hydrous oxides, I. Alumina*, J. Phys. Chem. **36,** 3010–29 (1932).

[41] R. Fricke and K. Meyring, *On the aging of fresh aluminum hydroxide gels*, Z. anorg. allgem. Chem. **214,** 269–74 (1933).

[42] L. Havestadt and R. Fricke, *On the dielectric relationships of hydrated oxides*, Z. anorg. allgem. Chem. **188,** 357–95 (1930).

[43] V. Kohlschütter, W. Beutler, L. Sprenger, and M. Berlin, *Investigations of the principles of genetic substance formation. III. On the chemistry and morphology of aluminum hydroxide*, Helv. Chim. Acta **14,** 3–49; 305–330; 330–354 (1931).

[44] R. Fricke, *On von Bonsdorff's crystalline alumina hydrate*, Z. anorg. allgem. Chem. **175,** 249–256 (1928).

[45] R. Fricke, *On von Bonsdorff's crystalline alumina hydrate. II.*, Z. anorg. allgem. Chem. **179,** 287–292 (1929).

[46] R. Fricke, *Some viewpoints on the changes of the hydrated oxides*, Kolloid-Z. **49,** 229–243 (1929).

[47] R. Fricke and H. Severin, *On the decomposition pressures of crystalline hydroxides, especially of aluminum and beryllium*, Z. anorg. allgem. Chem. **205,** 287–308 (1932).

[48] H. Lehl, *Böhmite and Bayerite*, J. Phys. Chem. **40,** 47–54 (1936).

[49] J. D. Edwards and M. Tosterud, *The oxides and hydrates of aluminum*, J. Phys. Chem. **37,** 483–488 (1933).

[50] H. Bassett, *Notes on the system lime-water, and on the determination of calcium*, J. Chem. Soc. 1270–1275. 1934.

[51] F. E. Jones, *The quaternary system* CaO-Al_2O_3-$CaSO_4$-H_2O at 25° C, Trans. Faraday Soc. **35,** 1484–1510 (1939).

[52] Wm. Lerch and R. H. Bogue, *Studies on the hydrolysis of compounds which may occur in portland cement*, J. Phys. Chem. **31,** 1627–46 (1927).

WASHINGTON, January 26, 1943.