# ON LIQUID IMMISCIBILITY IN THE SYSTEM $FeO\text{-}Fe_2O_3\text{-}Al_2O_3\text{-}SiO_2$.

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In an earlier paper[1] it was shown that a number of oxides are but partially miscible in the liquid state with silica. Siliceous mixtures of these oxides with silica form two liquids on melting. On the other hand there are certain oxides, notably alumina, soda, and potash, which do not exhibit this behavior. Moreover, the introduction of a small amount of one of these latter oxides is sufficient to cause a mixture, which would otherwise form two liquids, to melt to a single homogeneous liquid. It was shown that the compositions of igneous rocks could not be accounted for by the compositions of the immiscible liquids so formed. All the important rock-forming oxides with the exception of $Fe_2O_3$ were considered in that paper, namely, CaO, MgO, FeO, $Al_2O_3$, $Na_2O$, $K_2O$, $SiO_2$.

Since then the work has been extended to include mixtures of iron oxide and silica with a ferrous: ferric ratio of about one to one. The effect of the addition of alumina has also been determined. The results show that the equilibrium conditions here are similar to those in the other systems studied. Like the earlier work, this gives no support to the hypothesis that the differentiation observed in igneous rocks has come about through the splitting of a magma into immiscible liquids.

## IMMISCIBILITY IN THE SYSTEM $FeO\text{-}Fe_2O_3\text{-}SiO_2$.

If an appropriate mixture of iron oxide and silica is heated until melted two immiscible liquids result. Generally, when such a mixture is heated so that equilibrium is maintained, there is a short temperature interval through which cristobalite is in equilibrium with two liquids. The incomplete equilibrium diagram for a portion of the system $FeO\text{-}Fe_2O_3\text{-}SiO_2$, Fig. 1, has been drawn from data presented later. This is a projection of part of the fusion surface of silica on to the base of the solid temperature-concentration model.

In the field labeled "Cristobalite, Liquid A" and in that

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[1] Greig, J. W., Immiscibility in silicate melts, this Journal, 13, 1-44, 133-154, 1927.

labeled "Cristobalite, Liquid B" each point represents equilibrium between cristobalite and a liquid whose composition is given by the coördinates of the point. Each point in the field labeled "Cristobalite, Liquids A and B" represents equilibrium between cristobalite and two liquids the total composition of which is given by the point, and the actual compositions by the extremities of the tie line passing through the point. Two tie lines are shown. Mixtures with compositions represented by points within this field form two liquids when just melted: others form only one. Each of these points corresponds of course to a definite temperature which would ordinarily be indicated by isothermal lines on the diagram. In this case sufficient data to warrant the drawing of isotherms have not been obtained. Temperatures are indicated by numbers, and the directions of falling temperature by arrows. It will be seen that the surface slopes downward from the melting point

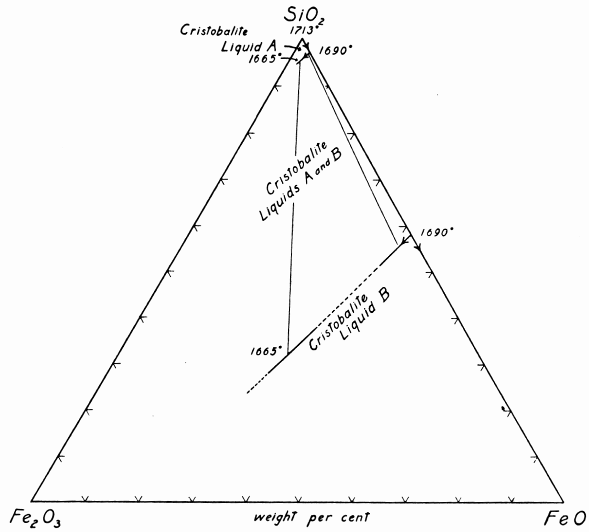

Fig. 1. Incomplete equilibrium diagram for the field of cristobalite in the system $FeO$-$Fe_2O_3$-$SiO_2$. This is a projection onto the base of the solid temperature-concentration model. The arrows indicate the direction of falling temperature. Points on the surface represent equilibrium between cristobalite and either one or two liquids as indicated. The light lines, crossing the field representing equilibrium between cristobalite and two liquids, are tie lines; two only are shown. The ends of tie lines indicate the compositions of pairs of liquids which are in equilibrium with cristobalite at the temperatures corresponding to the lines.

of cristobalite to the boundary of the field labeled "Cristobalite, Liquids A and B." The surface of this field is that generated by a straight line, parallel to the base, which moves from the $FeO$-$SiO_2$ side across the diagram, rotating as it goes so that in each position it is a tie line. The fusion surface of cristobalite in the field labeled "Cristobalite, Liquid B" falls very steeply again from the boundary of the field representing equilibrium with two liquids.

The data used to construct the equilibrium diagram were obtained as follows: To find the compositions of the two liquids, mixtures were heated to a temperature just above that of complete melting, held for a time sufficient to allow the liquids partially to segregate and then quenched by plunging under water and holding there until cold. This quenching is essential to avoid change in the state of oxidation during cooling.

The liquid richer in iron oxide is also much more fluid, and it collects rapidly into small globules and irregular shaped masses which are quite free from the other liquid, so that, after quenching and crushing the charge, this segregated material may be separated for analysis. This was picked out by hand when the segregation had been sufficient. As a check on the composition of this material several separations were also carried out to collect the minute globules which remained distributed through the siliceous liquid and consequently in intimate contact with it. This was done by the aid of a powerful electromagnet acting on the finely ground charge which was kept stirred up in alcohol. As such separations were never complete the amount of the siliceous phase was estimated under the microscope in order to use the material as a check.

The more siliceous phase was obtained by separation with the electromagnet and also by making up mixtures with decreasing amounts of iron oxide until they melted to a homogeneous liquid.

The compositions of the materials so prepared were found by analysis. $FeO$ was determined by a modified Pratt method.[2] Total iron was determined by titrating with permanganate after reduction with hydrogen sulphide. In several cases it was also determined gravimetrically. $SiO_2$ was found by difference. The results of analyses are listed in Table I. A

[2] Hillebrand, W. F., The analyses of silicate and carbonate rocks, U. S. G. S. Bull. 700, p. 203.

TABLE I.

A

| | | Analysis | | | FeO as oxalate | | Charge before heating | | Crucible[1] | Furnace[2] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | FeO | $Fe_2O_3$ | $SiO_2$ | $Al_2O_3$ | | $Fe_2O_3$ | $SiO_2$ | $Al_2O_3$ | | | |
| 1 | 2.94 | 0.13 | 86.8 | | 2.7 | | 96.3 | | S | S.C. | Almost entirely one glass |
| 2 | 2.38 | 2.05 | 95.6 | | | 40 | 60 | | P | S.C. | Perfect separation |
| 3 | 2.43 | 2.81 | 94.8 | | | 5 | 95 | | S | E | Not separated |
| 4 | 41.3 | 3.4 | 55.3 | | 38 | | 62 | | S | S.C. | Good separation |
| 5 | 40.8 | 6.3 | 52.9 | | | 31 | 69 | | P | M | Perfect separation |
| 6 | 38.7 | 7.0 | 54.3 | | | 31 | 69 | | P | M | Poor separation; around per cent siliceous phase |
| 7 | 31.4 | 35.5 | 33.1 | | | 50 | 50 | | P | E | Good separation |
| 8 | 31.7 | 36.7 | 31.6 | | | 44 | 56 | | P | S.C. | Excellent separation |
| 9 | 29.7 | 34.2 | 36.1 | | | 40 | 60 | | S | E | Around 5 per cent of si ceous phase |
| 10 | 29.6 | 34.6 | 35.8 | | | 40 | 60 | | P | E | Over 5 per cent of siliceo phase |
| 11 | 7.3 | 8.1 | 84.6 | | | 44 | 56 | | P | S.C. | A mixture, part of same r as 8 |

Analyses 2, 10, and also 8, 11 are of different parts of same charge and so determine tie lines.

B

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 8.5 | 6.2 | 80.3 | 5.0 | | 15.7 | 79.3 | 5 | P | E | 1 liquid |
| 13 | 15.3 | 15.0 | 59.7 | 10.0 | | 31.3 | 58.9 | 9.8 | P | E | 1 liquid |
| 14 | 16.4 | 15.1 | 61.4 | 7.0 | | 32.8 | 60.3 | 6.9 | P | E | 1 liquid |
| 15 | 16.5 | 15.7 | 61.8 | 6.0 | | 33.2 | 60.9 | 5.9 | P | E | 2 liquids, not separated |
| 16 | 16.9 | 16.5 | 61.7 | 4.9 | | 34.1 | 61.0 | 4.9 | P | E | 2 liquids, not separated |
| 17 | 24.2 | 31.7 | 40.1 | 4.0 | | 52.3 | 43.7 | 4.0 | P | E | Analysis of separated iron rich phase |
| 18 | 17.7 | 1.7 | 77.5 | 3.1 | | 22 | 75 | 3 | P | M | 1 liquid |
| 19 | 18.0 | 2.2 | 75.7 | 4.1 | | 22 | 74 | 4 | P | M | 1 liquid |
| 20 | 19.9 | 0.8 | 77.2 | 2.06 | | 22 | 76 | 2 | P | M | 2 liquids, not separated |

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[1] S = silica glass. P = platinum.

[2] E = electric furnace, either iridium or platinum-rhodium
S.C. = Surface Combustion gas furnace
M = Meker gas furnace.

*Purity of Materials used in Mixtures*

Silica: ground quartz, residue after evaporation with hydrofluoric and sulphuric acids ar subsequent treatment with ammonium carbonate = 0.0056 gram from a 10 gram sample.

Ferric oxide: Merck's Oxide, total impurities other than volatile <0.1 per cent. (R. B. Sosman, J. C. Hostetter, J. Am. Chem. Soc., 38, 812, 1916.)

Alumina: $Na_2O$, 0.15 per cent; $K_2O$, 0.09 per cent.

and also shown graphically by the diagram, Fig. 2. The numbers indicating the materials are the same in both table and diagram.

The charges were made up for the most part from pure ferric oxide and pure quartz, both finely ground. In a few cases ferrous oxalate was used instead of ferric oxide. The crucibles used in most of the runs were platinum. Analyses of the charges for platinum showed that some platinum was dissolved by the melt but in no case did it amount to 0.1 per cent. In a few heats silica glass crucibles were used.

The state of oxidation of the iron of any mixture at equilibrium is determined by the temperature and the oxygen pressure of the atmosphere in contact with the charge. Since no furnace was available in which the atmosphere could be controlled it was not possible to work at a range of oxygen pressures. Instead heats were made in an open electric furnace in which the oxygen pressure was that of the air, and in two gas furnaces, a Meker and a Surface Combustion furnace. In this way two general states of oxidation were obtained.

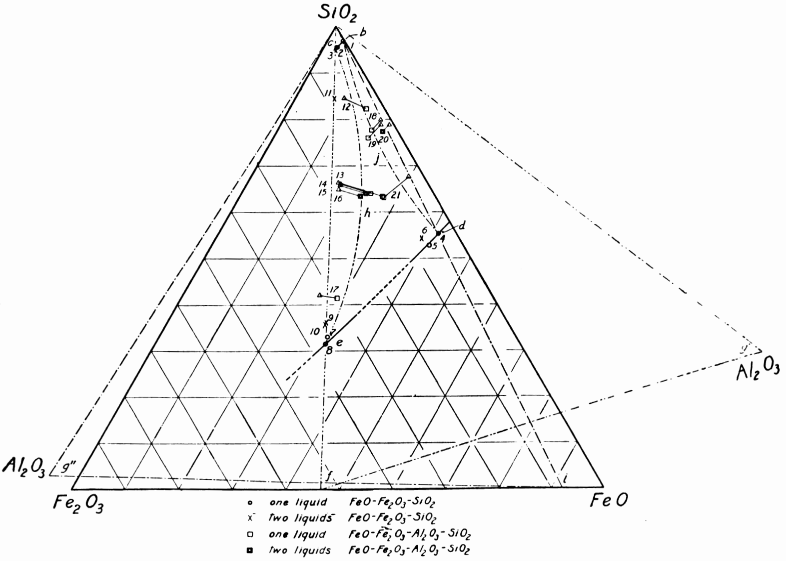

Fig. 2. Diagram showing graphically the compositions of materials analyzed and listed in Table I.

It is desirable that the equilibrium be determined at some ferrous: ferric ratio intermediate between these two. It will be some time before this is done. In the meantime we can only interpolate.

The temperature of the equilibrium between cristobalite and two liquids was found, for runs made in the electric furnace, by observing the temperature of melting of mixtures, measurements being made with an optical pyrometer. The charges were slowly brought to a definite temperature, held there, and after quenching examined to see whether or not they had melted. This temperature was checked by measurements with a thermocouple and potentiometer.

TABLE II.

| | Charge | | | |
|---|---|---|---|---|
| FeO | $Fe_2O_3$ | $SiO_2$ | $Al_2O_3$ | Temperatures determined in electric furnace open to air. |
| 16.4 | 15.1 | 61.4 | 7 | 1597° ± 10° temp. of complete melting. Thermocouple. |
| | 31 | 69 | | 1665° ± 10° temp. of complete melting. Thermocouple. |
| | 65 | 35 | | 1660° ± 10° 2 liquids + cristobalite in equilibrium. Optical pyrometer. |
| | 50 | 50 | | 1665° ± 10° 2 liquids + cristobalite in equilibrium. Optical pyrometer. |

State of oxidation of the last three charges at temperature of the runs given by diagram, Fig. 2. See also Table I, A.

Temperature of complete melting of mixtures forming 2 liquids with high ferrous: ferric ratio 1689° ± 10°. See text.

All temperatures referred to the following fixed points: Gold 1062.6° ± 0.8°; Palladium 1549.5° ± 2°; Platinum 1755° ± 5°.*

* Day, A. L., Sosman, R. B., and Allen, E. T., Carnegie Inst. Washington, Publication No. 157, 1911.

The temperature of melting of mixtures in which the iron was largely in the ferrous state was not determined as closely as that for melting in air. The method employed was to place small charges of ferrous oxalate and silica contained in platinum foil envelopes, together with similar charges of mixtures of $15CaO, 85SiO_2$ and $15BaO, 85SiO_2$, inside a small porcelain crucible and heat them in a Surface Combustion furnace, observing the temperature with an optical pyrometer. It was found that such charges melted at a temperature between the melting temperatures of the control mixtures, 1698° and 1679°,[3] that is, at 1689° ± 10°. A similar charge of ferric oxide and silica run with these was found to melt at a temperature lower than that of the ferrous oxalate silica mixture and also slightly below the $15BaO,85SiO_2$ charge.

The data are collected in Table II.

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[3] Greig, J. W., op. cit.

From these results it is possible to extrapolate to the binary system $FeO$-$SiO_2$ with fair certainty. The limits of immiscibility in that system are thus found to be $3FeO, 97SiO_2$ and $42FeO,58SiO_2$.[4] Since the increase in the temperature of equilibrium of cristobalite with two liquids is but slight for a small increase in the ferrous: ferric ratio, the temperature of this equilibrium in the binary system is placed at 1690° ± 10°.

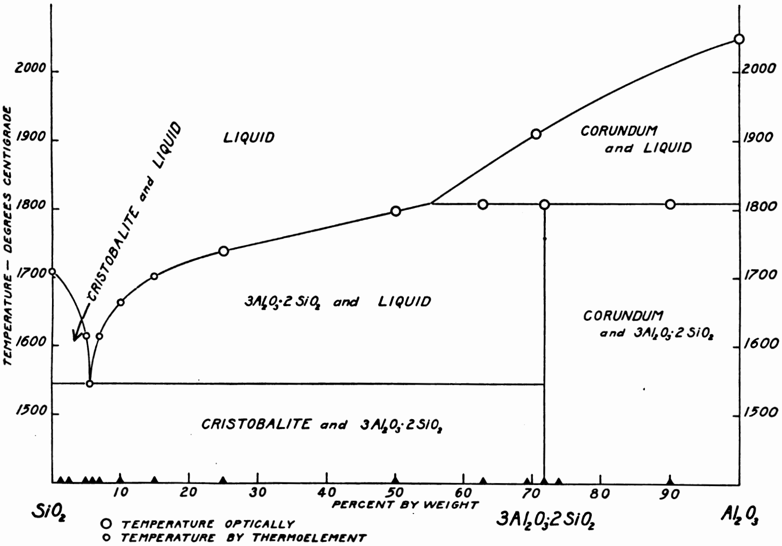

Fig. 3. Equilibrium diagram for the system $Al_2O_3$-$SiO_2$. (Bowen, N. L., and Greig, J. W., The system $Al_2O_3$-$SiO_2$; J. Am. Ceram. Soc., 238-54, 1924.)

## EFFECT OF ALUMINA.

When any mixture of alumina and silica is melted a single liquid results. (See Fig. 3.) The addition, therefore, of a certain proportion of alumina to mixtures of silica and some other oxide, which when melted form two liquids, will cause them to melt to single liquids. In the earlier paper[5] it was shown that for mixtures of silica with lime or magnesia only a small percentage of alumina was necessary to produce this result, which was accompanied by a marked lowering of the temperature of complete melting.

[4] In the earlier paper this was tentatively placed at $40FeO,60SiO_2$.

[5] Greig, J. W., op. cit.

The work described below was done to obtain some knowledge of the limits of immiscibility and of the temperatures of the equilibria between cristobalite and two liquids in the quaternary system $FeO$-$Fe_2O_3$-$Al_2O_3$-$SiO_2$. Equilibrium in such a system is expressible graphically in a regular tetrahedron. Consider such a tetrahedron resting on one face, the corners of which correspond to pure $SiO_2$, pure $Fe_2O_3$ and pure FeO, and with the apex corresponding to pure $Al_2O_3$.

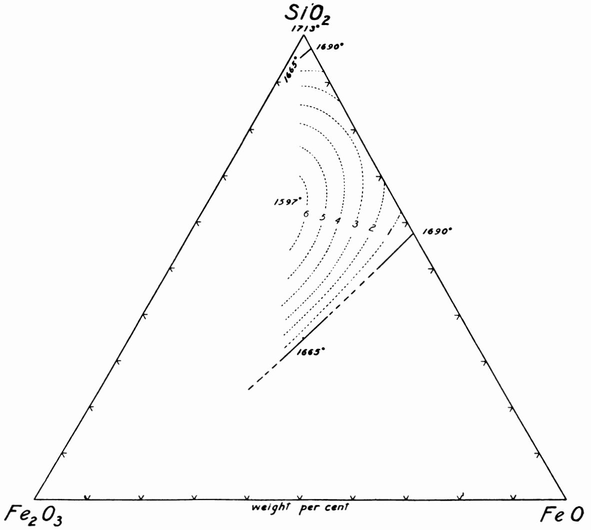

Fig. 4. Portion of the equilibrium diagram for the system $FeO$-$Fe_2O_3$-$Al_2O_3$-$SiO_2$. This is a projection of the curved surface bounding that portion of the tetrahedron which represents mixtures that form two liquids on melting. That apex of the tetrahedron which corresponds to pure $Al_2O_3$ is the pole of projection: the projection is onto the opposite face. The dotted lines are the projections of the intersections of the above surface with planes corresponding to 1, 2, 3, etc., per cent $Al_2O_3$; the numbers indicate the percentage of $Al_2O_3$. Projections of isothermal surfaces are not shown, but the temperatures of equilibrium of cristobalite with liquid are indicated by numbers for several compositions on the curved bounding surface.

Now imagine planes passed through it parallel to the base corresponding to 1, 2, 3, etc. per cent $Al_2O_3$. The compositions, which when melted form two liquids, are represented by points lying between the base and a curved surface that cuts the base along lines representing the limits of immiscibility in the ternary system $FeO$-$Fe_2O_3$-$SiO_2$ and that intersects the planes of 1, 2, 3, etc. per cent of $Al_2O_3$ in curved lines. If now such a surface is viewed with the eye at the apex of the tetrahedron corresponding to pure $Al_2O_3$, or if these lines of intersection are projected onto the base with the apex of the tetrahedron as the pole of projection, the diagram of Fig. 4 results. The compositions of mixtures which give a single liquid on melting are represented by points above or on this surface. The compositions of the pairs of liquids which can exist in equilibrium with cristobalite are represented by pairs of points on this surface.

To completely express the equilibrium up to the temperature of complete melting it would be necessary to construct the projections of the isothermal surfaces, i.e. surfaces which join the points representing the compositions of all liquids which are in equilibrium with cristobalite at the same temperature, and also to construct the projections of the tie lines or lines joining conjugate liquids. No tie lines except those in the ternary system $FeO$-$Fe_2O_3$-$SiO_2$ have been determined: nor have sufficient temperature determinations been made to warrant the construction of the isothermal surfaces. The temperatures which have been determined are indicated. These are at the projections of the intersections of the corresponding isothermal surfaces with the curved surface that defines the limits of immiscibility at the temperature of complete melting.

The data used to construct Fig. 4 were obtained as follows: Mixtures of ferric oxide, alumina and quartz were weighed out and heated in either a gas or electric furnace after which they were ground and the process repeated. They were then heated until just melted, quenched, and examined under the microscope to see whether one or two liquids were formed. The temperature control was by means of an optical pyrometer. The mixtures were then analyzed for ferrous and total iron and for alumina. These data are listed in Table I, B. The temperature of the liquidus in the case of the mixture 16.4 $FeO$, 15.1 $Fe_2O_3$, 7.0 $Al_2O_3$, 61.4 $Si_2$ was determined by means of a thermocouple and potentiometer.

In order to show graphically the compositions of the various mixtures investigated, the diagram, Fig. 2, had been constructed. Through the points within the tetrahedron, representing the compositions of the mixtures as found by analysis, lines are projected from the apex of tetrahedron onto the base. The projections are indicated by small triangles. The plane, containing the point representing the composition, the projection of the point on the base, and the edge of the tetrahedron representing mixtures of $SiO_2$ and $Al_2O_3$, is then rotated onto the plane of the base about the line joining the projection of the point and the corner $SiO_2$. The new position of the point is indicated by a square which is joined to the projection of the point by a straight line, the length of which is a measure of the proportion of alumina. The curved surface bounding those compositions which melt to two liquids must intersect the base along the lines *bc* and *de* and pass above the points representing mixtures that melt to two liquids, and below those representing mixtures which form a single liquid on melting. If a plane be passed through the apex of the tetrahedron and the line *cef* it will cut this curved surface. If now this plane be rotated about the line *cef* to the position *g′cef* the trace of the curved surface on this plane is given by the line *che*. Similarly the trace of this surface, on a plane through the apex of the tetrahedron and the line *bdi* and rotated to the position *g″bdi* in the plane of the base, is given by the line *bjd*.

## DISCUSSION AND APPLICATIONS.

Mixtures of silica and iron oxide with a ferrous:ferric ratio of about 1 : 1 have a greater range of immiscibility than has been found in any other case. This, however, does not show the extent of immiscibility in the system $Fe_2O_3$-$SiO_2$ nor indeed that immiscibility occurs there at all. Even to approach such compositions at these temperatures a high oxygen pressure would be necessary. It would seem, however, that equilibrium at high oxygen pressures and high temperatures can be of little or no importance in geological problems.

It has been found that the amount of alumina necessary to cause a single liquid to result from the melting of the mixtures varies with the silica content and with the ferrous-ferric ratio; a maximum of 6½ per cent being necessary in the case of a ferrous:ferric ratio of about unity. In the earlier work the effect of soda and potash on mixtures which form two liquids was investigated. Approximately half as much soda as alumina was found necessary to cause a single liquid to result from the melting of such mixtures. Potash was found to be similar to soda. Presumably the same would be true of their addition to mixtures of silica and iron oxide. This has, however, not been experimentally studied.

In the earlier paper the relationship of the compositions of igneous rocks to the compositions of the two liquids formed by various oxide mixtures was considered, and it was found that the compositions of igneous rocks, even in the extreme cases, were such as could not be accounted for by the compositions of these liquids. This work has added information as to the compositions of mixtures which may be expected to form two liquids when iron oxide is an important constituent. Here again the introduction of alumina, to say nothing of alkalies, in such quantities as are found in igneous rocks results in the formation of only one liquid on melting. No support therefore is found for the hypothesis of the differentiation of magmas by splitting into immiscible liquids.

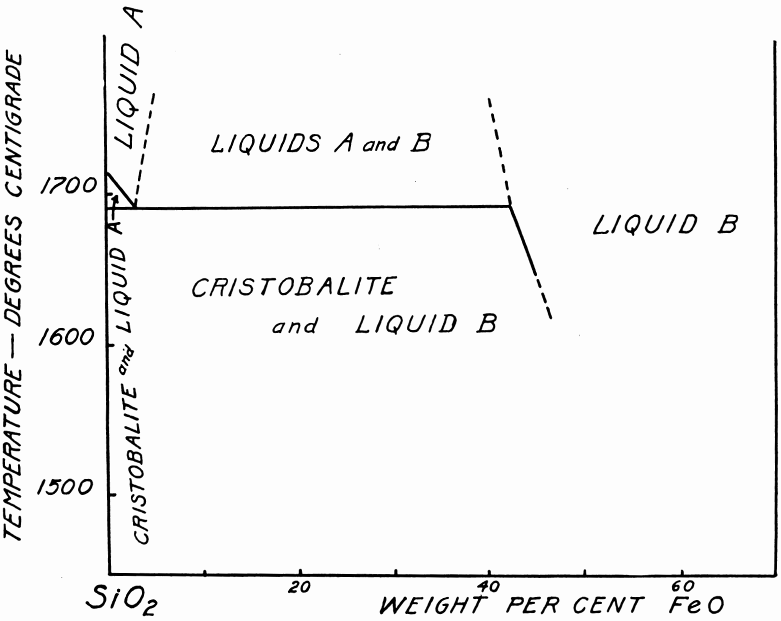

Fig. 5. Equilibrium diagram for a portion of the system $FeO$-$SiO_2$.

The silica brick from which the roofs of open hearth steel furnaces are built take up iron oxide in use. At the same time the original lime and alumina, in the form of a siliceous liquid, migrate between the grains of silica toward the cooler portions of the brick in front of an advancing liquid high in iron oxide.

The brick thus becomes zoned, with a composition and structure corresponding to the original brick at the outside, followed by a zone in which there is a concentration of lime and alumina, and then by a part much higher in iron oxide. In the acid furnace this iron oxide commonly amounts to between 20 and 25 per cent.

Tests have shown that the temperatures of melting of the parts high in iron oxides are not far below those of the original brick and are often higher than those of the much more siliceous portions in which the alumina has concentrated.

This may at first thought be a rather surprising state of affairs. It is, however, readily understood in the light of the equilibrium studies outlined above. Suppose the brick to have a ferrous:ferric ratio of 1 : 1. Analyses give a much lower ratio but they are made on brick that have been very slowly cooled in air and certainly oxidized. A mixture of silica and iron oxides with this ratio containing 65 per cent of iron oxide is completely liquid only at 1665.° Any other mixture up to 95 per cent silica with the same ferrous: ferric ratio is completely melted at the same temperature. If the mixture were 75 per cent silica the ratio of crystals to liquid would be 40 to 25 immediately below that temperature, and at lower temperatures still greater. The introduction of alumina, however, rapidly lowers the temperature of complete melting, and, since the composition of the liquid in equilibrium with cristobalite becomes at the same time rapidly more siliceous, the ratio of crystals to liquid is very much lowered at any given temperature. Since it is this ratio that determines whether or not the brick will stand, the behavior of the brick is seen to be exactly what is to be expected from the conditions of equilibrium.

It may be worth while to draw attention to the fact that the addition of iron oxide to a mixture of silica and alumina may raise the temperature of complete melting. As an example consider the mixture $Al_2O_3$ 5.5, $SiO_2$ 94.5 which is completely liquid at 1545° (see Fig. 3). To this add iron oxide and heat so as to form a mixture FeO 17.8, $Fe_2O_3$ 17.8, $Al_2O_3$ 3.54, $SiO_2$ 60.8. From the diagram, Fig. 4, it is readily seen that such a mixture will become liquid (2 liquids) at some temperature well above 1597°, probably about 1625°.

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