

433. The System CaO-Al₂O₃-H₂O at 5°.

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The solubility relations in this system at 5° have been studied by experiments in which lime was added to supersaturated calcium aluminate solutions, and also in which hydrated alumina, cubic hydrated tricalcium aluminate (3CaO,Al₂O₃,6H₂O), or hydrated monocalcium aluminate (CaO,Al₂O₃,10H₂O) was added to water or lime solutions. Stable or metastable solubility curves were determined for each of these compounds, and also for the hexagonal or pseudo-hexagonal hydrated calcium aluminates 2CaO,Al₂O₃,8H₂O and 4CaO,Al₂O₃,19H₂O. The approach to equilibrium was studied as well as the stable or metastable equilibrium states. The results differ from those reported at 21° or above, notably in the reduced rate of change of the other hydrated calcium aluminates into the cubic one, and in the existence of a well-defined metastable solubility curve for hydrated monocalcium aluminate. This compound has a virtually stable field of existence in the system at 5°, provided that equilibrium with well-crystallised gibbsite is not attained.

STUDIES on the system CaO-Al₂O₃-H₂O have great practical value as they throw light on the setting of high-alumina and Portland cements. Previous work on the phase equilibria at room temperatures and above was reviewed by Steinour,¹ and the system has since been studied by d'Ans and Eick² at 20°, Peppler and Wells³ at 50—250°, and Majumdar and Roy⁴ at 100—1000°. When high-alumina cement pastes with CaO,Al₂O₃ as the main constituent set at room temperature, the main product is a hydrated monocalcium aluminate, CaO,Al₂O₃,10H₂O. This compound was first described by Assarsson,⁵ who found that it was relatively persistent in aqueous suspensions at low temperatures, but not in those at room temperature. The present study was made to determine the solubility curves for the various compounds at 5°, and the stability of CaO,Al₂O₃,10H₂O relative to the others.

¹ Steinour, "Aqueous Cementitious Systems containing Lime and Alumina," Bull. 34 of the Portland Cement Association, Chicago, 1951.

² d'Ans and Eick, *Zement-Kalk-Gips*, 1953, **6**, 197.

³ Peppler and Wells, *J. Res. Nat. Bur. Stand.*, 1954, **52**, 75.

⁴ Majumdar and Roy, *J. Amer. Ceram. Soc.*, 1956, **39**, 434.

⁵ Assarsson, *Sver. Geol. Undersökn. Ansök.*, 1933, **27**, 22; 1936, **30**, 1; *Zement*, 1934, **23**, 1. 15; *Z. anorg. Chem.*, 1935, **222**, 321.

EXPERIMENTAL

Materials.—Calcium oxide was made by igniting "AnalaR" calcium carbonate and was used only when fresh. Hydrated alumina was made from pure aluminium turnings. These were degreased with ether, etched with aqueous sodium hydroxide, washed thoroughly, and placed for a few seconds in very dilute mercuric chloride solution. They were again washed and then left in a large volume of water until hydrated alumina had been formed. The solid was filtered off and washed with acetone, which was removed in a current of air. The Al₂O₃ content (60.08%) corresponded approximately to the composition Al(OH)₃; X-ray photographs of the product showed it to be quite well-crystallised bayerite. CaO, Al₂O₃, 10H₂O was made by hydrating finely ground pure CaO, Al₂O₃ (20 g.) with boiled distilled water (2 l.) at 5°. The solid was filtered off and dried in two lots (X and Y) (anhydrous CaCl₂). Carbon dioxide-free conditions were maintained throughout. Analyses gave for X: CaO, 20.0; Al₂O₃, 38.3; H₂O, 41.8%, and for Y, CaO, 18.4; Al₂O₃, 35.2; H₂O, 46.4%. The water contents were less than for CaO, Al₂O₃, 10H₂O (53.3%), which is thus only a nominal formula. The only solid phase detected by X-rays was CaO, Al₂O₃, 10H₂O, though a little alumina must have been present as the molar ratio CaO : Al₂O₃ was 0.95. Cubic hydrated tricalcium aluminate, 3CaO, Al₂O₃, 6H₂O, was a pure specimen kindly supplied by Dr. R. W. Nurse (Building Research Station, Watford, Herts.). Secar 250, used in some experiments, is a high-alumina cement made from commercial calcined alumina. A typical composition is Al₂O₃, 71.7; CaO, 27.6; Fe₂O₃, 0.30; SiO₂, 0.25; ignition loss, 0.20; total, 100.05%; insoluble in HCl, 7.85; whence, CaO, Al₂O₃, 55.5; CaO, 2Al₂O₃, 35.9; α-Al₂O₃ (corundum), 7.85%.

Phase-equilibrium Experiments.—Equilibrium was approached in different ways to obtain as much information as possible about both stable and unstable phases. Extreme care was always taken to avoid contamination by atmospheric carbon dioxide. Polythene bottles with screw caps and P.V.C. [poly(vinyl chloride)] gaskets were used, and were fitted with soda-lime guard tubes while the solid was being filtered off by suction through a covered Buchner funnel. With very few exceptions, this procedure was satisfactory. A room kept at 5° ± 0.5° was used for the work.

Supersaturated solutions were made by shaking Secar 250 (50 g.) with boiled distilled water (5 l.) for about 3 hr. and filtering. The clear filtrates generally had molar CaO : Al₂O₃ ratios slightly above 1, and contained about 1 g. of Al₂O₃ and 0.6 g. of CaO per l. Samples of the filtrate were analysed and weight aliquot parts of the rest taken in Polythene bottles, which were transferred to the 5° room and left for a day to cool. Precipitation did not usually occur during this time. Weighed amounts of solid calcium oxide were then added to the bottles, which were afterwards shaken continuously until the next batch was ready (never under a week), and then at least daily for the duration of the experiment. In a few experiments, lime solution was added to the supersaturated solutions, but this is inconvenient because the Al₂O₃ concentration is reduced. Addition of solid lime, although it does not reduce the Al₂O₃ concentration, also has disadvantages (see later). In some other experiments, no lime was added, the solutions being merely left to form precipitates. After suitable intervals the mixtures were filtered and the solutions analysed. CaO : Al₂O₃ ratios of solids were normally obtained by difference; a few solids were analysed directly, and the results agreed with those calculated.

Equilibrium was also approached by adding weighed amounts of CaO, Al₂O₃, 10H₂O, 3CaO, Al₂O₃, 6H₂O, or hydrated alumina to water or lime solutions contained in Polythene bottles. Subsequent procedure was as with experiments starting from supersaturation. In all, 112 experiments were made, with times varying between 1 and 574 days.

Analytical Methods.—A few analyses were done by classical gravimetric procedures, but most were done by using edta (disodium salt of ethylenediaminetetra-acetic acid) to form complexes both with calcium and aluminium. Calcium was determined by back-titration at pH 10 with manganese(II), and aluminium by a slight modification of Haar and Bazen's method.⁶ By these methods, it was possible to do duplicate CaO and Al₂O₃ analyses on a solution in about 30 min., with accuracies equal to those of the classical methods.

X-Ray Methods.—The solid products, and reference substances, were dried over saturated calcium chloride solution at room temperature, and X-ray powder photographs taken with 11.46 cm. diameter cameras with filtered copper radiation. Reference substances examined were 4CaO, Al₂O₃, 13H₂O, 2CaO, Al₂O₃, 8H₂O, CaO, Al₂O₃, 10H₂O, 3CaO, Al₂O₃, 6H₂O,

⁶ Haar and Bazen, *Analyt. Chim. Acta*, 1954, 10, 23.

FIG. 1. Definition of fields of bulk composition.

AF is the metastable solubility curve of 4CaO,Al₂O₃,19H₂O and 2CaO,Al₂O₃,8H₂O; *RS* is a line of slope CaO : Al₂O₃ (molar) = 1 passing close to *F*; *OT* is a line of slope CaO : Al₂O₃ (molar) = 3 passing through the origin.

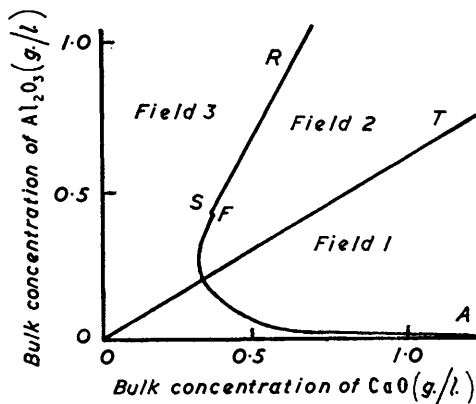
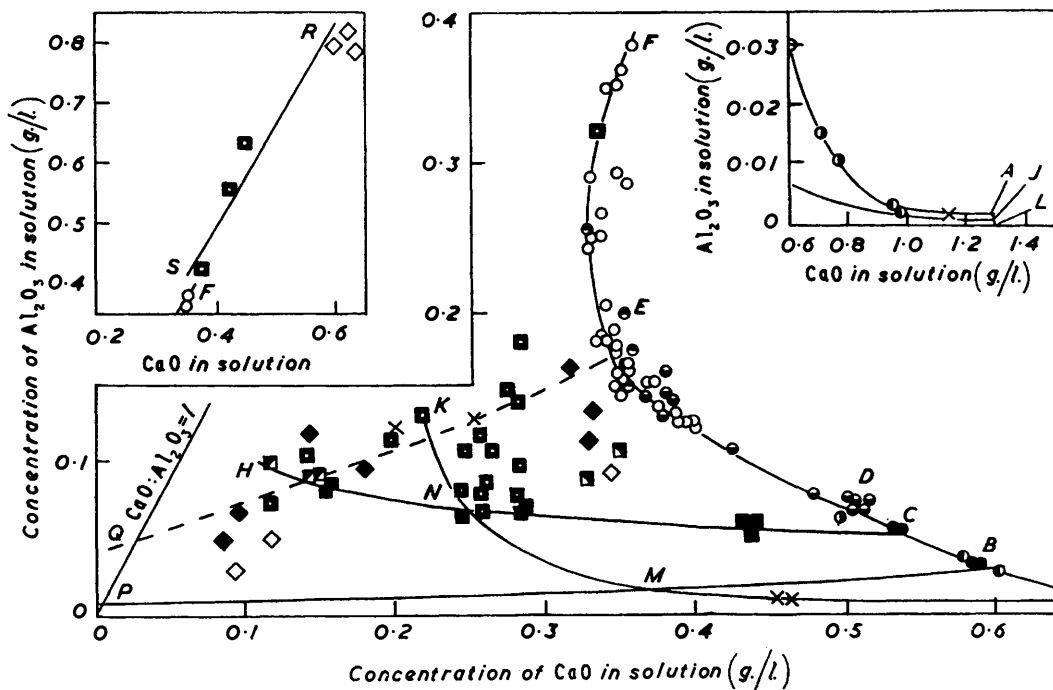


FIG. 2. Observed final solution compositions, and solubility curves in the system CaO-Al₂O₃-H₂O at 5°.*



Insets: continuations on different scales. For key to lettering see text. Key to experimental points:

- | Solid phase(s) present | Starting material |
|---|--|
| ● 4CaO,Al ₂ O ₃ ,19H ₂ O | Supersaturated solution (field 1) |
| ○ " " | CaO,Al ₂ O ₃ ,10H ₂ O |
| ○ " " | Alumina |
| ○ 4CaO,Al ₂ O ₃ ,19H ₂ O + 2CaO,Al ₂ O ₃ ,8H ₂ O | Supersaturated solution (field 1) |
| ○ 4CaO,Al ₂ O ₃ ,19H ₂ O and/or 2CaO,Al ₂ O ₃ ,8H ₂ O † | Supersaturated solution (field 2) |
| ○ " " † | Supersaturated solution (field 3) |
| ○ " " † | Supersaturated solution (field 2) |
| ■ CaO,Al ₂ O ₃ ,10H ₂ O | CaO,Al ₂ O ₃ ,10H ₂ O |
| ■ " " | Supersaturated solution (field 3) |
| ■ CaO,Al ₂ O ₃ ,10H ₂ O, usually + alumina | CaO,Al ₂ O ₃ ,10H ₂ O |
| ■ CaO,Al ₂ O ₃ ,10H ₂ O + alumina | Supersaturated solution (field 3) |
| ◇ Alumina | Alumina |
| ◇ Alumina | Alumina |
| × 3CaO,Al ₂ O ₃ ,6H ₂ O | 3CaO,Al ₂ O ₃ ,6H ₂ O |

* Trace constituents are sometimes ignored. † CaO,Al₂O₃,10H₂O and/or alumina usually also present; 2CaO,Al₂O₃,8H₂O usually more abundant than 4CaO,Al₂O₃,19H₂O.

3CaO, Al₂O₃, CaCO₃, 11H₂O, Ca(OH)₂, calcite, bayerite, and gibbsite. In general, the patterns agreed well with those in the literature.⁷ The alumina in the products was often very poorly crystallised. Except where the bayerite specimen had been used, and in certain other cases mentioned later, it gave a pattern most nearly resembling that of gibbsite. Occurrence of the two strong lines of gibbsite at about 4.8 and 4.4 Å, after allowance if necessary for the weak lines of CaO, Al₂O₃, 10H₂O in approximately the same positions, was regarded as the minimum test of its presence. It will be described simply as alumina. Powder patterns of preparations containing hydrated tetracalcium aluminate in contact with its mother-liquor showed basal spacings of about 10.6 and not 8 Å, confirming Roberts's view⁸ that the shorter spacing arises on drying; Roberts showed that the compound in contact with solution was 4CaO, Al₂O₃, 19H₂O. For simplicity, the latter description will be used throughout, although the hydrate actually detected in the dried precipitates was 4CaO, Al₂O₃, 13H₂O. No attempt was made to distinguish between the slightly differing reported forms^{1, 8} of 4CaO, Al₂O₃, 13H₂O and of 2CaO, Al₂O₃, 8H₂O.

In characterising the phases present in the solid products, account was taken of both *X*-ray and analytical evidence. With a few minor exceptions, the results of the two methods agreed satisfactorily, provided the difficulty of detecting very poorly crystallised phases by *X*-rays was allowed for.

Precipitation from Supersaturated Solutions.—(i) *Definition of fields of bulk composition.* For the description of these results it is convenient to divide the system into fields of bulk composition, which are defined in Fig. 1. The divisions are partly based on solubility and other curves subsequently established. The terms "bulk concentrations" imply the concentrations that would have existed had all the materials been in solution.

(ii) *Bulk compositions in field 1.* In all cases, the products were 4CaO, Al₂O₃, 19H₂O or 2CaO, Al₂O₃, 8H₂O or both, and final solution compositions were on *ADE* (Fig. 2). Where bulk CaO : Al₂O₃ (molar) exceeded 5, only 4CaO, Al₂O₃, 19H₂O was formed, and the final CaO concentration was at least 0.53 g./l. Where bulk CaO : Al₂O₃ was 3—5, 2CaO, Al₂O₃, 8H₂O and 4CaO, Al₂O₃, 19H₂O were both formed. Comparison experiments with the same bulk composition but differing times (Fig. 3) showed that true or apparent equilibrium was reached within a few days.

(iii) *Bulk compositions in field 2.* In nearly every case, the solid product contained several phases, and equilibrium is evidently not easily reached. 2CaO, Al₂O₃, 8H₂O was detected in the products of 32 out of the 35 experiments, CaO, Al₂O₃, 10H₂O in 25, alumina in 21, and 4CaO, Al₂O₃, 19H₂O in 16 (usually only as a minor constituent). In several cases all four compounds occurred together, though with increased time one or more tended to disappear. With two exceptions, final solution compositions were on *DF* (Fig. 2). For a given bulk composition, solution compositions moved down this curve with increased time (Fig. 3). The two exceptional experiments were both of over 570 days' duration, and the results (Fig. 2) suggested that with sufficiently long times, solution compositions may drop below *DF*. The observed trend in solution composition with time implies a decrease in the CaO : Al₂O₃ ratio of the precipitate. In agreement with this, products of short-term experiments tended to be rich in 2CaO, Al₂O₃, 8H₂O and sometimes contained 4CaO, Al₂O₃, 19H₂O while those of long-term experiments were usually rich in CaO, Al₂O₃, 10H₂O and alumina.

(iv) *Bulk compositions in field 3.* The main product was usually CaO, Al₂O₃, 10H₂O, often accompanied by alumina, and final solution compositions were mostly to the left of *CF* and on or above *HC* (Fig. 2). The alumina concentrations fell with time, and with many experiments of several months' duration the solution compositions were close to *HC*. The approach to equilibrium with a supersaturated solution to which no additional lime had been added is shown in Fig. 3. The points represent separate experiments with the same bulk composition but different times. Alumina was at first precipitated until the solution composition lay approximately on a line *RS*, which passes near *F* and has a slope corresponding to CaO : Al₂O₃ (molar) = 1. The composition of the precipitate was inferred from the change in solution composition, but it gave an anomalous and very weak *X*-ray pattern with the following spacings (Å) and relative intensities: 4.69 vw, 4.33 m, 3.88 s, 3.56 w, 3.30 m, 3.07 vw, 2.73 m, 2.07 w, 1.82 vw. It was not gibbsite or bayerite. CaO, Al₂O₃, 10H₂O was then precipitated, solution

⁷ Lea, "The Chemistry of Cement and Concrete" (revised edition of Lea and Desch), Edward Arnold and Co. Ltd., London, 1956, Appendix III, p. 604.

⁸ Roberts, *J. Appl. Chem.*, 1957, 7, 543.

compositions moving down *RS* into the region to the left of *CF* and above *HC*. Beyond *S*, both CaO,Al₂O₃,10H₂O and alumina were formed, with alumina tending to predominate. After 50—100 days, solution compositions approached a steady value a little above *HC*, and the precipitates were of CaO,Al₂O₃,10H₂O mixed with badly crystallised gibbsite.

In a few experiments with bulk compositions near *RS*, traces of 2CaO,Al₂O₃,8H₂O or 4CaO,Al₂O₃,19H₂O were formed, together with alumina, and the solution compositions were on or near *DF* (Fig. 2). In others, where the bulk lime and alumina concentrations were both very low, alumina was formed with little or no CaO,Al₂O₃,10H₂O, and solution compositions were below point *H*; in one such case, the alumina was in the form of bayerite.

Treatment of CaO,Al₂O₃,10H₂O with Water or Lime Solutions.—With water, CaO,Al₂O₃,10H₂O dissolved incongruently, the solid products being unchanged CaO,Al₂O₃,10H₂O and alumina.

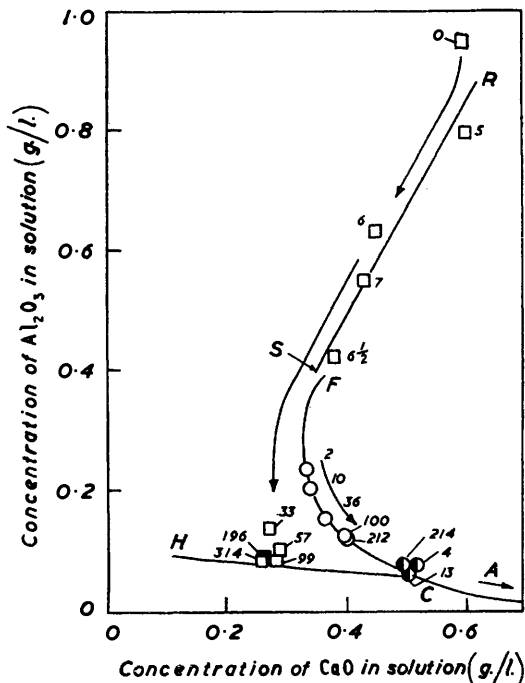


FIG. 3. *Course of precipitation from supersaturated solutions; three groups of experiments each with fixed bulk composition and varying times.*

Bulk compositions: ●, CaO 2.053 g./l., Al₂O₃ 0.768 g./l. (Field 1); ○, CaO 0.981 g./l., Al₂O₃ 1.016 g./l. (Field 2); □, CaO 0.600 g./l., Al₂O₃ 0.950 g./l. (Field 3). Time in days is shown against each point. Curves *HC*, *ACF*, and *RS* have the same significance as in Fig. 2.

Final solution compositions were near *H* (Fig. 2). With lime solutions containing initially 0.1—0.5 g. of CaO/l., it dissolved congruently or nearly so; final solution compositions were on *HC*, and the solids were unchanged CaO,Al₂O₃,10H₂O. With lime solutions containing initially more than 0.8 g. of CaO/l., the solids consisted chiefly of 4CaO,Al₂O₃,19H₂O, and solution compositions were on *AC*; small proportions of alumina and 3CaO,Al₂O₃,6H₂O were sometimes also formed. Comparison of experiments with similar bulk compositions and different times suggested that apparent equilibrium was probably always reached within about 30 days.

Treatment of Alumina with Lime Solutions.—Where hydrated alumina was treated with lime solutions containing 0.1—0.5 g. of CaO/l., it persisted largely unaltered in the products, and final solution compositions were near an ill-defined curve *QE* (Fig. 2). With lime solutions containing more than 0.8 g. of CaO/l., the products contained unchanged alumina and 4CaO,Al₂O₃,19H₂O, and final solution compositions were on *AD* (Fig. 2).

Treatment of 3CaO,Al₂O₃,6H₂O with Water or Lime Solutions.—This compound dissolved congruently in water or in lime solutions. Final solution compositions (Fig. 2) lay approximately on the solubility curve *JK* obtained at 21° by Wells, Clarke, and McMurdie.⁹ From one pair of experiments, equilibrium seemed to be established within about 30 days.

⁹ Wells, Clarke, and McMurdie, *J. Res. Nat. Bur. Stand.*, 1943, **30**, 367.

DISCUSSION

Stable Equilibria.—Because of the persistence of metastable phases, very few of the present results relate to thermodynamically stable equilibria. It nevertheless seems fairly safe to infer from results obtained at higher temperatures^{3,9} that the stable compounds in the system at 5° are gibbsite, 3CaO,Al₂O₃,6H₂O, and calcium hydroxide, and also that the solubility curves of the first two of these do not differ much from those obtained at 21°. In the case of 3CaO,Al₂O₃,6H₂O this view is supported by the present results. On this basis curves are included in Fig. 2 for gibbsite (*PMB*) and for 3CaO,Al₂O₃,6H₂O (*KMJ*). The short solubility curve *AJL* for calcium hydroxide is inferred from the known solubility at 5°. ¹⁰ Curves *PM*, *MJ*, and *JL* thus relate to stable equilibria; their prolongations, and all other curves in Fig. 2, relate to metastable equilibria.

Metastable Equilibria.—(i) 4CaO,Al₂O₃,19H₂O and 2CaO,Al₂O₃,8H₂O. These two compounds have closely similar crystal structures, and it is not easy to distinguish their solubility curves from each other. The curve *ADF* (Fig. 2) is associated with both of them. Its lime-rich end is the metastable solubility curve of 4CaO,Al₂O₃,19H₂O, and its alumina-rich end is that of 2CaO,Al₂O₃,8H₂O. The triple point for these two compounds with solution is hard to locate, as the curve seems continuous and there is a considerable portion between *D* and *E* over which the three phases can co-exist for a long time. The most likely position for the triple point is perhaps near *D*, which corresponds to the highest lime concentration at which 2CaO,Al₂O₃,8H₂O was found. The same difficulty in locating this triple point occurs at higher temperatures.^{1,2,9}

Both 4CaO,Al₂O₃,19H₂O and 2CaO,Al₂O₃,8H₂O are purely metastable phases in this system at 5°, but the first has a relatively stable field of existence at CaO concentrations above about 0.5 g./l. It was formed from both under- and over-saturation. 2CaO,Al₂O₃,8H₂O is a relatively transitory product; at certain concentrations it is stable relative to 4CaO,Al₂O₃,19H₂O, but it is always unstable relative to CaO,Al₂O₃,10H₂O. It was only formed from supersaturation, and usually occurred as an intermediate stage in the formation of that compound.

(ii) CaO,Al₂O₃,10H₂O. A metastable solubility curve *HC* (Fig. 2) is established from experiments starting from undersaturation and from supersaturation. In the former case the solution compositions lie substantially on the curve, while in the latter the curve can reasonably be considered to be the limit which they approach if given enough time. CaO,Al₂O₃,10H₂O is purely metastable in the system at 5°, but it is persistent and stable relative to 2CaO,Al₂O₃,8H₂O and 4CaO,Al₂O₃,19H₂O at CaO concentrations below about 0.5 g./l. At higher lime concentrations, it reacts with the solution, giving mainly 4CaO,Al₂O₃,19H₂O. There is a slight tendency to form the stable phases, 3CaO,Al₂O₃,6H₂O and alumina.

(iii) *Alumina.* The alumina formed or used was always imperfectly crystallised, and as improvement in crystallinity was slow, no definite solubility curve could be obtained. An infinite family of unstable curves lying above that of fully crystalline gibbsite (Fig. 2, *PB*) can be envisaged. The ill-defined curve *QE* obtained in the present work is a typical one for moderately well-crystallised hydrated alumina. It applies approximately both to the bayerite specimen and to the alumina formed by using CaO,Al₂O₃,10H₂O as starting material. With alumina formed in long-term experiments starting from supersaturation the Al₂O₃ concentrations in solution were lower.

Triple Points.—These are listed in the Table. All but the first two relate to metastable equilibria. Gibbsite implies well-crystallised natural material, and alumina implies the typical synthetic material (bayerite or gibbsite) mentioned above.

Variable Solubilities.—The effect of varying crystallinity on the apparent solubility of alumina has already been discussed; alumina concentrations were high relative to the assumed position of the stable gibbsite curve whether equilibrium was approached from

List of triple points.

Phases (in addition to solution)	Ref. letter on Fig. 2	Solution composition (g./l.)	
		CaO	Al ₂ O ₃
Ca(OH) ₂ -3CaO, Al ₂ O ₃ , 6H ₂ O	<i>J</i>	1.28	<0.002
3CaO, Al ₂ O ₃ , 6H ₂ O-gibbsite	<i>M</i>	0.4 app.	0.02 app.
Ca(OH) ₂ -4CaO, Al ₂ O ₃ , 19H ₂ O	<i>A</i>	1.28	<0.002
4CaO, Al ₂ O ₃ , 19H ₂ O-gibbsite	<i>B</i>	0.59 app.	0.04 app.
4CaO, Al ₂ O ₃ , 19H ₂ O-CaO, Al ₂ O ₃ , 10H ₂ O	<i>C</i>	0.53	0.06
4CaO, Al ₂ O ₃ , 19H ₂ O-2CaO, Al ₂ O ₃ , 8H ₂ O	<i>D</i>	0.51	0.07
2CaO, Al ₂ O ₃ , 8H ₂ O-alumina *	<i>E</i>	0.35	0.17
CaO, Al ₂ O ₃ , 10H ₂ O-alumina *	<i>H</i>	0.14	0.09
3CaO, Al ₂ O ₃ , 6H ₂ O-alumina *	<i>K</i>	0.22	0.12
3CaO, Al ₂ O ₃ , 6H ₂ O-CaO, Al ₂ O ₃ , 10H ₂ O	<i>N</i>	0.25	0.07

* Position variable depending on crystallinity of alumina.

under- or over-saturation. With calcium hydroxide, also, the apparent solubility depends on particle size, though to a smaller extent.¹⁰ With 2CaO, Al₂O₃, 8H₂O and 4CaO, Al₂O₃, 19H₂O there was no evidence of variable solubility. In nearly every case where either compound was formed, whether or not other solid phases were there as well, the solution compositions lay on *ADF*. This is readily explained by the fact that both compounds crystallise relatively well.

With CaO, Al₂O₃, 10H₂O, high apparent solubilities were generally obtained when equilibrium was approached from supersaturation. This could be described either as slowness in reaching equilibrium, or in terms of a series of unstable solubility curves lying above the metastable one *HC*. The second description appears reasonable, as CaO, Al₂O₃, 10H₂O crystallises very poorly. From this viewpoint, the metastable solubility curve *DF* of 2CaO, Al₂O₃, 8H₂O is also the locus of the unstable triple point for this compound with solution and poorly crystallised forms of CaO, Al₂O₃, 10H₂O. The line *RS* (Figs. 2 and 3) similarly represents a band of unstable triple points for solution with poorly crystallised forms of CaO, Al₂O₃, 10H₂O and alumina. The alumina in this case is not gibbsite or bayerite, but the unstable form giving the abnormal X-ray pattern described previously.

The Approach to Equilibrium from Supersaturation.—For bulk compositions in field 2, the CaO : Al₂O₃ ratio of the precipitate decreases markedly with time (Fig. 3). This can be attributed to the conditions under which precipitation occurs. Addition of calcium hydroxide solution, or especially of solid calcium oxide, to a supersaturated solution necessarily produces regions of high lime concentration, and it is in these regions that precipitation begins. The initial precipitates are therefore of higher CaO : Al₂O₃ ratio than those eventually formed, and the dissolution of the high-lime compounds and formation of those of lower CaO : Al₂O₃ ratio are slow processes. The same effect probably explains the formation and persistence of 4CaO, Al₂O₃, 19H₂O in cases where the bulk composition is in field 1 and the final solution composition above point *D* on curve *ADF* (Fig. 2). Dissolution of 4CaO, Al₂O₃, 19H₂O and formation of 2CaO, Al₂O₃, 8H₂O seem to be very slow in the range *DE* just above the triple point.

Comparison of Results with Those obtained at Higher Temperatures.—In Fig. 4, the solubility curves for 4CaO, Al₂O₃, 19H₂O-2CaO, Al₂O₃, 8H₂O, 3CaO, Al₂O₃, 6H₂O, and Ca(OH)₂ at 5° are compared with ones obtained at higher temperatures.^{3, 9, 11} The solubility curve for 4CaO, Al₂O₃, 19H₂O and 2CaO, Al₂O₃, 8H₂O rises sharply with temperature; at 90°, these compounds change so rapidly into 3CaO, Al₂O₃, 6H₂O that true metastable solubility curves are unobtainable. The solubility curve of 3CaO, Al₂O₃, 6H₂O also rises with temperature, though less markedly; the results for 5°, 21°, 25°, and even 50° are almost identical. The solubility of calcium hydroxide falls steadily with rising temperature.¹⁰

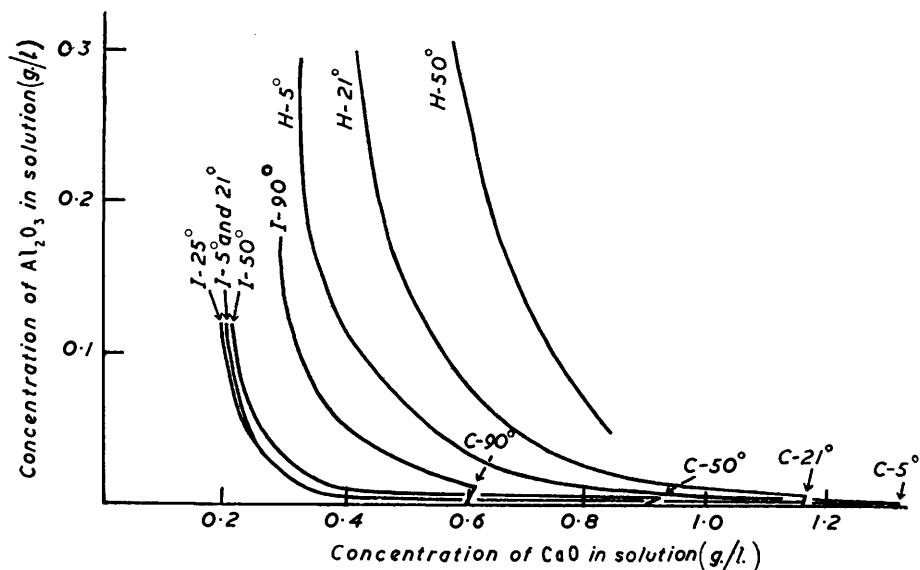
At 21° 4CaO, Al₂O₃, 19H₂O and 2CaO, Al₂O₃, 8H₂O change fairly quickly into

¹⁰ Bassett, *J.*, 1934, 1270.

3CaO,Al₂O₃,6H₂O when suspended in aqueous solutions; Wells, Clarke, and McMurdie⁹ found that out of 48 experiments starting from supersaturation, 21 gave amounts of 3CaO,Al₂O₃,6H₂O detectable by microscope within 10 days. In the present work at 5°, no experiments of this type gave 3CaO,Al₂O₃,6H₂O, even in more than 570 days. This compound was indeed formed in only three experiments of any kind, all starting from CaO,Al₂O₃,10H₂O. In these it was only a minor product.

CaO,Al₂O₃,10H₂O was apparently not formed in any of Wells, Clarke, and McMurdie's experiments in the course of their extensive investigation at 21°, and no metastable

FIG. 4. Influence of temperature on the stable or metastable solubility curves of 4CaO,Al₂O₃,19H₂O-2CaO,Al₂O₃,8H₂O (marked *H*), 3CaO,Al₂O₃,6H₂O (marked *I*), and Ca(OH)₂ (marked *C*). Sources of data: 5°, this investigation; 21° and 90°, Wells, Clarke, and McMurdie; 9° 50°, Peppel and Wells; 3° 25°, Bessey.¹¹



solubility curve for it at this or any other temperature has previously been reported. At 5°, however, a curve can be obtained, and in the absence of well-crystallised alumina, part of this curve (*HN*, Fig. 2) is stable, not only relative to that of 2CaO,Al₂O₃,8H₂O but also relative to that of 3CaO,Al₂O₃,6H₂O. A line through the origin with slope CaO : Al₂O₃ (molar) = 1 passes to the left of *H*; treatment of anhydrous or hydrated monocalcium aluminate with excess of water at 5° therefore gives a virtually stable mixture of CaO,Al₂O₃,10H₂O and alumina, as long as the alumina and CaO,Al₂O₃,10H₂O curves intersect to the left of *N*. If the crystallinity of the alumina approaches that of stable gibbsite, dissolution of CaO,Al₂O₃,10H₂O and formation of 3CaO,Al₂O₃,6H₂O are liable to occur.

Detailed Analytical and X-Ray Results.—Detailed analytical and X-ray data can be obtained from the authors.

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¹¹ Bessey, *Proc. Symp. Chem. Cements, Stockholm, 1938, 178.*