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THE SYSTEM, FeO-SiO_2.

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INTRODUCTION.

Of the various oxides that enter into the constitution of the silicate compounds of rocks the iron oxides are exceeded in abundance only by alumina and, of course, by silica itself. In studies of silicates designed to throw light upon the formation of rocks it is, therefore, of great importance to include those having iron as a significant constituent.

Silicates of Al_2O_3, CaO, Na_2O, MgO, and K_2O, to mention only the more abundant rock-forming oxides, have already been the subject of numerous investigations at the Geophysical Laboratory. Various attempts have been made during the course of this work to obtain data for the iron silicates that would have value comparable with those obtained for other silicates but these have not, for the most part, met with success. The difficulty is, of course, the controlling and defining the state of oxidation of iron. Some silicate systems in which the iron was kept entirely or almost entirely in the ferric state have proved amenable to accurate treatment,[1] but for studies concerned with the problems of the igneous rocks silicates bearing ferrous iron have, on the whole, a notably greater importance. Fundamental to all such silicates is, of course, the system, FeO-SiO_2, itself and its investigation may therefore be regarded as a natural, perhaps even a necessary, preliminary to the study of more complex related systems.

In addition, a knowledge of this simple system is of considerable industrial importance. In non-ferrous metallurgy the slags commonly employed are made up dominantly of FeO and SiO_2 with CaO as the principal other constituent, perhaps the nearest approach to our system being attained in copper converter slags. In ferrous metallurgy, the preliminary production of pig iron in the blast furnace is carried out in such a way as to reduce the losses of iron in the slag to a

[1] Bowen, Schairer, and Willems, this Journal, 20, 405-455, 1930.

minimum, but in the subsequent processes of refining to which the pig iron is subjected many of the slags produced are rich in FeO, indeed, some of them may be returned to the blast furnace. In such processes as the puddling of pig to produce wrought iron, and the acid open-hearth production of steel the slags frequently show a reasonably close approach to a binary constitution represented in the system, FeO-SiO_2. It is not surprising, therefore, that metallurgists have displayed much interest in this system; indeed, all previously published studies of it have been made by investigators primarily concerned with the application of their results to metallurgical problems. An exception is the work of Greig of this Laboratory, who discovered and partly delimited the two-liquid region existing at high temperatures.

EXPERIMENTAL METHODS.

In earlier studies of ferrous silicates at this Laboratory various methods have been employed, the principal method, perhaps, being one that involved the use of a vacuum furnace.[2] In this furnace it was possible under favorable conditions to reduce the air pressure to 0.0004 mm. of mercury and therefore the oxygen pressure to 1/5 that amount. Even with this seemingly low pressure of oxygen a large proportion of the iron of silicate melts remains in the ferric state. In the case of mixtures containing iron oxide (nearly all ferrous) and silica only, for example, one is thoroughly disappointed if he heats them in this furnace in a platinum crucible in the hope that the iron will remain largely in the ferrous state. From the great majority of such mixtures the product consists, as a matter of fact, mainly of magnetite and cristobalite with no more than a little liquid even at temperatures approaching 1500°. The atmosphere is plainly much too strongly oxidizing for the production of ferrous silicates or even a reasonably close approach to such compositions. At the same time the thermal behavior of the mixtures is wholly at variance with that exhibited by those in which the iron is nearly all ferrous.

In view of the above experience we sought a method by which the iron could be actively reduced to the ferrous condition. The use of a reducing atmosphere was not regarded favorably on account of the danger of reduction of an indefi-

[2] Sosman and Hostetter, J. Wash. Acad. Sci., **5**, 277-285, 1915.

nite proportion of the iron to the metallic state with consequent loss of control over the composition of the charge. We accordingly resorted to the use of an iron crucible in a "neutral" atmosphere, expecting the metallic iron to keep the iron of the melt in the ferrous state.

To obtain a "neutral" atmosphere a slow stream of nitrogen was passed through the furnace, entering near the bottom and escaping at the top. The inner tube of the furnace was, therefore, a gas-tight tube which protruded from the bottom of the furnace some six inches, at which distance it remains sufficiently cool that it can be closed by a rubber stopper. The well at the bottom of the furnace tube was connected through the stopper with a reservoir from which mercury could be caused to flow into the tube to any desired level. By allowing the charge to fall into the mercury a means of quenching it in the atmosphere of nitrogen was provided.

The nitrogen was purified in the conventional manner by passing it through ammoniacal copper solution and then over hot copper gauze. The partial pressure of oxygen in the nitrogen is thus reduced to that corresponding with the equilibrium $2Cu_2O \rightleftarrows 4Cu + O_2$ at the temperature of the gauze. This pressure is so low that for many purposes nitrogen so produced is regarded as furnishing a neutral atmosphere. In work with iron silicates, however, it is soon found to be by no means neutral. The iron crucible slowly acquires a black coating of FeO on the outside.[3] The inside of the crucible, in contact with melt, remains bright but the system, crucible plus melt, slowly acquires oxygen, the net result of the action being a slow increase in the FeO content of the charge during the period of the run. Nevertheless, it so happens that the rate of this addition of FeO is so small in comparison with the rate of establishment of equilibrium between crystals and melt that this latter equilibrium, wherein our interest lies, can be studied freely. In other words, during the period required to establish equilibrium between crystals and liquid, ordinarily not more than 15 minutes, the amount of increase in the FeO content of the charge is wholly negligible for most

[3] This fact obviously suggests the substitution of hot iron for hot copper in the nitrogen purification train but since the nitrogen resulting would still have oxygen corresponding with the equilibrium $2Fe + O_2 \rightleftarrows 2FeO$ it would be oxidizing to silicate solutions (melts) dilute with respects to FeO. It is doubtful therefore if any significant gain would have resulted from making this substitution. For this reason and because the results obtained by the above method of purification of nitrogen were found altogether satisfactory, we did not attempt to make this substitution of iron for copper.

charges. In some charges that melt at the higher temperatures a measurable change occurs in 15 minutes, but fortunately at these temperatures a much shorter time is adequate to establish equilibrium between crystals and liquid so that even here the change of composition of the melt during a run is negligible.

This procedure of studying equilibrium between crystals and liquid, in an atmosphere which is at equilibrium with neither, might seem, upon first thought, open to serious objection, but as a matter of fact it is a procedure frequently adopted in such work. For example, in studying the equilibrium between crystals and their aqueous solutions it is seldom necessary to insure that the partial pressure of water vapor above the solution is that in equilibrium with it at the temperature concerned. It is only necessary to insure that such gain or loss of water vapor as may occur induces no significant change in the composition of the solution. The procedure is thus strictly analogous to that here resorted to.

There is, of course, no one atmosphere that would be at equilibrium with all of the melts we studied at the various temperatures at which we worked. If absolutely pure nitrogen were at our disposal it would, theoretically at least, produce an eventual reduction to metallic iron of all the ferrous oxide in the melts. With pure nitrogen there would thus be a slow decrease of the amount of FeO in the melt, a process no more desirable than the slow increase we obtained. The only method of avoiding all possibility of change of composition would be to have the charge in an evacuated, closed container and permit it to establish its own atmosphere. Such a procedure can be and has been resorted to in some instances but is a comparatively tedious method, introducing much difficulty in the matter of quenching. At the same time it is a quite unnecessary precaution. Our method of studying equilibrium between crystals and liquid proved, as we shall see, wholly adequate and satisfactory.

The crucibles used in determining equilibrium were of electrolytic iron. They were of small capacity (0.2 $cm.^3$) and the charge was, therefore, always small, though notably larger than that ordinarily used as a quenching charge in silicate studies, a condition which was rendered desirable by the difficulty of obtaining perfect homogeneity in the original mixture from which the small samples for equilibrium studies were taken. At the same time the charges were small enough to

insure automatic uniformity of temperature throughout their mass and a prompt quenching when they were dropped into mercury. In this connection it should be pointed out that quenching of the liquid to a glass, an operation readily accomplished with most silicate melts, was found possible with only the more siliceous of our mixtures. The majority crystallize completely even with the most rapid cooling, but the fibrous or feathery aggregates so formed are readily distinguished under the microscope from primary crystals grown freely in contact with liquid during the run. Even the more siliceous tend to develop minute points of cristobalite, but these again are readily distinguishable from primary crystals of that phase.

The use of iron crucibles introduced a difficulty in the measurement of temperature but fortunately a ready means of overcoming this difficulty was at hand. For the routine, accurate measurement of temperatures in silicate studies, especially when some of the temperatures are as low as 1000°C., no device is as adaptable as the thermocouple of platinum rhodium, combined with a potentiometer system for the determination of its E.M.F. We wished to continue its use, but we found that in the presence of an iron crucible the E.M.F. of such a thermocouple rapidly changes so that after a few hours' use its reading may depart as much as 100° C. from the proper value. The difficulty was overcome simply by not measuring the temperature when the iron crucible with its charge was in the furnace, a procedure that was rendered possible by close control of the temperature with the Geophysical Laboratory furnace thermostat.[4] The procedure, then, consisted in bringing the furnace to the desired temperature with the thermocouple in place and its junction at the "hot-point" of the furnace and setting the thermostat so that the temperature remained constant at that value. The thermocouple was then removed and the small iron crucible with its charge was suspended in the furnace so that it occupied exactly the same position as that previously occupied by the thermocouple junction. Continued operation of the thermostat insures that the small crucible and its contents are thus brought to substantially the same temperature as that originally indicated for the thermocouple junction. The thermostat is, of course, not without its ailments, but fortunately these have obvious symptoms and when they are absent it has been found by experience that constancy of temperature to about 1° C. is assured.

[4] Roberts, H. S., J. Opt. Soc. Amer., etc., **11**, 171-186, 1925.

To be sure, the furnace regulator does not necessarily control the temperature at a given point in the furnace. It merely maintains at a constant value the total resistance of the platinum wire of the furnace winding. Such a requirement is not inconsistent with a different distribution of temperature in the furnace and, therefore, a different temperature at any given point. Therefore, a change of temperature might be induced by substituting for the thermocouple the charge with its suspension, even with the same setting of the regulator. To reduce this possible change to a minimum the "rig" placed in the furnace with the thermocouple was made as nearly identical as possible with the crucible suspension, both being reduced to a minimum of heat capacity and conductivity. The crucible suspension was, in fact, a single platinum wire, not however connected directly with the iron crucible, but with a small refractory ring which was in turn connected with the iron crucible by a wire of pure iron, for it was found that if platinum and iron were permitted to come into contact they soon became mechanically unsatisfactory on account of extreme brittleness of their alloys. In making this necessary reduction of bulk of the quenching "rig" we perforce abandoned the usual electrical method of quenching employed in this Laboratory and substituted for it a purely mechanical method. This consisted merely in holding the suspending wire at the top of the furnace in a spring clamp, which, upon release, permitted crucible and suspension to fall. The thermoelement "rig," likewise reduced to a minimum, consisted merely of the unjacketed couple, the wires being insulated from each other by a single refractory capillary which passed through a soapstone "head" fitting the top of the furnace tube and holding the thermocouple junction in a central position. Any small, possible residual difference surviving even with these precautions was readily taken into account in the calibration. This was carried out by suspending charges of substances of known melting point in exactly the same way as the charges under investigation and determining the thermocouple readings at which these standards were just melted. For this purpose the usual standards were employed—Li_2SiO_3 melting point 1201° C., $CaMgSi_2O_6$ melting point 1391.5° C., Pd melting point 1549.5° C. As a container for the two standard silicates a platinum crucible was, of course, substituted for the iron crucible used with the ferrous silicates, the platinum crucible

being made of the same size as the iron crucible. For the palladium a small porcelain crucible was used.

One limitation was imposed by the use of iron crucibles. The melting point of pure iron is 1535° C. approx., a fact

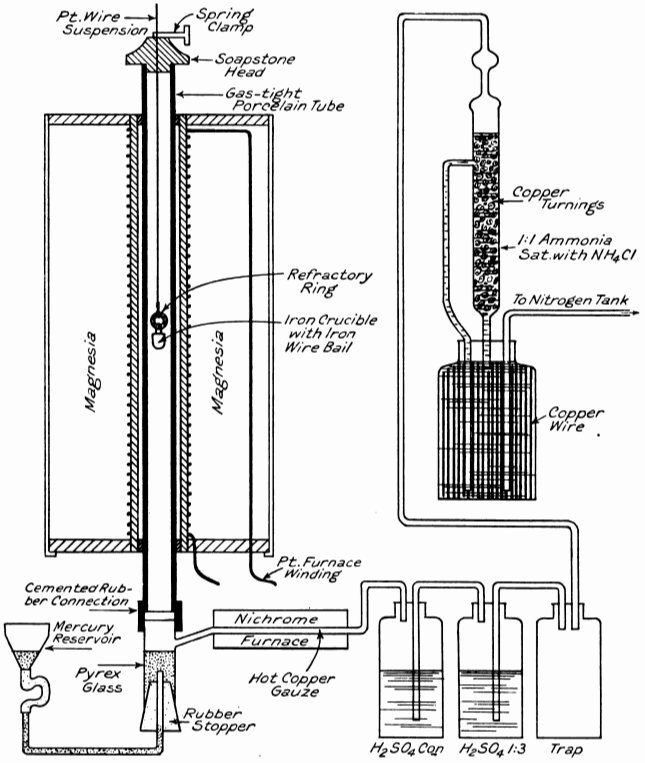

Fig. 1. Diagram of apparatus showing nitrogen purification train and crucible with charge in place in furnace and ready to be quenched by dropping into mercury at bottom of tube upon release of spring clamp at top.

which naturally placed an upper limit upon the temperature to which the investigations could be extended in the manner outlined. The actual temperature at which the highest run was made was 1523° C., this being the temperature of melting of iron under the conditions prevailing in our furnace, a matter that will be discussed at a later point. In Fig. 1 a diagrammatic sketch of the experimental arrangements is given.

Preparation of the Mixtures.

Before investigating equilibrium in the small samples of each mixture, it was necessary to prepare a considerable quantity of the mixture in a homogeneous condition. Here iron crucibles were not adaptable and we resorted to the use of platinum. The ingredients used were ground quartz and either Fe_2O_3 or ferrous oxalate, $FeC_2O_4.2H_2O$. These were mixed and ground together in the desired proportions and then were melted in the platinum crucible in a gas furnace. Platinum has a marked disadvantage for this purpose. Except under strongly oxidizing conditions it reduces iron from its compounds and takes it into solid solution. Oxidizing conditions were, of course, to be avoided since we wished to convert as much of the iron as possible into the ferrous state. The result was that in all cases some iron was removed from the charge by the platinum crucible, but by making the charge sufficiently large this was reduced to a small but not negligible proportion of the total iron. This action of platinum has the further disadvantage that it renders impossible the obtaining of a charge that is perfectly homogeneous. Close to the crucible the charge always contains less iron than it does elsewhere, a fact that is readily ascertained in glassy charges, where the refractive index of the glass is always low close to the platinum. When the mixture has thus been melted three times with intermediate grindings the product is a somewhat inhomogeneous material, containing a little less total iron than that calculated from the original ingredients and with a small proportion of the iron in the ferric state. The reduction of most of the iron to the ferrous state is a matter of experience in the use of the gas furnace and is attended with variable success.

Chemical Behavior of Charges in Iron Crucibles.

It has already been stated that a somewhat larger charge is taken for the study of equilibrium than is usually taken in our silicate studies. The reason for this procedure lies in the somewhat inhomogeneous character of the mixture as prepared above, but careful mixing and grinding assure that the sample taken shall be representative of the whole. The charge placed in the iron crucible has, then, a somewhat smaller percentage of total iron than that used in making the mixture and some of this is in the ferric state. When it is melted in the iron

crucible ferric iron is reduced by reaction with iron and there is an addition of FeO to the charge. Here we have an action that is compensatory to the subtraction of iron by the platinum crucible. The one effect may, at times, balance the other so that the final product after meltng in the iron crucible may have sensibly the proportion of total iron that was originally used but such a result cannot be depended upon. Usually the one effect or the other predominates and for this reason all charges must be analyzed. It is necessary to analyze a charge which has been run in an iron crucible in exactly the same way as the charges used in determining this equilibrium, that is, for the same period of time and at the same temperature as that previously fixed as the liquidus point for any particular charge. For this purpose a somewhat larger iron crucible was used so that a product weighing about a gram was obtained for analysis.

Chemical Analyses of Charges.

Ferrous iron was determined by the Pratt[5] method modified somewhat. The exact procedure was as follows: Weigh 0.2 to 0.3 gram sample into a 150 cc. transparent silica glass[6] Erlenmeyer flask, add about 60 cc. distilled water. Displace the air in the flask by a stream of CO_2 (free from air) entering by a silica tube through a two-hole rubber stopper. Heat to boiling, remove flame and add 15 cc. (1:1 by volume) H_2SO_4 and 5 cc. of 40% hydrofluoric acid from a platinum dish by just lifting the stopper while CO_2 is still running. Replace stopper and boil gently until sample is completely dissolved (3 to 8 minutes). Cool in ice bath for 15 minutes, with CO_2 stream still running. Stop CO_2, remove from ice bath and add a large excess of solid boric acid (about 5 or 6 grams), titrate at once with standard $KMnO_4$ solution.

Total iron was determined by dissolving 0.2 to 0.3 gram sample in 15 cc. (1:1 by volume) H_2SO_4 and 8 cc. of 40% hydrofluoric acid in a large platinum dish and heating on a hot plate until all H_2F_2 had disappeared. The dish was cooled, contents diluted, 5 cc. of concentrated HNO_3 added and the liquid transferred to a 250 cc. beaker. The iron was precipitated with an excess of NH_4OH and the precipitate ignited

[5] This Journal, **48**, 149, 1894.

[6] Silica glass was used to obtain the advantage of observing the progress of solution of the sample. Other glasses would meet this requirement but were found to affect the FeO determination seriously.

and weighed as Fe_2O_3. The difference between total iron and FeO gave Fe_2O_3. In a few cases Fe_2O_3 was determined directly by titration with a standardized titanous sulphate solution and the results were in good agreement with those determined by the above method.

Experimental Procedure in Brief.

Mixtures were made up by taking silica and ferrous oxalate (or Fe_2O_3) in the proportion calculated to give the desired product and melting them together three times in a platinum crucible in a gas furnace. Thus was obtained a product deviating somewhat from the desired product by reason of a slight deficiency in iron and the existence of some of the iron in the ferric state. Small samples of the mixture were then heated at measured temperatures in iron crucibles in a stream of nitrogen and the temperatures of beginning of melting, completion of melting and of any other changes of phase were determined by the method of quenching, combined with microscopic determination of the phases in the quenched product. Upon heating in the iron crucible, a small change of composition of the charge occurs which is principally due to reduction of ferric oxide by the iron crucible and consequent increase of the total iron content of the charge. This increase may partly balance or more than balance the deficiency produced by melting in platinum but the extent of balance cannot be predicted. A charge of each mixture was, therefore, subjected to chemical analysis after a run in an iron crucible at the temperature at which a change of phase was found to occur. Ordinarily the temperature of the run was that at which completion of melting occurs and the analysis thus gave the composition of the liquid at the liquidus point for that composition. By repeating this procedure for a series of mixtures and plotting the determined liquidus temperatures and analyzed compositions (with microscopic determination of the crystalline phases) the data given in Table I were obtained.

EXPERIMENTAL RESULTS.

Discussion of Table I.

Inspection of Table I shows that a definite and in some instances a rather large amount of F_2O_3 is shown upon analysis of the charge run in an iron crucible quenched from the temperature at which it is just completely melted. We

have already pointed out that our "nitrogen" atmosphere is gently oxidizing with respect to our melts. The question arises as to whether the oxidizing action at the free surface of the liquid takes place at such a rate that the reducing action of the iron crucible is unable to keep pace with it, or whether the presence of Fe_2O_3 is due to other causes. In order to investigate this point we resorted to the method of melting the charge, again in an iron crucible, but now sealed up in an

TABLE I.

Liquidus temperatures for various mixtures.

Liquidus temperature °C.	Composition of liquid at liquidus temperature			Solid phases in equilibrium with liquid
	FeO	Fe_2O_3	SiO_2	
1380 ± 5	88.44	11.56	0.00	Wüstite and Fe
1315 ± 5	82.73	9.00	8.27	Wüstite and Fe
1215 ± 5	75.19	4.73	20.08	Wüstite and Fe
1193 ± 2	71.53	3.32	25.15	Fayalite and Fe
1202 ± 2	70.21	2.50	27.29	Fayalite and Fe
1205 ± 2	68.36	2.25	29.39	Fayalite and Fe
1203 ± 2	66.36	2.21	31.43	Fayalite and Fe
1187 ± 2	62.65	1.39	35.96	Fayalite and Fe
1260 ± 2	60.22	1.32	38.46	Tridymite and Fe
1365 ± 2	58.98	1.31	39.71	Tridymite and Fe
1475 ± 5	56.56	1.15	42.29	Cristobalite and Fe
1515 ± 5	55.37	1.14	43.49	Cristobalite and Fe

evacuated tube of silica glass. The amount of oxygen remaining in the small free space of this tube when it is thus evacuated or, indeed, even without that precaution, is wholly negligible in comparison with the weight of the charge; and again the amount of oxygen (in excess of the ferrous ratio) present in the original charge is wholly negligible as compared with the weight of the iron crucible. Therefore the system, charge + iron crucible, is free to establish its own atmosphere, in other words that pressure of oxygen which is in equilibrium with it, and the melt is free to come to equilibrium with the iron crucible and the established oxygen pressure. If metallic iron is capable of reducing all the iron oxide of the melt to the ferrous state, here are the conditions under which it is free to occur without disturbance from any extraneous source of oxygen. We accordingly investigated three of our melts in the manner described.

The compositions chosen were the pure iron oxide mixture without silica and two mixtures in the neighborhood of the composition of fayalite, Fe_2SiO_4. These we shall now discuss.

Sealed Tube Experiments Compared with Nitrogen Runs.

The invariant point, liquid + iron $\rightleftarrows$ *wüstite.*—A great deal of investigation has already been carried out upon the composition of the liquid phase that is in equilibrium with solid iron and solid oxide (wüstite) in the binary system, iron-oxygen; and while there is some disagreement of the results, the evidence, especially the more recent evidence, is strongly in favor of the conclusion that the composition of the liquid lies on the high-oxygen side of the composition FeO, in other words, metallic iron is incapable of reducing all the iron of the liquid to the ferrous condition or, in yet other words, ferrous oxide melts incongruently with separation of metallic iron. Dissenting voices have claimed in the past that inadequate precautions against oxidation of the liquid are the cause of its higher oxygen content. Since our own experiments with ferrous oxide melted in an iron crucible were conducted in a "nitrogen" atmosphere admittedly somewhat oxidizing, this objection would, no doubt, be urged against the results which we obtained in that manner. It was necessary, therefore, to investigate equilibrium under conditions precluding access of oxygen, which was done by conducting the melting in an iron crucible in a sealed silica glass tube in the manner described.

It is desirable at this place that we should point out the details of the procedure, and in order to make these clear it will be necessary to refer to an iron-oxygen diagram. The latest published diagram is that of Mathewson, Spire, and Milligan,[7] which we reproduce in Fig. 2, omitting the solidus relations between iron and wüstite which were, in fact, not determined by them. These workers determined the composition of the points C and M at one blow by holding an iron oxide melt in an iron crucible at or near the temperature of the point C, cooling slowly to the temperature of point M (with separation of Fe as primary phase), and thereafter more rapidly to obtain consolidation of the liquid M as a homogeneous solid solution, wüstite. By determining analytically the proportions of Fe, FeO and Fe_2O_3 they located the two points. For our purposes the point C has no importance. We are concerned only with the point M and we determined it by holding an iron oxide melt in an iron crucible a little above

[7] Trans. Am. Soc. Steel Treating, **19**, 66-88, 1931. Their diagram is based partly on their own results and partly upon compilation of the results of others.

the temperature of the point M and cooling rapidly to procure consolidation of the liquid as the crystalline oxide phase, wüstite. Actually the runs were made at 1390°, about 10° above the temperature of M. The initial material may be any iron oxide, for the liquid will eventually be brought to the same composition by reaction with the iron crucible. We used either an oxide made by heating ferrous oxalate at 1200° in "nitrogen" which gave a wüstite containing approximately 20 per cent of magnetite in solid solution or, alternatively, we used a mixture of Fe_2O_3 and filings of electrolytic iron taken

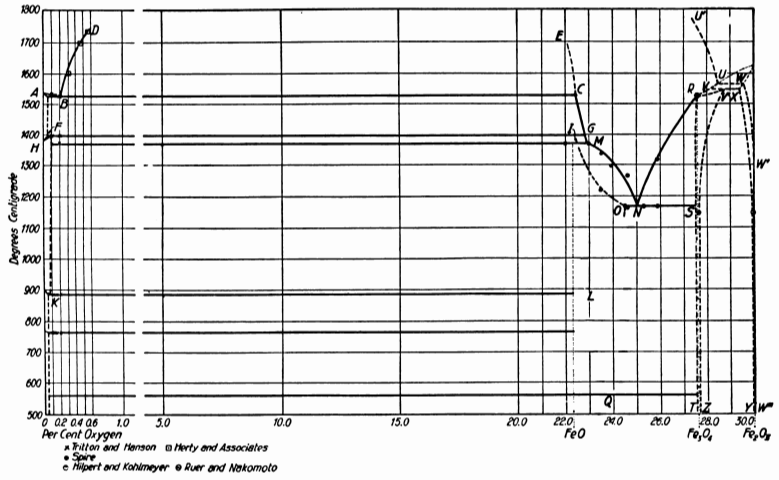

Fig. 2. The iron-oxygen diagram. (In part determined by and in part compiled by Mathewson, Spire, and Milligan. Wüstite solidus relations, not determined by them, are here omitted.)

in the proper proportion to give FeO, though such a proportion was not essential nor indeed particularly advantageous. In Table II the results of the work are summarized.

A word is necessary as to the treatment of the material before analysis. The crystallized oxide phase always contained some metallic iron as mechanically included particles resulting from irregular attack of the oxide upon the iron crucible or from failure of complete solution of the iron filings. Mathewson, Spire, and Milligan had a similar experience. They were able to get a satisfactory separation of the mechanically included particles by passing their product through an appropriate screen, thus obtaining a concentrate of the oxide

phase with its small primary crystals of iron from whose chemical constitution they fixed the points C and M. Their "determination of total ferrous iron was carried out on a separate sample from which the metallic iron had not been removed. It was considered preferable to analyze the oxides in this manner, notwithstanding the possible reduction of some ferric chloride by hydrogen generated during solution of the

TABLE II.

Composition of liquid phase at invariant point, $Fe + \text{liquid} \rightleftarrows FeO$ (1380°).

	FeO	Fe_2O_3
Iron oxide (from ferrous oxalate) held at 1390° ..... 15 min. in Fe crucible in "nitrogen"*	89.40	10.60
Iron oxide (from Fe and Fe_2O_3) held at 1390° ..... 30 min. in Fe crucible in "nitrogen" (0.8% Fe present and corrected for except as to reducing effect of released hydrogen)	89.83	10.17
Iron oxide (from Fe and Fe_2O_3) held at 1390° ..... 30 min. in Fe crucible in evacuated, sealed SiO_2 tube	88.44	11.56
Mathewson, Spire, and Milligan, 1931 ..... (2.2% Fe present and corrected for except as to hydrogen effect)	90.5	9.5

metallic iron. In this way, the possibility of oxidizing iron in the supercooled ferrous oxide, during removal of free iron, was avoided."[8] We have made a test of this effect using material of known Fe_2O_3 content to which iron filings were added and we find that the reducing effect of the hydrogen is real. Their value for the percentage of Fe_2O_3 in the oxide phase (9.5 per cent) is, therefore, necessarily somewhat lower than the actual Fe_2O_3 content of their oxide phase, a correction which would bring their results into closer agreement with our own, although no definite value can be assigned to this correction.

In our efforts to determine the composition of the oxide phase (wüstite) we found that a satisfactory separation of the iron could, in favorable cases, be obtained magnetically. Wüstite is non-magnetic, in the ordinary every-day usage of the term, even when it contains large amounts of magnetite in solid solution, and simply by drawing magnetized tweezers

* In this run the iron crucible with its charge was covered with iron foil, placed inside a deeper iron crucible which was then filled to the top with iron filings. The charge was thus completely surrounded by iron, and any gas that came in contact with it was filtered through iron filings.

[8] Op. cit., p. 86.

through the powder and rejecting the powder that adheres to them one eventually gets, in some cases, a residue of oxide that contains no more than a small fraction of one per cent of Fe, as determined by comparison of areas in polished section under the reflecting microscope, which method was necessary for the examination of all the wüstite-metallic iron products. We thus obtained material that gave directly, upon analysis, the composition of the oxide phase. Table II compares our results by various methods and those of Mathewson et al. We have every reason to believe that our highest value of Fe_2O_3 (11.5 per cent) is the best, for the analysis was made upon a product practically freed from metallic iron.

While we have the iron-oxygen diagram (Fig. 2) before us we may now explain the melting of our iron crucibles at 1523° (Pd = 1549.5), a matter to which reference has already been made. Under the partial pressure of oxygen in our "nitrogen" atmosphere the melting of iron takes place at the temperature of the horizontal BC and our observations therefore constitute an independent determination of that temperature. The point A can be realized only in a hydrogen atmosphere.

Sealed tube runs with silicate melts.—In addition to these comparison runs made upon "FeO" to check the validity of the results obtained in "nitrogen," similar comparison runs were made with a like purpose upon two other mixtures. These were run in an iron crucible in a sealed, silica glass tube at a temperature about 5 degrees above the melting point, the charge being thus held in the molten condition for 30 minutes. Again it was found that under these conditions of complete exclusion of oxygen the iron crucible fails to reduce all the iron oxide of the melt to the ferrous state. The analyses of the charges resulting from these runs are compared in Table III with those of charges of the same material run in an iron crucible in the "nitrogen" atmosphere and cooled in two contrasted manners, viz., instantaneously and slowly.

Inspection of Table III shows that the runs made in sealed tubes do indeed show a somewhat lower Fe_2O_3 content than the runs made in "nitrogen" and quenched. On the other hand they are nearly identical with the runs made in "nitrogen" and slowly cooled. The explanation of the lower results for Fe_2O_3 in the case of the sealed tube runs is, in part, as follows. In the tube at the temperature of the run there is established the very low vapor pressure of oxygen in equilibrium with the

charge. When the tube with its contents is then cooled, the fall of temperature of the charge is much less rapid than is obtained with a quenched charge and crystallization takes place in a somewhat different manner. The first crystals formed in a slowly cooled mass contain less Fe_2O_3 than the charge as a whole, a relation that is to be expected on theoretical grounds but is actually demonstrated by the fact that in a charge close to the composition of fayalite the central portions of the

TABLE III.

Showing effect of three different methods of procedure upon composition of two charges.

	I.	II.	III.	I.	II.	III.
FeO	68.36	68.92	68.93	66.36	67.23	67.12
Fe_2O_3	2.25	1.60	1.67	2.21	1.35	1.65

I. Run in Fe crucible in nitrogen and quenched.
II. Run in Fe crucible in nitrogen and cooled slowly.
III. Run in Fe crucible in evacuated, sealed silica tube.

fayalite crystals are less deeply colored than their rims. The subtraction of these less ferric early crystals tends to push the liquid over to a more ferric composition than that of the original liquid. This more ferric liquid has, however, a higher oxygen pressure than that which had been established in the sealed tube, and the charge therefore loses oxygen into the free space of the tube. Indeed, all charges run in a sealed tube are found upon examination to have become pumice as a result of this action. During cooling the swelling of the charge and the development of a "spatter cone" on its surface can be observed. We have here the phenomenon of the second boiling point.[9] It is plain that the liquid charge in equilibrium with the iron crucible at the temperature of the run had at least a little more oxygen (more Fe_2O_3) than that revealed upon analysis of the cold pumice. A correction is, therefore, applicable to the analysis which would bring it nearer to the composition of the quenched charge from the "nitrogen" run. The amount of the correction cannot be determined but it can be said that it is very small, for the pressure of oxygen built up in the tube by vesiculation of the charge must itself be very small, the free space of the tube is not large, so the actual weight of oxygen lost is of small magnitude. A part of the difference between the results of closed tube runs and quenched,

[9] Morey, G. W., The development of pressure in magmas as a result of crystallization, J. Wash. Acad. Sci., **12**, 219-230, 1922.

"nitrogen" runs is to be accounted for otherwise. The necessarily somewhat slow cooling of the charge enclosed in the silica tube brings in another effect that can be demonstrated in charges cooled slowly in "nitrogen" and these latter charges do not exhibit any second boiling-point phenomena. This effect of slow cooling is, in some measure, set forth in Table III by the figures for runs made by the three different methods there listed. It will now be discussed more fully as exhibited in a greater number of mixtures.

The Effect of Rate of Cooling upon the Composition of the Charge.

In Table IV we present the results of comparison runs made in "nitrogen" upon six different mixtures that were cooled instantaneously from the liquidus temperature by dropping into mercury, in the case of the runs marked "quenched," and on the other hand, in the case of runs marked "cooled slowly,"

TABLE IV.

Comparison runs showing differences in composition depending upon rate of cooling, for six mixtures.

	I.		II.	
	FeO	Fe_2O_3	FeO	Fe_2O_3
Quenched	71.53	3.32	68.36	2.25
Cooled slowly	72.52	2.67	68.92	1.60
Quenched	70.21	2.50	62.65	1.39
Cooled slowly	70.90	1.51	63.00	0.93
Quenched	60.22	1.32	58.98	1.31
Cooled slowly	60.56	1.00	59.23	0.69

were cooled in the furnace by resetting the regulator so that the temperature fell to a value a few degrees below that at which the charge was completely crystalline, *i.e.*, below the temperature of the nearest eutectic. It will be noted in the table that there is no single exception to the rule that for any given mixture the ferric oxide is higher and the ferrous oxide lower in the quenched charge than in the slowly cooled charge. The table shows two groups marked I and II. Under II runs are shown that were made before we suspected the existence of the effect and had merely happened to cool charges of the three listed mixtures in the two contrasted manners. They were the only examples of mixtures that had been so treated. They were made at different times, in some cases months apart, and we could not guarantee that some of the condi-

tions had not varied. Accordingly we made a series of comparison runs on three other mixtures (listed under I) with all of the conditions identical except the rate of cooling. Each mixture shows the described effect.

The explanation of this effect is, no doubt, the following. We may take for simplicity a mixture close to fayalite in composition. Such a mixture, melted in the iron crucible, adjusts itself in composition so that the content of Fe_2O_3 is 2.25 per cent and, if it is cooled instantaneously by quenching in mercury, analysis of the product reveals that quantity of Fe_2O_3. If, on the other hand, it is cooled slowly, a more complicated behavior is presented. The first crystals that separate are fayalite, possibly pure Fe_2SiO_4, but certainly containing much less Fe_2O_3 than the liquid. This tends to enrich the liquid in Fe_2O_3, but such a liquid is no longer in equilibrium with iron and will react with the iron crucible in the effort to maintain a composition in equilibrium with iron. Indeed, the composition of the liquid would, with perfect equilibrium, move along the reaction boundary curve between the fields of fayalite and iron (see Fig. 3), a motion which represents nearly constant Fe_2O_3 content. In consequence of the fact that the liquid is thus at least partially restrained from moving on to the more highly ferric compositions that are complementary in composition to the highly ferrous early crystals of fayalite, the slowly cooled charge is, in total composition, more ferrous than the original liquid. We have already pointed out that no second boiling-point phenomena (vesiculation) occur in charges thus cooled slowly in "nitrogen," the reason being that the external pressure is now 1 atm. and any small portion of the liquid that does attain a fairly high Fe_2O_3 content never exerts an oxygen pressure remotely approaching that value. Any oxygen that might escape could do so only as a result of evaporation rather than of boiling and the amount must be quite negligible.

In the slow cooling of the charges a period of some 8 to 10 minutes was required for the temperature to fall to that of complete crystallization, but in most cases not more than 2 or 3 minutes could have elapsed before a sufficient proportion of the charge had crystallized that the remaining liquid could no longer freely react with the iron crucible. We have then in these runs plain evidence of how sensitive the composition of the charge is to the presence of iron and how rapidly it adjusts its composition accordingly.

Equilibrium attained between Metallic Iron and the Silicate Liquids.

In view of all the considerations detailed in the foregoing, we are forced to conclude that those runs that were made in iron crucibles in "nitrogen" and were quenched give the appropriate values for real equilibrium between iron crucible and silicate melt, and that the small content of Fe_2O_3, that is

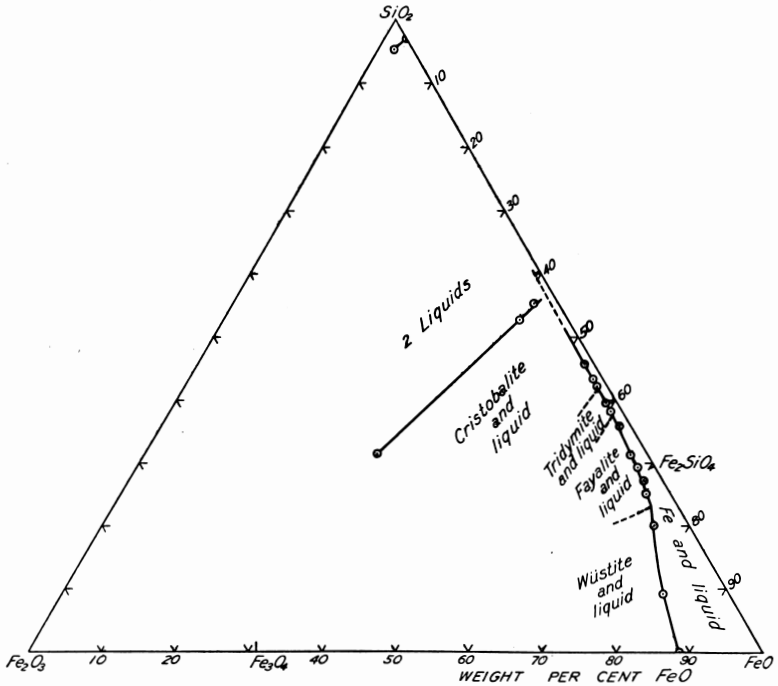

Fig. 3. Equilibrium diagram showing, principally, the boundary curves of the field of metallic iron against adjacent fields in the system, FeO-Fe_2O_3-SiO_2. (Boundaries of two-liquid region by Greig.)

the excess of oxygen in the liquid above that corresponding to the ferrous ratio, is a true equilibrium relation.

We therefore present the ternary equilibrium diagram (Fig. 3) as the correct phase diagram for our mixtures. It shows the field of Fe encroaching upon the FeO-Fe_2O_3-SiO_2 triangle, the more complete representation of equilibrium requiring the more general triangle Fe-O-SiO_2, but in this triangle the subsidiary triangle FeO-Fe_2O_3-SiO_2 is reduced to

such dimensions that the relations brought out in our Fig. 3 would be scarcely legible, for which reason we have not used the more general triangle.

Iron cannot further reduce the Fe_2O_3 content of these silicate melts at their respective liquidus temperatures. Not only is this true, but the Fe_2O_3 content cannot in any manner be further reduced at the liquidus temperature. An attempt at further reduction with the aid of, say, a powerful reducing agent would result only in the separation of iron metal without decreasing the Fe_2O_3 content of the liquid. It should be noted, however, that this limitation upon the composition of *liquid* iron silicates at the temperatures where their crystallization begins has no necessary counterpart in the composition of the *crystalline* phases that separate. These could be purely ferrous.

Incongruent melting with separation of metallic Fe is thus characteristic not only of ferrous oxide but of all mixtures along the FeO-SiO_2 join.

The compound, fayalite, for example, if it be perfectly pure Fe_2SiO_4, melts incongruently according to the diagram and the amount of Fe separating should be about ¾ per cent. Fayalite must contain some 2.25 per cent Fe_2O_3 in order that it shall lie outside the field of Fe and thus melt without this separation of iron. A very satisfying way of clinching the analytical evidence of the encroachment of the field of iron beyond the FeO-SiO_2 join would, therefore, be to demonstrate the incongruent melting of fayalite, with separation of metallic Fe.

Incongruent Melting of Natural Fayalite.

The best material for this demonstration would be perfectly pure fayalite, but from all that has gone before it will be plain that perfectly pure fayalite is not so easily obtained. To prepare most silicate compounds it is ordinarily necessary only to prepare a liquid of the precise composition of the compound and cause that liquid to crystallize completely. In the case of fayalite, however, all our results show that no such liquid exists, at least up to temperatures as high as the melting point of iron. In all probability pure fayalite can be prepared by baking together its solid ingredients in the absence of oxygen and at a temperature below that at which any liquid forms, but its formation would be a slow process and we have not carried it out. The fact of incongruent melting should be equally demonstrable with any fayalite containing less than

2.25 per cent Fe_2O_3 and we have resorted to the use of natural fayalite.

The iron crucibles ordinarily used in our investigation were here not adaptable since it could not be guaranteed that any metallic iron found had not come from the crucible. Platinum was to be avoided on account of its action upon iron compounds. We therefore tried very rapid melting in a crucible of refractory porcelain in "nitrogen." To accomplish this we adjusted the temperature of the furnace at 1255°, *i.e.*, 50° above the melting temperature of fayalite, suspended in it the small porcelain crucible with its charge of natural fayalite for a period of 1 minute, then dropped it into mercury and examined the quenched charge in polished section in reflected light. The fayalite was thus above its melting point a small fraction of a minute and the conditions were unfavorable to the development of iron, being somewhat oxidizing, but in both the natural fayalites used metallic iron was developed. The fayalites were from Rockport, Massachusetts, and from Mourne Mountains, Ireland, selected material from each being powdered and freed from magnetite inclusions by means of a magnet. The metallic iron was identified in the quenched product not merely by its appearance in reflected light under the microscope but by its precipitation of copper from a copper sulphate solution, also observed under the microscope and, to make assurance doubly sure, the original minerals were examined for metallic iron and none found.

This approach to equilibrium from a totally different direction completes the demonstration that the field of iron passes over to compositions beyond the FeO-SiO_2 join, *i.e.*, to more ferric compositions.

Slope of the Liquidus Surface of Iron.

We have made runs on some of our mixtures to determine the slope of the Fe liquidus surface that rises from the boundary curves limiting the field of Fe and liquid (Fig. 3). One would expect on theoretical grounds that there would be at least some inclination of this surface towards the composition of iron; in other words, that the liquids in equilibrium with metallic Fe would have less Fe_2O_3 at higher temperatures than at lower temperatures. Mathewson et al. have found this to be true in the iron-oxygen mixtures without silica. Thus at a temperature near the melting point of iron they find that the liquid is nearly pure FeO (point C, Fig. 2), whereas at

1380° their determinations indicate, as we have seen, about 9.5 per cent Fe_2O_3 in the liquid (point M, Fig. 2). We have not investigated the slope of the Fe liquidus in the iron-oxygen system, but in the silicate mixtures we have not been able to detect any effect of that kind. In Table V are given the

TABLE V.

Showing effect of varying the temperature upon the composition of liquid in equilibrium with iron for three mixtures.

		Quenched from 1500°	Quenched from 1215°
I.	FeO	75.28	75.19
	Fe_2O_3	4.68	4.73
II.	FeO	70.13	70.21
	Fe_2O_3	2.88	2.50
III.	FeO	62.54	62.65
	Fe_2O_3	1.83	1.39

results of runs made to investigate this matter. We selected mixtures whose liquidus temperature for silicate + metallic Fe was in the neighborhood of 1200°, held them at 1500° in an iron crucible in "nitrogen," and quenched in mercury. They were thus some 300° above their silicate liquidus temperature and not far below the melting point of iron, but inspection of the table shows that there is no less Fe_2O_3 in the liquid at the higher temperature than at the lower. Indeed, the figures alone would suggest a slight variation in the opposite direction but the differences are within the error of analytical determination. We can only conclude, therefore, that for the silicate mixtures investigated, the iron liquidus surface is sensibly vertical and that, even at the temperature where iron melts, the silicate liquid in equilibrium with molten iron contains about the same amount of Fe_2O_3 as does the liquid in equilibrium with solid iron around 1200°. The bi-liquidal region thus overlaps the FeO-SiO_2 join in the more general triangle, at least in compositions with from 20 to 36 per cent SiO_2.

RESULTS REPRESENTED AS A BINARY SYSTEM.

Although the system we have set out to study cannot be accurately treated as a binary system because the liquids are never purely ferrous, nevertheless the approach to the binary system, FeO-SiO_2, is very close except at the iron-rich end.

Moreover, in their actual behavior the mixtures are sensibly binary. They begin to melt sharply and, as in a binary system, after the first formation of liquid at the "eutectic" only one crystalline phase is left. The mixture having nearly the composition of theoretical fayalite melts about as sharply as the purest silicate compounds in spite of its content of Fe_2O_3. Without serious misrepresentation, therefore, and with enormous gain in the utility of the diagram we have drawn a binary diagram by calculating all iron in each mixture to FeO and plotting the results accordingly. With this diagram (Fig. 4) before us we may speak, for convenience, of the eutectic, fayalite-tridymite, of the eutectic, fayalite-wüstite, and so

TABLE VI.

The data of Table I recalculated to a binary basis by expressing all iron oxide as FeO.

Composition of liquid at liquidus temperature		Liquidus temperature °C.	Solid phase in equilibrium with liquid
FeO	SiO_2		
100		1380 ± 5	Wüstite
90.83	9.17	1315 ± 5	Wüstite
79.45	20.55	1215 ± 5	Wüstite
74.52	25.48	1193 ± 2	Fayalite
72.46	27.54	1202 ± 2	Fayalite
70.39	29.61	1205 ± 2	Fayalite
68.35	31.65	1203 ± 2	Fayalite
63.90	36.10	1187 ± 2	Fayalite
61.41	38.59	1260 ± 2	Tridymite
60.16	39.84	1365 ± 2	Tridymite
57.59	42.41	1475 ± 5	Cristobalite
56.40	43.60	1515 ± 5	Cristobalite

Invariant points expressed as if system were binary.

	Temperature °C.	Composition of liquid FeO	Composition of liquid SiO_2
FeO melting point	1380 ± 5		
Eutectic: Wüstite-fayalite	1177 ± 5	76	24
Fayalite (Fe_2SiO_4) melting point ..	1205 ± 2	70.5	29.5
Eutectic: Fayalite-tridymite	1178 ± 2	62.0	38.0
Inversion: Tridymite-cristobalite...	1470 ± 5	57.5	42.5
Two liquids and cristobalite	1690 ± 10 (Greig)	42.0	58.0
		3.0	97.0
Cristobalite melting point	1713 ± 5 (Greig)		100.0

forth, although such points as invariant points in a binary system have no real existence. In Table VI we give the data of Table I with all iron oxide calculated as FeO. It is with these figures as a basis that Fig. 4 has been drawn.

The Silica Liquidus.

The diagram (Fig. 4) shows no break on the silica liquidus at the temperature of the inversion, cristobalite-tridymite (1470° C.). In most diagrams the angular discontinuity at this point is very small and only the most careful determinations on especially favorable mixtures are competent to bring it out.[10] If any such change of slope exists it is possible that

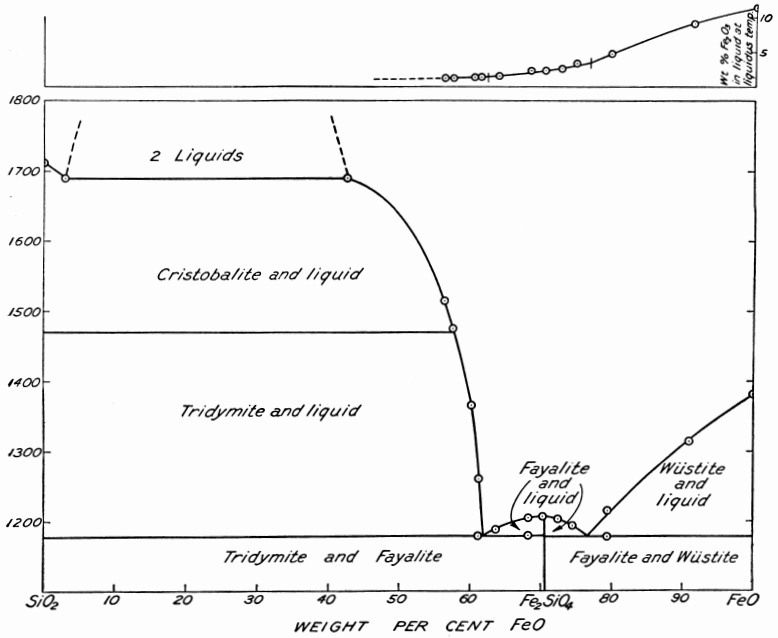

Fig. 4. Equilibrium diagram of the system, FeO-SiO_2, constructed by calculating all iron oxides in the liquids to FeO. Upper figure gives actual amounts of Fe_2O_3 in liquids at liquidus temperatures, indicating extent of departure from binary character.

it lies within the limit of error of measurement in this case. It should, however, be pointed out that although we have indicated on the diagram and in the table that the curve below 1470° is the liquidus of tridymite, nevertheless we are not sure that the solid phase present was tridymite. In most runs at temperatures well below the liquidus the silica was in the form of cristobalite, but in some cases tridymite was probably present also. That in the runs very close to the liquidus, upon

[10] Kracek, F. C., J. Phys. Chem., **34**, 1588, 1930.

which its location depends, the last surviving trace of small crystals was tridymite we cannot affirm. It is, therefore, possible that the curve drawn as the liquidus of tridymite, in accordance with the known stability relations of the forms of silica, is really the metastable downward extension of the cristobalite liquidus. If this is true, there would, necessarily, be no discontinuity at 1470° and the real curve for tridymite would depart slightly from our determined curve, lying at a slightly higher temperature at any given composition.

We were unable to determine any point on the cristobalite liquidus above 1515° on account of the limitation imposed by the melting point of our iron crucibles. We have, therefore, merely extended our curve as a smooth curve meeting the point of equilibrium of two liquids and cristobalite as determined by Greig[11] by a short extrapolation from mixtures containing small amounts of Fe_2O_3, the basis of extrapolation (his determined points) being shown on the ternary diagram (Fig. 3).

APPLICATION OF RESULTS.

Petrologic.

The principal importance of our results petrologically lies in their constituting a starting point for the investigation of more complex silicates, a matter for the future. Their direct application will be discussed now.

The melting point of fayalite, synthetic and natural.—We have already shown that the melting point of our synthetic fayalite is 1205 ± 2° C. Perhaps the purest natural fayalite is that from Rockport, Massachusetts. The specimen available to us contains small magnetite inclusions which can be separated almost completely from the powdered material by means of a magnet. The powder so obtained, examined under the microscope, is found to contain a very small amount of blades of another mineral with $\gamma = 1.73$, multiple twinning and small extinction angles against the twinning plane. This is, no doubt, grünerite. The presence of grünerite makes the material melt through an appreciable range of temperature as determined in an iron crucible by the method of quenching. The formation of a definite though very small amount of liquid is detectable some 10 degrees below the melting point,

[11] Greig, J. W., this Journal, **14**, 479, 1927.

but the melting point (temperature of completion of melting)[12] is found to be exactly the same, within the limits of error, as that of the synthetic fayalite 1205 ± 2° C. The fayalite maximum is so flat (see Fig. 4) that a small amount of grünerite would make a scarcely appreciable difference. It is possible, however, that Rockport fayalite free from grünerite would melt some 2 or 3 degrees higher, a raising that is to be regarded as likely on account of the presence of a small amount of manganese orthosilicate in solid solution in the fayalite (MnO = 0.65 per cent).[13] We have tested one other fayalite, that from Mourne Mountains in Ireland. Powder of this mineral after magnetic treatment contains no grünerite but there is locally a brownish staining. The melting temperature is a little higher than that of the synthetic fayalite and there is a definite melting interval of some 10° C. The values found were 1207 to 1217° C. The melting interval is apparently not due to any extraneous substance but to the existence of some substance in solid solution, no doubt principally manganese. Old analyses of fayalite from Mourne Mountains show 5 per cent MnO and 0.3 per cent MgO.

The low melting point of fayalite is noteworthy in connection with the high value for the magnesian end member of the common series of rock-forming olivines, forsterite (1890°).

Non-existence of $FeSiO_3$ as a crystalline compound.—There is no indication of the formation of a crystalline compound of the composition of the metasilicate, $FeSiO_3$, at any temperature where liquid forms in the binary system. The liquidus at the composition, $FeSiO_3$, about 1550°, is a little above our highest determined point and the solid phase is cristobalite. Moreover, we were unable to induce the crystallization of $FeSiO_3$ at any temperature. On account of the fact that the melting temperature lies above the melting temperature of our iron crucibles we were unable to prepare a glass of the composition, $FeSiO_3$, but by the method of quenching we did prepare a glass close to it in composition such that if the meta-

[12] This refers, of course, to the temperature of final disappearance of silicate, the small amount of metallic iron, whose presence has been demonstrated in an earlier section, being neglected for the purposes of the present discussion.

[13] Penfield and Forbes, this Journal, 1, 1929, 1896. Since the above was written we have analyzed the Rockport fayalite material actually used by us and find that it contains 3.20 per cent MnO and 0.83 per cent Fe_2O_3 and thus differs somewhat from Penfield's material. This fact necessitates no change in the above remarks.

silicate compound formed in it, it would upon complete crystallization make up 85 per cent of the mass, the rest being fayalite. This glass when reheated and thus crystallized at a temperature as low as 660° gives a feathery devitrification product apparently completely crystalline but wholly unsuited for microscopic determination. The X-ray powder pattern of this material, kindly made for us by Dr. Posnjak, shows only the lines of fayalite with a general blackening of the film, probably due to amorphous silica or glass, so the material probably consist of 80 per cent fayalite and 20 per cent SiO_2. The product is thus strictly analogous to, and indeed closely resembles under the microscope, the form of $MgSiO_3$ which was regarded formerly as amphibole, but has been proved to be an intergrowth of the olivine forsterite (Mg_2SiO_4) and glass.[14] The difference between the magnesian and the ferrous material lies in the fact that the "amphibole" form of $MgSiO_3$ is prepared only under special conditions on account of the comparative stability and ready crystallization of the compound as clino-enstatite, whereas the "compound" $FeSiO_3$ cannot be induced to assume any form other than this peculiar intergrowth of olivine (fayalite) and amorphous material.

Quartz and fayalite occur together in rocks, a condition that has been assumed by some investigators to be due to a special action of volatile constituents which prevents their combination to form metasilicate, but the facts pointed out above show that any such assumption is unnecessary. Indeed, it would appear that the opposite is true, for in the presence of the volatile constituent water, ferrous oxide and silica can, under proper conditions, combine in a ratio that approaches, though it does not attain, the metasilicate ratio. The amphibole, grünerite, is sometimes assigned the formula, $FeSiO_3$, but the recent X-ray studies of Warren have shown that one molecule of H_2O is associated with each 8 molecules of SiO_2, the formula being $Fe_7H_2(SiO_3)_8$ just as the formula for tremolite is $Ca_2Mg_5H_2(SiO_3)_8$.[15]

All of the evidence thus points to the failure of formation of a compound of composition, $FeSiO_3$, in nature, just as it fails to form in synthetic mixtures.

[14] Bowen and Posnjak, this Journal, **22**, 193-202, 1931.
[15] Warren, Z. Krist., **72**, 42, 1929. Posnjak and Bowen, this Journal, **22**, 203-214, 1931.

Technologic.

Properties of slags.—The technologic importance of a knowledge of the system, FeO-SiO_2, lies in the fact that metallurgical slags, except iron blast furnace slags, are dominantly made up of these two ingredients. In the original blast-furnace or reverberatory furnace reduction even of non-ferrous metals from their ores the departure of slags from the binary composition is notable, either as a result of the nature of the gangue or of deliberate addition of other ingredients. Speaking generally, therefore, it is to the subsequent processes of purifying metals and mattes that our system is more directly applicable since it is here that slags with a closer approach to our mixtures are produced. Thus in the enrichment of an impure copper in the copper converter the principal impurity to be removed is iron, and this is accomplished by oxidizing it in the presence of SiO_2 which immediately combines with the FeO formed to give a slag. In the metallurgy of iron and steel the reaction, $2FeO + Si \rightleftarrows SiO_2 + 2Fe$, is of great importance. The puddling of pig iron to produce wrought iron involves the addition of iron oxide to it with the object, among others, of oxidizing the silicon of the pig according to the above reaction, the resulting silica immediately fluxing with excess of the iron oxide to form a slag. Conversely silicon may be added to steel to rid it of its last trace of FeO, and again the same reaction with resultant formation of an FeO-SiO_2 slag applies. In the acid processes (Bessemer or open-hearth) for the production of steel, which consist in removing the impurities of pig-iron by oxidizing them, FeO-SiO_2 slags are produced by fluxing of FeO with the acid (SiO_2) lining or hearth, though many of these slags bear large quantities of MnO.

The slags formed in the production of wrought iron must be of such a character as to permit the removal of the greater part by squeezing of the spongy iron and to facilitate the production of optimum distribution of the retained part during the working of the metal; the slag inclusions produced during deoxidation of steel by silicon should have properties that facilitate their elimination from steel; the slags of the other processes mentioned must be in the proper condition to enter freely into the various reactions involved in the processes and to be, in general, "workable." It is but natural that metallurgists have been much interested in the fundamental slag system, FeO-SiO_2, and have made various attempts to deter-

mine melting equilibrium in that system. In Fig. 5 we have plotted, together with our own results, those of others upon the same subject. We give only diagrams of those investigators who have made up mixtures especially for the investigation of this system itself. Many other diagrams of the system have been produced, that were based upon extrapolation from impure mixtures and upon other considerations, but these are omitted, though we may mention the shrewd estimate

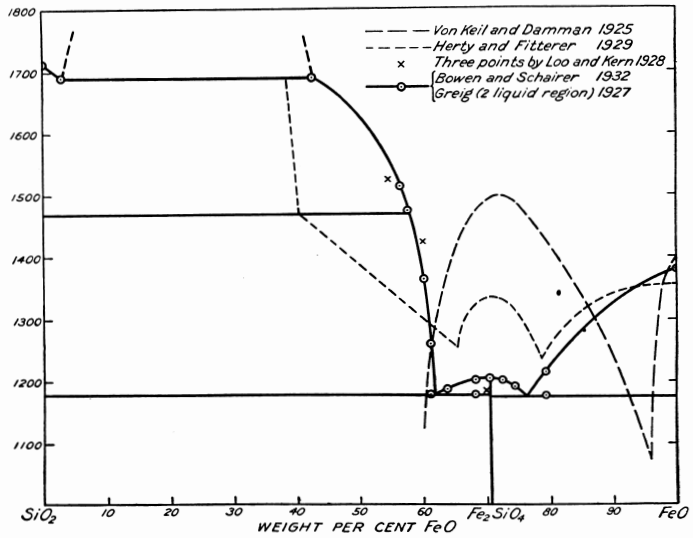

Fig. 5. Comparison diagram giving results of various investigations of the system, FeO-SiO_2.

by Whitely and Hallimond.[16] The great discrepancies between our work and that of others are to be seen at a glance. It is obvious that it would be a matter of some concern to metallurgists whether there is a maximum at 1500° at the composition of fayalite, as indicated in the diagram of von Keil and Damman.[17] If this were true, a slag approaching such composition would require to be avoided as the plague, and it is well known that this is not so. We are at a loss to account very satisfactorily for their result except to suggest that, if the mixture really consisted principally of magnetite and cristobalite, as it is very likely to do if the precautions against

[16] J. Iron & Steel Institute, **99**, 212, 1919.
[17] Stahl und Eisen, **45**, 890, 1925.

oxidation are inadequate, and if the crucible is platinum, as it was, some such value might readily be obtained. Herty and Fitterer[18] place this maximum at 1335°, more than 100° above our value. They made their determinations on a platinum strip in a nitrogen atmosphere, measuring their temperatures with an optical pyrometer and observing "softening points" and "melting points," regarding the former as the temperature of melting of a eutectic and the latter as giving a point on the liquidus. The mechanical behavior of the charge at any temperature depends upon the relative proportion of liquid and crystals, upon the fluidity of the liquid, and somewhat upon the shape of the crystals, but in any case there should be in most mixtures no abrupt increase of fluidity at the point where the last crystals disappear, and the method of observing the mechanical behavior of a charge is in general quite incapable of locating such points, *i.e.,* points on the liquidus. They are to be dependably located only by quenching experiments as a general procedure. Nevertheless, the method of observing the deformation of the charge should be capable of giving a reliable value for any eutectic temperature in mixtures reasonably close to the eutectic in composition, and for the melting temperature of a compound which melts at a point of maximum, especially in these mixtures for they give thin liquids. The high value found for the melting point of fayalite, which does present such a maximum, is probably to be attributed to the fact that, in using a minute charge on a platinum strip, ideal conditions obtain for bringing practically all of the charge into intimate contact with platinum, with consequent abstraction of iron from the charge and conversion of a considerable proportion of the remaining iron into the ferric condition. It would, therefore, be necessary to analyze the charge after the run, the composition of the initial material not being pertinent.

The three points by Loo and Kern[19] shown on the diagram (Fig. 5) were determined in an atmosphere probably somewhat reducing. This prevents the formation of an excess of Fe_2O_3 in the charge and the formation of a little iron could do no harm. They, too, worked by the method of observing deformation which, as we have seen, should give a reliable value for the fayalite maximum. Their determination of the fayalite melting point agrees reasonably well with ours, lying,

[18] Ind. Eng. Chem., **21**, 51, 1929.
[19] Trans. Am. Inst. Mining & Metall. Eng., **76**, 504, 1928.

as it does, 20 degrees lower. The lower value may, perhaps, be accounted for by the fact that they worked with mixed oxides without the preliminary precaution of combining them into the compound fayalite. Such a charge would inevitably be minutely inhomogeneous and give locally some liquid corresponding to the two eutectics on either side of the fayalite maximum. This would increase in amount upon rise of temperature, with consequent deformation between the temperature of these eutectics and the fayalite point. Curiously enough, the other determinations by these workers also show fair agreement with ours. The method of observing deformation of the charge was used here as well, and we are at a loss to see how such observation could locate a point on the silica liquidus. Their mixture, $60FeO.40SiO_2$, for example, should become 96 per cent liquid at the temperature of the adjacent eutectic and should there deform completely. It is scarcely credible that the presence of 4 per cent of crystals could endow the mass with any suggestion of rigidity, and even if it did, this rigidity should decrease gradually as the temperature was raised and the crystals gradually dissolved. When the slow solution of the crystals finally became complete at the temperature of the liquidus there could be no abrupt further increase of fluidity, indeed, we are unable to imagine what sort of melting process is mentally pictured by observers who seek to determine a point on a liquidus curve, other than a maximum or minimum, by any procedure which depends upon observing deformation of the material. We have dealt with this matter at some length in this section of our paper because the method referred to is frequently used by metallurgists and it cannot be expected to give reliable results. Of course, for certain practical purposes, the information desired may be a knowledge of the temperatures at which various mixtures become thin fluid, and observations which determine these temperatures may be quite to the point, but there is no reason, ordinarily, to believe that a satisfactory equilibrium diagram can be based upon such results.

Action of slags on siliceous hearths.—Determination of the FeO-SiO_2 diagram is of service in permitting a prediction of the action of FeO-rich slag upon siliceous furnace linings or, perhaps better expressed, it explains many facts already known concerning such action. Consideration of this matter in its more general aspects is best left in the hands of those more intimately concerned. There is just one point upon which

we wish to remark. Greig has already given an excellent discussion of the relative fluxing effects of a number of oxides upon silica, in connection with his determination of the immiscible region and the silica liquidus of each of these oxides.[20] The one point we shall discuss in connection with our determination of the silica liquidus and the high-silica eutectic in

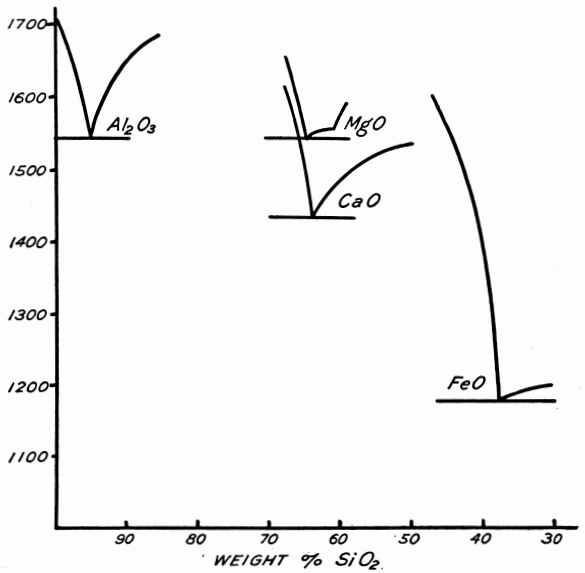

Fig. 6. Diagram to illustrate the relative fluxing power of different oxides upon silica. Authorities:
Al_2O_3-SiO_2, Bowen and Greig, J. Am. Ceram. Soc., 7, 238-254, 1924.
MgO-SiO_2, Bowen and Andersen, this Journal, 37, 487-500, 1914; and Greig, this Journal, 13, 15, 1927.
CaO-SiO_2, Day, Shepherd, and Wright, this Journal, 22, 282, 1906; and Greig, op. cit., p. 18.

FeO mixtures is the prevalence of the two apparently contradictory opinions that FeO has a powerful fluxing effect upon SiO_2 and the opposite opinion that it has a weak fluxing effect. Both opinions are correct. The apparent discrepancy arises merely from the fact that in reaching the one opinion attention has been focussed upon low temperatures, and in reaching the other, upon high temperatures. The fluxing power of any oxide upon silica is a relative matter and for that reason is

[20] Greig, J. W., this Journal, **13**, 1-44 and 133-154, 1927; and **14**, 473-484, 1927.

best discussed with the aid of a comparison diagram such as that given in Fig. 6 which shows the silica liquidus and the high-silica eutectic for several oxides that are of importance in this connection. Reference to the diagram shows that if we had a silica mass into which, say, 30 weight per cent FeO became introduced, melting would occur as soon as the temperature was raised above 1178° and the proportion of liquid formed at that temperature would be but little less than one-half the mass. No melting would occur at such temperatures if the introduced material were any one of the other oxides shown, so at these temperatures FeO is a relatively potent flux. Up to temperatures of 1400°, and somewhat above, there is no change in the situation but if we consider a temperature of about 1450° there is a marked change. At this temperature if the introduced material were CaO some melting would occur, and if the amount of CaO were 30 per cent the mass would be some 83 per cent liquid, whereas a mass into which FeO had been introduced in the same amount (30 per cent) would still be, at this temperature, but little more than one-half liquid. At 1450°, then, as compared with that of CaO, the fluxing power of FeO upon silica is relatively weak. Moreover, if we consider a temperature of 1550°, even the very refractory oxide, MgO, becomes a more potent flux than FeO, as measured by the proportion of liquid formed in a mass containing equal amounts of MgO on the one hand and of FeO on the other. All of the liquids considered in the above are thin liquids, so that for all ordinary purposes the factor mentioned, viz., the amount of liquid formed, is an adequate measure of the fluxing power whether we focus attention upon such deformation under load as might be induced by small additions of the several oxides mentioned or whether we consider the ready flowing of the material produced by larger additions.

In the case of Al_2O_3 the matter is somewhat more complicated. It is true even here that an addition of a small amount of that oxide to silica at 1550° will produce more liquid than a like amount of FeO. Five per cent Al_2O_3, for example, will convert the mass entirely into liquid whereas the same amount of FeO gives only about 10 per cent liquid. However, the liquid, 95 per cent SiO_2, 5 per cent Al_2O_3, is so extremely viscous that its deformation or flow might not be more readily produced than would these phenomena in the corresponding FeO mixture though 90 per cent crystalline.

Minimum amounts of Fe_2O_3 in slags.—The equilibrium diagram (Fig. 3) shows the minimum possible percentage of Fe_2O_3 in iron oxide-silica liquids *at their liquidus temperatures.* Theoretically, one might expect that it should be possible to induce greater reduction of the amount of Fe_2O_3 at higher temperatures without separation of iron, but our determinations show that there is no measurable change (see Table V). What influence the presence of other oxides in the liquid may have upon the minimum amount of Fe_2O_3 at any temperature it is impossible to predict. The proportion of Fe_2O_3 in the

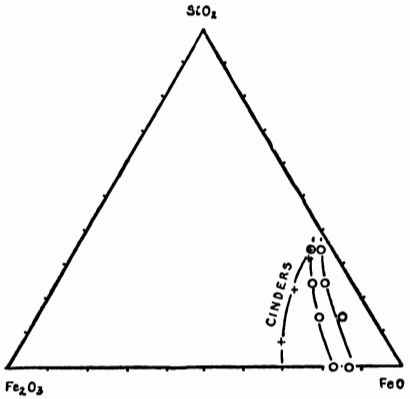

Fig. 7. Composition of melts containing SiO_2, FeO, and Fe_2O_3 in contact with furnace gases under varying conditions (three series) after Whitely and Hallimond.

slag is regarded by some as of importance in furnace practice on account of its function as a "carrier" of oxygen to the metal bath. Whitely and Hallimond have determined the variation with silica of the amounts of Fe_2O_3 and FeO in slags made of these materials only, and the effect of different furnace gases on these amounts.[21] Their innermost (least ferric) curve (Fig. 7) lies close to the position of our wüstite-iron boundary curve (Fig. 3), a fact which suggests that the gas conditions to which their mentioned curve pertains gave about the maximum possible reduction of Fe_2O_3. In connection with the determination of the amount of Fe_2O_3 in the slag it is desirable to point out that this amount will be somewhat decreased during crystallization of slag upon cooling, if iron

[21] Whitely and Hallimond, J. Iron & Steel Inst., **99**, 231, 1919.

globules are present, unless cooling is rapid enough to prevent reaction with these globules. It is to be doubted whether even a spoon sample could be cooled quickly enough to prevent some effect of that kind.

Some reflection of this equilibrium of Fe, FeO, and Fe_2O_3 as it appears in iron silicate melts is to be found in the varying constitution of scale formed during the working of metal, especially at a high temperature where the scale melts. McCance notes that, "as the percentage of SiO_2 increases the amount of FeO also increases and that of Fe_2O_3 gets less," and then adds, "There seems to be a physical equilibrium between these three substances wholly independent of their chemical grouping."[22] Our equilibrium diagram (Fig. 3) shows that the initial thin film of molten scale in equilibrium with iron would necessarily show the relation noted by McCance since it must lie along the boundary curves limiting the field of iron against adjacent fields.

SUMMARY.

The importance to petrology of silicates bearing iron in the ferrous condition has led us to investigate melting relations in the fundamental system involved, viz., the system, FeO-SiO_2. The work was carried out by using crucibles of pure electrolytic iron as containers for the melts and an atmosphere of nitrogen as a protection against oxidation. It is found that iron cannot reduce all the iron oxide of the melts to the ferrous condition, that all melts in equilibrium with iron contain some Fe_2O_3. The composition of the liquids cannot, therefore, be accurately expressed in a binary diagram and the full relations are expressed only with the aid of a ternary diagram in which FeO, Fe_2O_3, and SiO_2 may conveniently be taken as components. The diagram is given in Fig. 3. The amount of Fe_2O_3 in the liquid is greatest when no SiO_2 is present, the solids in equilibrium with the liquid being wüstite (FeO solid soluition) and iron, and the content of Fe_2O_3 in the liquid 11.5 per cent, a value which is in substantial agreement with recent work by others upon the same question. The amount of Fe_2O_3 in the liquid decreases rapidly as SiO_2 is added and while wüstite and iron are the solid phases in equilibrium. As soon as fayalite and iron become the solid phases

[22] McCance, Andrew, J. Iron & Steel Institute, **97**, 263, 1918.

the amount of Fe_2O_3 decreases less rapidly with added SiO_2, and finally when SiO_2 and iron are the solid phases the amount of Fe_2O_3 falls off at a still lower rate. The amount of Fe_2O_3 in the liquid at compositions close to fayalite (Fe_2SiO_4) is about 2.25 per cent. The pure compound, Fe_2SiO_4, like ferrous oxide and, indeed, all compositions on the FeO-SiO_2 join, therefore melts incongruently with separation of iron.

The amount of this departure from a truly binary character is, as these figures show, very small, especially for all compositions with enough SiO_2 to render them of interest to petrologists. With great gain in convenience the results may, therefore, be presented as a binary diagram by calculating all iron oxides as FeO. This has been done in Table VI and the data represented diagrammatically in Fig. 4. The diagram thus obtained shows a maximum at the composition of fayalite at 1205°, a eutectic between fayalite and tridymite at 1178° at the composition 62 per cent FeO, 38 per cent SiO_2, and a eutectic between fayalite and wüstite at 1177° and at the composition 76 per cent FeO, 24 per cent SiO_2.

These results are widely at variance with most earlier studies of the system, but these earlier studies bear internal evidence of inadequate precautions to insure equilibrium.

To petrologists it is of importance that there is but one crystalline compound between FeO and SiO_2, the orthosilicate, fayalite. The synthetic mineral melts at $1205 \pm 2°$ and the natural mineral from Rockport, Massachusetts, at sensibly the same temperature. Fayalite from Mourne Mountains, Ireland, has a melting interval of about 10° (1207 to 1217°), which fact is probably to be referred to manganese in solid solution in it. Both natural fayalites melt incongruently with separation of a small amount of metallic iron. No crystalline compound of the composition, $FeSiO_3$, forms at any temperature where liquid occurs in the system, nor have we been able to find any evidence of its crystallization even at temperatures as low as 660°.

The system is of much interest to metallurgists because it is the fundamental system of most slags. The results, therefore, give the melting temperatures of the pure iron silicate slags and indications of the thermal behavior of non-metallic (slag) inclusions in wrought iron and steel, as well as of the composition of scale formed on these metals while being "worked" under certain conditions.

ACKNOWLEDGMENTS.

We wish to express our indebtedness to Professor Hutchinson of Cambridge University for the specimen of fayalite from Mourne Mountains, Ireland; to Dr. Foshag of the U. S. National Museum for fayalite from Rockport, Massachusetts; to our colleague, Dr. Greig, for examining under the reflecting microscope the products containing opaque phases (iron or wüstite), where his experience with the iron oxides was of great value to us; and to our colleague, Dr. Posnjak, for X-ray photographs of the crystalline material approaching $FeSiO_3$ in composition. We also thank Mr. Swanger of the U. S. Bureau of Standards, under whose supervision our electrolytic iron was rolled into sheet from which we were able to stamp crucibles in our own shops.

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