[CONTRIBUTION FROM THE PORTLAND CEMENT ASSOCIATION FELLOWSHIP, BUREAU OF STANDARDS]

STUDIES ON THE SYSTEM CALCIUM OXIDE-ALUMINA-FERRIC OXIDE[1]

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Introduction

This investigation of the system calcium oxide-alumina-ferric oxide has been undertaken as one step in a program to determine the constitution of portland cement and the role played by each component in the manufacture and utilization of cement. The system has been found to be complex and only that part has been explored which appears to be of significance in the above-mentioned problem. This part, however, includes a large portion of the system.

Very little pertaining to the system CaO-Al_2O_3-Fe_2O_3 is found in the literature. Three contributions have been made, however, which are of interest.

Le Chatelier[2] believed that a compound existed of the composition $3CaO.Al_2O_3.Fe_2O_3$.

Shepherd, Rankin and Wright[3] observed that $2CaO.Fe_2O_3$ and $5CaO.3Al_2O_3$ reacted, but the reaction products were not determined.

Campbell[4] found that alumina and ferric oxide were capable of replacing each other in certain combinations with calcium oxide.

The Binary Systems

Two of the binary systems making up the ternary system under consideration have been studied. These are the systems CaO-Al_2O_3[5] and CaO-Fe_2O_3.[6] The system Al_2O_3-Fe_2O_3 has not been reported but a knowledge of it is not necessary for the investigation given here.

The data from these systems are plotted[7] on the sides of the triangular diagram, Fig. 1. Dotted lines have been drawn out from the quadruple points to indicate the origin of the boundary curves. With this preliminary information we are in a position to determine the ternary combinations and temperature relations existing in a part of the ternary system

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[1] Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce. Paper No. 13 of the Portland Cement Association Fellowship at the Bureau of Standards.

[2] Le Chatelier, *Compt. rend.*, **94**, 13 (1882).

[3] Shepherd, Rankin and Wright, *J. Ind. Eng. Chem.*, **3**, 211 (1911).

[4] Campbell, *J. Ind. Eng. Chem.*, **11**, 116 (1919).

[5] Rankin and Wright, *Am. J. Sci.*, **39**, 11 (1915).

[6] Sosman and Merwin, *J. Wash. Acad. Sci.*, **6**, 532 (1916).

[7] Abbreviated formulas are used in Fig. 5 to conserve space. These are as follows $C = CaO$; $A = Al_2O_3$; $F = Fe_2O_3$.

and the stability fields for calcium oxide and some of the binary and ternary compounds.

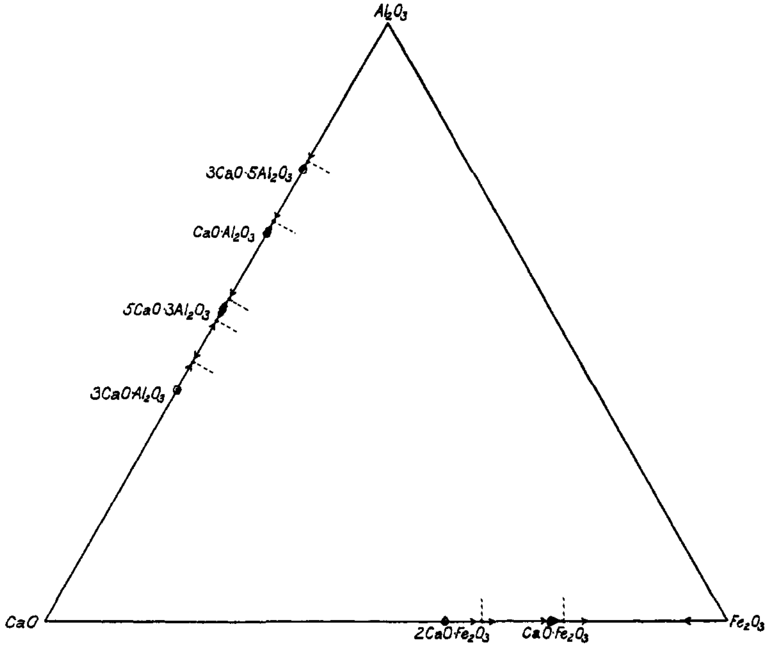

Fig. 1.—Compositions of the binary compounds and quadruple points projected on the ternary diagram.

The Ternary System

Experimental Procedure

The raw materials employed in this study consisted of precipitated calcium carbonate, alumina and ferric oxide.

Analyses of these materials are given in Table I.

TABLE I

ANALYSIS OF PURIFIED RAW MATERIALS[8]

	Calcium carbonate	Alumina	Ferric oxide
SiO_2	nil	0.01	...
Al_2O_3	0.08	98.50	...
Fe_2O_3	.01	0.002	99.15
FeO	...	...	nil
CaO	55.73	...	...
MgO	0.01	...	...
Alkalies	.04	...	...
CO_2	44.10	...	...
SO_3	trace	trace	nil
Cl	trace	trace	...
Loss on ignition	...	1.43	0.93

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[8] By H. C. Stecker.

The general principles involved in phase equilibria studies and the methods of experimentation have been very fully discussed by Rankin and Wright.[5]

The samples for study were prepared by mixing the finely powdered raw materials in a beaker with distilled water. These mixtures were placed on a hot-plate and stirred several times as evaporation proceeded to prevent segregation. When dry the mixtures were melted in platinum in an electric resistance furnace.[9] These melts of about 20 g. each were crushed in a steel mortar and ground in an agate mortar for use in the experiments described later.

Sosman and Hostetter[10] have shown that the dissociation of ferric oxide to ferro-ferric oxide increases with rise in temperature and time of heating. To minimize this dissociation as far as possible these preliminary samples were melted in an interval of about twenty minutes and at as low a temperature as possible. After a few samples had been studied the temperatures at which the others would melt could be estimated.

Crystallization was found to be very rapid in melts in this system, as it is in the $CaO-Fe_2O_3$[6] and $CaO-Fe_2O_3-SiO_2$[11] systems. Many of the melts obtained as described above crystallized completely so that their crystalline phases could be studied without additional treatment. Small charges of those that were not entirely crystallized were remelted in the quenching furnace[11] and cooled slowly to allow complete crystallization.

The crystalline phases were studied microscopically and their indices of refraction determined by the immersion method. The necessary high index media were prepared by the methods described by Larsen and Merwin[12] and by Brownmiller.[13]

Undercooled glasses could not be obtained by quenching melts in this system. It was necessary, therefore, to determine the melting relations by means of heating curves and to deduce the phase relations from the microscopic and heating curve data with the aid of the phase rule. This method is not so accurate nor so satisfactory as the quenching method, but it is believed that the phase relations reported herein are correct. Further work will be necessary to establish some of the boundary curves more exactly and to clear up other minor points in this part of the system.

Experimental Results

One ternary compound was found in the system $CaO-Al_2O_3-Fe_2O_3$. It has the oxide formula $4CaO.Al_2O_3.Fe_2O_3$ and the composition[14] CaO,

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[9] Hansen and Bogue, *Ind. Eng. Chem.*, **19**, 1260 (1927).

[10] Sosman and Hostetter, THIS JOURNAL, **38**, 1188 (1916).

[11] Hansen and Bogue, *ibid.*, **48**, 1261 (1926).

[12] Larsen and Merwin, *Am. J. Sci.*, **34**, 42 (1912).

[13] Brownmiller, *Am. Mineralogist*, **12**, 43 (1927).

[14] All compositions are given in percentage by weight.

46.1%; Al_2O_3, 21.0%; Fe_2O_3, 32.9%. It melts[15] congruently at 1415 ± 5°. This compound forms easily from the finely powdered components at temperatures well below its melting point. Its density[16] was found to be 3.77.

The optical properties of $4CaO.Al_2O_3.Fe_2O_3$ are as follows: biaxial, negative, with a medium optic axial angle. $\alpha_{Li} = 1.96 \pm .01$, $\beta_{Li} = 2.01 \pm .01$, $\gamma_{Li} = 2.04 \pm .01$. The indices for the yellow mercury line ($\lambda = 578$) are $\alpha = 1.98 \pm .01$, $\beta = 2.05 \pm .01$, $\gamma = 2.08 \pm .01$. Occasional polysynthetic twinning was observed. The compound often occurs as prismatic grains with extinction angle against the prismatic faces very small. Pleochroism γ = brown and α = yellow-brown.

$4CaO.Al_2O_3.Fe_2O_3$ and CaO form a eutectic mixture of the composition CaO, 56%; Al_2O_3, 17%; Fe_2O_3, 27%; which melts at 1395 ± 5°. A partial temperature-concentration diagram of this system is given in Fig. 2.

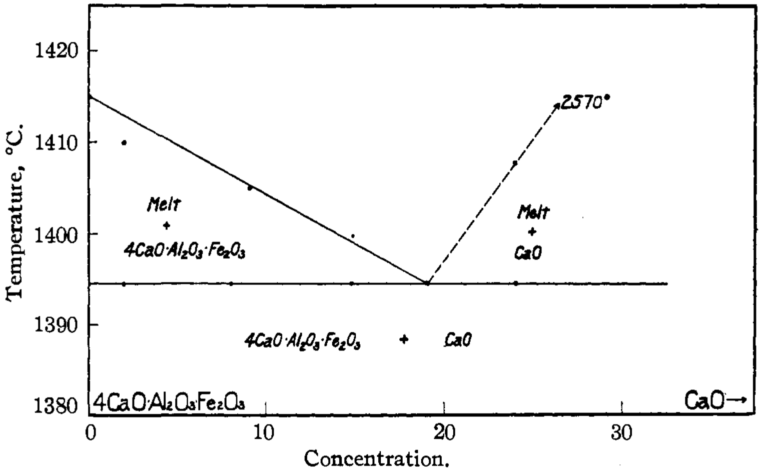

Fig. 2.—Partial temperature-concentration diagram of the system $4CaO.Al_2O_3.Fe_2O_3$-CaO.

$4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ form a complete series of solid solutions. The melting range of these solid solutions could not be determined from the heating curves. Only one distinct break was obtained on each of the heating curves. It appears, therefore, that the melting range of these solid solutions is very narrow, probably less than ten degrees. The temperatures of the observed thermal breaks are plotted against composition in Fig. 3. $2CaO.Fe_2O_3$ dissociates at 1435° into CaO and liquid. A thermal change was observed at this temperature in the heating curve obtained from the composition CaO, 41.5%; Al_2O_3, 1.5%; Fe_2O_3, 57.0% or $2CaO.Fe_2O_3$, 93% and $4CaO.Al_2O_3.Fe_2O_3$, 7%. This observation, in con-

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[15] All temperatures are given in centigrade degrees.

[16] Determined by Wm. Lerch using Le Chatelier's method, described in U. S. Bureau of Standards, *Circular 33*, 1917.

junction with the curve obtained in Fig. 3, indicates that CaO and solid solution are in equilibrium with liquid and vapor at 1435° in the above composition. That is, therefore, a quadruple invariant point. Charges of this composition were quenched from 1435° and examined microscopically for CaO. It was not possible, however, positively to identify CaO in those quenched charges.

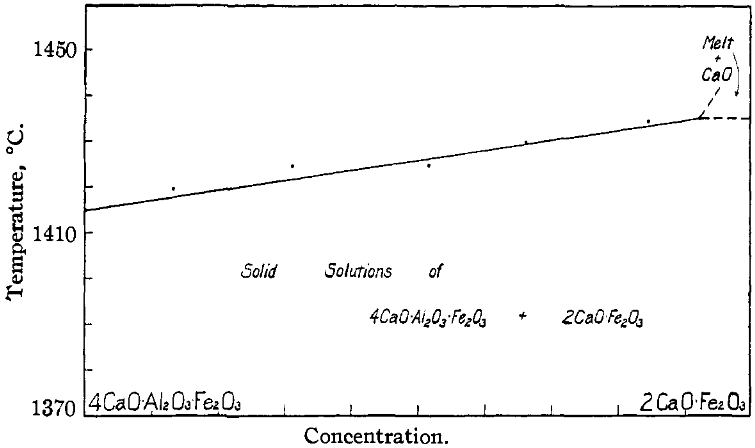

Fig. 3.—Temperature-concentration diagram showing the melting relations in the solid solution of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$.

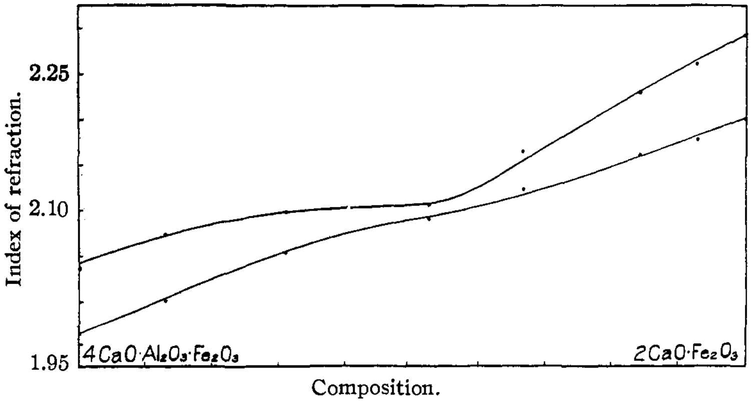

Fig. 4.—Indices of refraction of the solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ plotted against composition.

The α and γ indices of refraction of this series of solid solutions are shown graphically in Fig. 4. $2CaO.Fe_2O_3$ is biaxial, positive and $4CaO.Al_2O_3.Fe_2O_3$ is biaxial, negative. The solid solutions rich in $2CaO.Fe_2O_3$ are positive while those rich in $4CaO.Al_2O_3.Fe_2O_3$ are negative. The exact composition at which the character changes has not been determined.

In Fig. 5 there are shown the fields below the line $CaO.Al_2O_3$-$CaO.Fe_2O_3$ which were studied in this investigation. The region above that line has not been explored. The five fields below this line show the regions in which the various compounds and solid solutions occur as the final products of crystallization of melts of these compositions.

In Fig. 6 the fields are shown in which CaO, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and solid solutions occur as primary phases. The dots in that figure represent the compositions studied during the investigation.

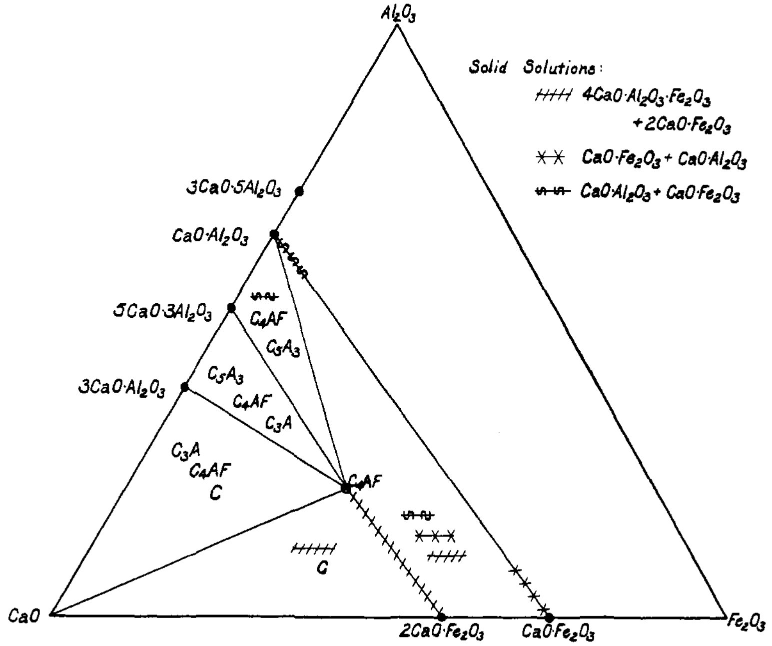

Fig. 5.—Diagram showing the final products of crystallization of melts in a portion of the ternary system CaO-Al_2O_3-Fe_2O_3.

The final melting temperatures of some of the compositions are given in that figure. These temperatures with those in the other figures are sufficient for the construction of a solid model of the liquidus surface of this portion of the system.

The two dashed lines (Fig. 6) radiating from the composition $4CaO.Al_2O_3.Fe_2O_3$ are not true boundary curves. A boundary curve is a line representing the compositions and temperatures at which two solid phases are in equilibrium with liquid and vapor. Since the compound $4CaO.Al_2O_3.Fe_2O_3$ forms a continuous series of solid solutions with $2CaO.Fe_2O_3$ there can be no boundary curve separating the fields in which $4CaO.Al_2O_3.Fe_2O_3$ and the solid solutions with $2CaO.Fe_2O_3$ separate as primary phases. It seems desirable, however, to indicate, in some manner, the compositions at which the primary phase changes from $4CaO.Al_2O_3.Fe_2O_3$ to a solid solution of $4CaO.Al_2O_3.Fe_2O_3$ with $2CaO.Fe_2O_3$.

The quintuple invariant point (Fig. 6) at which CaO, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, liquid and vapor are at equilibrium was found to have the composition CaO, 54%; Al_2O_3, 37%; Fe_2O_3, 9%; and to melt at 1345 ± 5°. If a line is drawn from $3CaO.Al_2O_3$ to $4CaO.Al_2O_3.Fe_2O_3$ in Fig. 6, as it is in Fig. 5, and the two figures are compared, it will be observed that CaO occurs as a primary phase in a part of the triangle $3CaO.Al_2O_3$—$4CaO.Al_2O_3.Fe_2O_3$—$5CaO.3Al_2O_3$. When crystallization is allowed to take place slowly in melts whose compositions fall within that triangle, the CaO combines with the liquid and disappears so that CaO is not a final product of crystallization in that field. It was found possible to quench the charges in which CaO occurs as the primary phase in this field and prevent its recombination. That made it possible to establish the quintuple point, referred to above, by both heating curves and quenches.

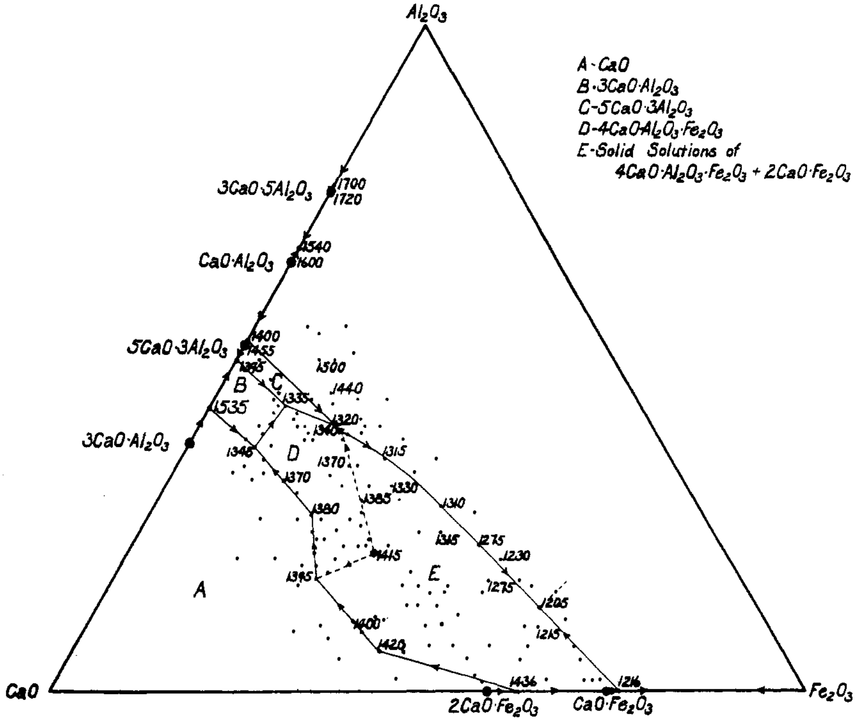

Fig. 6.—Diagram showing the fields in which CaO, $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$ and solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ + $2CaO.Fe_2O_3$ separate as primary phases. The dots represent the compositions studied.

$4CaO.Al_2O_3.Fe_2O_3$ and $5CaO.3Al_2O_3$ form a eutectic mixture of the composition CaO, 47%; Al_2O_3, 43%; Fe_2O_3, 10%; which melts at 1335 ± 5°. The temperature-concentration diagram of this system is given in Fig. 7.

The quintuple invariant point at which $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, liquid and vapor are at equilibrium appears to have very nearly the same composition and melting temperature as the binary eutectic of $5CaO.3Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$. Perhaps these two points can be differentiated when a greater number of samples are studied in the region of that point. This quintuple point, therefore, is given tentatively as CaO, 47%; Al_2O_3, 43%; Fe_2O_3, 10%; and 1355 ± 5°.

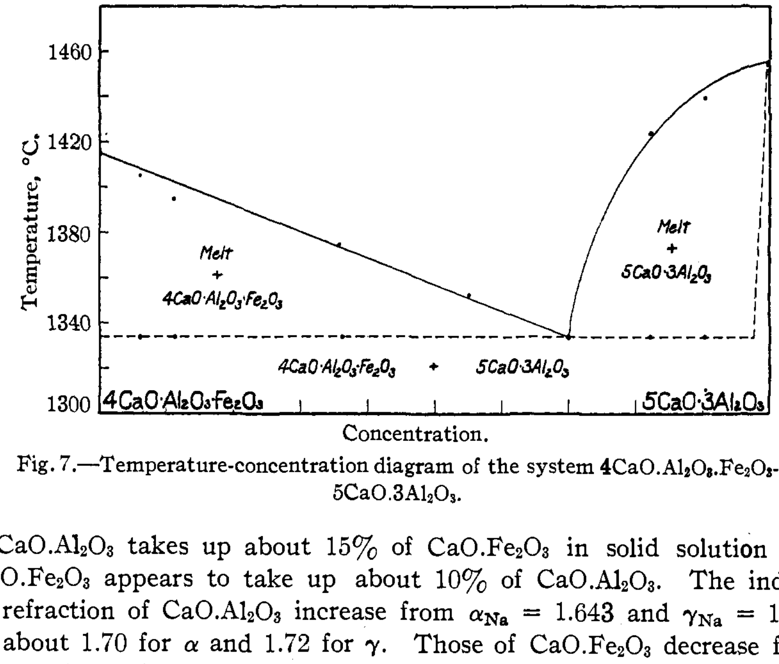

Fig. 7.—Temperature-concentration diagram of the system $4CaO.Al_2O_3.Fe_2O_3$-$5CaO.3Al_2O_3$.

$CaO.Al_2O_3$ takes up about 15% of $CaO.Fe_2O_3$ in solid solution and $CaO.Fe_2O_3$ appears to take up about 10% of $CaO.Al_2O_3$. The indices of refraction of $CaO.Al_2O_3$ increase from $\alpha_{Na} = 1.643$ and $\gamma_{Na} = 1.663$ to about 1.70 for α and 1.72 for γ. Those of $CaO.Fe_2O_3$ decrease from $\omega_{Li} = 2.465$ and ϵ_{Li} 2.345 to about 2.25 for ω and 2.13 for ϵ.

The melting relations existing between $CaO.Al_2O_3$ and $CaO.Fe_2O_3$ are shown in Fig. 8. It may be seen there that a eutectic mixture of the composition CaO, 28%; Al_2O_3, 13%; Fe_2O_3, 59% is formed. This mixture melts at 1205 ± 5°. This melting was observed in all of the samples within the four-sided figure (Fig. 5) $CaO.Al_2O_3$-$CaO.Fe_2O_3$-$2CaO.Fe_2O_3$.-$4CaO.Al_2O_3.Fe_2O_3$. In that region, when crystallization of the melts is completed, three crystalline phases are found. They are solid solutions of $CaO.Al_2O_3$ in $CaO.Fe_2O_3$, $CaO.Fe_2O_3$ in $CaO.Al_2O_3$ and $4CaO.Al_2O_3$.-Fe_2O_3 in $2CaO.Fe_2O_3$.

This point is, therefore, the quintuple invariant point at which the three solid solutions are in equilibrium with liquid and vapor. It would seem, therefore, that $CaO.Fe_2O_3$, which melts incongruently at 1216° into $2CaO.Fe_2O_3$ and liquid, in taking up $CaO.Al_2O_3$ in solid solution, has its incongruent melting point lowered to 1205 ± 5°. At this temperature this solid solution of $CaO.Al_2O_3$ in $CaO.Fe_2O_3$ dissociates into liquid and solid solutions of $2CaO.Fe_2O_3 + 4CaO.Al_2O_3.Fe_2O_3$.

Samples having compositions falling on the line $CaO.Al_2O_3$-$4CaO.Al_2O_2.Fe_2O_3$ (Fig. 5) do not consist of those two compounds at equilibrium. The $CaO.Al_2O_3$ takes up some $CaO.Fe_2O_3$ which raises its indices of refraction. In some of the samples, small amounts of $5CaO.3Al_2O_3$ were found. The phase that should correspond to $4CaO.Al_2O_3.Fe_2O_3$ had somewhat lower indices of refraction. This phase was found to have α about 1.95 and γ 2.04 for the mercury yellow light.

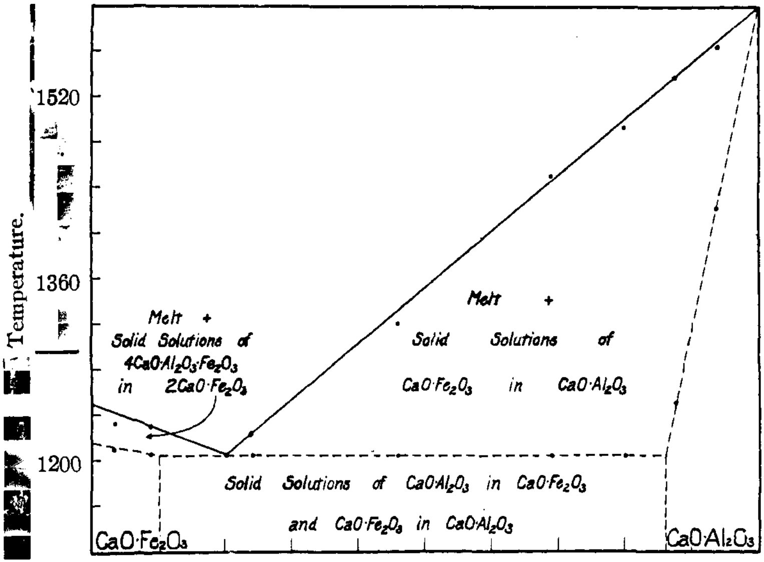

Fig. 8.—Diagram showing melting relations existing between $CaO.Fe_2O_3$ and $CaO.Al_2O_3$.

These results may be explained as follows. If $CaO.Al_2O_3$ takes up a certain amount of $CaO.Fe_2O_3$, the ratio of the remaining Al_2O_3 and CaO to the Fe_2O_3 is too great to form $4CaO.Al_2O_3.Fe_2O_3$ or its solid solutions with $2CaO.Fe_2O_3$. Therefore, some of the Al_2O_3 and CaO is combined as $5CaO.3Al_2O_3$. The other phase then is $4CaO.Al_2O_3.Fe_2O_3$ with a little $2CaO.Fe_2O_3$ in solution. From the lowered indices of refraction it would seem that $4CaO.Al_2O_3.Fe_2O_3$ and its solid solutions with $2CaO.Fe_2O_3$ are capable of taking up very small amounts of $CaO.Al_2O_3$ in solid solution. Therefore, in Fig. 5, the line $CaO.Al_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$ should be drawn from $CaO.Al_2O_2$ to some point on the solid solution line of 4CaO.-

$Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$. The exact course of this line has not been established and is therefore shown as ending at $4CaO.Al_2O_3.Fe_2O_3$.

The indices of refraction of $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ are raised slightly in this system. Values as high as 1.735 were found for $3CaO.Al_2O_3$ and 1.720 for $5CaO.3Al_2O_3$.

None of the binary compounds of CaO with Al_2O_3 and Fe_2O_3 are found as the pure compounds within the ternary system as shown by their optical properties. The exact amount and nature of all of the solid solutions formed within this system have not been fully determined.

The compositions and melting temperatures of the quadruple and quintuple points found in this ternary system are given in Table II.

Table II

Quadruple and Quintuple Points in the System $CaO-Al_2O_3-Fe_2O_3$

Crystalline phases	Composition, weight percentage CaO	Al_2O_3	Fe_2O_3	Temp., °C.
Quadruple Points				
CaO, $4CaO.Al_2O_3.Fe_2O_3$	56	17	26	1395 ± 5
CaO, solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ + $2CaO.Fe_2O_3$	41.5	1.5	57.0	1435 ± 5
Quintuple Points				
CaO, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$	54	37	9	1345 ± 5
$3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, $5CaO.3Al_2O_3$	47	43	10	1335 ± 5
$4CaO.Al_2O_3.Fe_2O_3$, $5CaO.3Al_2O_3$, solid solutions of $CaO.Al_2O_3$ + $CaO.Fe_2O_3$	42	40	18	1320 ± 5
Solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ + $2CaO.Fe_2O_3$, $CaO.Al_2O_3$ + $CaO.Fe_2O_3$, $CaO.Fe_2O_3$ + $CaO.Al_2O_3$	28	13	59	1205 ± 5

In this paper the experimental results obtained in the system $CaO-Al_2O_3-Fe_2O_3$ have been presented. The application of these findings to the problem of the constitution of portland cement will be presented in another paper.

The authors take pleasure in expressing their appreciation to Dr. Herbert Insley of the Bureau of Standards for advice and assistance in the microscopical studies.

Summary

A part of the $CaO-Al_2O_3-Fe_2O_3$ system has been studied. One ternary compound of the composition $4CaO.Al_2O_3.Fe_2O_3$ was found in this part of the system. Its melting point and optical properties have been determined.

$2CaO.Fe_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$ form a complete series of solid solutions. The melting relations and optical properties of these solutions are given.

$CaO.Al_2O_3$ and $CaO.Fe_2O_3$ form limited solid solutions with each other.

$3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ have higher indices of refraction than they have in the binary system.

The fields in which CaO, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ separate as primary phases from these ternary melts are shown diagrammatically.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 21]

A RESISTANCE WIRE TO BE USED IN THE CHEMICAL LABORATORY

BY JEAN PICCARD

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Resistance coils which must have a perfectly constant resistance are always made of constantan (identical with ideal) or of manganin, as the resistances of both alloys are nearly independent of the temperature. These wires corrode easily. Nevertheless, the bad surface quality due to this corrosion causes no inconvenience since the whole coil is protected by paraffin. The very low thermoelectric force of manganin against copper renders its use almost imperative whenever direct current is involved. The somewhat better surface qualities of constantan are more than offset by its exceptionally high thermoelectric force against copper.

If, however, a measuring wire with slide contact is needed, as in the Wheatstone Bridge, then one faces an entirely different problem. One does not need in this case the very low temperature coefficient of the resistance because the different parts of the wire have nearly the same temperature, but one needs a wire with a bright surface which is not attacked either by the air or by the acid fumes of the laboratory. For this reason many authors favor the use of platinum wire. Its surface remains always perfectly clean, but its electric resistance has too high a temperature coefficient. It increases by 30 to 40% if the temperature rises from 0 to 100°, so that even the small changes of temperature which one produces when moving the contact slide with the hand have a noticeable effect on the position of the zero point.

The best resistance wire for Wheatstone Bridges, which, on request, was offered by Hereus for the use in the chemical laboratory, is platin-iridium. Apart from its very high price, however, it still has too high a temperature coefficient. An American company which manufactures resistance wires as a specialty was also unable to make us any satisfactory offer.

The question arose as to whether one could not replace the copper in constantan (60% Cu + 40% Ni) by the more noble metals of the same group, silver or gold. Since the jewelers recently began to use nickel-