Summary.

The results of this research may be summarized briefly as follows:

(1) More than one hundred determinations of the surface tension of forty-eight concentrations of sulfuric acid in water, at various temperatures, have been made by aid of the drop-weight method, and formulas provided by which the surface tension and specific cohesion can be calculated at any concentration and temperature between $0°$ and $50°$. A method is also given which obviates any difficulty produced in the drop-weight method by high viscosity and poor covering power.

(2) It is found that both the addition of sulfuric acid to water, as well as that of water to sulfuric acid, causes an increase in the surface tension, so that different concentrations of sulfuric acid may have identical surface-tension values at the same temperature. The addition of SO_3 to sulfuric acid ($SO_3.H_2O$) also increases the surface tension.

(3) If the property-composition curve means anything as to chemical interaction, it can be assumed, perhaps, from the surface-tension results to indicate the existence of the hydrate $H_2SO_4.H_2O$ at 85% acid.

(4) The application of the theory of Denison, that the deviation of a property from the mixture law plotted against the composition, shows at the point of maximum deviation the presence of a compound identical in composition with that of the solution leading to that maximum deviation, indicates the following hydrates in water solutions of sulfuric acid, according to the property which is taken as a criterion:

$H_2SO_4.H_2O$ by density, compressibility viscosity (and refraction);

$H_2SO_4.2H_2O$ (by refraction);

$H_2SO_4.3H_2O$ by surface tension;

$3H_2SO_4.H_2O$ by conductivity (and viscosity);

$H_2SO_4.12H_2O$ by conductivity and density;

$4H_2SO_4.H_2O$ or $5H_2SO_4.H_2O$ (by viscosity).

NEW YORK CITY.

THE TERNARY SYSTEM CaO–Al₂O₃–MgO.

BY G. A. RANKIN AND H. E. MERWIN.

The study of a three-component system can be undertaken only if the equilibrium relations in the three systems of two components have previously been ascertained, a prerequisite of which again is that the properties of the pure components be adequately known. Similarly, before one can proceed to the investigation of a four-component system—at least with the hope of a successful outcome—one must have elucidated the equilibrium relations in the four possible systems made up of combinations

of three of the components. The study of the important system of the oxides CaO, Al$_2$O$_3$, SiO$_2$, MgO has reached the point that two of the ternary systems have now been completed; the results obtained on the system CaO–Al$_2$O$_3$–SiO$_2$ were published recently,[1] while the present paper is a record of the study of the system CaO–Al$_2$O$_3$–MgO.[2] The present system has involved no problem as interesting as that of the constitution of Portland cement clinker, a knowledge of which was one of the results of the work on the system CaO–Al$_2$O$_3$–SiO$_2$; nevertheless it was necessary to work this system out, since the relation in any ternary system cannot be deduced by analogy with any similar system, but can only be learned by experiment. In this system, as it happens, the substances stable in contact with melts containing only the three components include no ternary compounds, and are only eight in number (inclusive of the components themselves) whereas in the CaO–Al$_2$O$_3$–SiO$_2$ system the corresponding number is fourteen.

In the following pages we discuss the equilibrium relations of the several crystalline phases which separate from anhydrous melts containing only the oxides CaO, Al$_2$O$_3$, MgO—in other words, the solubility of the several solid phases in such liquids. These relations have been ascertained, by means of determinations of melting temperatures and optical characteristics of the components and compounds, throughout the range of concentrations within which they occur as stable solid phases. The general principles upon which the mode of experiment is based, as well as most of the actual methods employed, have been fully described in a previous paper, to which the reader is referred.[3]

One paper dealing with the three binary systems[4] has already been published. In the present paper we are able to give some new data on the systems MgO–Al$_2$O$_3$ and CaO–MgO.

The Components and Binary Systems.

In presenting the results obtained from a study of the components and binary systems, we will consider only such new data as has not already been published. This will include a study of the component MgO, a new form of the component Al$_2$O$_3$ and the binary systems MgO–CaO and MgO–Al$_2$O$_3$. The results obtained from the study of CaO and the system CaO–Al$_2$O$_3$ are given in the previous paper.

Magnesia, MgO.—The melting point of MgO as determined by

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[1] Rankin and Wright, *Am. J. Sci.*, [4] **39,** 1 (1915).

[2] A portion of the system CaO–MgO–SiO$_2$ has also been investigated already. See paper by N. L. Bowen, "The Ternary System Diopside–Forsterite–Silica," *Am. J. Sci.*, [4] **38,** 207 (1914).

[3] Rankin and Wright, *Am. J. Sci.*, [4] **39,** 1 (1915), referred to hereafter as the previous paper.

[4] *Am. J. Sci.*, [4] **28,** 293 (1909).

Kanolt is 2800°.[1] No indications of a second form have so far been observed.

In silicate melts MgO crystals are not faceted,[2] but with CaO and Al_2O_3 present sharply bounded and skeletal octahedrons, sometimes modified by the cube, were seen frequently.

Alumina, Al_2O_3.—This investigation has shown that alumina occurs in two distinct forms: (1) α-Al_2O_3 (artificial corundum) is the only form which has previously been described; the melting point of this form as determined by Kanolt is 2050°;[3] (2) β, the new form of alumina, is found to occur occasionally in charges of pure alumina which have been melted and slowly cooled. Having once formed, it has not been found possible to cause this β form to revert to the α form, even when held at temperatures above or below that required for melting. The presence of a small amount of MgO (0.5%) materially assists the formation of this new form, while melted alumina containing small amounts of either CaO or SiO_2 when cooled has been found to crystallize as the α form (corundum). It would appear therefore that β-Al_2O_3 may be monotropic with respect to the α form, although the exact relation existing between these two forms is uncertain by reason of the experimental difficulties involved in investigations requiring such extremely high temperature.

β-Al_2O_3 is hexagonal, often appearing in groups of over-lapping triangular plates with perfect basal cleavage. *The refractive index* ϵ appears to vary, even in preparations made from our purest alumina, due account being taken of the difficulty of getting properly oriented sections. The values found are 1.635 to 1.650. In the same preparations ω was 1.677 $\pm$ 0.003. In preparations containing MgO, ϵ may be as low as 1.629, and ω may vary between 1.665 and 1.680. But no relation between the content of MgO in the melt and the refractive index of the crystals has appeared.

Some artificial alumina[4] abrasives have been found to contain small amounts of this β-Al_2O_3 having ϵ = 1.631 and ω = 1.674.

The Binary System: Lime–Magnesia.—It was found that in all fused mixtures of CaO and MgO the two oxides crystallize out side by side, showing no evidence of combination, that is, there is no compound formed stable in contact with melt. The concentration temperature diagram for the system CaO–MgO is given in Fig. 1. The melting points of CaO and MgO are taken as 2570° and 2800°, respectively, the values determined by Kanolt at the Bureau of Standards. The eutectic, as obtained

[1] Kanolt, *J. Wash. Acad. Sci.*, **3**, 315 (1913).

[2] Anderson, *Am. J. Sci.*, [4] **39**, 421 (1915).

[3] *J. Wash. Acad. Sci.*, **3**, 315 (1913).

[4] β-Al_2O_3 separated from an artificial alumina abrasive was analyzed by H. S. Washington and found to have the chemical composition Al_2O_3; its density is 3.30 $\pm$ 0.01.

by extrapolation of the CaO–MgO boundary in the ternary system CaO–Al$_2$O$_3$–MgO, has the approximate composition 67% CaO, 33% MgO and its melting point is 2300° ± 50°.

The Binary System: Magnesia – Alumina. — MgO and Al$_2$O$_3$ combine to form but a single compound, MgO.Al$_2$O$_3$ (MgO 28.4 %, Al$_2$O$_3$ 71.6%). This compound is stable at its melting point,

Fig. 1.—Concentration-temperature diagram for the system lime-magnesia.

which is 2135° ± 20°. With MgO, MgO.Al$_2$O$_3$ forms a eutectic of the composition MgO 45%, Al$_2$O$_3$ 55%; its melting point is 2030° ± 20°.

Fig. 2.
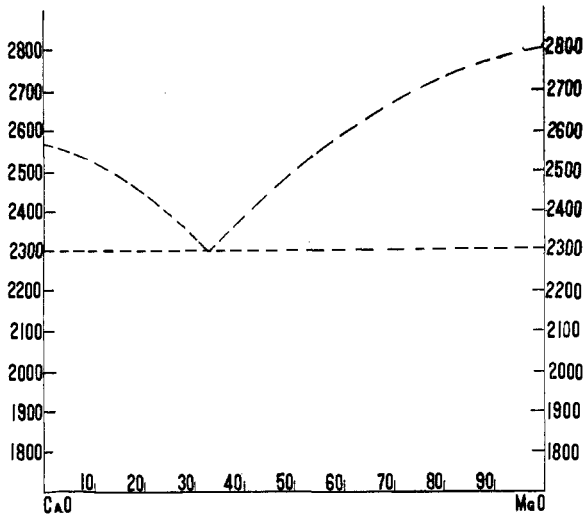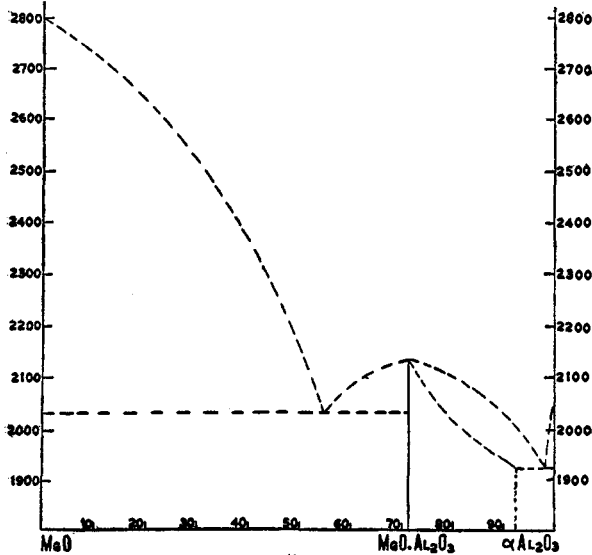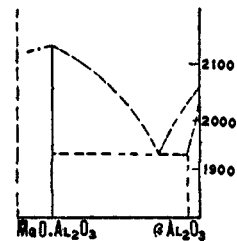
Fig. 2.—Concentration-temperature diagram for the system magnesia–alumina.
Fig. 2a.—Concentration-temperature diagram for the system spinel–alumina.

It was found exceedingly difficult to establish definitely the relations existing between the compound MgO.Al$_2$O$_3$ and the two forms of Al$_2$O$_3$. This is due to the fact that since β-Al$_2$O$_3$ is apparently monotropic with

respect to the α form, it is not possible to define conditions for the preparation of melts which on cooling will crystallize to give $MgO.Al_2O_3$ and the desired form of Al_2O_3. However from the optical examination of the crystals which have separated in a large number of experiments, it appears that the compound $MgO.Al_2O_3$ forms with α-Al_2O_3 a nearly complete series of solid solutions, but with β-Al_2O_3 it does not enter into solid solution except that the β-Al_2O_3 seems to take a limited amount of $MgO.$-Al_2O_3 in solid solution. Nevertheless, one cannot predict which alternative will happen in any particular case; for under apparently identical conditions of melting and cooling sometimes the solid solution will be formed, sometimes the $MgO.Al_2O_3$ along with the β-Al_2O_3. These relations are represented by concentration-temperature diagrams; Fig. 2, that for the system MgO–α-Al_2O_3 and Fig. 2a, that for the system $MgO.$–Al_2O_3–β-Al_2O_3. In these diagrams the melting temperatures for the various mixtures are represented by dotted lines, for the reason that no satisfactory melting temperatures could be obtained except for pure MgO—2800°; pure $MgO.Al_2O_3$ —2135° ± 20°; pure Al_2O_3—2050° ± 20°; the eutectic MgO–$MgO.Al_2O_3$ (45% MgO, 55% Al_2O_3)—2030° ± 20°; the eutectic α-Al_2O_3–$MgO.Al_2O_3$ (98% Al_2O_3, 2% MgO)—1925° ± 40°; and the eutectic β-Al_2O_3–$MgO.Al_2O_3$ (92% Al_2O_3, 8% MgO)—1925° ± 40°.

The Optical Properties of the crystals separating in the different parts of the spinel field are not very different from those of pure spinel, although some of these crystals do not contain more than 8% of theoretical spinel. For example, from the melt Al_2O_3 98%, MgO 2% there separated about 90% spinel and 10% of the two forms of Al_2O_3. The refractive index, n, of this spinel was 1.733. From another melt spinel containing its own weight of dissolved alumina had a refractive index of 1.726. A practically pure spinel made in the iridium furnace[1] had $n = 1.718 \pm 0.002$. The mean refractive index of α-Al_2O_3 (corundum) is 1.765 and of β-Al_2O_3 is about 1.665. Thus the refractive index of spinel crystals of intermediate composition is not even an approximate additive function of the refractive indices of two end members. Such a relation might, however, exist if both forms of Al_2O_3 are dissolved in the same spinel crystal. The spinel is strictly isotropic unless the alumina is greatly in excess, in which case double refraction appears and increases with the content of alumina to perhaps 0.003. The value is hard to estimate for the grains then contain a fine, irregular lattice which extinguishes as a unit, and the elements of which seem to extend in three rectangular directions.

The Identification of Spinel in Presence of Periclase was found to be im-

[1] A similar preparation melted in the arc furnace had $n = 1.723 \pm 0.002$. *Am. J. Sci.*, **28**, 326 (1909).

practicable by an optical method alone owing to their being isotropic and similar in refractive index, and often having the same crystal habit. Spinel—unless in the process of dissolving—always appeared in faceted or skeleton octahedra; periclase appeared in rounded grains as well as in the same habits as spinel. In cases of doubt in identification, the powdered preparation was warmed on the slide with a few drops of mixed nitric and hydrochloric acids diluted with an equal amount of water. The glasses, containing the crystals, and the periclase dissolved leaving the spinel. By interrupting the process of solution partly dissolved grains of periclase could be identified.

The Binary System: Lime–Alumina.—The results obtained from the investigation of this system have already been published. Some new optical data, however, have been obtained for two of the calcium aluminates as they occur in ternary mixtures of CaO, Al_2O_3, MgO. The compound $5CaO.3Al_2O_3$ was here observed in skeleton tetrahedrons. The compound $CaO.Al_2O_3$ was seldom twinned in these preparations while in silicate mixtures it was almost invariably twinned. The value of 2V of this compound in silicate preparations is given at 36°; variations to nearly uniaxial were observed during this investigation. Besides irregular grains and fibers many crystals which appeared to be orthorhombic were observed. No variations in refractive index from crystals found in the silicate melts were noted.

The Ternary System CaO–Al₂O₃–MgO.

The results obtained from the investigation of the three binary systems show that in the study of the ternary system we must delimit the regions of stability of the three components CaO, Al_2O_3, MgO; the five binary compounds $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$, $MgO.Al_2O_3$, and in addition to these any other compounds, binary or ternary, which may be stable in contact with melt. As a matter of fact, in the present system no substances other than those already encountered in the binary system appear.

The first step in this investigation consisted in the preparation of charges whose compositions represented random intervals over the entire range of ternary mixtures. The primary crystalline phase was then determined for each of these charges which could be quenched at some temperature below 1600° in such a way that a single crystalline phase imbedded in glass could be obtained. From this preliminary reconnaissance we located approximately the fields with their limiting boundary curves and quintuple points. With these general data as a basis, other intermediate charges were prepared and their primary phases determined; this secured a more exact location of the boundary curves and quintuple points, the compositions along boundary curves (lines) being accurate to within

TABLE I.

Quenchings Which Determine the Limits of the Field of CaO.

Phases present, glass + CaO.

Composition wt. %.				Time in
CaO.	Al₂O₃.	MgO.	Temp.	hours.
55	42	3	1525°	0.25
53	41	6	1460°	0.5
52	42	6	1480°	0.5
62	37	7	1450°	1.0
53	39	8	1550°	0.25
55	35	10	1570°	0.5

TABLE II.

Quenchings Which Determine the Limits of the Field of 3CaO.Al₂O₃.

Phases present, glass + 3CaO.Al₂O₃.

Composition wt. %.				Time in
CaO.	Al₂O₃.	MgO.	Temp.	hours.
54	43	3	1480°	0.25
48	48	4	1378°	0.5
51	43	6	1435°	0.25
47	47	6	1360°	1.0

TABLE III.

Quenchings Which Determine the Limits of the Field of 5CaO.3Al₂O₃.

Phases present, glass + 5CaO.3Al₂O₃.

Composition wt. %.				Time in
CaO.	Al₂O₃.	MgO.	Temp.	hours.
48	50	2	1410°	0.5
48	48.5	5.5	1370°	0.5
42.5	51.5	6	1370°	0.5
44.5	49	6.5	1400°	0.25

TABLE IV.

Quenchings Which Determine the Limits of the Field of CaO.Al₂O₃.

Phases present, glass + CaO.Al₂O₃.

Composition wt. %.				Time in
CaO.	Al₂O₃.	MgO.	Temp.	hours.
35.2	62	2.8	1550°	0.25
45	52	3.0	1390°	0.5
34	63	3.0	1560°	0.25
37	58.5	4.5	1515°	0.5
42	53	5	1400°	0.5
42	52	6	1360°	0.5
41	53	6	1375°	0.5

TABLE V.

Quenchings Which Determine the Limits of the Field of 3CaO.5Al₂O₃.

Phases present, glass + 3CaO.5Al₂O₃.

Composition wt. %.				Time in
CaO.	Al₂O₃.	MgO.	Temp.	hours.
33	64.5	2.5	1590°	0.25
32	65	3	1585°	0.5
30.5	66	3.5	1600°	0.25

TABLE VI.

Quenchings Which Determine the Limits of the Field of MgO.Al₂O₃.

Phases present, glass + MgO.Al₂O₃.

Composition wt. %.				Time in
CaO.	Al₂O₃.	MgO.	Temp.	hours.
33.5	63.5	3	1563°	0.25
32	64	4	1570°	0.25
30.5	65.5	4	1610°	0.25
34.5	61	4.5	1545°	0.5
30	64	6	1585°	0.5
40	53	7	1400°	0.5
37	53	10	1500°	0.25
34	54	12	1575°	0.25

TABLE VII.

Quenchings Which Determine the Limits of the Field MgO.

Phases present, glass + MgO.

Composition wt. %.				Time in
CaO.	Al₂O₃.	MgO.	Temp.	hours.
50	43.5	6.5	1435°	0.5
45.5	48	6.5	1375°	0.5
51.7	41.3	7	1465°	0.5
48	45	7	1400°	0.5
46	47	7	1375°	2.0
44	49	7	1375°	0.5
42.5	50.5	7	1355°	2.5
41	52	7	1375°	0.5
51.5	40.5	8	1500°	0.5
45	47	8	1500°	0.25
43	49	8	1450°	0.5
52	39.5	8.5	1550°	2.5
52.5	37.5	10	1610°	0.25
50	40	10	1465°	0.5
45	45	10	1600°	0.25
40	50	10	1425°	1.5
35	52.5	12.5	1580°	0.25
45	40	15	1430°	0.5
45	35	20	1500°	0.5
35	45	20	1400°	0.5
35	30	35	1550°	0.25

TABLE VIII.

Quenchings Which Determine the Limits of the Field of β-Al_2O_3.

Phases present, glass + Al_2O_3.

Composition wt. %.				Time in
CaO.	Al_2O_3.	MgO.	Temp.	hours.
20	75	5	$1700°$[1]	0.25

$\pm 1.0\%$, and quintuple compositions being accurate within a radius of 0.5%.

The data obtained in this way are given in Tables I–VIII. Each of these tables contains the data for the location of the boundaries and quintuple points which delimit the field for one crystalline phase. The limits
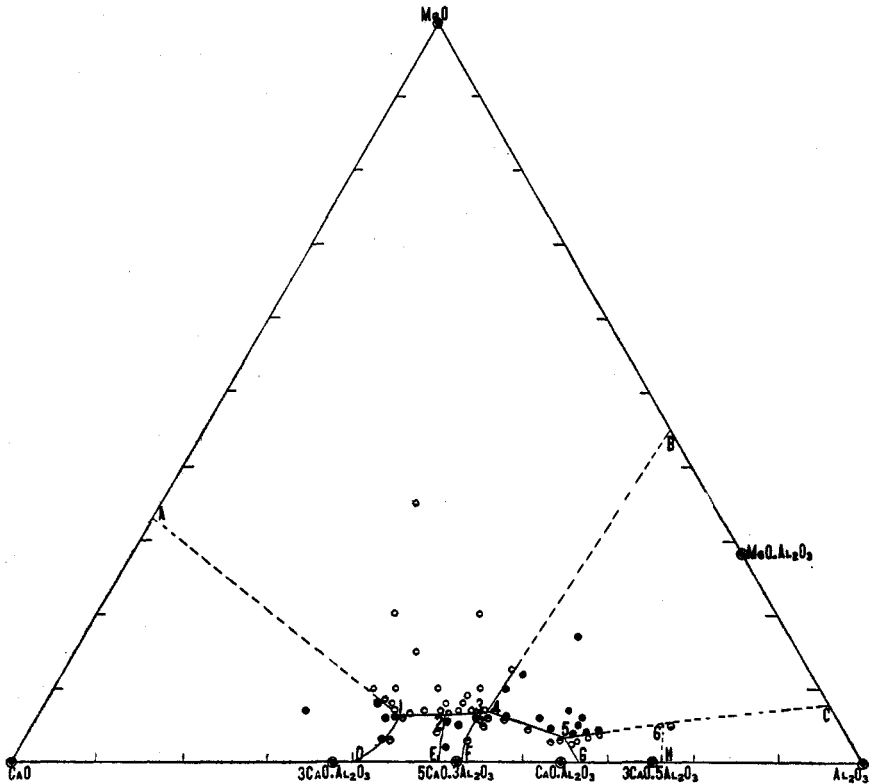

Fig. 3.—Projection of concentration-temperature diagram for the ternary system $CaO–Al_2O_3–MgO$, giving compositions whose primary phases determined the location of boundary curves and quintuple points.

of the field of stability, as determined by these data, are represented in the triangular diagram, Fig. 3. The dots given in the diagram represent the compositions examined.

[1] Heated in iridium furnace.

When the compositions within each field, along each boundary curve and at each quintuple point are known it is still necessary to determine the composition of each unknown crystalline phase and the equilibrium temperature within the fields, along the boundary curves and at each quintuple point. Examination of Fig. 3 shows that there are no crystalline phases not found in the binary series, $i.\ e.$, that there are no ternary compounds stable in contact with the melts; altogether, therefore, there are 8 fields, 13 boundary curves and 6 quintuple points.

The Fields.

In the complete $CaO-Al_2O_3-MgO$ diagram there proved to be 8 separate fields of stability; that is, there are 8 separate regions—one for each chemical compound (including the original components) which occurs in the system—within which a single particular compound is in equilibrium with solution and vapor. Each field may be regarded as the solubility region of a single compound in solutions of two other definite compounds or the melting region of a single compound in solutions of three definite compounds.

The melting temperatures within each field are obtained by quenching to determine the temperature above which glass (liquid) is obtained and below which a single crystalline phase is obtained imbedded in glass, as determined by optical examination with the microscope. By this method of procedure it is possible to determine melting temperatures up to 1600°— the limit of the platinum resistance furnace in which quenchings are made.

We shall now consider the fields separately, the numbers and letters used to designate them being those given in Fig. 3. Examination of Fig. 3 shows that the field of each of several of the compounds of CaO and Al_2O_3 covers approximately the same area that it did in the equilibrium diagram for CaO, Al_2O_3 and SiO_2. This is merely a strange coincidence which could not be predicted, since the solubility of a compound in one series of ternary solutions is not necessarily the same as for any other series of ternary solutions.

1. **The field of lime** (CaO)(D–1–A–CaO).—Practically all the melting temperatures within this field are too high for determination, and hence the slope of its melting surface was deduced from the melting temperature of the boundaries.

2. **The field of** $3CaO.Al_2O_3$ (D–1–2–E).—$3CaO.Al_2O_3$ is a compound unstable at its melting point, wherefore its composition lies outside of its field of stability. Table IX gives the quenchings which determine the melting temperature of various compositions within this field.

3. **The field of** $5CaO.3Al_2O_3$ (E–2–3–F).—$5CaO.3Al_2O_3$ occurs in two forms, a stable form and an unstable form which occurs in melts with considerable frequency. The melting slope of the narrow field for the stable

form follows from the melting temperature of the boundaries which have been ascertained.

TABLE IX.

Quenchings Which Determine Melting Temperature[1] of Various Compositions within Field D–1–2–E; Primary Phase is $3CaO.Al_2O_3$.

Composition wt. %.

CaO.	Al₂O₃.	MgO.	Temp.	Time in hours.	Phases present.
54	43	3	1490°	0.25	Glass
			1480°	0.25	Glass + $3CaO.Al_2O_3$
48	48	4	1385°	1.0	Glass
			1378°	0.5	Glass + $3CaO.Al_2O_3$
51	43	6	1450°	0.5	Glass
			1435°	0.25	Glass + $3CaO.Al_2O_3$

4. The field of $CaO.Al_2O_3$ (F–3–4–5–G).—Table X gives the quenchings which determine the melting temperatures of various compositions within this field.

TABLE X.

Quenchings Which Determine Melting Temperature of Various Compositions within Field F–3–4–5–G; Primary Phase is $CaO.Al_2O_3$ (m. p. 1600° $\pm$ 5°).

Composition wt. %.

CaO.	Al₂O₃.	MgO.	Temp.	Time in hours.	Phases present.
35.2	62	2.8	1560°	0.25	Glass
			1550°	0.25	Glass + $CaO.Al_2O_3$
45	52	3	1395°	0.5	Glass
			1390°	0.5	Glass + $CaO.Al_2O_3$
42	52	6	1390°	0.5	Glass
			1360°	0.5	Glass + $CaO.Al_2O_3$

5. The field of $3CaO.5Al_2O_3$ (G–5–6–H).—$3CaO.5Al_2O_3$ occurs in two forms, a stable form and an unstable form, which is occasionally found in melts. Practically all the melting temperatures within this field are too high for determination, and hence the melting surface was deduced from the melting temperatures of the boundaries.

6. The field of alumina (Al_2O_3) (H–6–C–Al_2O_3).—All the melting temperatures within this field are too high for determination and hence the slope of its melting surface was deduced from the melting temperature of its boundaries.

7. The field of $MgO.Al_2O_3$ (B–4–5–6–C).—Most of the melting tempera-

[1] The melting temperatures, given in this table and those which follow for fields and boundary curves, were not determined with the greatest possible accuracy, for two reasons: (1) It was possible to establish the equilibrium relations in this system with approximate determinations of these temperatures. (2) The essential points (quintuple points) in this system are all contained within a small area of compositions, so that the accurate determination of the melting temperature of each of these points, together with the melting temperatures of pure compounds and quadruple points, enables one to give rather accurately the melting slopes of the various ternary fields and boundary curves.

tures within this field are too high for determination; those of certain compositions are given in Table XI.

TABLE XI.

Quenchings Which Determine Melting Temperatures of Various Compositions within Field B–4–5–6–C; Primary Phase is MgO.Al$_2$O$_3$ (m. p. 2135° ± 20°).

Composition wt. %.					
CaO.	Al$_2$O$_3$.	MgO.	Temp.	Time in hours.	Phases present.
37	53	10	1525°	0.25	Glass
			1500°	0.25	Glass + MgO.Al$_2$O$_3$
34	54	12	1610°	0.25	Glass
			1575°	0.25	Glass + MgO.Al$_2$O$_3$

8. **The field of magnesia** (MgO) (A–1–2–3–4–B–MgO).—MgO, which occurs in but a single form, is the primary crystalline phase for over one-half of the area of compositions of CaO, Al$_2$O$_3$, MgO, represented in Fig. 3. Most of the melting temperatures within this area (field) are too high for determination. Those of certain compositions determined by quenching are given in Table XII.

TABLE XII.

Quenchings Which Determine Melting Temperatures of Various Compositions within Field A–1–2–3–4–B–MgO; Primary Phase is MgO (m. p. 2800°).

Composition wt. %.					
CaO.	Al$_2$O$_3$.	MgO.	Temp.	Time in hours.	Phases present.
51.5	40.5	8	1500°	0.5	Glass + MgO
			1540°	0.5	Glass
45	47	8	1450°	0.25	Glass + MgO
			1500°	0.25	Glass
43	49	8	1450°	0.25	Glass + MgO
			1500°	0.25	Glass
40	50	10	1510°	0.5	Glass + MgO
			1535°	0.5	Glass

The Boundary Curves.

A boundary curve is the line which separates two fields and represents the temperatures and concentrations at which the solid phase of one field is in equilibrium with the solid phase of the other field in coexistence with solution and vapor.

The boundary lines in Fig. 3 represent the projection upon the horizontal plane of the lines on the concentration-temperature solid model. In order to make clear the way in which the temperature varies along these lines, we have made projections upon a vertical plane, obtaining in this way the series of boundary curves reproduced in Fig. 4, in which the numbers and letters used correspond to those in Fig. 3. The ordinates represent temperatures, which were determined experimentally.

These temperatures are ascertained by quenching to determine the temperature above which one solid crystalline phase is obtained im-

bedded in glass and below which two crystalline phases are obtained im-
bedded in glass, as observed by the microscope. Data obtained in this
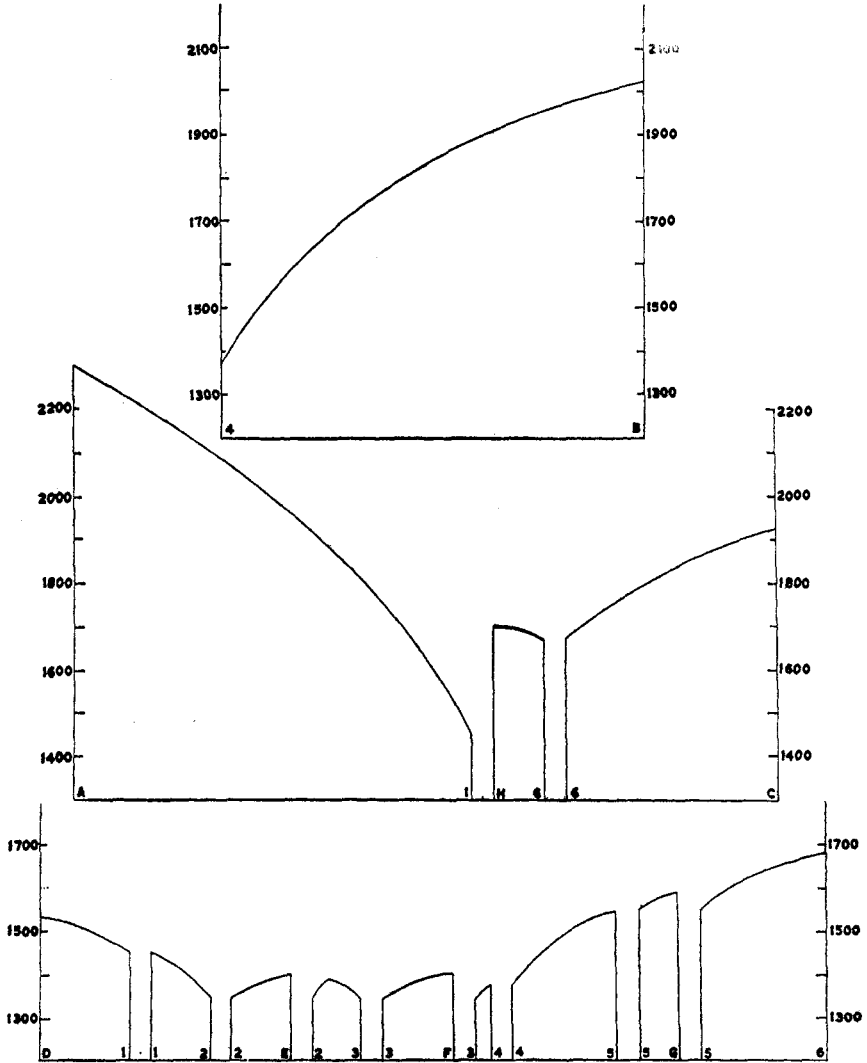way giving the temperatures determined for points on the boundaries,

Fig. 4.—Temperature-concentration diagram of the 13 boundary curves which fix the limits of the fields within the ternary system CaO–Al₂O₃–MgO.

are contained in Table XIII. The temperatures at the ends of the bound-
ary curves are given later as quintuple and quadruple point tempera-
tures.

<div align="center">TABLE XIII.</div>

Quenchings Which Determine Temperatures for Points on the Boundary Curves.

CaO.	Al₂O₃.	MgO.	Temp.	Time in hours.	Phases present.	Boundary.
55	42	3	1465°	0.5	Glass + 3CaO.Al₂O₃	D–1
			1500°	0.25	Glass + 3CaO.Al₂O₃ + CaO	
48	48	4	1378°	0.5	Glass + 3CaO.Al₂O₃	E–2
			1375°	1.0	Glass + 3CaO.Al₂O₃ + 5CaO.3Al₂O₃	
52	39.5	8.5	1550°	0.25	Glass + MgO	1–A
			1510°	0.5	Glass + MgO + CaO	
52.5	37.5	10	1610°	0.25	Glass + MgO	
			1590°	0.25	Glass + MgO + CaO	
48	45	7	1400°	0.5	Glass + MgO	1–2
			1380°	0.5	Glass + MgO + 3CaO.Al₂O₃	
44.5	49	6.5	1400°	0.25	Glass + 5CaO.3Al₂O₃	2–3
			1360°	0.5	Glass + 5CaO.3Al₂O₃ + MgO	
45	52	3	1390°	0.5	Glass + CaO.Al₂O₃	F–3
			1375°	0.5	Glass + CaO.Al₂O₃ + 5CaO.3Al₂O₃	
42	52	6	1360°	0.5	Glass + CaO.Al₂O₃	
			1350°	1.0	Glass + CaO.Al₂O₃ + 5CaO.3Al₂O₃	
41	52	7	1375°	0.5	Glass + MgO	3–4
			1365°	0.5	Glass + MgO + CaO.Al₂O₃	
34	54	12	1520°	0.5	Glass + MgO.Al₂O₃	4–B
			1475°	0.5	Glass + MgO + MgO.Al₂O₃	
35	52	12.5	1580°	0.25	Glass + MgO	
			1550°	0.25	Glass + MgO + MgO.Al₂O₃	
37	53	10	1500°	0.25	Glass + MgO.Al₂O₃	
			1475°	1.5	Glass + MgO.Al₂O₃ + MgO	
37	58.5	45	1515°	0.5	Glass + CaO.Al₂O₃	4–5
			1485°	0.5	Glass + CaO.Al₂O₃ + MgO.Al₂O₃	
40	53	7	1400°	0.5	Glass + MgO.Al₂O₃	
			1385°	0.5	Glass + MgO.Al₂O₃ + CaO.Al₂O₃	
30.5	65.5	4	1610°	0.25	Glass + MgO.Al₂O₃	5–6
			1600°	0.25	Glass + MgO.Al₂O₃ + 3CaO.5Al₂O₃	

The Quintuple Points.

A quintuple point, a common point for three boundaries, is the point at which three solid phases are in equilibrium with solution and vapor. A quintuple point is known as a eutectic if it is the lowest temperature of the three boundaries of which it is a common point.

The temperature of a quintuple point may be determined in any mixture of the solid phases present at that quintuple point, either from heating curves or quenches to determine the temperature above which two crystalline phases are obtained imbedded in glass (liquid) and below which three solid crystalline phases are obtained; that is, the temperature at which glass first appears in a ternary mixture is the temperature of the quintuple point for that mixture.

Following is a list of the 6 quintuple points giving compositions in weight percentages of CaO, Al₂O₃, MgO and the corresponding temperatures

determined both by heating curves and quenches. The numbers assigned to each quintuple point correspond to the numbers in Fig. 3.

Point 1 is the quintuple point for CaO, MgO and 3CaO.Al₂O₃ (CaO 51.5, Al₂O₃ 43.3, MgO 6.2). Its melting temperature ($1450° \doteq 5°$) is based on the values obtained from various compositions as given in Table XIV.

TABLE XIV.

Melting Temperature: Quintuple 1 for CaO, MgO, and 3CaO.Al₂O₃ as Determined from Various Compositions.

Composition, wt. %	CaO......	52.5	55	45	52	51.7	50
	Al₂O₃.....	37.5	35	35	42	41.3	40
	MgO.....	10.0	10	20	6	7	10
Temperature..................		1446	1450	1449	Quench	Quench	Quench
		1449	1450	1450	1460	1455	1450
		1445	1450	1449	....	....	....
		1447	1450	1446	....	....	....
		1449	....	1450	....	....	....
Mean,		1447	1450	1449	1460	1455	1450

Point 2 is the eutectic point for MgO, 3CaO.Al₂O₃ and 5CaO.3Al₂O₃ (CaO 51, Al₂O₃ 42.7, MgO 6.3). Its melting point $1345° \doteq 5°$ is based on the values obtained from compositions given in Table XV.

TABLE XV.

Melting Temperature: Eutectic 2 for MgO, 3CaO.Al₂O₃ and 5CaO.3Al₂O₃ as Determined from Various Compositions.

Composition, wt. %	CaO......	45	50	52.5
	Al₂O₃.....	35	43.5	37.5
	MgO.....	20	6.5	10.0
Temperature..................		1340° Quench	1350° Quench	1340° Quench

Point 3 is the eutectic for MgO, 5CaO.3Al₂O₃ and CaO.Al₂O₃ (CaO 41.5, Al₂O₃ 51.8, MgO 6.7). Its melting temperature is $1345 \doteq 5°$.

Point 4 is the quintuple point for MgO, MgO.Al₂O₃ and CaO.Al₂O₃ (CaO 40.7, Al₂O₃ 52.4, MgO 6.9). Its melting temperature, $1370 \doteq 5°$, is based on the values obtained from various compositions as given in Table XVI.

TABLE XVI.

Melting Temperature: Quintuple Point 4 for MgO + MgO.Al₂O₃ + CaO.Al₂O₃ as Determined from Various Compositions.

Composition, wt %	CaO...............	39	31	35	40	34
	Al₂O₃.............	55	62	52.5	53	54
	MgO.............	6	7	12.5	7	12
Temperature.......................		1373	1371	1370	1370	1370
		1374	1373	Quench	Quench	Quench
		1372	1375	....	....	....
		1372	1371	....	....	....
		1374	....	....	....	....
Mean,		1373	1372	1370	1370	1370

Point 5 is the quintuple point for $MgO.Al_2O_3$, $CaO.Al_2O_3$ and $3CaO.-5Al_2O_3$ (CaO 33.3, Al_2O_3 63.2, MgO 3.5). Its melting temperature, $1550° \pm 5°$, is based on the values obtained from various compositions as given in Table XVII.

TABLE XVII.

Melting Temperature: Quintuple Point 5 for $MgO.Al_2O_3$ + $CaO.Al_2O_3$ + $3CaO.5Al_2O_3$ as Determined from Various Compositions.

Composition, wt. %				
	CaO.............	32	29	30
	Al₂O₃...........	65	67	64
	MgO...........	3	4	6
Temperature........................		1555	1554	1550
		1554	1553	1449
		1555	1553	1550
		1554	1555	1549
Mean,		1555	1554	1549
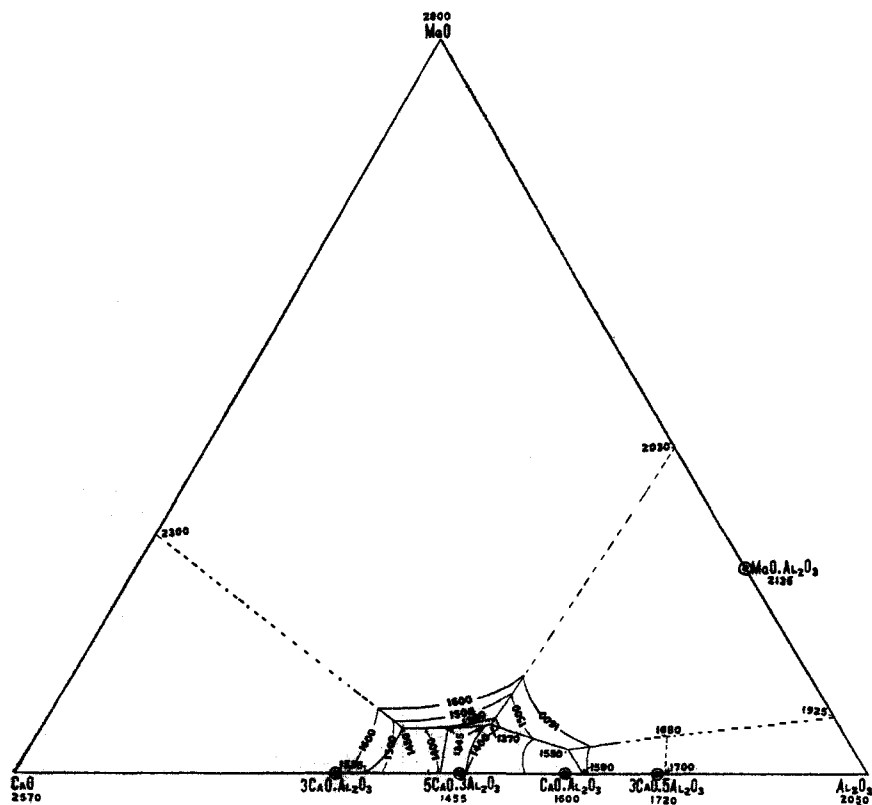
Fig. 5.—Projection of a concentration-temperature diagram of the ternary system CaO–Al₂O₃–MgO with isotherms and melting temperatures of compounds and invariant points.

Point 6 is the quintuple point for $MgO.Al_2O_3$, $3CaO.5Al_2O_3$ and Al_2O_3 (CaO 21, Al_2O_3 74, MgO 5). Its melting temperature determined in the iridium furnace is $1680° \pm 20°$.

Point 6 was located by extrapolation of the boundary curves 5–6, H–6 and C–6.

The Concentration-Temperature Model.

In the preceding pages we have recorded equilibrium temperatures as determined within the limits of our apparatus for the three binary systems and for the ternary system; in other words, we have presented the temperature corresponding to quintuple points, boundary curves and fields. By interpolation from the determined melting temperatures we may draw constant temperature lines or isotherms; this has been done for every $100°$ from $1400°$ to $1600°$ and the resulting diagram is given in Fig. 5, which shows, moreover, the melting temperatures of each compound, component, quadruple and quintuple point.
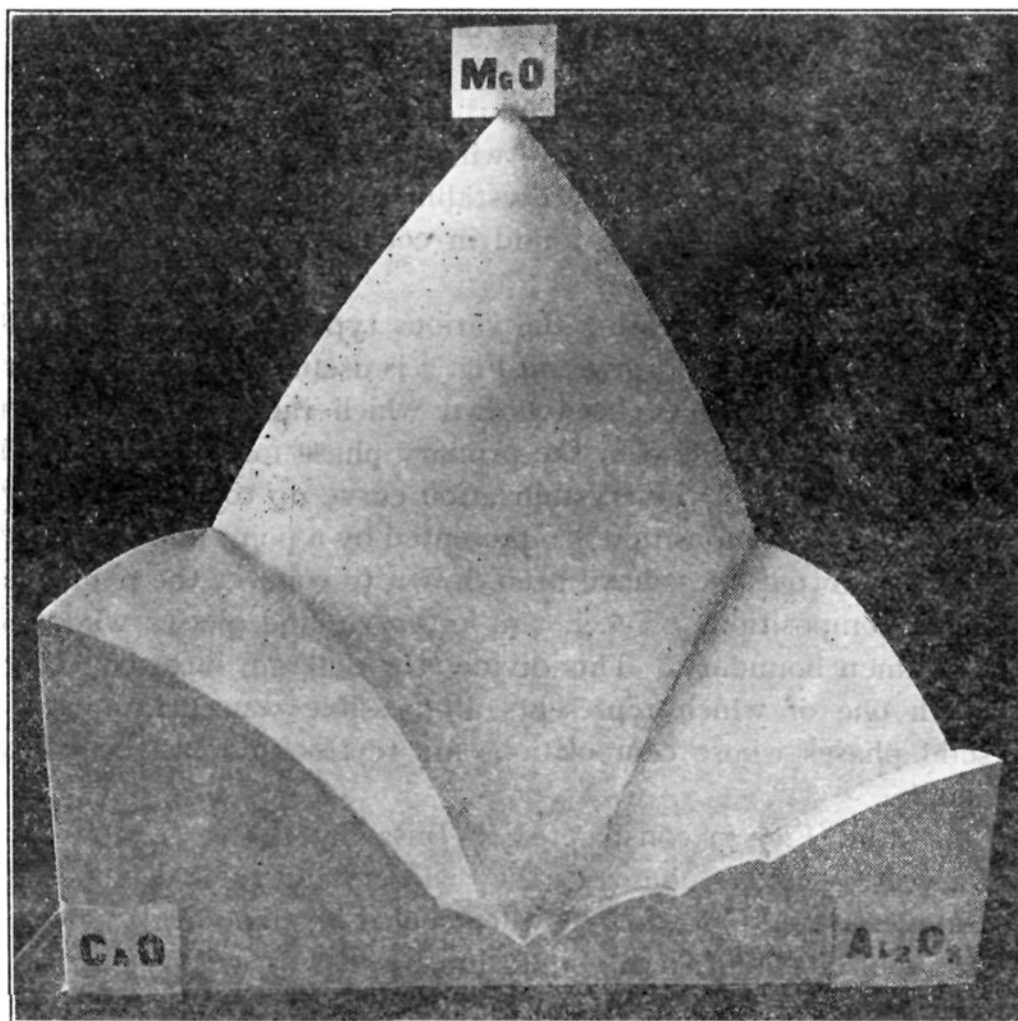

Fig. 6.—Photograph of solid model of concentration-temperature diagram of the system $CaO-Al_2O_3-MgO$.

By erecting the diagram (Fig. 4) for each boundary curve (Fig. 3) perpendicular to the plane of the corresponding projection of each boundary curve (Fig. 3) one can construct a concentration-temperature solid model whose surface represents the melting temperatures of all ternary compositions of $CaO-Al_2O_3-SiO_2$. A photograph of a solid plaster of Paris model constructed in this way is given in Fig. 6. Fig. 6 is taken from in front of the $CaO-Al_2O_3$ side and shows the slopes of the various fields.

Crystallization of Ternary Solutions of $CaO-Al_2O_3-MgO$.

The results of this investigation thus far, have been plotted graphically in diagrams to show the equilibria between the various phases of this system $CaO-Al_2O_3-MgO$. To the end that these data be utilized in practical work it is desirable to know what is the composition of the solid phases which separate when any ternary solution is cooled. In the previous paper the systematic elaboration of phase separations has been carried out, the deductions being based on the actual data contained in the system $CaO-Al_2O_3-SiO_2$. The data contained in the equilibrium diagram for the present system shows that the same types of ternary crystallization are found here as in the system $CaO-Al_2O_3-SiO_2$. For that reason in the present paper we will treat the subject of crystallization rather briefly, giving merely crystallization curves, to illustrate the various types of crystallization found in cooled solutions of CaO, Al_2O_3 and MgO.

For the purpose of illustrating the various types of ternary crystallization, a diagram such as that given in Fig. 7 is useful. In this equilibrium diagram, straight lines have been drawn which radiate from the point representing the composition of the primary phase for each field. These lines show the course of the crystallization curve up to the boundary for any solution whose composition is represented by a point in a field. Other straight lines (dotted lines) have been drawn to connect the points representing the compositions of each pair of crystalline phases whose fields have a common boundary. This divides the diagram into six triangular areas, each one of which represents all possible concentrations of the three solid phases whose compositions are represented by the apices of the triangle.

The diagram (Fig. 7) constructed in this way enables one to readily ascertain the crystalline phases as they will crystallize or disappear from a solution of CaO, Al_2O_3 and MgO when cooled in such a way as to secure the continuous attainment of equilibrium.

The experimental data represented in this diagram show that there are five types of ternary crystallization found therein. Each of these types involves only crystalline phases of constant composition, that is, there is no solid solution. These five types are: (1) Crystallization in

which the crystallization of each solid phase is continuous. (2) **Crystallization** in which a solid having crystallized along a boundary partially disappears at a quintuple point. (3) Crystallization in which a solid having crystallized along a boundary entirely disappears at a quintuple
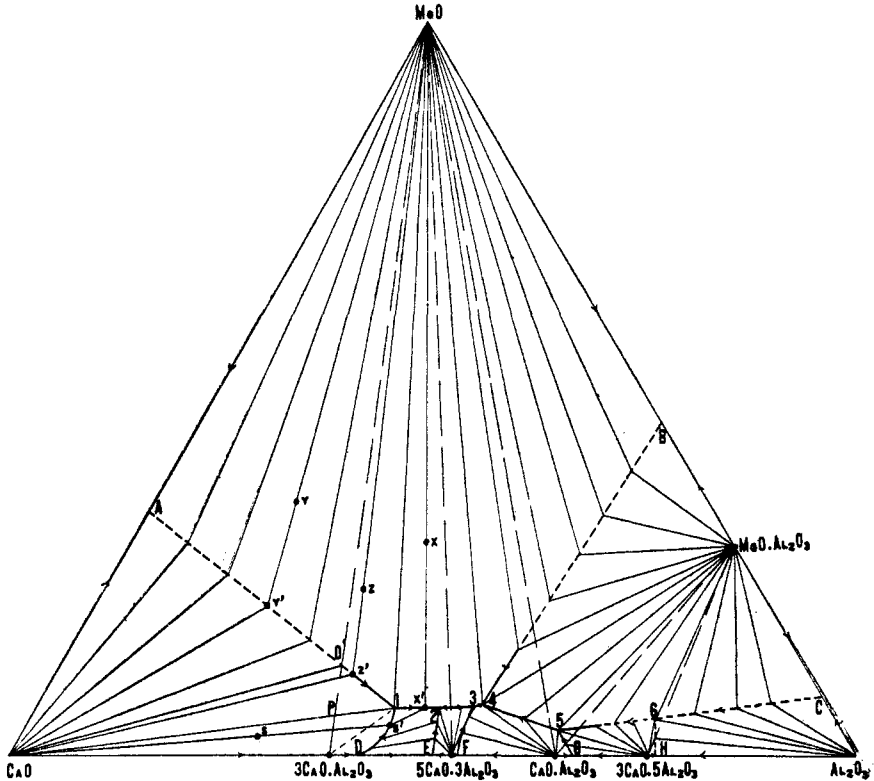

Fig. 7.—Equilibrium diagram to show the course of crystallization when ternary solutions of CaO, Al$_2$O$_3$, MgO are cooled.

point. (4) Crystallization in which a solid phase having crystallized within a field partially disappears along a boundary curve. (5) Crystallization in which a solid phase having crystallized within a field entirely disappears along a boundary.

We will now consider each of these five types separately, giving the course of the crystallization curve for a single particular solution and the areas which represent the compositions of all solutions which on cooling show the same type of ternary crystallization.

1. **Crystallization in which the Crystallization of Each Solid Phase is Continuous.**—The crystallization curve follows a straight line to a boundary, along which two phases crystallize until the quintuple point (a eutectic) is reached when three phases crystallize and the solution

completely solidifies. As an example consider a saturated solution whose composition is represented by point X. The course of its crystallization curve is from X to X′ and from X′ to 2. The solid phases in the order in which they crystallize are pure MgO; MgO and $3CaO.Al_2O_3$ together; and finally MgO, 3CaO, Al_2O_3 and $5CaO.3Al_2O_3$. Examination of Fig 7 shows that there are 4 areas which represent the compositions of solutions which on cooling have this type of crystallization, *viz.*, D–1–2–E E–2–3–F; F–3–4–$CaO.Al_2O_3$; 1–MgO–4–3–2.

2. **Crystallization in which a Solid having Crystallized Along a Boundary Partially Disappears at a Quintuple Point.**—The crystallization curve follows a straight line to a boundary along which two phases crystallize until a quintuple point (not a eutectic) is reached. At the quintuple point one of the two phases which has crystallized partially disappears— unites with a component in solution to form the third crystalline phase. As an example consider the crystallization curve for solution y. Its course is from y to $y′$ and from $y′$ to 1 where it ends. The solid phases in the order in which they appear are MgO; MgO and CaO together; and finally MgO, CaO and $3CaO.Al_2O_3$. Part of the CaO which crystallized with MgO unites with Al_2O_3 in solution to form $3CaO.Al_2O_3$. There are 4 areas which represent the compositions of solutions which on cooling show this type of ternary crystallization, *viz.*, CaO–A–MgO–P; MgO–B– $MgO.Al_2O_3$–$5CaO.Al_2O_3$; $CaO.Al_2O_3$–$MgO.Al_2O_3$–6–$3CaO.5Al_2O_3$; Al_2O_3– $MgO.Al_2O_3$–$3CaO.5Al_2O_3$.

3. **Crystallization in which a Solid having Crystallized Along a Boundary Entirely Disappears at a Quintuple Point.**—The crystallization curve follows the same course as in (2) up to the quintuple point. At this point one phase which has crystallized along a boundary is entirely used up in the formation of the third solid phase. The crystallization curve now leaves the quintuple point and follows a boundary along which the two remaining solid phases continue to crystallize until a second quintuple point is reached which is the end of the curve. As an example consider the crystallization for a solution whose composition is represented by point z within the field of MgO. Its course is from z to $z′$, from $z′$ to 1 and from 1 to 2, where it ends. The solid phases in the order in which they appear are: MgO; MgO and CaO; MgO, CaO and $3CaO.Al_2O_3$; CaO and $3CaO.Al_2O_3$; and finally MgO, $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$. All of the CaO which crystallized united with Al_2O_3 in solution to form $3CaO.Al_2O_3$. There are 4 areas which represent the compositions of solutions which on cooling show this type of ternary crystallization, *viz.*, o–MgO–1–P; $3MgO$–$CaO.Al_2O_3$; $CaO.Al_2O_3$–5–$MgO.Al_2O_3$; 6–$MgO.Al_2O_3$–$3CaO.5Al_2O_3$.

4. **Crystallization in which a Solid having Crystallized Within a Field Partially Disappears Along a Boundary.**—The crystallization curve follows a straight line to a boundary, one phase crystallizing until the

boundary is reached when part of the primary phase is used up in the formation of a second solid phase. Proceeding in this way, one phase disappearing while the other crystallizes, the crystallization curve follows a boundary to a quintuple point. As an example consider Solution S within the field of CaO. The course of its crystallization curve is from S to S' and from S' to 1, where it ends. The solid phases in the order in which they appear are: CaO; CaO and $3CaO.Al_2O_3$; and finally CaO, $3CaO.Al_2O_3$ and MgO. The CaO which crystallized as primary phase unites with Al_2O_3 in solution to form the secondary phase $3CaO.Al_2O_3$. There are two areas which represent the compositions of solutions which on cooling show this type of ternary crystallization, *viz.*, CaO–P–$3CaO.$-Al_2O_3; and P–1–$3CaO.Al_2O_3$. Crystallization curves for area CaO–P–$3CaO.Al_2O_3$ will end at 1 while those for area P–1–$3CaO.Al_2O_3$ will end at quintuple point 2, since this area is included within the triangle which represents all possible concentrations of $3CaO.Al_2O_3$, MgO and $5CaO.$-$3CaO.Al_2O_3$ whose quintuple point is point 2.

5. Crystallization in which a Solid Phase having Crystallized Within a Field Entirely Disappears Along a Boundary Curve.—The crystallization curve follows a straight line to a boundary along which the primary phase is entirely used up in the formation of the secondary phase. The curve now leaves the boundary and crosses a field, a single solid crystallizing until a second boundary is reached when two phases crystallize and the curve proceeds along the boundary to a quintuple point, where it ends. As an example consider any solution whose composition is represented by a point within area D–1–$3CaO.Al_2O_3$. The crystallization curve for any such solution will intercept boundary D–1, leaving boundary D–1 and cross the field D–1–2–F, intercept either boundary 1–2 or E–2 and end at 2. The solid phases in the order in which they appear are: CaO; CaO and $3CaO.Al_2O_3$; $3CaO.Al_2O_3$; $3CaO.Al_2O_3$ and MgO if the curve intercepts boundary 1–2 and $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ if it intercepts boundary E–2; and finally MgO, $3CaO.Al_2O_3$ and $5CaO.$-$3Al_2O_3$. There is but one area which represents the compositions of solutions which on cooling show this type of ternary crystallization, *viz.*: D–1–$3CaO.Al_2O_3$.

We have now given an example of each type of ternary crystallization and the areas which represent the compositions of solutions which on cooling give the same type. Knowing, then, the original composition of a ternary solution of CaO, Al_2O_3 and MgO, one can ascertain from the equilibrium diagram precisely which phases separate, their order of crystallization and the final product of crystallization.

The final product of crystallization of ternary solutions of CaO, Al_2O_3 and MgO always consists of three solid phases whose fields are adjacent. The same three solid phases will be the final product of crystallization

from any solution whose composition lies within the triangle formed by lines joining the compositions of these three phases.

These composition lines which have been drawn in Fig. 7 divide the diagram into 6 triangular areas. Each of these triangles represents all possible mixtures of those three compounds whose compositions are represented by the apices of the triangle. Though three certain, definite compounds can exist together in only one triangle, yet, as can be seen in the diagram, any one of these three compounds may be in a number of different triangles.

Summary.

The foregoing pages are a record of an investigation of the system $CaO-Al_2O_3-MgO$. This ternary system proved to be rather a simple one, there being no ternary compounds stable in contact with melt. The working out of this system, therefore, simply involved the equilibrium of the components (CaO, Al_2O_3, MgO) and the binary compounds ($3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$, $MgO.Al_2O_3$) in ternary solutions.

The relations found to subsist between the components and compounds in binary systems and in the ternary system are exhibited in a series of concentration-temperature diagrams.

The optical and crystallographical properties of the components and pure compounds are given in the previous papers, but a few additional notes are made here on the compounds $5CaO.3Al_2O_3$ and $CaO.Al_2O_3$. A new form of Al_2O_3 has been described. The relation of this new form (β-Al_2O_3) to αAl_2O_3 (corundum), the only form previously observed, could not be definitely established, although it would appear that β-Al_2O_3 is monotropic with respect to α-Al_2O_3. The relation of each of these forms, in the binary system $MgO-Al_2O_3$, involved solid solution, the extent of which was determined.

WASHINGTON. D. C.

THE EFFECT OF FREEZING ON CERTAIN INORGANIC HYDROGELS.[1]

BY H. W. FOOTE AND BLAIR SAXTON.

The composition and nature of precipitated colloids or hydrogels, such as silicic acid and ferric hydroxide, have been the subjects of repeated investigations which have varied greatly in their results. In the earlier work, the composition of inorganic hydrogels was determined chiefly

[1] Part of a dissertation presented by Blair Saxton to the Faculty of the Graduate School of Yale University, 1915, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.