EQUILIBRIUM AT HIGH TEMPERATURES IN SYSTEMS CONTAINING IRON OXIDES.

Thesis for the Degree of Doctor of Science

by

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SECTION 1.

INVESTIGATIONS INTO THE DISSOCIATION OF FERRIC OXIDE AT HIGH TEMPERATURES, AND INTO THE INFLUENCE OF LIME AND SILICA ON SUCH DISSOCIATION.

INTRODUCTION.

The oxides of iron play an important part in many high temperature processes, and knowledge of their behaviour at high temperatures is capable of wide application in the fields of geophysics, ceramics, metallurgy and general high temperature chemistry. Because of this they have been the subject of a considerable number of investigations, and by workers drawn from many different branches of scientific activity. Nevertheless, probably because of the inherent difficulties associated with research at elevated temperatures, knowledge concerning them has remained very incomplete.

The investigations described in the following pages comprise a detailed study of the equilibria existing at high temperatures in solid and liquid systems containing the oxides of iron, alone, and in the presence of certain other oxides, and of the factors affecting these equilibria. The work was inspired primarily by requirements in the field of ferrous metallurgy, and had as its object the provision of additional information of a fundamental nature concerning the reactions occurring in the slag in the open hearth steel furnace. The results obtained are, however, perfectly general in character and are applicable to any high temperature reactions involving the oxides of iron.

In the following section is given a brief statement of the metallurgical considerations which led to the present investigation.

THE MECHANISM OF OXYGEN TRANSFER THROUGH SLAGS CONTAINING IRON OXIDES, AND ITS RELATIONSHIP WITH SLAG CONSTITUTION.

In both the acid and the basic open hearth steel furnace a considerable amount of the oxidation essential to the refining process is brought about by the agency of oxygen from the furnace atmosphere. Whiteley and Hallimond[1] found that in the case of an acid charge, approximately fifty per cent of the carbon removal after melting down was due to oxygen from this source. In the basic process it may be even higher than this. After the initial melting-down period there is little possibility of direct contact between metal and gas, and it is now generally recognized that the bulk of this "gas-oxidation" is brought about by the diffusion of oxygen through the layer of liquid slag to the underlying metal. The mechanism of this oxygen transfer through the slag has been the subject of considerable study. Whiteley[2] early realised the importance of the part played by the iron oxide content of the slag. He showed that both ferrous and ferric oxide occur in normal slags, the proportion of the latter varying in significant fashion during the working of a charge. During the early stages, when there is a high content of oxidizable materials in the metal, the ferric oxide content of the slag remains low, this being particularly noticeable during the boil, when rapid oxidation of the metalloids is fostered by the increased intimacy of contact between slag and metal resulting from the turbulence of the bath at this stage. Towards the end of the process, however, the ferric oxide content of the slag shows a decided tendency to increase, even though no additions are made to it. At the same time the total iron oxide content of the slag also increases. The following figures given by Whiteley[2] show these changes occurring during the later stages of the working of an acid charge.

Carbon in bath. %	SLAG ANALYSIS.					Metallic globules found in slag. %.
	Fe %	FeO %	Fe_2O_3 %	MnO %	SiO_2 %	
0.30	23.6	30.1	0.25	11.6	53.5	0.30
0.20	23.3	29.3	0.50	-	-	0.10
0.15	23.9	29.5	1.20	-	-	-
0.10	24.5	29.6	2.10	-	-	-

In the basic process the same effect is observable but to a much more marked degree. Throughout the process the proportion of ferric oxide to ferrous oxide is notably higher, and towards the end the ferric oxide and total iron oxide contents of the slag increase in a very marked fashion, which has come to be recognized as a characteristic feature of basic practice. Whiteley's figures for the working of a basic charge are given in the table below.

Carbon in bath. %.	SLAG ANALYSIS.							Metallic globules in slag. %.
	Fe_2O_3 %	FeO %	MnO %	CaO %	MgO %	SiO_2 %	P_2O_5 %	
0.80	0.85	5.8	6.75	42.3	8.23	24.8	8.01	0.56
0.70	1.0	4.9	5.26	49.1	6.8	20.4	7.28	0.7
0.52	2.0	7.7	4.56	50.6	6.4	18.2	7.74	1.8
0.24	2.3	9.1	4.41	51.6	6.31	16.0	6.69	2.5
0.145	3.1	9.5	4.18	52.9	6.17	15.6	6.56	0.3
0.09	3.4	10.4	4.2	51.7	5.91	14.6	6.56	0.5
0.13	3.0	11.4	3.9	52.0	5.87	14.8	6.0	0.25
0.165	3.0	11.8	4.5	51.4	5.91	15.3	5.76	Trace

As was pointed out by Whiteley with reference to the above tables, the increase in ferric oxide in the slag in the absence of additions can be due only to atmospheric oxidation. At the same time the increase in the total iron oxide content of the slag must be due to oxidation of metallic iron of the bath. The two effects are closely parallel to one another, and hence, in view of the established fact that ferric oxide is reduced by metallic iron at high temperatures, it is reasonable to suppose that the second occurs as a consequence of the first. The generally accepted view is that an oxidation and reduction cycle involving the oxides of iron is set up in the slag, ferrous oxide undergoing continuous oxidation to the ferric state at the slag-air surface, while ferric oxide is continually undergoing reduction to the ferrous condition at the slag-metal interface, with consequent oxidation of part of the metal of the bath. The nett effect is a continuous diffusion of oxygen through the slag to the underlying metal. During the early stages of the refining process the effect of this is masked by the rapidity with which the iron oxides of the slag are reduced by the action of the metalloids in the metal bath, and it is only towards the end of the process, when the concentration of the metalloids has dropped considerably, that the consequences of these reactions are manifest.

That the mechanism pictured above is essentially correct has been confirmed by the observations of many investigators. Furthermore, examination of the relevant data available indicates that the cycle of reactions postulated is at least feasible thermochemically. Reliable quantitative data concerning the reactions involved have, however, always been lacking. For one thing the stability relationships between the oxides of iron at the appropriate temperatures have been very incompletely known. Again, as to how far these relationships are likely to be modified by the influence of the slag in which these oxides are embodied, little of a definite nature could be stated, though it has long been recognized that powerful constitutional influences must be involved to give rise to the well-marked differences that are observed between acid and basic slags in the matter of gas oxidation. In this connection several workers have indicated that a definite relationship appears to exist between the acidity - or, conversely, the basicity - of a slag and the proportion of ferrous to ferric oxide in it. Whiteley and Hallimond[1], Whiteley[2] and M'Cance[3] all describe experiments which show that, as the acidity increases the ferric oxide content tends to decrease, while increased basicity causes an increase in the ferric oxide content. Bainbridge[4] seems to have been the first to suggest that the reason for the high ferric oxide content of basic slags lay in the formation of stable compounds between ferric oxide and lime. These compounds have been repeatedly identified in basic slags[5] especially towards the end of the process, and the view that they stabilize the ferric oxide in this way has been widely accepted. Similarly the low ferric oxide content of acid slags is held to be due to the fact that the bulk of the ferrous oxide of the slag is combined with silica as stable ferrous silicates, and is thus prevented from oxidizing. Such statements have always remained purely qualitative, and to a certain extent hypothetical, however, owing to the lack of direct information on the subject. The whole matter is intimately related to the problem of slag constitution. In this connection it may be mentioned that for the past seven years the present writer has been associated with Professor Hay of the Royal Technical College in a series of investigations intended to increase the available information on this aspect of steel-making. During this period many important systems of slag-forming oxides have been studied at high temperatures, and their thermal equilibrium diagrams determined. These include the binary systems $MnO - SiO_2$[6], $FeO - SiO_2$[7], $FeO - MnO$[7], and $CaO - Fe_2O_3$[8], and the ternary systems $FeO - MnO - SiO_2$[9], $FeO-Al_2O_3-SiO_2$[10] and $FeO - MnO - Al_2O_3$[11]. As a result of these and of the similar investigations of other workers in the same field considerable light has been thrown on the question of the molecular constitution of slags. It should be pointed out, however, that the knowledge of constitution obtained from thermal equilibrium studies is quantitatively applicable to solid slags only, and has only qualitative significance when applied to problems involving liquid slags. There may be considerable differences between the molecular constitution of a liquid slag and that of the same slag after solidification. That such is probably the case is indicated by the fact that most of the compounds occurring in solid slags have been shown to melt incongruently.

IRON OXIDE EQUILIBRIA - PREVIOUS INVESTIGATIONS.

In the study of systems containing iron oxides at high temperatures the gaseous phase is of primary importance, since the oxygen pressure exerts a determinative influence on the composition of the oxide or oxides. The changes involved can be represented by the following general equations, each of which represents a reversible equilibrium, and the corresponding reactions can be made to proceed in either direction according to the conditions, the controlling factors being temperature and oxygen pressure.

$$6Fe_2O_3 = 4Fe_3O_4 + O_2$$

$$2Fe_3O_4 = 6FeO + O_2$$

$$2FeO = 2Fe + O_2.$$

It follows on ordinary chemical grounds, that, for each pair of oxides there is at any temperature a characteristic oxygen pressure at which they are in equilibrium, and at which they can co-exist in a stable condition. Changes in the oxygen pressure cause a pick-up or evolution of oxygen with consequent change in the composition of the oxide. In this respect investigations of iron oxide equilibria can be conveniently divided into two groups, (1) those which are concerned with the equilibria under directly measurable oxygen pressures, and (2) those which are concerned with the equilibria at extremely low oxygen pressures such as exist in mixtures of CO and CO_2 at high temperatures. The former group comprises studies of the dissociation of ferric oxide and of equilibrium in oxide mixtures ranging in composition from Fe_2O_3 to Fe_3O_4 approximately, depending on the temperature at which the investigation is carried out. The present series of investigations are primarily of this category. The latter group deals principally with the equilibria between Fe_3O_4, FeO, and oxygen-saturated iron, which have been subjected to exhaustive study by numerous investigators including Matsubara[12], Schenck and co-workers[13], and others.

Of previous researches with a bearing on the present project it will be sufficient to mention only those in which a systematic study was attempted. Walden[14] attempted to measure the dissociation pressure of ferric oxide at various temperatures by enclosing a sample in a sealed, evacuated tube and measuring the pressure developed when equilibrium had been attained at selected temperatures. This method is only valid if there is no solubility between the dissociating oxide and the product of dissociation. Sosman and Hostetter[15] showed that this was not true. They studied the dependence of the oxygen pressure on the composition of the dissociating oxides at constant temperature. At the temperatures studied (1100 and 1200°C.) the form of the oxygen-pressure/composition isotherm showed continuous and progressive variation of oxygen pressure with composition over the range Fe_2O_3 to Fe_3O_4, and they therefore assumed, justifiably, that there was complete solid solubility between Fe_2O_3 and Fe_3O_4 at these temperatures. Considerable doubts were thrown on this conclusion by Benedicks and Lofquist[16], who pointed out that in the light of microscopic evidence this was highly improbable. White, Graham and Hay[8] (see later) from a study of the dissociation pressure of ferric oxide at temperatures up to 1450°C. concluded that there was only partial solubility between the solid oxides at high temperatures. Shortly afterwards, and while the present investigations were in progress, a second paper on the subject was published by the U. S. Geophysical Laboratory, again bearing the name of Sosman, but with a number of other collaborators[17]. This paper reversed the finding of the first from this source, and confirmed that there was only partial solubility between the oxides. The solubility limits differ considerably from those fixed by White, Graham and Hay, however.

As regards the behaviour of ferric oxide in liquid melts, with which this present investigation is largely concerned, little systematic work has previously been attempted. Isolated observations have been made, as for instance those of Whiteley and Hallimond[1], Whiteley[2] and McCance[3] previously alluded to. During the course of the present work the results of an investigation by Krings and Schackmann[18] on the oxygen pressure of iron oxide melts were published. The method employed was similar to that previously used by White, Graham and Hay, but the determinations were extended to higher temperatures to embrace the liquid oxides. This was made possible by the use of fused alumina tubes in which to heat the experimental samples. Several compositions containing lime and silica were also investigated. The results obtained, however, do not appear to be particularly accurate, even when allowance is made for the difficulty of the study, and the work appears to have been rather hurriedly carried out.

The behaviour of the oxides of iron in glasses has also been investigated by several workers, and it has been shown[19] that the dissociation of ferric oxide in glasses is dependent on the composition of the glass.

PRESENT INVESTIGATIONS.

GENERAL CONSIDERATIONS: The present series of investigations originated from, and may be regarded as a continuation and extension of the investigation of ferric oxide described by White, Graham and Hay[8] to which reference has already been made. The findings of this paper may be briefly summarized here. It was found that ferric oxide developes measurable dissociation pressure in the neighbourhood of 1100°C. The dissociation pressure was measured at various temperatures and was found to increase rapidly and almost logarithmically with temperature. In the solid state the product of the dissociation is Fe_3O_4 which is partially soluble in the residual Fe_2O_3, the solubility increasing with rise of temperature. When the amount of Fe_3O_4 formed is in excess of that required to form a saturated solution in the residual Fe_2O_3 a new solid phase appears which is a saturated solution of Fe_2O_3 in Fe_3O_4. The system then becomes monovariant, the oxygen pressure, so long as the two solid phases are present, being a function of temperature only and increasing approximately logarithmically as the temperature increases. Further dissociation leads ultimately to complete disappearance of the Fe_2O_3-rich solid solution, and the system becomes once more divariant. The reaction involved appeared to be reversible at all stages, though with some difficulty if the oxide had been strongly sintered by the process of dissociation, and it was concluded that, at any temperature and oxygen pressure, a true equilibrium is reached, the amount of dissociation occurring being a function of these two variables. Liquid melts containing lime to Fe_2O_3 in the proportions of monocalcium ferrite ($CaO.Fe_2O_3$) and dicalcium ferrite ($2CaO.Fe_2O_3$) respectively were also investigated, these being the two compounds of lime and ferric oxide whose existence had been established in determining the thermal equilibrium diagram of the system CaO-Fe_2O_3 as described in the earlier part of the same paper. It was found that in these melts dissociation of the ferric oxide appeared to proceed until an equilibrium was reached between the ferrous and ferric contents just as in the case of the solid oxide previously investigated, but it was not possible to say at that stage whether the ferrous oxide formed existed in the free condition in the liquid melts, or whether it was combined with ferric oxide liberated by the peritectic dissociation of the ferrite on melting. As before the factors controlling the equilibrium were temperature and pressure, the dissociation increasing as the temperature was raised or as the oxygen pressure was decreased. It was also shown that the lime present in the melts did not act merely as an inert diluent, but that it caused a displacement in equilibrium in the direction of higher Fe_2O_3 concentration, this being more marked in the high lime melt than in the low lime melt. From these observations it was concluded that mono- and dicalcium ferrite, though they underwent partial dissociation on melting, had appreciable stability in the liquid state. This was, of course, in agreement with the suggestion made by Bainbridge (see earlier), and explained the high concentration of ferric oxide formed in basic slags as compared with acid slags.

The present investigations constitute an attempt to make a systematic study of the equilibria which had thus been shown to exist in systems containing iron oxides at high temperatures. The project was to study the equilibrium in systems in which the oxides of iron alone were present, and also in systems in which there were (1) a typical strongly basic oxide, (2) a typical strongly acid oxide, in addition to the iron oxides. In ordinary slags the most important base and acid are lime and silica respectively, and so these substances were chosen for the investigation. It was also intended to study the equilibrium in melts containing both of these substances together in various proportions so that the connection between acid and basic slags should be made clear.

In carrying out the actual experiments it was found most convenient to use ferric oxide as a starting product. Theoretically, since the equilibria studied are all reversible, any of the oxides of iron could have been used, since the final state reached in any experiment was independent of the initial composition of the iron oxide, and depended only on the conditionsof the experiment. It was, however, essential that the initial composition of the oxide should be known accurately, since the accuracy of the final determinations depended on this, and, of the three oxides of iron, ferric oxide was found easiest to prepare with a standard and regular composition. With a known weight of ferric oxide embodied in the original experimental sample, the composition of the sample at equilibrium under any conditions could be got by measuring the amount of dissociation which had occurred. This could be done by measuring the amount of oxygen lost by the system in reaching equilibrium, this being a direct measure of the amount of ferrous oxide formed. Furthermore, the presence of lime and silica caused no interference, since these substances are stable at high temperatures under the conditions of the experiments. Two general methods of measuring the oxygen evolution were possible, (1) by measuring the increase of pressure taking place in a closed system, or (2) by finding the weight lost by the sample due to oxygen evolution. Both of these methods were tried out.

PREPARATION OF THE STARTING MATERIALS.

FERRIC OXIDE: It was necessary to use ferric oxide of standard composition, and absolutely free from ferrous oxide, since the starting composition was the basis of all calculations of equilibrium compositions. Considerable time was, therefore, devoted to the development of a suitable method of preparation. Finally the following method was adopted, pure, recrystallized ferrous oxalate being used as the starting material. The ferrous oxalate was first ignited over a small flame in air, which caused it to decompose and oxidize spontaneously, giving a bulky red powder. This consisted of ferric oxide mainly, contaminated with carbonaceous matter, and usually analyzed about 69 per cent total iron. From this a uniform product was obtained by heating to about 1200°C in oxygen and cooling slowly from that temperature. Under this treatment an irreversible loss of weight occurred, accompanied by an evolution of gas, and the total iron content increased to a value approximating closely to 69.94 per cent which is the theoretical iron content of pure ferric oxide. Over a large number of determinations carried out with samples of the oxide prepared by this method the deviation from this value was practically always within the limits of experimental error, typical values ranging from 69.90 to 70.05 per cent. It was, however, necessary to avoid too high a temperature during this final reheating in case the small amount of dissociation of the ferric oxide which occurred at the high temperature might not be completely reversed during cooling. As it was, any deviation in the final analysis was always towards too high a value for the iron content of the oxide, indicating the presence of ferrous oxide in the sample. With care, however, using this method, it was possible to prepare a standard and reproducible product. In practice it was found convenient to analyse the ferrous oxalate for total iron, and to weigh out the necessary amount of oxalate from a sealed bottle each time an experimental sample was to be made up. This was then ignited at a low temperature in a platinum basin as described above, transferred to the weighed platinum crucible in which the experiment was to be carried out (this operation requiring considerable care to avoid loss), and it was then ignited at the high temperature in oxygen. This latter operation was conveniently carried out in the apparatus used for the equilibrium investigations. After ignition the sample was weighed in the crucible. If the weight of ferric oxide formed in this way did not tally with the weight of oxalate taken, the sample was rejected. In this way a double check was kept on the ferric oxide used. It was found that, theoretically, 10 grams of ferrous oxalate should have been equivalent to 4.4453 grams of ferric oxide, this figure being got from the average of a considerable number of determinations of the iron content of the oxalate.

LIME: Owing to the comparative rapidity with which lime gains in weight in the atmosphere, and the necessity for accuracy in weighing out all the constituents, it was found best to make all lime additions in the form of weighed amounts of calcium oxalate. Pure calcium oxalate was used for the purpose, and the lime content was found by the ignition of weighed samples to lime, followed by cooling in desiccators containing fresh calcium chloride, since it was found that lime could abstract moisture from the atmosphere over the partly spent material. The samples were then weighed as quickly as possible. Thereafter the calcium oxalate was kept in a sealed bottle, the composition being checked periodically by the same method. After the construction of the high temperature balance described later, it was used to check the composition of the oxalate, the sample being ignited while suspended from the pan of the balance, and weighed at once at high temperature as soon as the weight had become constant. The values so obtained agreed very closely with the earlier ones. It was found that one gram of the calcium oxalate was equivalent to 0.3826 grams of calcium oxide, the variation in the actual values being never more than two or three in the fourth decimal place on either side of this figure.

SILICA : Two sources of silica were employed - pure silica sand and pure precipitated silica. The latter had to be ignited to over 1000°C before use to remove moisture. No systematic difference was detectable between the results obtained with the different forms, but the sand was usually preferred since it was much less bulky and therefore more convenient to add to the melts.

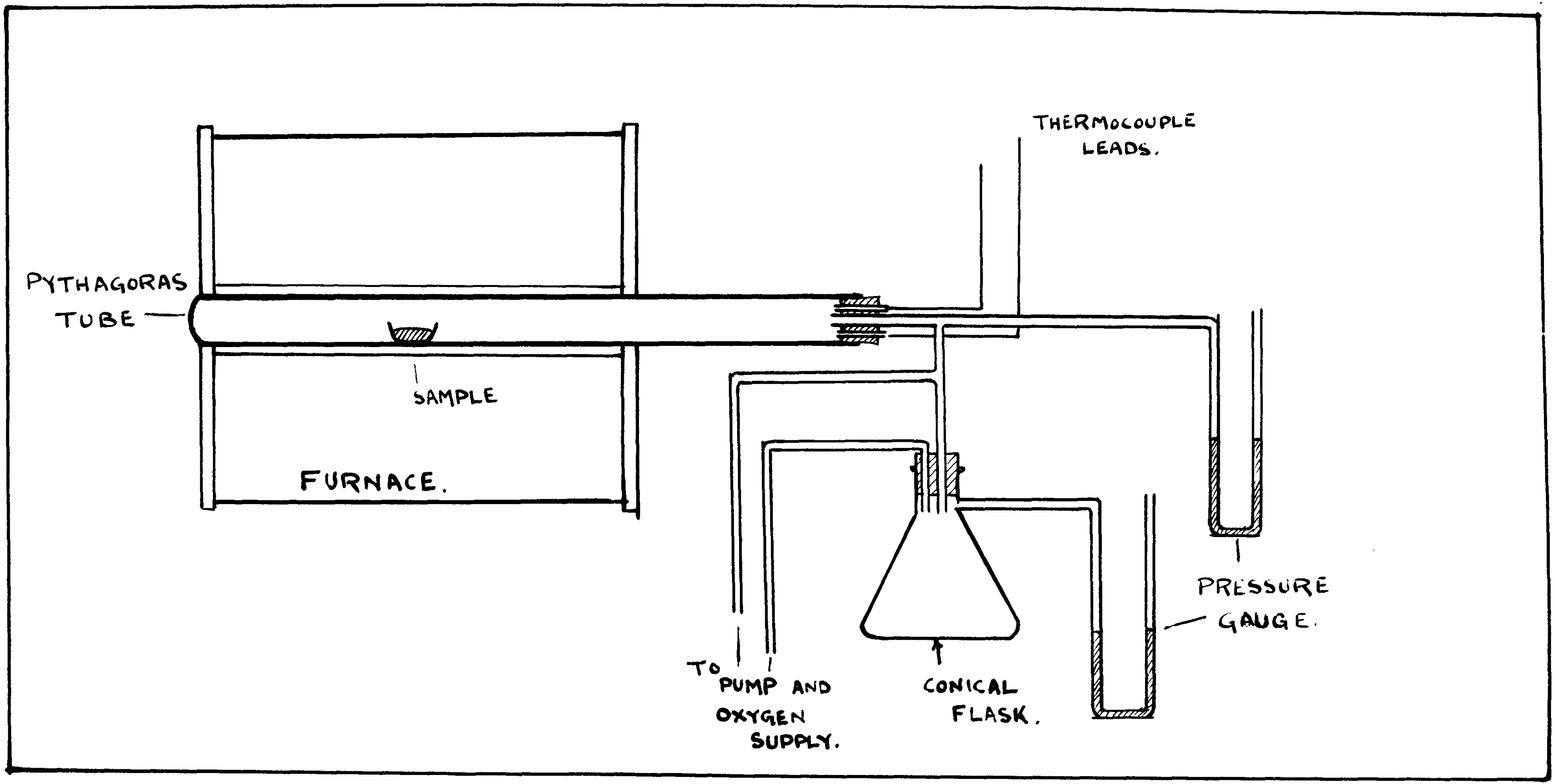
EXPERIMENTAL PROCEDURE.

Three different methods of attack were employed in the investigations. These were used in turn, and each represented an advance in accuracy over its predecessor, the last of the three being decidedly more accurate than the other two, and giving results that were eminently consistent and reproducible. It was, therefore, adopted and employed for most of the experiments. These methods are fully described below.

The same type of furnace was employed throughout the course of the work. This was a molybdenum-wound tube furnace, which has been described many times previously[20]. The furnace tube proper, which carried the molybdenum winding, was constructed of Norton's "Alundum", and was enclosed in a steel case inside which a reducing atmosphere was maintained,while the furnace was at high temperatures,to prevent oxidation of the molybdenum. The reducing atmosphere was produced by passing a mixture of nitrogen and hydrogen into the furnace casing, this mixture being got by"cracking" ammonia gas by passing it over iron turnings at approximately 900°C. To allow of the experiments being carried out in controlled atmospheres, an impervious, refractory tube of Pythagoras composition was inserted in the furnace,and kept the melts from coming into contact with the reducing atmosphere of the furnace.

A platinum/platinum-rhodium thermocouple was used for temperature measurement. This was calibrated before use and

FIG. 1.


THERMOCOUPLE LEADS.
PYTHAGORAS TUBE
SAMPLE
FURNACE.
PRESSURE GAUGE.
TO PUMP AND OXYGEN SUPPLY.
CONICAL FLASK.

checked at intervals against the melting points of various pure substances, including gold and palladium.

METHOD OF OXYGEN PRESSURE MEASUREMENT: The first method employed was based on the measurement of the oxygen evolution from the ferric oxide of the experimental samples by means of oxygen pressure measurements. Both the method and the apparatus employed have been fully described intthe paper by White, Graham and Hay to which reference has already been made. Figure 1 shows the apparatus employed. As can be seen the furnace was used in a horizontal position. The "Pythagoras" tube was closed at one end, and the other end carried a rubber bung, through which passed connections to the mercury pressure gauge and to the "Cenco Hyvac" pump used to evacuate the apparatus. The thermocouple leads were also passed through the bung, and thence made connection with a "Tinsley" Vernier Potentiometer, which was used in conjunction with a "Tinsley" mirror galvanometer for temperature measurement. Special precautions were taken to prevent the heat from reaching the rubber bung, baffles and a water-cooled copper coil being placed at the end of the tube for this purpose. For reading the mercury levels in the pressure gauge a vernier cathetometer capable of reading to 0.0001 centimetres was employed. Between the pump and the bung a T-piece was inserted, and one leg of this was connected to a conical pressure flask and thence to an oxygen cylinder. This flask was also connected to another pressure gauge, so that, if necessary, known volumes of oxygen could be added to, or withdrawn from, the system, stopcocks being provided for the purpose. It was, of course, necessary to know the volume of the flask.

As already mentioned this apparatus was used successfully to investigate the dissociation of ferric oxide in the solid state, and when embodied in melts of monocalcium and dicalcium ferrite composition. In the former case the following [illegible] method was adopted. A weighed sample of the oxide was placed in the "Pythagoras" tube in a platinum crucible. The apparatus was then evacuated and a predetermined pressure of oxygen was then admitted, after which the temperature was raised gradually. At suitable intervals during the course of the heating the temperature was held steady in the hot zone of the tube until the temperature distribution along the tube had reached a steady state. This was shown when the pressure reading on the manometer had become constant. In each case the temperature and pressure were recorded. When these values were plotted on a temperature/pressure curve, it was found that at low temperatures a regular curve was obtained, but that at higher temperatures a deviation was observable due to gas evolution in the tube. The exact temperature at which this occurred was a function of the oxygen pressure in the tube, the temperature of initial evolution tending to increase as the pressure was raised. It was found that, by producing the initial regular part of the curve, which was almost linear at temperatures over 1100°C, the increase in pressure due to gas evolution on heating to any temperature could be got by direct measurement of the extent of the deviation. Provided that the total enclosed volume of the apparatus was known, and that the equivalent of the pressure difference due to gas evolution could be estimated at room temperature (i.e. that the effect of temperature as recorded in the hot zone of the tube could be allowed for), the volume of oxygen given off by the ferric oxide in heating to the particular temperature could be calculated. The volume of the apparatus was got directly by noting the pressures developed when known amounts of gas were admitted into the evacuated apparatus. As regards the correction for temperature, by making a series of "blank" runs with no oxide in the tube it was found possible to draw a curve showing the fractional increase in pressure occurring in the apparatus on heating the tube from room temperature to any particular temperature within the range covered by the experiments. It was, of course, necessary for the application of the data thus obtained that the apparatus should be left unaltered from day to day. In particular it was important that the position of the "Pythagoras" tube in the furnace should be left unaltered, since any change altered the temperature distribution along the tube when thermal equilibrium had been reached at any temperature, and consequently altered the value of the factor at that temperature. Even as it was, it was found that the curve of fractional pressure increase was not perfectly reproducible from day to day. The error was not, however, excessive, and it was estimated that the maximum error to be expected in the results from this source would be of the order of three per cent, this being the extent of the "spread" observed over a considerable number of blank runs. At the time, in view of the difficulties associated with such high temperature researches, this was regarded as quite satisfactory. Room temperature was assumed constant at 15°C for all experiments since it was found that the effect of the deviations from this figure that were likely to occur would be negligible. A more serious effect of the room temperature, and one that probably contributed to the observed "spread" in the calibration factors, would be that it would have a direct effect on the temperature distribution along the tube at any temperature. Hence it was tried to keep the temperature of the room constant as far as possible.

By varying the pressure of oxygen that was initially introduced into the tube it was possible to obtain figures for the dissociation occurring at various oxygen pressures, and temperatures.

In the case of the ferrite melts mentioned above a slightly different procedure was adopted. It was first necessary to prepare the ferrite from the appropriate mixture of lime and ferric oxide. This was done by heating to above the melting point in an atmosphere of oxygen at about one and one third atmospheres pressure, followed by slow freezing under the same oxygen pressure, since it was found as the result of experiments that both of the ferrites, though they remained stable in oxygen up to their melting points, underwent partial dissociation on melting with liberation of oxygen and formation of ferrous oxide in the melts. This could not be prevented even at the highest oxygen pressure obtainable in the apparatus, though the extent of the dissociation could be decreased by increasing the oxygen pressure. By slow cooling from the liquid state in oxygen at the above-mentioned pressure, it was possible to obtain mono- and dicalcium ferrites containing no detectable ferrous oxide. The dissociation of these compounds could then be studied by the method already described for ferric oxide. After each run it was necessary to cool slowly at about one and a third atmospheres of oxygen to make sure that all of the iron was once more oxidized to the ferric state before the commencement of the next run. As far as could be ascertained from the curves, dissociation of the ferrites below the melting point was negligible (except possibly at very low oxygen pressures when a slight gas evolution was apparent, which may, however, have been due to the action of platinum on the iron of the ferrite at these very low pressures - an effect which is discussed later). On melting there was a sudden evolution of gas till equilibrium was attained causing a definite "step" to appear on the pressure/temperature curve. As the temperature was raised above this point, the gas evolution increased progressively, but at a much slower rate. As before the amount of gas evolution taking place on heating to any temperature was estimated by measuring the extent of the deviation from the normal curve at that temperature. Hence the composition of the melt at that particular temperature and oxygen pressure could be calculated. By varying the initial pressure of oxygen put into the tube the dissociation was studied over a range of pressures. The application of this method obviously involved the assumption that no pick-up or evolution of oxygen by the melt had occurred below the temperature at which the first noticeable deviation from the normal curve took place, since such pick-up or evolution would produce an alteration in the composition of the melt which was not allowed for in computing the final composition. For the ferrite melts, so long as the lime present was sufficient to combine with all of the ferric oxide (i.e. so long as the molecular ratio of lime to ferric oxide was not less than unity), and so long as the melt was free from ferrous oxide, this seemed to be justified, as consistent results were obtained by this method as shown in the published account of the research. Attempts to extend the method at the commencement of the present investigation were, however, much less successful, and it was found that these assumptions were not justified in the case of melts in which (a) the lime to ferric oxide ratio was less than unity, (b) melts which contained appreciable silica as well as lime. It was found that many of these melts underwent changes in oxygen content in the solid state, these changes being too sluggish in nature to show as definite deviations on the pressure/temperature curves. Hence the oxygen evolution above the melting point was not a true measure of the total change in composition occurring. The most frequent source of error seemed to be due to the presence of ferrous oxide (combined as Fe_3O_4 in the solidified melts) which underwent slow oxidation on heating in oxygen. The device previously employed, of cooling slowly in oxygen from the liquid state, was not sufficient to ensure complete oxidation of this free iron oxide to the ferric state owing to the sluggishness of the reaction involved. Even fairly prolonged soaking at temperatures below the melting point was not sufficient to ensure that the oxidation was complete,for crystalline magnetite is markedly inert. Because of this it was necessary to weigh the melts before each run to find the starting composition, the difference between this weight and that of the constituents originally used to make up the melt representing the weight of oxygen lost during the run. On the other hand the presence of free ferric oxide in these crystallized melts could also produce errors, as it was liable to dissociate below the melting point to a certain extent. All these considerations were not appreciated till later work had revealed all the factors involved. At the time it was clear that considerable errors were arising, owing to the lack of agreement between the results from different runs. Theoretically it should have been possible to assess all the changes occurring on heating from room temperature to high temperatures above the melting point by using the fractional-pressure-increas factors determined for the apparatus to calculate, at any temperature, the pressure that would have been exerted by the initia oxygen that was admitted to the tube, if no changes in the melt had taken place. The difference between this and the actual recorded pressure at that temperature would then have given the oxygen evolved or absorbed by the melt, and hence the compositio could have been calculated. As already explained, however, there was a variation from day to day in these factors. The error arising from this was not of serious dimensions so long as the factors were used only to convert to room temperature the pressu increases got by measuring the deviations on the pressure/temperature curves. An error of say three per cent in assessing the expansion would simply produce an error of three per cent in the final result. A little consideration will, however, show that this was not the case when the factors were used to estimate the pressure exerted at high temperatures by the original oxygen in the tube. The possible error due to

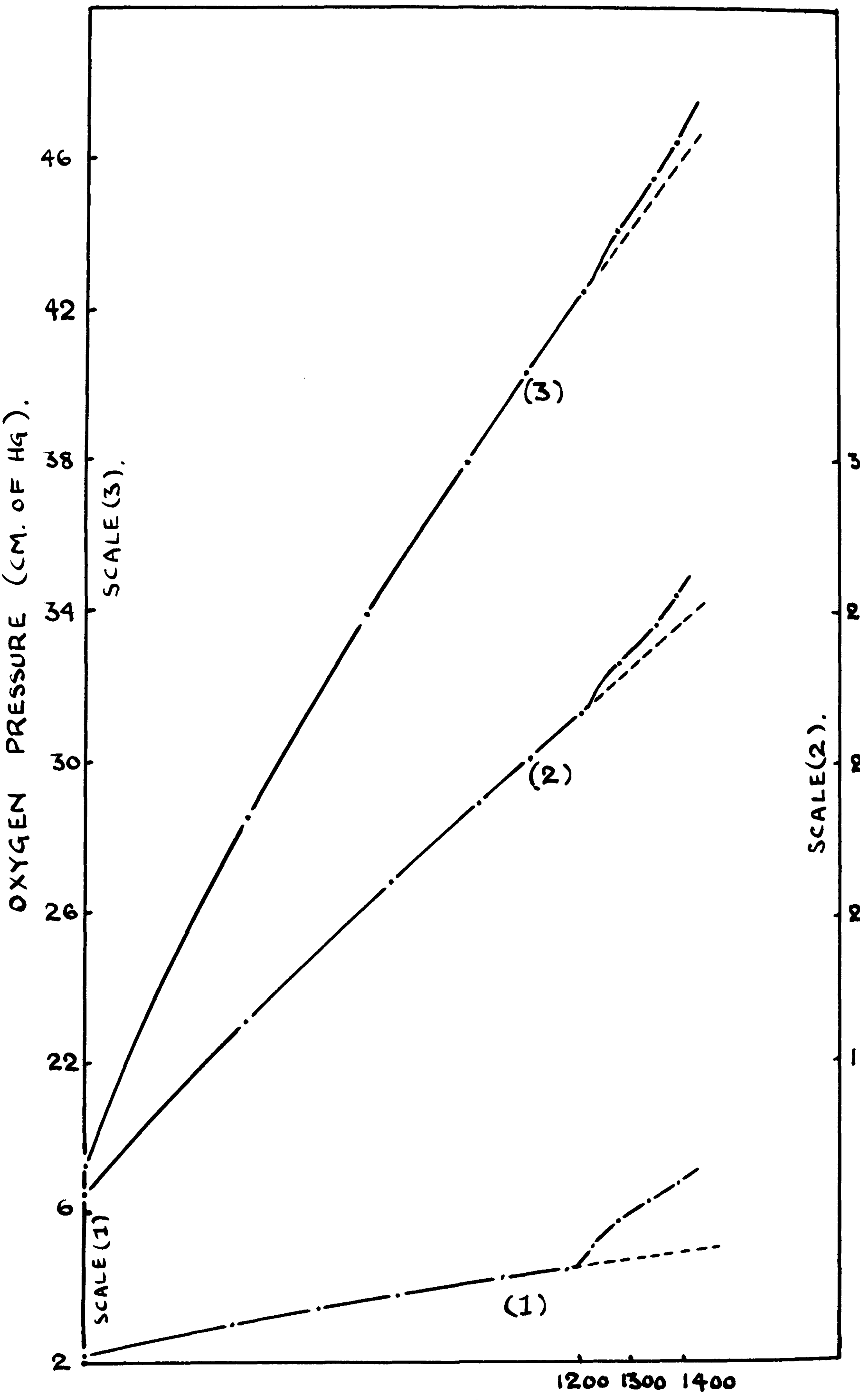

OXYGEN PRESSURE (CM. OF HG).
SCALE (3).
SCALE (2).
SCALE (1)
46
42
38
34
30
26
22
6
2
32
28
24
20
16
(3)
(2)
(1)
1200
1300
1400
TEMP. °C.

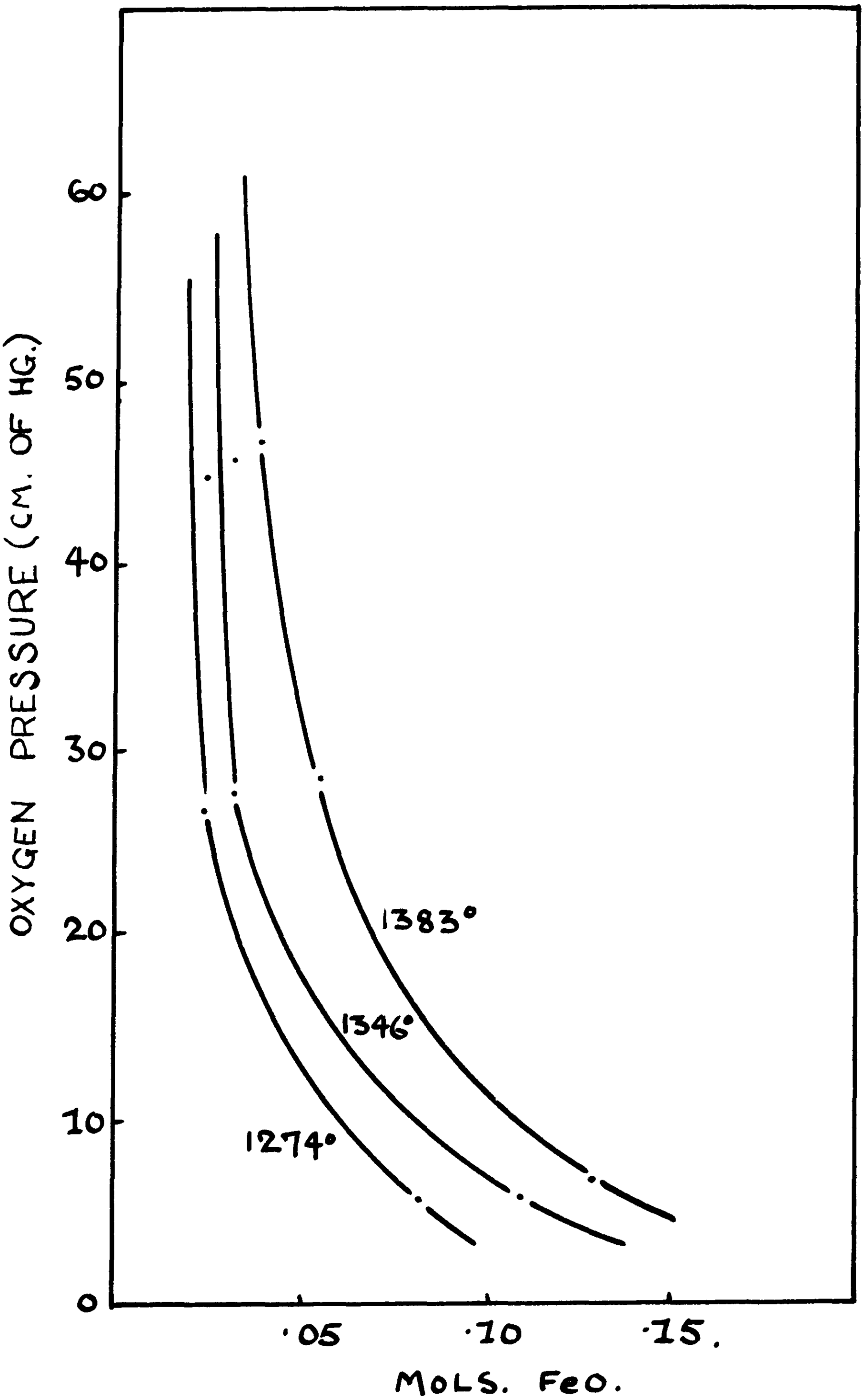
FIG. 2.

variations in the factors was then very much larger. An error of three per cent in the value of the pressure-increase-factor would produce an error of three per cent in the calculated pressure, which would represent a very much larger percentage error in the value got for oxygen evolution from the melt, since this was got by subtracting the calculated value of the pressure from the actual value. In practice this was found to be the case, and attempts to increase the accuracy of the determinations by this method were unsuccessful, the agreement between the results of different experiments being very unsatisfactory.

EXPERIMENTAL RESULTS GOT BY THE METHOD OF OXYGEN PRESSURE MEASUREMENT: In view of the bulk of the more accurate experimental data got later by other methods, most of the work done by this method was rejected. In Figure 2, however, are shown the pressure/temperature curves got during the investigation of a melt by this method. The deviations occurring on melting can be seen. By production of the regular part of the curves as shown the extent of the deviation can be got at any temperature, and hence the composition of the melt at that temperature can be calculated, as indicated in the table below. It will be noticed that the composition of the original melt is such that the bases are in excess of the acids. Hence, on slow cooling in oxygen, all the ferric oxide will be combined as ferrite, as there is enough lime left to do this even allowing for the formation of calcium silicates. Hence the troubles discussed above should not be encountered with this composition.

In the table below the column headed "dP" gives the pressure increase resulting from dissociation at the various temperatures. The next column gives the "fractional-pressure-increase-factors" at the various temperatures, derived in calibrating the apparatus. By means of these factors the measured deviations are calculated to room temperature.

FIG. 3.



OXYGEN PRESSURE (CM. OF HG.)
60
50
40
30
20
10
0
·05
·10
·15.
MOLS. FeO.
1383°
1346°
1274°

Hence, since the volume of the apparatus is known, the weight of oxygen liberated can be got by simple calculation. From this the weight of FeO formed in the melt can be calculated. In the last column the number of gram-molecules of FeO formed from that weight of the melt containing originally 1.000 gram-molecules of Fe_2O_3 is given.

EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELT AT VARIOUS TEMPERATURES AND OXYGEN PRESSURES.

Original composition of melt:- 1.371 mols CaO; 0.039 mols SiO_2; 1.000 mol Fe_2O_3.

Actual weight of Fe_2O_3 taken = 4.4450 gm.

Volume of apparatus = 1850 c.c. Room Temperature = 15°C.

Temp. °C.	Oxygen Pressure. cm. of Hg.	dP cm. Hg.	Fractional Pressure Increase	Weight of O_2 Liberated	FeO formed mols.	FeO from 1 mol Fe_2O_3. mols.
1274	44.2	.35	2.055	.0056	.00070	.025
1346	45.7	.50	2.12	.0077	.00096	.035
1383	46.5	.60	2.15	.0092	.00115	.042
1274	26.6	.35	2.055	.0056	.00070	.025
1346	27.65	.45	2.12	.0070	.00088	.032
1383	28.5	.80	2.15	.0123	.00154	.055
1274	5.7	1.15	2.055	.0185	.00231	.083
1346	6.2	1.65	2.12	.0257	.00321	.116
1383	6.7	2.00	2.15	.0306	.00384	.138

From the data thus obtained oxygen-pressure/ferrous-oxide isotherms have been constructed and are shown in Figure 3. The agreement between the experimental points is only fair.

THE METHOD OF QUENCHING:

In addition to the drawbacks described in the previous section, the original method suffered from the disadvantage that, with the apparatus as it was, it could not readily be used for temperatures over 1450°C. Above this temperature "Pythagoras" composition begins to soften and collapse of the tube occurs if the pressure inside is much below atmospheric. For high temperatures it was necessary to use an inert gas in the tube if the oxygen pressure desired was lower than this. The accuracy of the method was still further decreased by this device. In an attempt to find a more satisfactory method, which could be used to at least 1600°C, a series of quenching experiments was carried out. For this purpose the "Pythagoras" tube and furnace were used in a vertical position, and, to lessen the stresses on the tube in the hot zone, it was partly suspended from above. When this precaution was taken, temperatures of 1650°C have been reached without serious damage to the tube. During these quenching experiments the tube was open to the atmosphere so that the melts were under an oxygen pressure of 15.2 cm. of mercury.

The procedure adopted was as follows. A platinum crucible, containing the appropriate amounts of the desired constituents, was weighed accurately. For the purpose of these experiments an accuracy of at least 0.0005 grams was desired in all weighings, and a balance capable of giving this was employed. The crucible was then suspended inside the "Pythagoras" tube in the hot zone of the furnace, which was heated up to the desired temperature. For simplicity the thermocouplesleads were used to support the crucible. After sufficient time had been allowed for equilibrium to be attained, the crucible was rapidly pulled from the tube. An "air quench" was thus obtained, any more drastic method being impractible owing to the necessity for accurate weighing afterwards. Actually this method gave quite a rapid quench, as the crucible and its contents weighed only about 20 grams. Further, freezing, at least of the surface, occurred practically instantaneously, and rapid oxygen pick up was only possible while the melt remained liquid. The crucible and its contents were then weighed when cold, after the thermocouple leads had been detached. The initial composition being known, the final composition at equilibrium could be arrived at from the change in weight recorded, on the assumption that no change had occurred on cooling.

A melt of ferric oxide was first investigated at 1592°C. Progressive additions of silica were then made to it, the equilibrium being determined after each addition at the same temperature. This gave a series of determinations with increasing silica contents. In making the necessary calculations, the change in the initial weight due to the silica additions was, of course, allowed for. As in the earlier series of experiments, the determination of the oxygen lost from the initial ferric oxide, was made use of to give the total amount of ferrous oxide formed in the melts, and hence the amount of ferrous oxide formed in that weight of the melt containing 1.000 gram molecules of ferric oxide initially before dissociation occurred. A similar series of experiments was also carried out to find the effect of increasing lime content on the dissociation of ferric oxide, the lime additions being made in the form of calcium oxalate of known lime content, as previously mentioned. The oxalate was then carefully decomposed to avoid loss by slowly heating the crucible to over 1000°C.

With both lime and silica a series of results was obtained which appeared to be quite consistent and coherent, and individual results appeared to be repeatable within reasonably narrow limits. Over the ranges of composition covered it was found that an increasing silica content caused a progressive increase in the dissociation of the ferric oxide as measured by the ferrous oxide formation, while an increasing lime

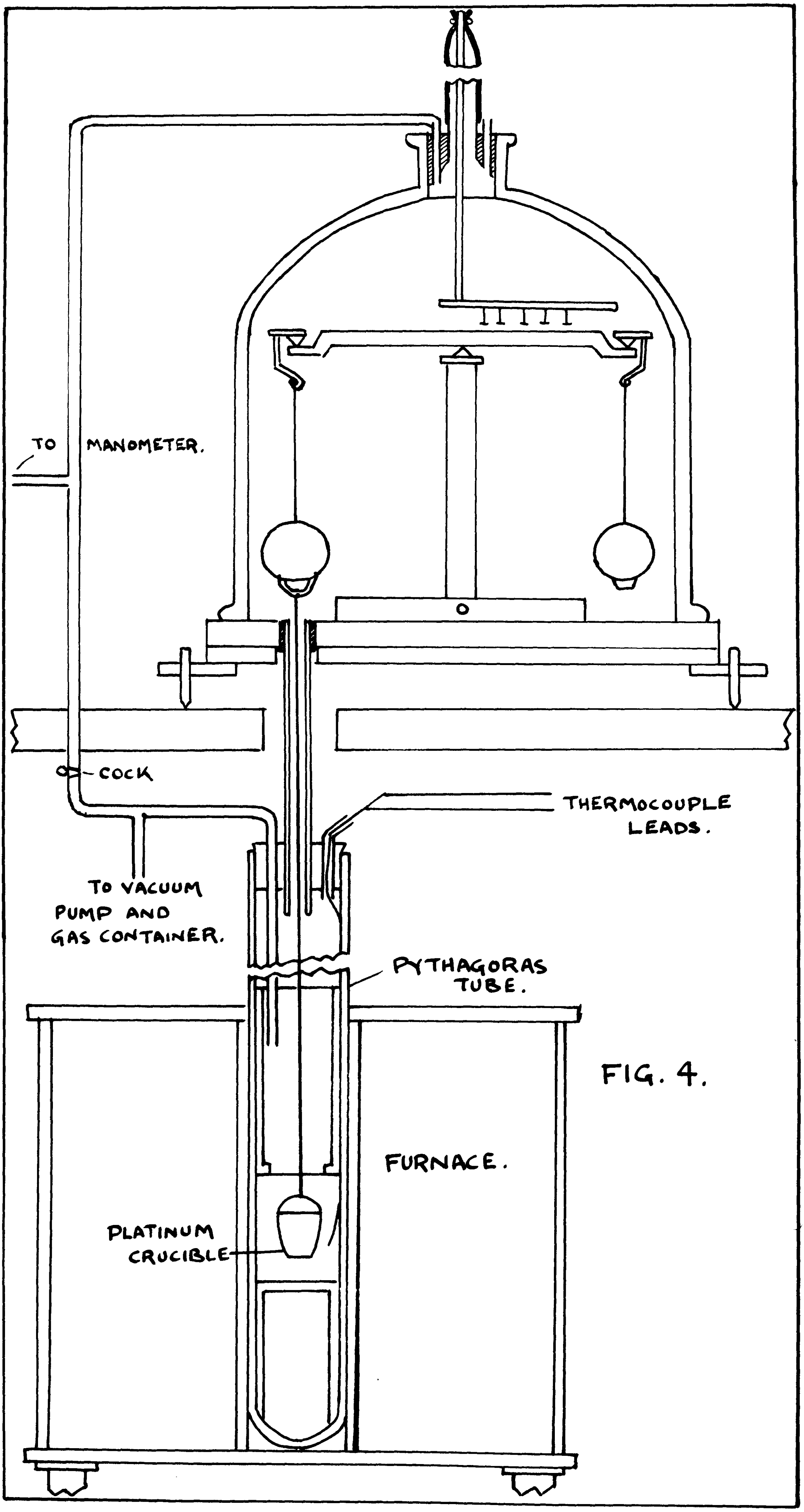

TO MANOMETER.
COCK
TO VACUUM PUMP AND GAS CONTAINER.
THERMOCOUPLE LEADS.
PYTHAGORAS TUBE.
FURNACE.
PLATINUM CRUCIBLE

FIG. 4.

content caused the dissociation to decrease progressively. The results for lime addition are given later in Table VIIB, and for silica (also later) in Table XIIIB.

THE METHOD OF THE HIGH TEMPERATURE BALANCE:

The accuracy of the results obtained by a quenching method depends on the rapidity of the quench. With a view to estimating the accuracy of the method, and, if possible, to improving on it, it was decided to make an attempt to weigh the melts while they were actually at the temperatures under investigation. Difficulties were anticipated, but, in practice, the method proved very successful, and was adhered to throughout the remainder of the investigation. A sketch of the apparatus employed, in its final form, is given in Figure 4, which is largely self-explanatory. The balance employed was a sensitive assay balance suitably modified. It was placed on a specially-constructed shelf above the furnace, the crucible being suspended in the hot zone of the furnace by means of a platinum suspension wire attached to one pan of the balance as shown. The original apparatus was open to the atmosphere, but it was later completely enclosed to allow of the use of controlled atmospheres. This was carried out by enclosing the balance by means of a specially-constructed bell-jar resting on a glass plate as indicated in the sketch, a hole having been drilled in the plate to allow the suspension wire to pass through. Enclosure was completed by inserting rubber bungs into the hole in the glass plate and into the open upper end of the "Pythagoras" tube, through these bungs being passed a glass tube of about half an inch internal diameter. In practice it was found most convenient to use two lengths of glass tubing connected by a length of rubber tubing of suitable bore. The suspending wire was cut at the level of the rubber tube, and the ends bent into the form of hooks which could readily be connected or disconnected on slipping back the rubber. This made it possible to lower the crucible into the "Pythagoras" tube, and complete the enclosure without disturbing the balance after it had been adjusted and the zero determined, which was always done with the suspension wire attached to it, counterpoises being added to the other pan of the balance to compensate for the weight of the wire. Thus only the weight of the crucible and its contents were recorded during the experiments. The balance was, of course, adjusted before each experiment. With the set up described it was found that the balance was sufficiently well-protected from the heat of the furnace to avoid measurable error from this source. Further, by using a small diameter glass tube to enclose the suspending wire errors due to convection currents entering the balance case were rendered negligible. Provision was made for the fitting of baffles inside the "Pythagoras" tube to diminish the effect of such currents in the tube, but in practice this was found to be unnecessary. The cold end of the tube was, however, filled up with "Alundum". During tests with an empty crucible, the greatest error noted was an apparent decrease in weight of 0.0005 grams as the temperature rose from room temperature to about 1600°C. Actually it was not necessary to correct even for this slight error, since the method depended on the measurement of weight differences, and all of the weights were recorded at temperatures of over 1000°C. The balance, fitted up in this fashion, could detect with certainty differences in weight of 0.0005 grams. It could actually be made to measure weight differences somewhat less than this, but, for most of the work, this accuracy was quite sufficient, and was a big improvement on the methods previously employed. It was also necessary to measure weight differences up to 0.1300 grams in some of the experiments, and with the balance totally enclosed. This was done by using two platinum riders, one of 10 milligrams and the other approximately ten times this weight. It was found possible to move these riders by means of an L-shaped lever to which were attached a number of equally-spaced hooks as indicated in the sketch. It was necessary to provide a flexible seal where the lever passed out from the bell-jar. This was done by inserting in the bung at the top of the bell-jar a length of $\frac{3}{4}$ inch diameter brass tubing, to the upper end of which was attached about eight inches of thick-walled rubber tubing of suitable bore. The upper end of the rubber tube was sealed down tightly on the arm of the lever as shown in the sketch. The locking mechanism of the balance was operated by means of a piece of flexible motor-car speedometer drive, which was also passed outwards through the bung at the top of the bell-jar, and a flexible seal obtained in the same fashion as that just described. This simple device, though somewhat crude mechanically, operated quite successfully, and it was fitted up much more quickly and, incidentally, more cheaply than the complex mechanisms usually employed for the purpose.

Owing to the high temperature reached, it was necessary to maintain the gas pressure inside the apparatus at approximately one atmosphere.. In all cases in which the oxygen pressure was appreciably below this, an inert gas was also added, nitrogen being used for this purpose. At a temperature of 1600°C the possibility of reaction between the two gases had to be considered, but calculations based on published data for the reactions involved showed that the error to be expected from this source could be neglected. The volume of the apparatus was such that the changes in oxygen pressure produced by reactions in the melt would be negligible provided that the gases remained homogeneously mixed. To ensure this various stirring and circulatory devices were tried out but with limited success, owing to the rather involved shape of the enclosed volume. These difficulties were increased by the fact that closed end "Pythagoras" tubes were employed and it was desired to avoid altering the apparatus in this respect, if possible, owing to the complications involved. Finally the problem was solved by passing a slow stream of gas of the appropriate composition into the "Pythagoras" tube by means of the tube and jet indicated in the sketch. A corresponding amount of gas was allowed to escape by a controlled leak from the bell-jar. The gas stream was, of course, cut off while weighings were being made. The necessary nitrogen and oxygen were previously mixed in the desired proportions and stored under pressure in a large container connected to the apparatus. At the start of each experiment the apparatus was first evacuated and filled with gas of the appropriate composition.

RESULTS OF INVESTIGATIONS.

PART I - DISSOCIATION OF FERRIC OXIDE IN THE LIQUID AND SOLID STATES.

(Chronologically this investigation should follow the others since it was not carried out until the rest of the experimental work had been completed. The reason for this was that it was anticipated that,for a comprehensive study, the determinations would have to be extended to higher temperatures than were required for the other investigations, because of the high melting temperature of iron oxide under oxidizing conditions. This greatly increased the risk of damage to the high temperature part of the apparatus, so it was decided to delay this part of the work to the last. Systematically, however, it is best perhaps to describe the results of this investigation first.)

The dissociation of ferric oxide in the liquid and solid states was studied at various oxygen pressures and temperatures by means of the high temperature balance.

Known weights of ferric oxide were heated in a previously weighed platinum crucible under predetermined pressures of oxygen, and the weight recorded at various temperatures after equilibrium had been established. From the loss in weight at any temperature the ferrous oxide formed in the system could be calculated. It was found most convenient to make a series of determinations at each of a series of chosen pressures, the pressure being kept constant during the series while the temperature was raised progressively.

The results obtained are given in Tables I to V. All the determinations grouped in any one table are for the same oxygen pressure, the value of the pressure being denoted at the head of the table. In these tables the first column of figures indicates the serial number of the particular batch of ferric oxide being investigated. Whenever a new batch was prepared a new serial number was given for reference purposes. The initial weight of ferric oxide prepared is given in the third column, while the loss in weight which has occurred on heating to any temperature is entered in the next. From this by a simple calculation the weight of ferrous oxide formed in the weight of ferric oxide taken initially is obtained. Hence the number of gram-molecules of ferrous oxide formed from one gram-molecule of ferric oxide can be calculated as given in the last column.

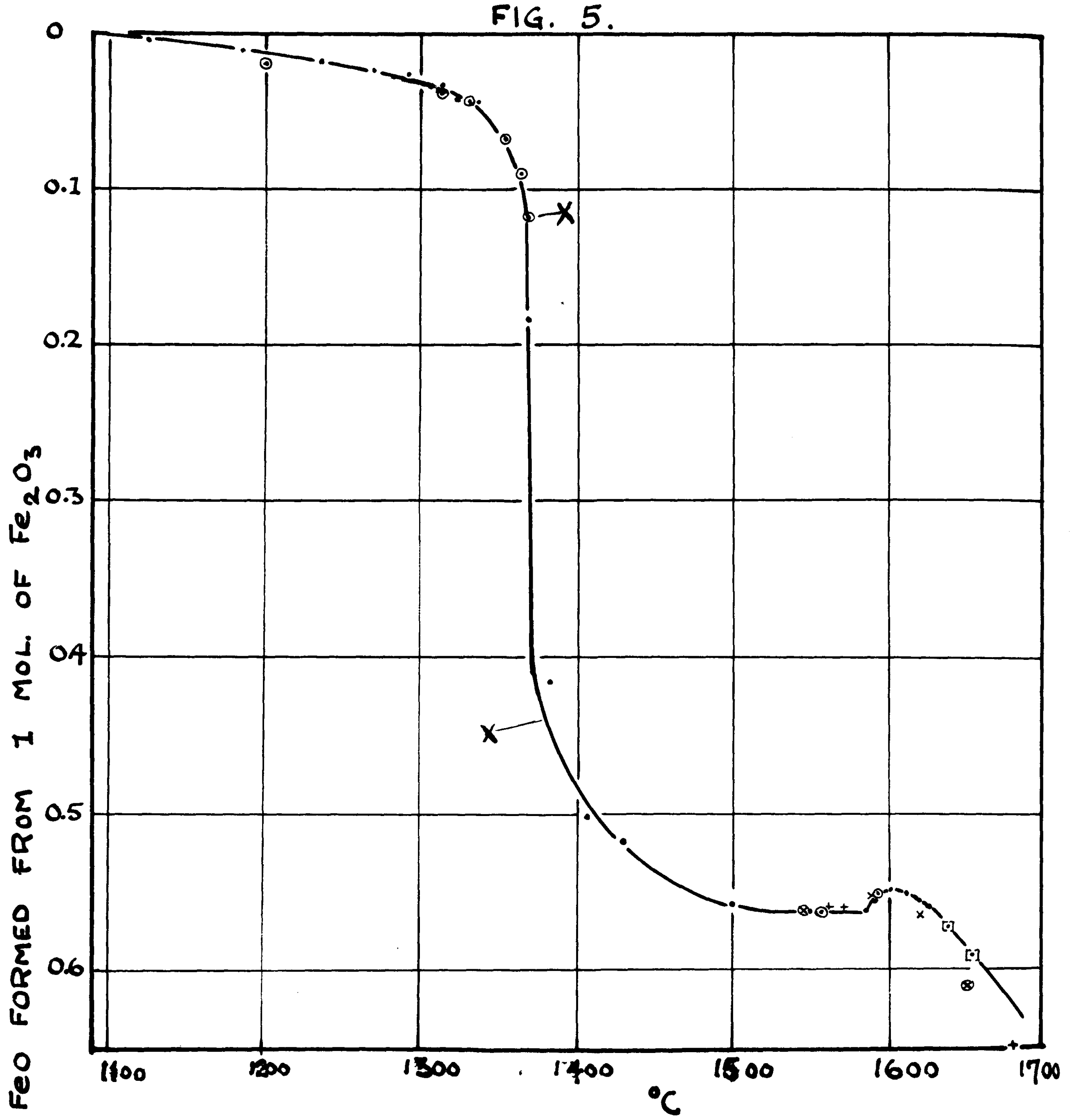
TABLE I.

EQUILIBRIUM IN IRON OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols of FeO.
5	1000	4.4457	0	0
"	1059	"	0	0
"	1106	"	0	0
"	1127	"	0.0005	0.0023
"	1186	"	0.0020	0.0090
"	1235	"	0.0040	0.0180
"	1270	"	0.0050	0.0226

FIG. 5.



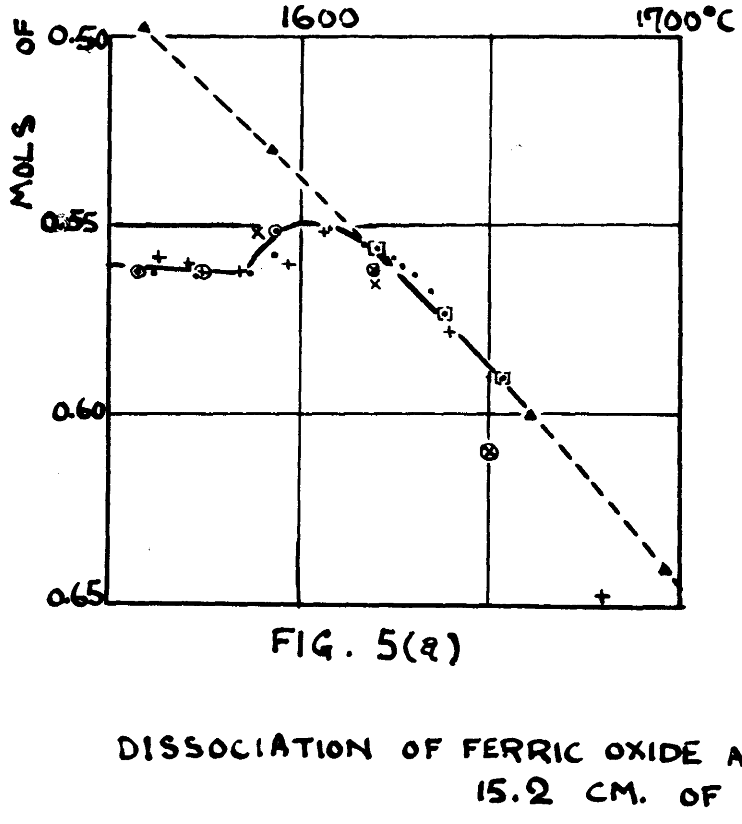
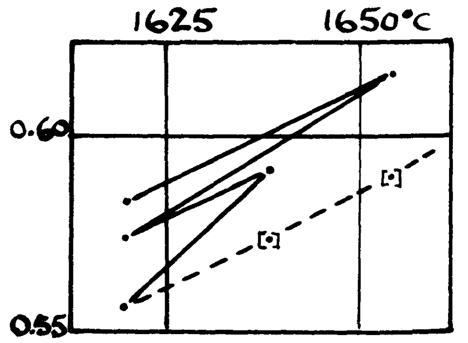


FIG. 5(a)



5(b)

· SERIES 5
⊙ " 6
■ " 7
× " 20
⊗ " 21
\+ " 22
● " 24

[•] CORRECTED VALUES.

▲ CALCULATED VALUES.

DISSOCIATION OF FERRIC OXIDE AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

(IN THIS, AS IN LATER DIAGRAMS, THE CALCULATED VALUES WERE OBTAINE
AS DESCRIBED IN SECTION II.)

TABLE 1 (CONTINUED).

EQUILIBRIUM IN IRON OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
5	1292	4.4457	0.0055	0.0248
"	1314	"	0.0075	0.0338
"	1338	"	0.0099	0.0446
"	1369	"	0.0410	0.1849
"	1383	"	0.0925	0.4170
"	1405	"	0.1115	0.5020
"	1429	"	0.1150	0.5175
"	1500	"	0.1215	0.5570
"	1546	"	0.1245	0.5600
"	1562	"	0.1250	0.5624
"	1573	"	0.1250	00.5624
"	1586	"	0.1250	0.5624
"	1593	"	0.1240	0.5578
"	1610	"	0.1230	0.5530
"	1618	"	0.1235	0.5550
"	1625	"	0.1240	0,5578
"	1627	"	0.1245	0.5600
"	1631	"	0.1250	0.5624
"	1635	"	0.1260	0.5670
6	1200	4.4455	0.0040	0.0180
"	1313	"	0.0075	00.0338
"	1331	"	0.0095	0.0427
"	1353	"	0.0150	0.0675
"	1363	"	0.0200	0.0900
"	1369	"	0.0260	0.1170
"	1557	"	0.1250	0.5620
"	1593	"	0.1225	0.5510
7	1324	4.4455	0.0095	0.0427
"	1559	"	0.1250	0.5620
"	1593	"	0.1240	0.5578
11	1545	4.4453	0.1248	0.5620
"				
20	1588	4.4455	0.1225	0.5510
"	1620	"	0.1255	0.5650
21	1540	4.4453	0.1238	0.5510
"	1575	"	0.1248	0.5620
22	1564	4.4455	0.1240	0.5578
"	1571	"	0.1245	0.5600
"	1585	"	0.1250	0.5620
"	1597	"	0.1245	0.5600
"	1607	"	0.1225	0.5510
"	1625	"	0.1245	0.5600
"	1640	"	0.1285	0.5784
"	1680	"	0.1440	0.6480
24	1620	4.4450	0.1250	0.5620
"	1650	"	0.1355	0.6100

TABLE Ib.

EQUILIBRIUM IN IRON OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Attempt to correct for reduction by platinum at high temperatures (determinations given in chronological sequence).

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in Weight. gm.	Mols of FeO.
25	1619	4.4455	0.1235	0.5560
"	1638	"	0.1315	0.5920
"	1619	"	0.1275	0.5740
		Permanent Loss	=	00.018
		Corrected Value at 1638°		0.5740
"	1654	4.4455	0.1370	0.6170
"	1619	"	0.1295	0.5830
		Permanent Loss	=	0.027
		Corrected Value at 1654°		0.5900

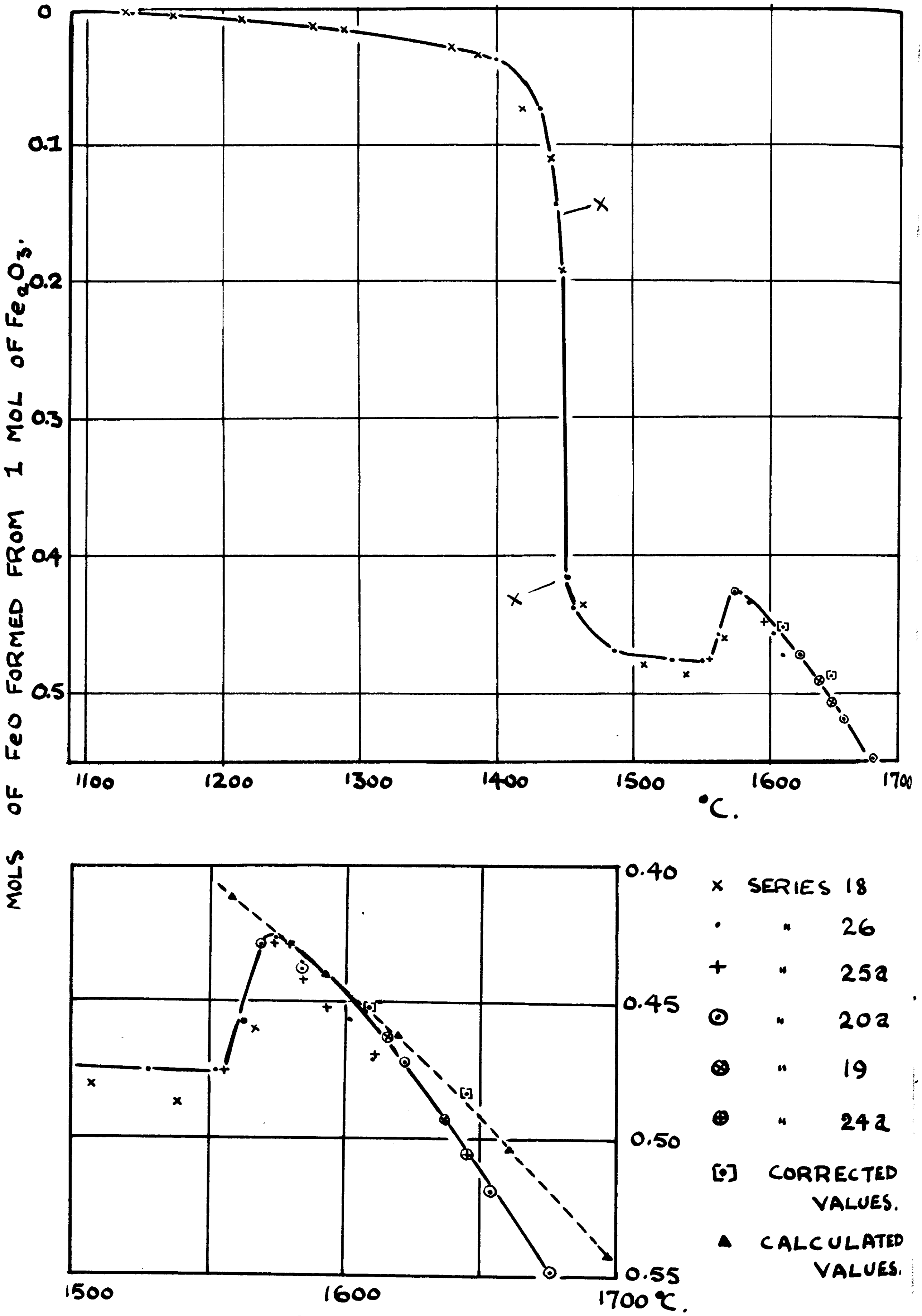
TABLE II.

EQUILIBRIUM IN IRON OXIDE MELTS.

Oxygen Pressure = 76.0 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols of FeO.
18	1000	4.4461	0	0
"	1054	"	0	0
"	1128	"	0.0003	0.0014
"	1165	"	0.0006	0.0027
"	1212	"	0.0012	0.0054
"	1267	"	0.0023	0.0103
"	1290	"	0.0032	0.0144
"	1367	"	0.0055	0.0248
"	1386	"	0.0072	0.0324
"	1418	"	0.0163	0.0734
"	1440	"	0.0241	0.1084
"	1464	"	0.0966	0.4350
"	1506	"	0.1068	0.4800
"	1538	"	0.1081	0.4870
"	1566	"	0.1021	0.4600
26	1055	4.4453	0	0
"	1133	"	0.0005	0.0023
"	1404	"	0.0078	0.0351
"	1432	"	0.0164	0.0739
"	1444	"	0.0317	0.1429
"	1448	"	0.0424	0.1909
"	1451	"	0.0920	0.4145
"	1445	"	0.0970	0.4370
"	1485	"	0.1042	0.4696
"	1527	"	0.1054	0.4750
"	1552	"	0.1054	0.4750
"	1562	"	0.1014	0.4565

FIG. 6.



6(a)

DISSOCIATION OF FERRIC OXIDE AT AN OXYGEN PRESSURE OF 76.0 CM. OF MERCURY.

TABLE II (CONTINUED).

IRON OXIDE EQUILIBRIUM.

Oxygen Pressure = 76.0 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols of FeO.
26	1574	4.4453	0.0946	0.4260
"	1580	"	0.0951	0.4280
"	1584	"	0.0966	0.4350
"	1601	"	0.1012	0.4560
"	1609	"	0.1045	0.4710
		Permanent Loss on Cooling		0.0200
		Corrected Value at 1609°		0.4510
25a	1555	4.4453	00.1034	0.4750
"	1573	"	0.0950	0.4278
"	1578	"	0.0950	0.4278
"	1584	"	0.0982	0.4420
"	1592	"	0.1002	0.4510
"	1610	"	0.1042	0.4694
20a	1568	4.4453	0.0950	0.4280
"	1583	"	0.0970	0.4370
"	1622	"	0.1047	0.4720
"	1654	"	0.1153	0.5196
"	1676	"	0.1217	0.5480
19	1615	4.4453	0.1027	0.4625
"	1636	"	0.1092	0.4922
"				
24a	1645	4.4453	0.1124	0.5060
		Permanent Loss on Cooling =		0.0230
		Corrected Value at 1645° =		0.4830

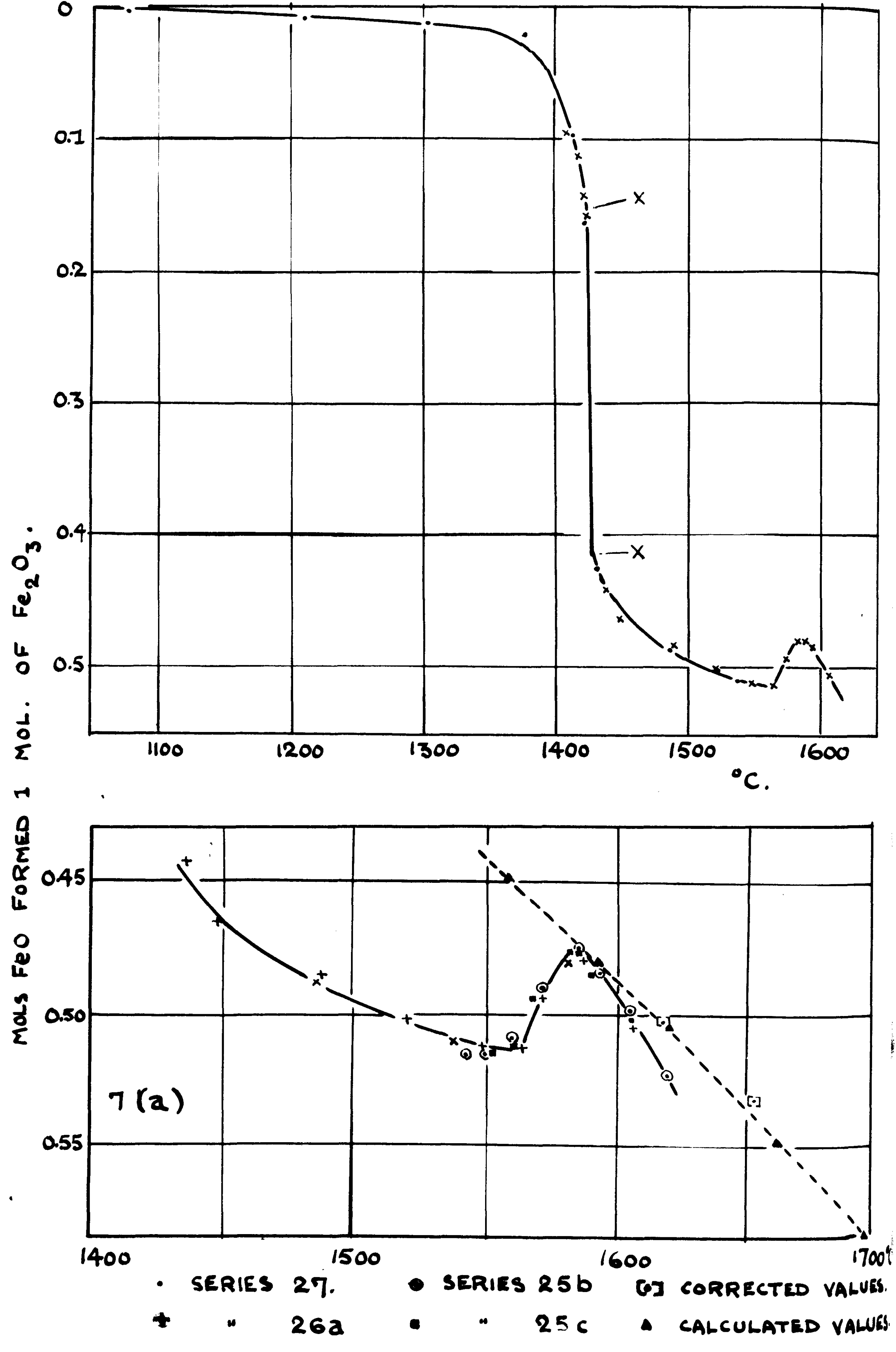
TABLE III.

IRON OXIDE EQUILIBRIUM.

Oxygen Pressure = 37.0 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
27	1060	4.4444	0	0
"	1083	"	0.0005	0.0023
"	1209	"	0.0015	0.0068
"	1302	"	0.0024	0.0108
"	1376	"	0.0044	0.0198
"	1411	"	0.0218	0.0980
"	1421	"	0.0364	0.1639
"	1436	"	0.0954	0.4290
"	1485	"	0.1084	0.4880
"	1536	"	0.1131	0.5100

FIG. 7



DISSOCIATION OF FERRIC OXIDE AT AN OXYGEN PRESSURE OF 37.0 CM. OF MERCURY.

TABLE III (CONTINUED).

IRON OXIDE EQUILIBRIUM.

Oxygen Pressure = 37.0 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
26a	1407	4.4426	0.0211	0.0951
"	1416	"	0.0251	0.1131
"	1419	"	0.0311	0.1402
"	1422	"	0.0341	0.1536
"	1437	"	0.0981	0.4420
"	1448	"	0.1031	0.4645
"	1489	"	0.1076	0.4844
"	1520	"	0.1111	0.5005
"	1549	"	0.1135	0.5110
"	1564	"	0.1140	0.5130
"	1572	"	0.1096	0.4930
"	1581	"	0.1066	0.4800
"	1586	"	0.1066	0.4800
"	1593	"	0.1076	0.4844
"	1606	"	0.1121	0.5052
25b	1543	4.4453	0.1143	0.5150
"	1551	"	0.1143	0.5150
"	1560	"	0.1127	0.5090
"	1572	"	0.1087	0.4900
"	1585	"	0.1052	0.4740
"	1593	"	0.1063	0.4790
"	1605	"	0.1106	0.4980
"	1620	"	0.1158	0.5220
25c	1543	4.4453	0.1143	0.5150
"	1551	"	0.1143	0.5150
"	1560	"	0.1135	0.5110
"	1566	"	0.1096	0.4935
"	1582	"	0.1057	0.4755
"	1586	"	0.1058	0.4760
"	1590	"	0.1078	0.4850
"	1605	"	0.1113	0.5010
"	1620	"	0.1158	0.5220
		Permanent Loss on Cooling		0.0190
		Corrected Value at 1620°		0.5030

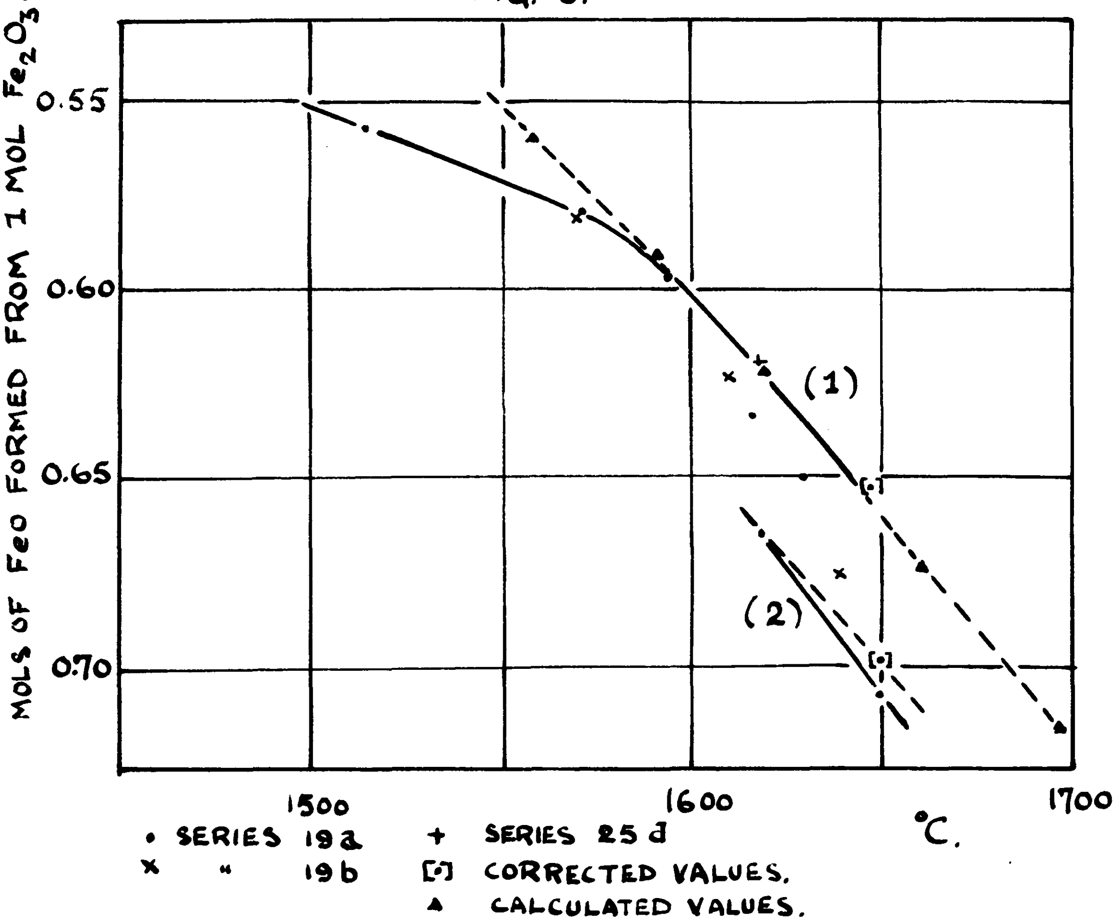
TABLE IV.

IRON OXIDE EQUILIBRIUM.

Oxygen Pressure = 4.0 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in Weight. gm.	Mols. of FeO.
19a	1515	4.4455	0.1235	0.5553
"	1571	"	0.1286	0.5790
"	1594	"	0.1329	0.5970
"	1616	"	0.1409	0.6330
"	1630	"	0.1446	0.6500
19b	1570	4.4455	0.1289	0.5810
"	1609	"	0.1381	0.6235

FIG. 8.



DISSOCIATION OF FERRIC OXIDE AT AN OXYGEN PRESSURE OF (1) 4.0 CM. (2) 2.0 CM. OF MERCURY

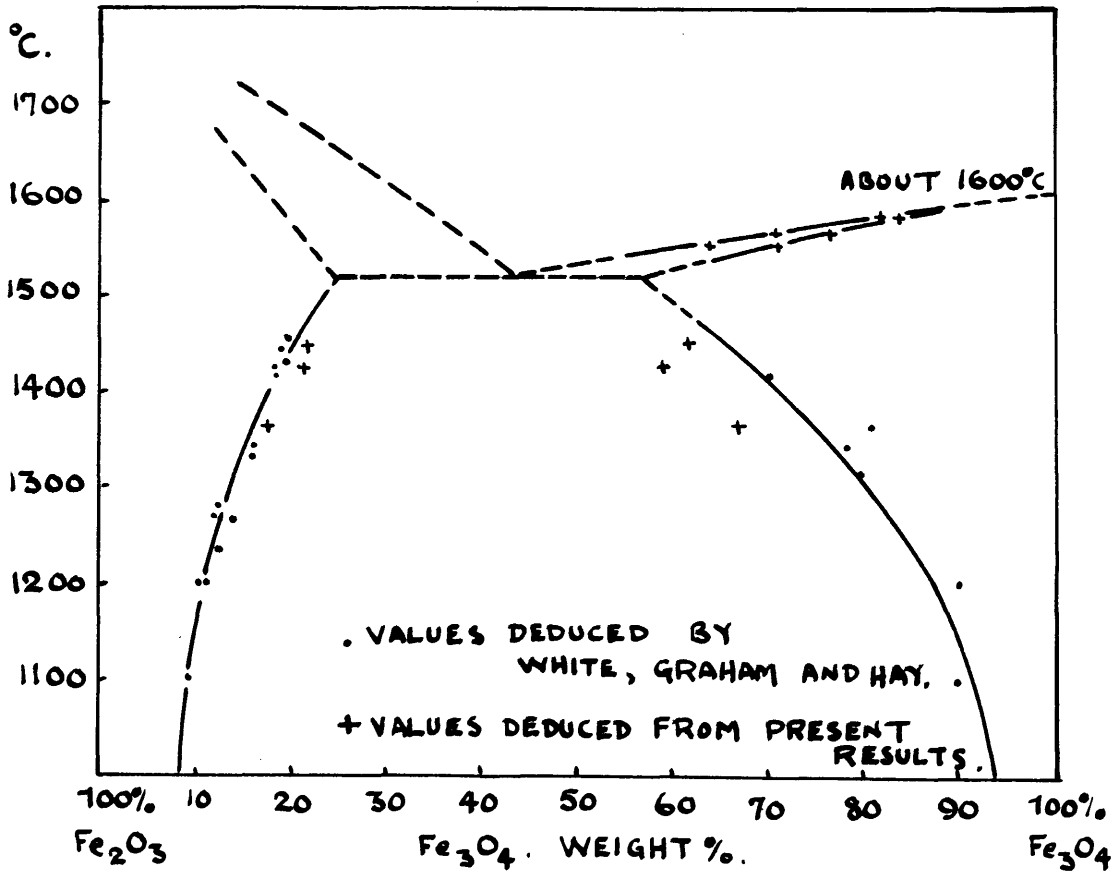


FIG. 9 – THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM Fe_2O_3 – Fe_3O_4.

TABLE IV (CONTINUED).

IRON OXIDE EQUILIBRIUM.

Oxygen Pressure = 4.0 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in Weight. gm.	Mols. of FeO.
19b	1639	4.4455	0.1498	0.6750
25d	1619	4.4453	0.1375	0.6190
"	1648	"	0.1460	0.6570
		Permanent Loss on Cooling		0.0040
		Corrected Value at 1648°		0.6530

TABLE V.

IRON OXIDE EQUILIBRIUM.

Oxygen Pressure = 2.0 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	Loss in Weight. gm.	Mols. of FeO.
25c	1619	4.4453	0.1473	0.6640
"	1650	"	0.1569	0.7060
		Permanent Loss on Cooling		0.0082
		Corrected Value at 1650°		0.6978

The above results are given graphically in Figures 5 to 8, the gram molecules of ferrous oxide formed from one gram molecule of ferric oxide (as given in the last column of the tables), being plotted against temperature with the oxygen pressure constant. No assumption is made, at the moment, as to whether the ferrous oxide is combined with ferric oxide as magnetite or not.

DISSOCIATION OF FERRIC OXIDE IN THE SOLID STATE:

As described in the paper by White, Graham and Hay, to which reference has already been made, the dissociation in the solid state of finely powdered ferric oxide is completely reversible so long as the mass remains porous and open. The dissociation is, however, accompanied by sintering, due presumably to the process of recrystallization involved, and, if it is allowed to proceed to a stage at which the composition of magnetite is approached, the mass becomes dense and hard and there is considerable shrinkage, and, on cooling, it reconverts very sluggishly to ferric oxide. In practice complete reconversion was never actually observed under these conditions. This was also found to be the case with samples which had been heated till molten. Apart, however, from this limitation, which is due to physical rather than chemical reasons, the equilibrium between the oxides of iron in the solid state at high temperatures appears to be a truly reversible one. This is borne out by the work of other investigators.

The results obtained by the present method of investigation agree well with those given in the earlier paper for the dissociation of ferric oxide in the solid state. The dissociation appears to begin at even lower temperatures than were then observed. This was not altogether unexpected since it was then found that the dissociation of ferric oxide on heating at constant oxygen pressure is at first very gradual, and it was surmised that a certain amount of dissociation would have occurred before it became detectable. The present method, gave better oppurtunities for observing the onset of dissociation, and showed that this was the case. The curves obtained indicate that the dissociation increases steadily and at a progressively increasing rate with temperature corresponding to the formation of Fe_3O_4 which enters into solid solution in the residual Fe_2O_3. At a temperature which depends on the oxygen pressure of the system, there is a sudden increase in the amount of the dissociation, which appears to indicate that the saturation limit of the solid solution has been reached, with liberation of another phase, a solid solution of Fe_2O_3 in Fe_3O_4. While these two solid solutions are present the system is monovariant, and hence at constant pressure the change over from the one solid solution range to the other should occur at a constant temperature. This appears to be the case, though experimentally it is rather difficult to demonstrate it with absolute conclusiveness. Several hours are necessary to allow the change over to complete itself, and, towards the end, as the new equilibrium condition is approached, the system becomes increasingly sluggish.

There seems to be a certain amount of hysteresis associated with the change over, which is not difficult to understand in the case of a reaction involving two solid solutions. There are indications that the lower the temperature is, the more pronounced does the hysteresis become, and this may explain the earlier results of Sosman and Hostetter[15], at 1100 and 1200°C. Other factors to be considered are traces of impurities in the oxide, and the presence of temperature gradients throughout the sample.

The dissociation of the Fe_3O_4-rich solid solution increases further as the temperature rises, but at a steadily decreasing rate till the curve becomes almost horizontal. When melting takes place a pick up of oxygen by the system occurs, so that the liquid formed has a lower content of FeO than the solid at the melting point. At higher temperatures the dissociation of the liquid oxide increases progressively as the temperature rises. Only in the case of the incompleted curve at 4.0 cm. oxygen pressure is no oxygen pick-up observed. Pick-up would be more difficult at the lower partial pressure of oxygen in the apparatus.

Some time was spent in checking the determinations in the neighbourhood of the melting point at the other three pressures given. It was found that oxygen was invariably picked up on melting. Further, the pick-up was strictly reversible, for on freezing a corresponding loss in weight occurred. It was also noted that as the oxygen pressure was increased the melting point was decreased to a slight but quite definite and reproducible extent; the temperatures at which melting and oxygen pick-up began are stated in Table VI.

TABLE VI.

DATA ON THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM Fe_2O_3-Fe_3O_4.

Source.	Description.	Oxygen Pressure cm. of mercury.	Temp. °C.	Fe_3O_4.% by weight.
	A. - Solid Solubility Limits.*			
Fig.5	Limit of Fe_2O_3-rich solid solution.	15.2	1368	17.4
"	Limit of Fe_3O_4-rich solid solution.	15.2	1368	66.8
Fig.6	Limit of Fe_2O_3-rich solid solution.	76.0	1450	21.2
"	Limit of Fe_3O_4-rich solid solution.	76.0	1450	61.5
Fig.7	Limit of Fe_2O_3-rich solid solution	37.0	1425	21.2
"	Limit of Fe_3O_4-rich solid solution.	37.0	1425	59.0
	B. - Liquidus and Solidus Compositions and Temperatures.			
Fig.5	Beginning of melting	15.2	1585	83.6
"	End of melting	15.2	1605	81.9
Fig.6	Beginning of melting	76.0	1555	70.5
"	End of melting	76.0	1575	63.1
Fig.7	Beginning of melting	37.0	1565	76.5
"	End of melting	37.0	1585	70.5

In the currently accepted form of the Iron-Oxygen thermal equilibrium diagram, as given by Benedicks and Lofquist[21]; Matthewson, Spire and Milligan[22] and others, a peritectic reaction is postulated between the two solid solutions (Fe_2O_3-rich and Fe_3O_4-rich) of the system Fe_2O_3-Fe_3O_4. This form of the diagram would indicate that a loss of oxygen should occur on melting under constant pressure, and also that an

* Denoted by X on Figures 5, 6 and 7.

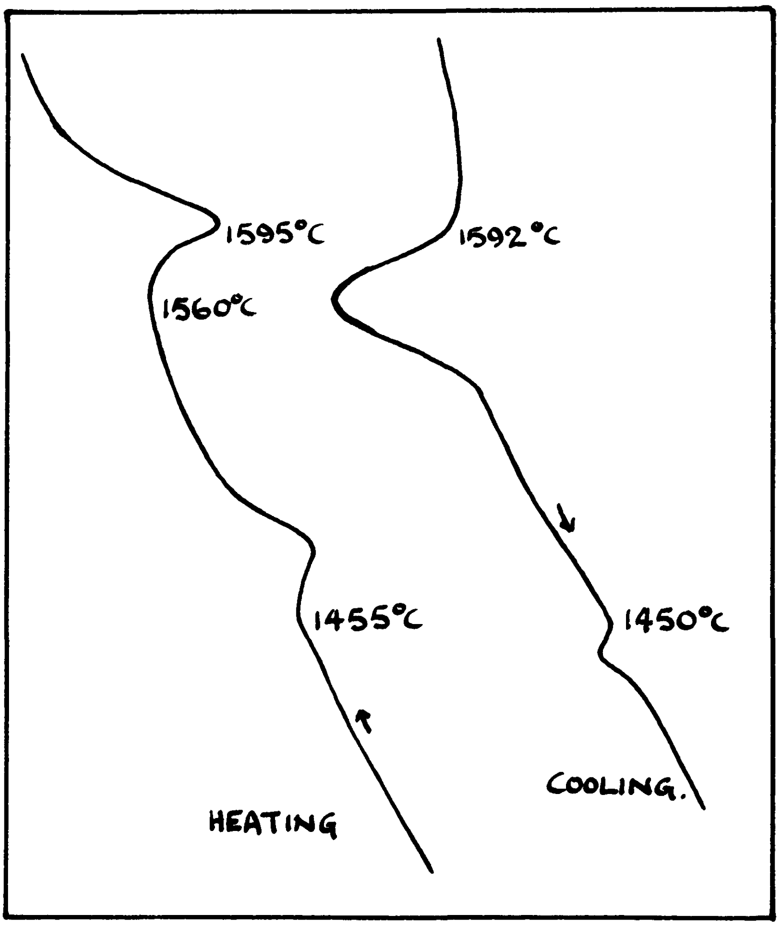


FIG. 10 – HEATING AND COOLING CURVES OF FERRIC OXIDE (DIFFERENTIAL METHOD) AT 1 ATMOSPHERE OF OXYGEN.

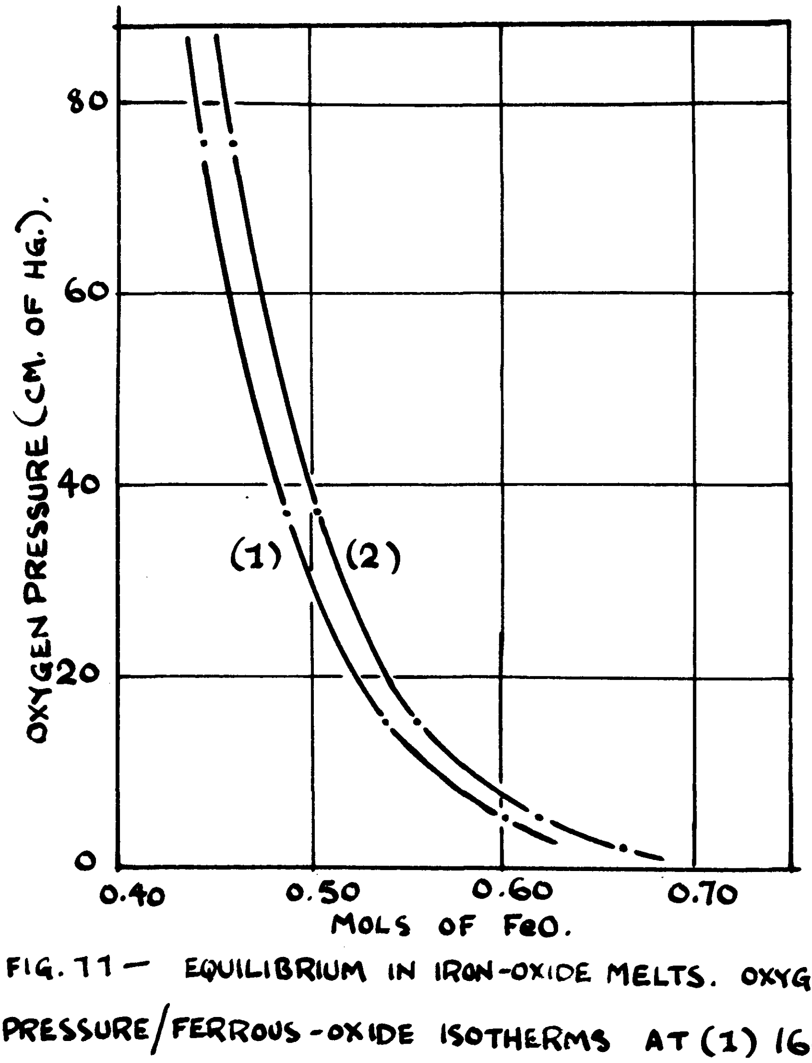


FIG. 11 – EQUILIBRIUM IN IRON-OXIDE MELTS. OXYGEN-PRESSURE/FERROUS-OXIDE ISOTHERMS AT (1) 1600°C. (2) 1619°C.

increase in the oxygen pressure should raise the melting temperature. The presence of a eutectic between the two solid solutions would, however, explain both of the phenomena actually observed. Theoretically, at constant oxygen pressure, melting and oxygen pick up should take place invariantly. This was found, however, not to be the case. Various reasons might be suggested for this - the presence of impurities, the existence of temperature gradients in the oxide sample and (see later) reaction between the crucible and the oxide.

Figure 9 shows the thermal equilibrium diagram of the system Fe_2O_3-Fe_3O_4 modified in the light of the present evidence, the fresh data from which it is mainly constructed being that given in Table VI. Compositions at the beginning and end of melting are used to give liquidus and solidus for the melting of the Fe_3O_4-rich solid solution, the temperature difference between the two being neglected. It is difficult to obtain accurate figures for the limits of solubility in the solid state from the present data owing to the difficulty of establishing the extent of the truly vertical portions of the curves of Figures 5, 6 and 7. The limits can, however, be approximately fixed (points marked X in these figures), and when replotted on Figure 9 they show reasonable agreement with the values previously given in the paper by White, Graham and Hay, particularly as regards the limits of the Fe_2O_3-rich solid solution.

It is of interest to consider the form of the thermal curves of Fe_2O_3 in the light of the new information. Figure 10 shows a heating and cooling curve taken on a sample of ferric oxide in a platinum crucible under an oxygen pressure of just over an atmosphere. Both curves are difference curves and were taken by the method of Roberts-Austen. On both two thermal changes are to be observed, beginning at 1450-55°C. and at 1555-60°C. respectively on the heating curve, and corresponding closely to those on the cooling curve. On comparison with the dissociation curve of ferric oxide at 76.0 cm. oxygen pressure given in Figure 6, an explanation of these thermal changes is provided. The lower one corresponds closely as regards temperature with the change over from one solid solution to the other. The upper one agrees closely with the temperature range over which oxygen pick-up occurs, and is due to melting of the oxide. Incidentally by the time melting occurs it is no longer ferric oxide that is being investigated. Actually complete conversion to the Fe_3O_4-rich phase occurs at the temperature of the lower arrest, and it is the melting of this substance which gives rise to the observed arrest at the higher temperature. Very large pressures indeed would be required to maintain ferric oxide stable up to its melting point. The literature contains many references to the lower arrest got on heating ferric oxide. Various explanations have been put forward, but there seems little doubt that the correct explanation is that now given.

EQUILIBRIUM IN LIQUID IRON OXIDE MELTS:

As it was intended to attempt an analysis of the experimental work from the point of view of the law of mass action some importance was attached to the elucidation of the equilibria in simple liquid iron oxide melts. Considerable trouble was, however, encountered in obtaining reliable values for the dissociation in the liquid state. It was first of all noticed that the equilibrium in these melts was apparently not completely reversible, and that a permanent loss of weight seemed to occur every time the liquid oxide was raised in temperature and then cooled again. Chronologically this work was carried out towards the end of the investigation, as mentioned earlier. During the earlier part of the work on systems containing lime and silica the equilibrium had always appeared readily reversible, and this discovery was rather unexpected. Owing to the high melting point of the iron oxides alone, the determinations were extended to higher temperatures than had previously been the case, and it was thought that volatilization of the oxide might be occurring. Indications of this were completely lacking, however.* The possibility of loss due to splashing caused by effervescence of the oxide was also ruled out by fitting a perforated platinum lid to the crucible. No traces of splashing could be seen on the lid but the loss continued. It was finally established that the platinum of the crucible was picking up iron from the melts. It was observed that, after heating at low temperatures for some time, the outside of the crucible became discoloured by iron oxide due to the oxidation of iron picked up at higher temperatures. Sosman and Hostetter[15] have previously mentioned the possibility of this occurring at certain temperatures and oxygen pressures. It appears that over 1600°C it occurs even at an oxygen pressure of 76 cm. of mercury. It was established that it only becomes serious above the melting point. In the solid state the contact between the platinum and oxide which had not been previously melted was relatively slight, and became even less on heating due to the large amount of shrinkage that occurred causing the oxide to shrink away from the sides of the crucible. Further, iron oxide melts containing lime or silica appeared to be little affected by the platinum. Only in the case of those melts having low lime or silica was any discrepancy from this cause observed, and then only when the oxygen pressure/ferrous oxide isotherms were being determined, which necessitated the taking of a considerable number of high temperature determinations on the same melt. A progressively increasing error was then noticeable in some cases. With iron oxide melts it was also observed that the loss of weight was comparatively slow while the temperature remained steady, but appeared to be much

* See note at the end of this section (page 65).

accelerated by a rising temperature. This being so, attempts to minimise the effect by taking determinations as rapidly as possible were only partially successful. In most cases, however, the rate of loss just above the melting point was fairly slow (though on repeated meltings a slight progressive loss was found). An attempt was, therefore, made to estimate the permanent loss occurring on heating to higher temperatures. The equilibrium was first determined just above the melting point, then, as quickly as possible at a higher temperature, after which it was cooled quickly back to the previous temperature and the equilibrium redetermined. The difference between the two low temperature determinations was a measure of the permanent loss which had occurred due to platinum reduction on heating to the higher temperature. Thus a correction could be applied to the higher temperature determination. Some time was spent in trying to obtain, in this way, values on which reliance could be placed. The results obtained indicated that the increase with temperature of the ferrous oxide content of these melts took place at an appreciably slower rate than the earlier results had seemed to show. It was also evident that the rate of increase was practically the same at the different oxygen pressures used. Table I B and Figure 5 B give in detail the history of a melt which was investigated in the manner just described. Other determinations corrected in this way are also given in the other Tables. From the corrected ferrous-oxide/temperature curves thus obtained at the various oxygen pressures employed oxygen-pressure/ ferrous oxide isotherms have been drawn for two temperatures as shown in Figure 11. To get certain of the values on the isotherm at 1600°C it was necessary to extrapolate the liquid-state portion of the ferrous-oxide/temperature curves since, at some pressures, this temperature is within the melting range as can be seen by referring to Figures 5, 6, 7, and 8. Because of the difficulties involved this part of the work is probably less reliable in character than the remainder.

PART II - EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.

The effect of lime on the equilibrium in iron-oxide melts was studied by all three of the methods described. The quenching values, on the whole, tend to lie somewhat lower than the others, particularly in the case of the more fusible compositions, and of the higher-temperature determinations. This is as might be expected.

In making these determinations fresh melts were not made up each time. Ferric oxide was first melted and calcium oxalate was added progressively to give a series of determinations with regularly increasing lime contents. Care had to be taken in heating up with the calcium oxalate additions in the crucible, as too rapid decomposition of the oxalate caused a loss of lime and gave too high a figure for the ferrous-oxide content, the effect being cumulative if the loss was repeated. For this reason it was not desirable to make too many lime additions to any one melt without checking the values obtained against entirely fresh melts, and this was done whenever possible. Each time a fresh melt embodying a fresh batch of ferric oxide was made, a new series number was allocated to it. Several entirely different melts were made up during the investigation of the lime/ferric-oxide equilibrium The results obtained are given in Tables VII A and VII B, the latter being the figures for the quenching experiments. From the weight lost on heating the original components to the stated temperature the number of gram-molecules of ferrous oxide formed in that weight of the melt which would have contained initially one gram-molecule of ferric oxide was calculated and is entered in the penultimate column. The last column gives the number of gram-molecules of lime present in this latter amount of melt, i.e. the number of gram-molecules of lime that would have been added to 1 gram-molecule

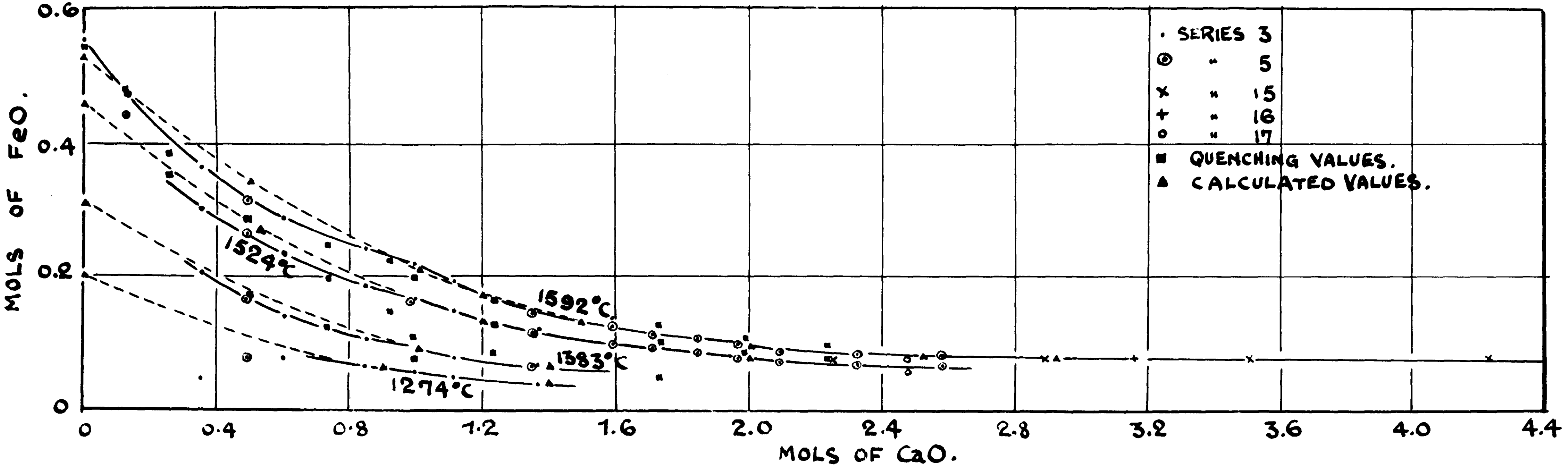


FIG. 12. EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

of ferric oxide to give a melt of the composition under investigation. The results are recorded graphically in Figure 12. The range of compositions studied at the lower temperatures is restricted by the narrowness of the range of lime concentrations which are completely fusible at these temperatures. Some of the compositions for which figures are given (marked with an asterisk in the Tables) would not be completely liquid at some of the temperatures studied. This would be expected to affect the equilibrium conditions, and the values so obtained do, in fact, lie off the curves. In drawing the curves the results with the high-temperature balance have been assumed to be more accurate than the others. As the lime content of the melts is increased, the liability to error increases, since any error in computing the lime content of the calcium oxalate added becomes of progressively greater significance, while, at the same time, the weight loss due to dissociation becomes smaller. The chief tendency to error lay in the direction of higher dissociation values than were actually the case, this being due to small lime losses as already mentioned. This tendency can be observed in some of the results given in Table VII A. and in the series of quenching experiments. Some of the earlier results were obviously considerably in error for this reason and have been rejected.

The effect of a change of oxygen pressure on melts with various lime contents is shown in Tables VIII to XII and, graphically, in Figures 13 to 17. As before, the results are given in terms of gram -molecules of ferrous oxide formed at equilibrium from one gram molecule of ferric oxide, and in the diagrams this is plotted against the oxygen pressure at various constant temperatures.

There were indications that the melt containing 0.4920 gram-molecules of lime was being affected to some extent by the platinum of the crucible. The effect was minimised

TABLE VII A.

EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO gm.	Loss in weight. gm.	Mols. of FeO	Mols. of CaO.
3	1274	4.4453	0.5570	0.0101	0.0455	0.3580
	1383	"	"	0.0453	0.2040	"
	1525	"	"	0.0670	0.302	"
	1592	"	"	0.0820	0.368	"
	1274	"	0.9396	0.0174	0.0779	0.6050
	1383	"	"	0.0304	0.1366	"
	1525	"	"	0.0519	0.2330	"
	1592	"	"	0.0639	0.2875	"
	1274	"	1.3222	0.0142	0.0637	0.8500
	1383	"	"	0.0230	0.1035	"
	1525	"	"	0.0415	0.1865	"
	1592	"	"	0.0535	0.2409	"
	1274	"	1.5521	0.0129	0.0580	0.9970
	1383	"	"	0.0204	0.0917	"
	1525	"	"	0.0369	0.1660	"
	1592	"	"	0.0489	0.2200	"
	1274	"	1.7434	0.0107	0.0481	1.199
	1383	"	"	0.0172	0.0772	"
	1525	"	"	0.0327	0.1470	"
	1592	"	"	0.0427	0.1920	"
	1274	"	2.1260	0.0080	0.0395	1.364
	1383	"	"	0.0148	0.0665	"
	1525	"	"	0.0268	0.1205	"
5	1525	4.4457	0.1913	0.0998	0.4485	0.1230
	1592	"	"	0.1063	0.4780	"
	1274	"	0.7599	0.0169	0.0759	0.4880
	1383	"	"	0.0359	0.1616	"
	1525	"	"	0.0579	0.2610	"
	1592	"	"	0.0698	0.3141	"
	1525	"	1.5251	0.0361	0.1630	0.9820
	1383	"	2.0990	0.0140	0.0618	1.346
	1525	"	"	0.0255	0.1146	"
	1592	"	"	0.0320	0.1442	"
	1525	"	2.4816	0.0216	0.0971	1.595
	1592	"	"	0.0276	0.1242	"
	1525	""	2.6729	0.0204	0.0918	1.7150
	1592	"	"	0.0254	0.1142	"
	1525	"	2.8642	0.0192	0.0862	1.841
	1592	"	"	0.0235	0.1056	"
	1524	"	3.055	0.0175	0.0787	1.964
	1592	"	"	0.0218	0.0980	"
	1524	"	3.2468	0.0161	0.0724	2.086
	1592	"	"	0.0196	0.0880	"
	1524	"	4.0120	0.0155	0.0697	2.580
	1592	"	"	0.0179	0.0804	"
15	1592	4.4453	3.4805	0.0168	0.0755	2.240
	1592	"	4.4805	0.0163	0.0740	2.886

TABLE VII A (CONTINUED).

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO. gm.	Loss in weight. gm.	Mols. of FeO.	Mols. of CaO.
15	1592	4.4453	5.4655	0.0168	0.0755	3.510
	1592	"	6.5775	0.0198	0.0757	4.23
16	1592	4.4453	4.9085	0.0158	0.0712	3.16
17	1524	4.4453	3.8420	0.0113	0.0510	2.472
	1592	"	"	0.0163	0.0740	"

TABLE VII B.

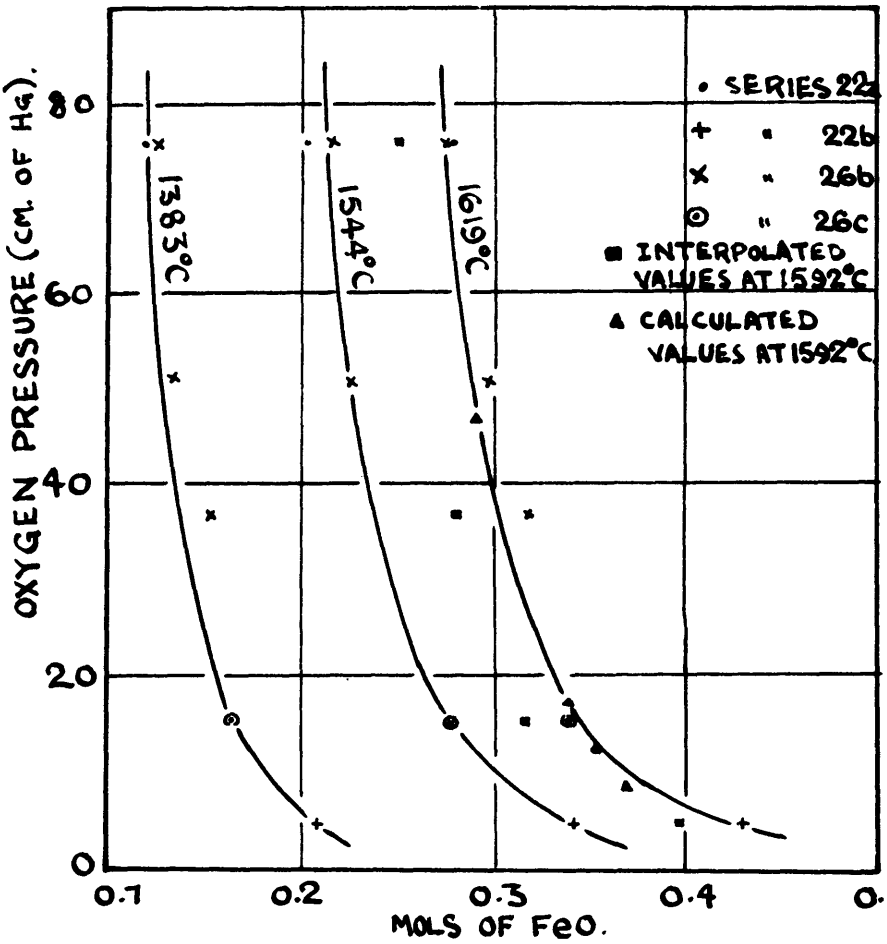
EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.- QUENCHING EXPERIMENTS.

Oxygen Pressure = 15.2 cm. of mercury.

Temp. °C.	Initial Fe_2O_3. gm.	CaO. gm.	Loss in weight. gm.	Mols. of FeO.	Mols of CaO.
1592	4.4505	0	0.1225	0.5485	0
1592	"	0.1913	0.1068	0.4800	0.1230
1524	"	0.3826	0.0791	0.3550	0.2460
1592	"	"	0.0846	0.3850	"
1383	"	0.7652	0.0372	0.1672	0.4920
1592	"	"	0.0637	0.286	"
1383	"	1.1478	0.0273	0.1234	0.7380
1524	"	"	0.0444	0.1995	"
1592	"	"	0.0538	0.2415	"
1524	"	1.4351	0.0481	0.2210	0.9200
1592	"	"	0.0345	0.1550	"
1274	"	1.5430	0.0170	0.0763	0.990
1383	"	"	0.0240	0.1076	"
1592	"	"	0.0538	0.2415	"
1383	"	1.9256	0.0196	0.0879	1.234
1524	"	"	0.0291	0.1305	"
1592	"	"	0.0366	0.1640	"
1383	"	2.6908	0.0108	0.0485+	1.725
1524	"	"	0.0228	0.1022	"
1592	"	"	0.0283	0.1270	"
1524	"	3.0920	0.0182	0.0815	1.983
1592	"	"	0.0233	0.1046	"
1524	"	3.4746	0.0169	0.0758	2.226
1592	"	"	0.0219	0.0982	"

+ Not completely molten at this temperature.

FIG. 13. EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS. OXYGEN-PRESSURE/FERROUS-OXIDE ISOTHERMS OF MELT CONTAINING 0.4920 MOL. OF CaO TO 1.000 MOL OF Fe_2O_3.



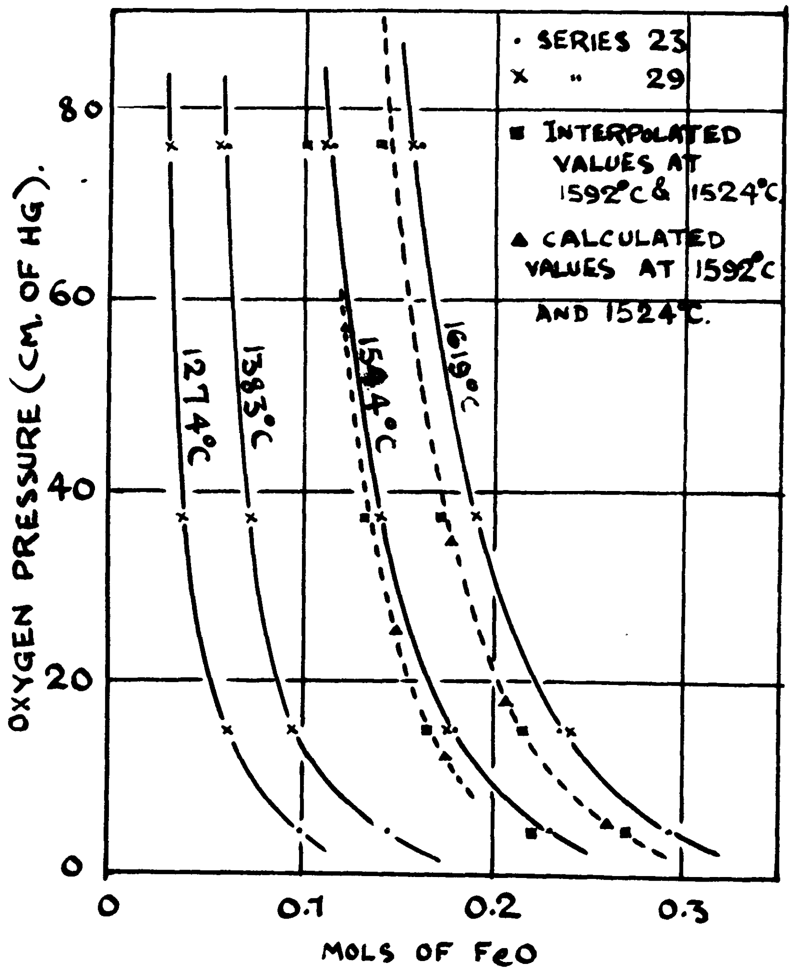


FIG. 14 — EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS. OXYGEN-PRESSURE/FERROUS-OXIDE ISOTHERMS OF MELT CONTAINING 1.000 MOL CaO TO 1.000 MOL Fe_2O_3.

TABLE VIII - EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.

Constant CaO content = 0.7652 gm. i.e. 0.4920 mol per mol of Fe_2O_3.

Oxygen Pressure Varying.

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols of FeO.
22a	1383	76.0	4.4455	0.0260	0.1172
	1544	"	"	0.0453	0.2042
	1619	"	"	0.0610	0.2750
22b	1383	5.0	4.4453	0.0576	0.2595
	1544	"	"	0.0752	0.3388
	1619	"	""	0.0956	0.4300
26b	1383	51.0	4.4453	0.0290	0.1308
	1544	"	"	0.0499	0.2246
	1619	"	"	0.0658	0.2966
	1383	76.0	"	0.0274	0.1232
	1544	"	"	0.0477	0.2144
	1619	"	"	0.0609	0.2739
	1383	37.0	"	0.0335	0.1510
	1619	"	"	0.0705	0.3178
26c	1383	15.2	4.4454	0.0359	0.1620
	1524	"	"	0.613	0.2760
	1619	"	"	0.0750	0.3380

TABLE IX - EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.(MONOCALCIUM FERRITE).

Constant CaO content = 1.5540 gm. i.e. 1.000 mol per mol of Fe_2O_3.

Oxygen Pressure Varying.

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
23	1544	15.2	4.4453	0.0412	0.1855
	1619	"	"	0.0537	0.2420
	1274	76.0	"	0.0072	0.0326
	1383	"	"	0.0141	0.0636
	1544	"	"	0.0259	0.1169
	1619	"	"	0.0354	0.1596
	1274	5.0	"	0.0213	0.0961
	1383	"	"	0.0315	0.1420
	1544	"	"	0.0509	0.2295
	1619	"	"	0.0645	0.2910
9	1274	15.2	4.4454	0.0133	0.0599
	1383	"	"	0.0205	0.0923
	1544	"	"	0.0402	0.1810
	1619	"	"	0.0533	0.2400
	1274	76.0	4.4454	0.0073	0.0329
	1383	"	"	0.0125	0.0564
	1544	"	"	0.0254	0.1144
	1619	"	"	0.0353	0.1590

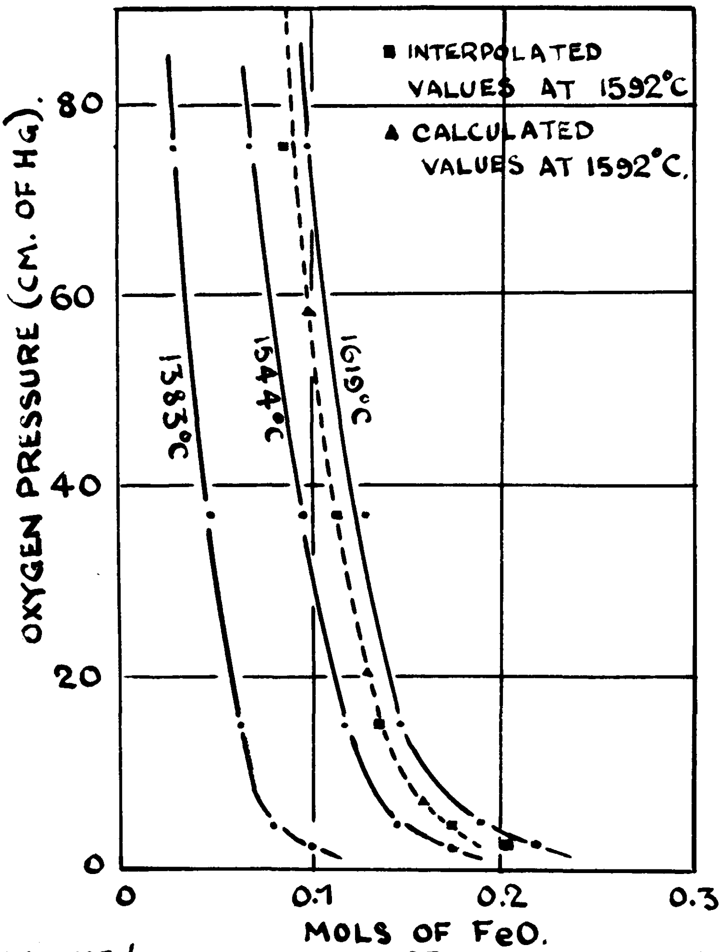


FIG. 15 – EQUILIBRIUM IN LIME/FERRIC OXIDE MELTS. OXYGEN-PRESSURE/FERROUS-OXIDE ISOTHERMS OF MELT CONTAINING 1·4920 MOLS CaO TO 1.00 MOL Fe_2O

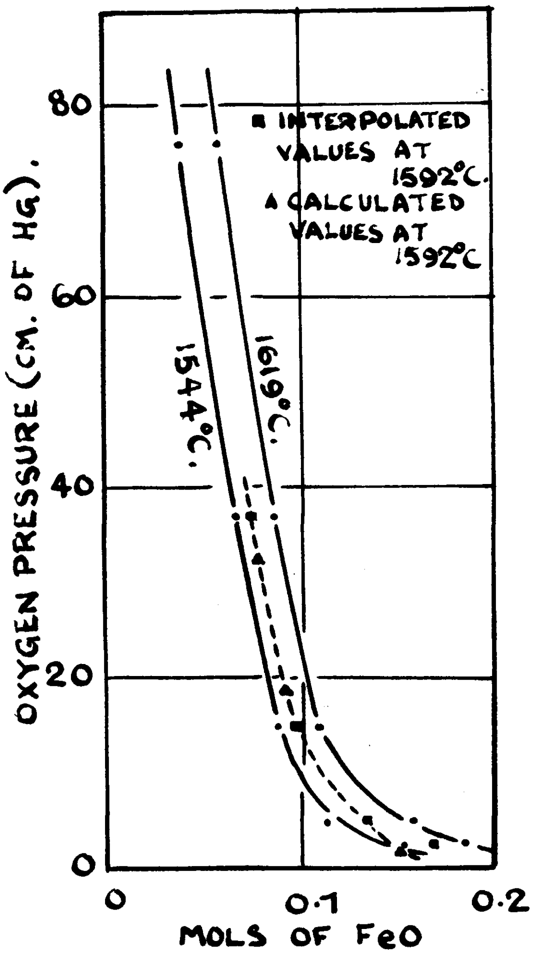


FIG. 16. EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS. OXYGEN-PRESSURE/FERROUS OXIDE ISOTHERMS OF MELT CONTAINING 2.000 MOLS CaO TO 1.000 MOL Fe_2O_3.

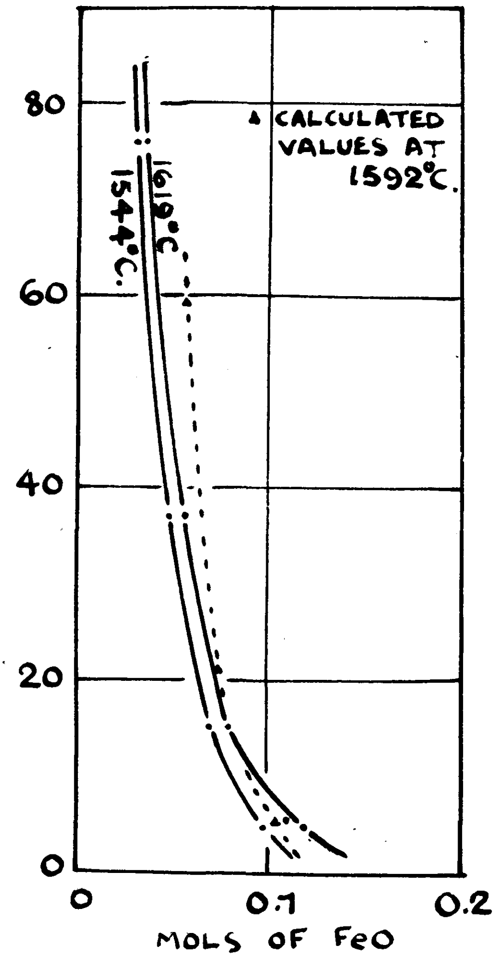


FIG. 17 – EQUILIBRIUM IN LIME/FERRIC OXIDE MELTS. OXYGEN-PRESSURE/FERROUS-OXIDE ISOTHERMS OF MELT CONTAINING 2.500 MOLS CaO TO 1.000 MOL Fe_2O_3.

TABLE IX. (CONTINUED).

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
29	1274	37.0	4.4454	0.0088	0.0397
	1383	"	"	0.0167	0.0734
	1544	"	"	0.0313	0.1410
	1619	"	"	0.0423	0.1908

TABLE X - EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.

Constant CaO Content = 2.3192 gm. i.e. 1.492 mol per mol Fe_2O_3.

Oxygen Pressure Varying.

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
23	1383	15.2	4.4453	0.0144	0.0649
	1544	"	"	0.0256	0.1154
	1619	"	"	0.0321	0.1449
	1383	76.0	"	0.0061	0.0275
	1544	"	"	0.0145	0.0653
	1619	"	"	0.0215	0.0969
	1383	36.0	"	0.0107	0.0482
	1544	"	"	0.0211	0.0951
	1619	"	"	0.0284	0.1281
	1383	5.0	"	0.0173	0.0779
	1544	"	"	0.0318	0.1433
	1619	"	"	0.0414	0.1864
	1383	2.5	"	0.0222	0.1000
	1544	"	"	0.0381	0.1717
	1619	"	"	0.0483	0.2179

TABLE XI - EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.

Constant CaO Content = 3.1062 gm. i.e. 2.000 mols per mol Fe_2O_3.

Oxygen Pressure Varying.

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3 gm.	Loss in weight. gm.	Mols of FeO.
23	1544	15.2	4.4453	0.0192	0.0864
	1619	"	"	0.0237	0.1068
	1544	76.0	"	0.0084	0.0378
	1619	"	"	0.0125	0.0564
	1544	37.0	"	0.0146	0.0658
	1619	"	"	0.0189	0.0851
	1544	5.0	"	0.0247	0.1113
	1619	"	"	0.0347	0.1564
	1544	2.5	"	0.0334	0.1506
	1619	"	"	0.0410	0.1849

TABLE XII - EQUILIBRIUM IN LIME/FERRIC-OXIDE MELTS.

Constant CaO Content = 3.8800 gm. i.e. 2.500 mols per mol of Fe_2O_3.

Oxygen Pressure Varying.

Series No.	Temp. °C.	Oxygen Pressure. cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
29	1544	76.0	4.4454	0.0068	0.0306
	1619	"	"	0.0078	0.0352
	1544	37.0	"	0.0106	0.0477
	1619	"	"	0.0126	0.0566
	1544	15.2	"	0.0153	0.0690
	1619	"	"	0.0173	0.0779
	1544	5.0	"	0.0213	0.0960
	1619	"	"	0.0263	0.1184

(Continued from page 43.)

by using fresh melts whenever evidence of reduction was noted. Its influence can, however, be seen in the case of the melt of series 26b, the results for which are given in chronological order. It will be seen that these oxygen-pressure/ferrous-oxide isotherms have a general characteristic shape. Their steepness tends, however, to increase somewhat as the lime content increases and, to a less extent, as the temperatures fall. It will be seen that very high oxygen pressures would be needed to prevent entirely the dissociation of these liquid melts. It has been found, however, that slow freezing in an atmosphere of oxygen gives crystalline ferrites with a negligible content of ferrous oxide, provided that sufficient lime is present to combine with all of the ferric oxide. Conversely, on melting the ferrites, there is always a sudden evolution of oxygen, until the liquid melt reaches equilibrium with the atmosphere over it. If the lime is not sufficient to combine with all of the ferric oxide, crystals of magnetite separate out on freezing, along with the ferrite, and these oxidize completely only with great difficulty.

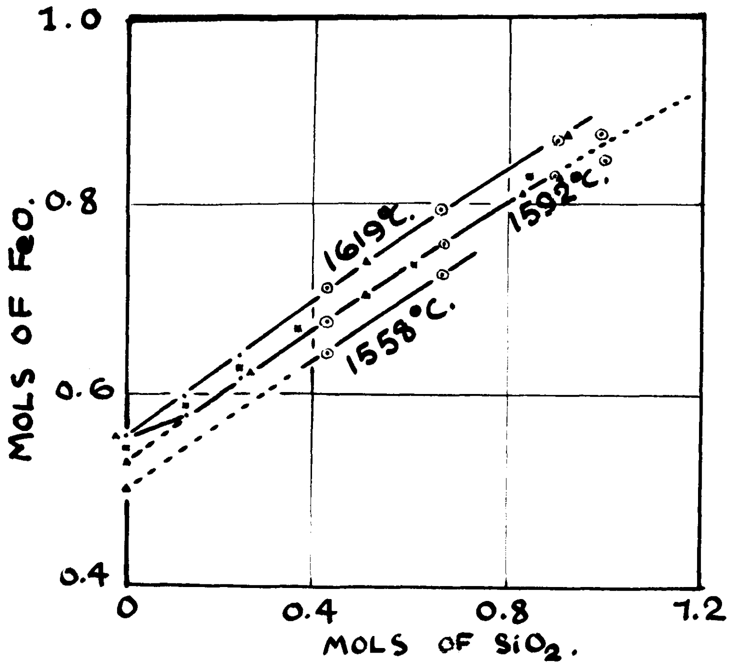


FIG. 18 - EQUILIBRIUM IN SILICA/FERRIC-OXIDE MELTS AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

· SERIES 6 ■ QUENCHING EXPERIMENTS.

⊙ " 7 ▲ CALCULATED VALUES.

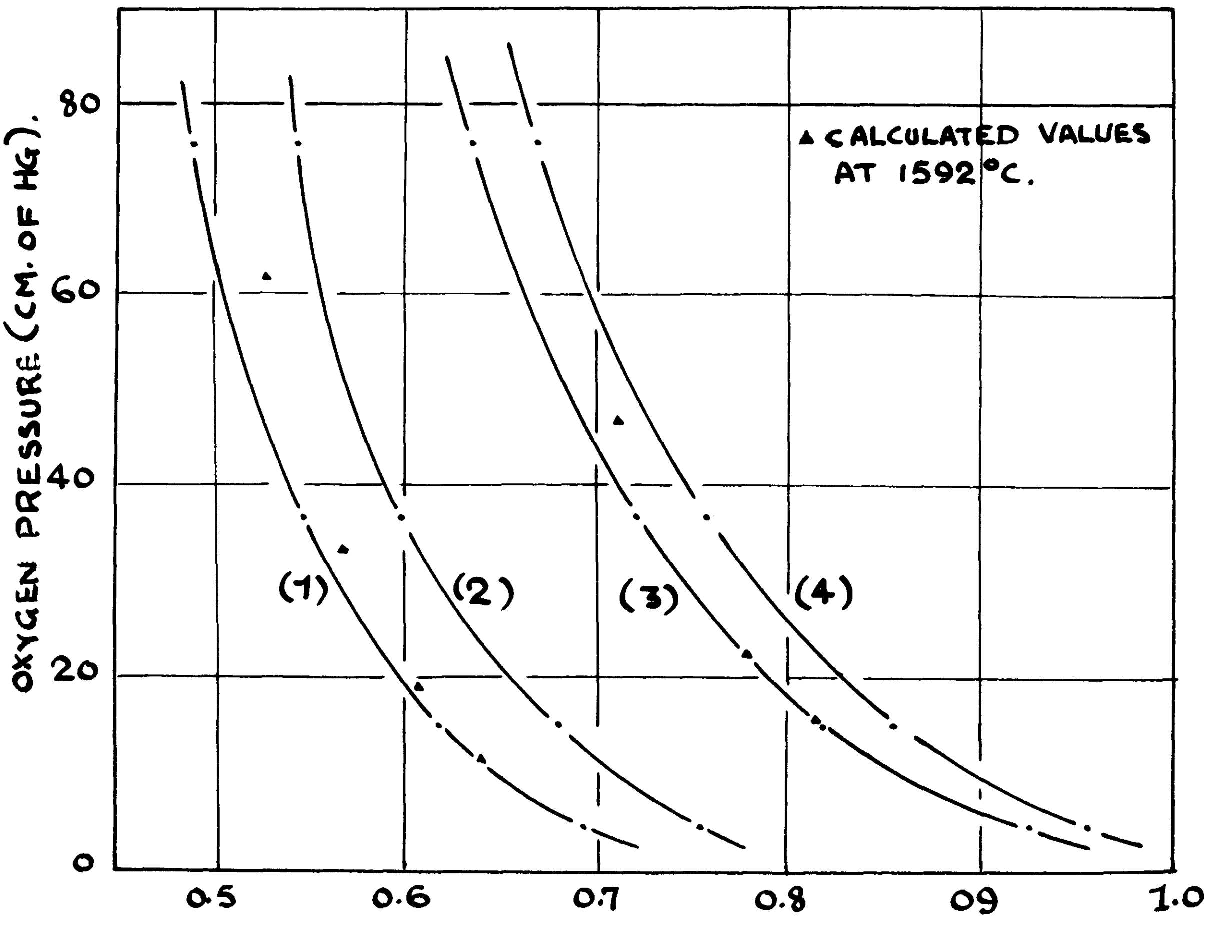


FIG. 19. EQUILIBRIUM IN SILICA/FERRIC-OXIDE MELTS. OXYGEN-PRESSURE/FERROUS-OXIDE ISOTHERMS.

(1) MELT CONTAINING 0.2400 MOLS SiO_2 PER MOL Fe_2O_3 AT 1592°C.
(2) " " " " " " " " " 1648°C.
(3) " " 0.8400 " " " " " " 1592°C.
(4) " " " " " " " " " 1619°C.

PART III - EQUILIBRIUM IN SILICA/FERRIC OXIDE MELTS.

The procedure adopted in studying the equilibrium in silica/ferric oxide melts was the same essentially as that used in the case of the lime/ferric oxide melts. Progressive additions of silica were made to iron oxide melts, and the equilibrium was determined with the various silica contents thus obtained at various temperatures. It was found that the time required to reach equilibrium increased as the silica content rose, owing probably to the marked increase in viscosity which occurred. Because of the high melting points of these melts it was considered desirable to make a series of determinations at a higher temperature than had been used in the case of the lime/ferric-oxide melts. It is of interest to note that, though fayalite ($2FeO.SiO_2$) melts in vacuo or in neutral atmosphere at 1205°C, the same melt, heated under equilibrium conditions in air requires a temperature of over 1600°C for complete fusion. The corresponding mixture of ferric oxide and silica will, at equilibrium under the same conditions, yield a melt of the same composition as is obtained from fayalite. In the solid state, however, such a mixture behaves very sluggishly and silica and ferric oxide interact very slowly below 1550°C.

The effect of silica in ferric oxide melts is to increase the dissociation at equilibrium under any conditions, presumably because of the formation of ferrous silicates, which must therefore be presumed to have at least partial stability in the liquid melts. The results obtained (Table XIII A and B and Figure 18) indicate that the increase in ferrous oxide content takes place almost linearly as the silica content increases. The variation of the equilibrium with the oxygen pressure was studied with silica contents of 0.2400 and 0.8400 gram-molecules per gram molecule of ferric oxide, and the results obtained are given in Tables XIV and XV and in

Figure 19. It will be seen that the oxygen-pressure/ferrous oxide isotherms are of the usual charactertistic form. They are, however, less steep than those obtained with iron oxide alone or with the lime/ferric-oxide melts. Further, the indications are that the steepness decreases progressively as the silica content increases. Silica thus acts in this respect in the directly opposite sense to lime which causes a progressive increase in the steepness of the isotherms. It follows that the melts containing silica were much more sensitive to the influence of the atmosphere than the lime/iron-oxide melts.

At the temperatures employed it was not possible to extend the investigation to higher silica concentrations than are stated in the Tables, since the melts became saturated with silica at a concentration of between 0.900 and 1.000 gram-molecules. Even after heating to 1619°C, the silica added to bring the silica content up to the latter figure could be seen undissolved on top of the melt.

TABLE XIII A - EQUILIBRIUM IN SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	SiO_2 gm.	Loss in weight. gm.	Mols. of FeO.	Mols.of SiO_2.
6	1592	4.4455	0	0.1231	0.5540	0
	1592	"	0.2000	0.1286	0.5790	0.1200
	1619	"	"	0.1331	0.599	"
	1592	"	0.4000	0.1371	0.617	0.2400
	1619	"	"	0.1431	0.644	"
7	1592	4.4455	0	0.1240	0.558	0
	1558	"	0.7000	0.1450	0.652	0.4200
	1592	"	"	0.1500	0.674	"
	1619	"	"	0.1579	0.714	"
	1558	"	1.1000	0.1625	0.730	0.6600
	1592	"	"	0.1695	0.7620	"
	1619	"	"	0.1770	0.796	"
	1592	"	1.5000	0.1865	0.833	0.9000
	1619	"	"	0.1935	0.870	"
	1592	"	1.6667	0.1882	0.845	1.000
	1619	"	"	0.1942	0.877	"

TABLE XIII B.- EQUILIBRIUM IN SILICA/FERRIC-OXIDE MELTS.

QUENCHING EXPERIMENTS.

Oxygen Pressure = 15.2 cm. of mercury.

Temp. °C.	Initial Fe_2O_3. gm.	SiO_2. gm.	Loss in weight. gm.	Mols. of FeO.	Mols. of SiO_2.
1592	4.4445	0	0.1222	0.5480	0
1592	"	0.2000	0.1315	0.5920	0.1200
1592	"	0.4000	0.1400	0.6300	0.2400
1592	"	0.6000	0.1495	0.672	0.3600
1592	"	1.0000	0.1650	0.742	0.6000
1592	"	1.4000	0.1855	0.832	0.8400
1592	"	1.5700	Melt saturated with SiO_2.		

TABLE XIV.- EQUILIBRIUM IN SILICA/FERRIC-OXIDE MELTS.

Constant SiO_2 Content = 0.4000 gm.i.e. 0.2400 mol per mol of Fe_2O_3.

Oxygen Pressure Varying.

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3 gm.	Loss in weight. gm.	Mols. of FeO.
28	1592	76.0	4.4450	0.1083	0.4890
	1648	"	"	0.1207	0.5444
28a	1592	37.0	4.4450	0.1213	0.5470
	1648	"	"	0.1322	0.5960
	1592	15.2	"	0.1370	0.6175
	1648	"	"	0.1510	0.6805
	1592	4.5	"	0.1540	0.6940
	1648	"	"	0.1670	0.7530

TABLE XV. - EQUILIBRIUM IN SILICA/FERRIC-OXIDE MELTS.

Constant SiO_2 = 1.4000 gm. i.e. 0.840 mol per mol of Fe_2O_3.

Oxygen Pressure Varying.

Series No.	Temp. °C.	Oxygem Pressure cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols. of FeO.
30	1592	76.0	4.4453	0.1409	0.6345
	1619	"	"	0.1483	0.6680
	1592	37.0	"	0.1600	0.7205
	1619	"	"	0.1680	0.7560
	1592	15.2	"	0.1815	0.8175
	1619	"	"	0.1895	0.8535
	1592	4.5	"	0.2055	0.9250
	1619	"	"	0.2115	0.9530

PART IV. - EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

In studying the equilibrium in the presence of both lime and silica it was found most convenient to examine the effect of progressively increasing the lime content while the silica content was kept constant at various selected values. For this purpose melts with the appropriate proportions of ferric oxide and silica were made up, and the equilibrium was determined over a range of lime concentrations; the results obtained are recorded in Tables XVI to XXIV and in Figures 20 to 27. In all cases the final figures for the lime, silica and ferrous oxide contents are given as gram-molecules calculated on the basis of one gram-molecule of ferric oxide initially. Two compositions were also investigated for the effect of oxygen pressure on the equilibrium; the results appear in Tables XXI and XXII and Figure 25.

The range of lime and silica concentrations studied covers practically all the field of compositions completely fusible at the temperatures employed. On some of the curves divergencies can be observed, arising from the fact that the compositions involved were incompletely fused. The curves obtained with a silica content of 2.478 gram-molecules (Table XXIV and Figure 26) suddenly shifts to a higher ferrous oxide value when the lime content exceeds 4.6 gram-molecules. There is reason to believe that this also is due to the appearence of a solid phase in the melt, as there were definite signs of incomplete fusion at this point. Separation of a constituent having a high lime to silica ratio (e.g. $2CaO.SiO_2$ or $3CaO.SiO_2$) might produce such an effect, since it would leave the remaining liquid impoverished in lime. Further information is, however, required on this point.

With many of the compositions studied an unforeseen difficulty arose in that the melts crumbled to a fine dust on cooling below red heat. This "dusting" was accompanied by a considerable volume expansion, which usually resulted in rupture of the crucible walls. It occurred with all the melts in which the silica exceeded 0.24 gram-molecules whenever the lime content was greater than a certain, fairly definite, amount, this amount being dependent on the silica content. For example, dusting began at lime contents of approximately 2.2, 1.0, and 1.4 gram-molecules of lime in melts in which the silica contents were 1.0, 0.673 and 0.498 gram- molecules respectively. These figures were obtained incidentally in the course of the work, and no attempt was made to determine systematically the range of dusting compositions, since the effect of the phenomenon on the crucibles was altogether too drastic. It was apparently due to the crystallization of calcium orthosilicate from many of these melts on freezing. This material, as is well-known, undergoes a transformation on cooling that is accompanied by a considerable volume expansion, which causes the substance (and slags containing it) to crumble to a powder.

This dusting tendency provided a serious problem for a while. It was possible in some cases to suppress it by rapid cooling from high temperatures, but this served no useful purpose, since on the next heating, after the desired amount of calcium oxalate had been added, dusting took place at some temperature below redness. It was out of the question to clean out the crucible each time, and start each heat with a fresh mixture, owing to the time required to remove these very hard and insoluble melts from the crucibles. The problem was finally overcome by constructing a small electric muffle furnace, into which the crucible and its contents could be transferred on removing it from the high temperature balance, which was done while the temperature was still above 1000°C. The muffle was held at approximately 600°C. and the crucible was kept in it overnight, and at the weekends when necessary. All additions of calcium oxalate, for the purpose of increaseing the lime content, had to be made to the hot crucible. This was done by making the oxalate into pellets in a pellet press, and adding these from a weighing-bottle by tilting it over the crucible, the weighing-bottle being weighed before and after the addition. With a little practice it was possible to do this without any sacrifice in accuracy and yet sufficiently rapidly to avoid cooling the crucible below the transition point of the orthosilicate.

At the end of a series of determinations it was necessary to clean out the crucible without cooling it to room temperature. Several fluxes were tried as additions to prevent the formation of the orthosilicate, but considerable difficulties in cleaning were encountered. The most

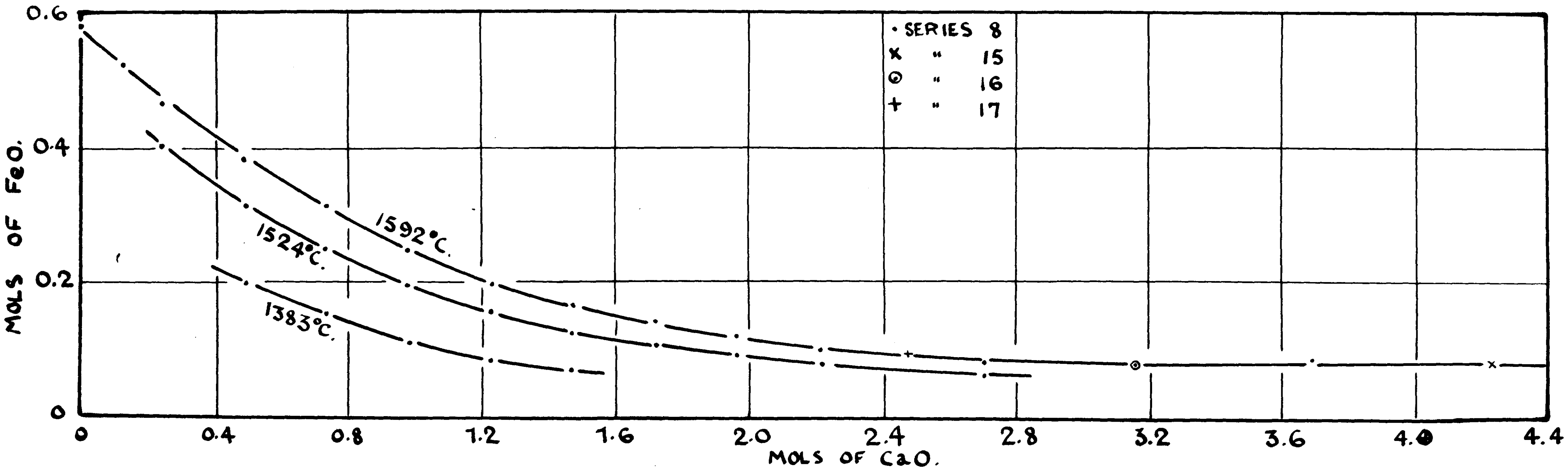


FIG. 20. EQUILIBRIUM IN LIME/SILICA/FERRIC OXIDE MELTS AT AN OXYGEN-PRESSURE OF 15.2 CM. OF MERCURY.

CONSTANT SiO_2 CONTENT = 0.1200 MOLS PER MOL Fe_2O_3.

successful method was to invert the crucible over a fireclay pot in the furnace and heat it to 1600°C.

TABLE XVI - EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Constant SiO_2 Content = 0.2000 gm. i.e. 0.1200 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO gm.	Loss in weight. gm.	Mols.of FeO.	Mols.of CaO.
8	1592	4.4453	0	0.1293	0.5820	0
	1592	"	0.1913	0.1166	0.5240	0.1230
	1524	"	0.3826	0.0889	0.4005	0.2460
	1592	"	"	0.1040	0.468	"
	1383	"	0.7652	0.0440	0.1980	0.492
	1524	"	"	0.0595	0.3130	"
	1592	"	"	0.0855	0.3845	"
	1383	"	1.1478	0.0336	0.1513	0.7380
	1524	"	"	0.0556	0.2500	"
	1592	"	"	0.0696	0.3135	"
	1383	"	1.5304	0.0235	0.1057	0.9840
	1524	"	"	0.0430	0.1937	"
	1592	"	"	0.0545	0.2453	"
	1383	"	1.9130	0.0181	0.0813	1.2300
	1524	"	"	0.0341	0.1543	"
	1592	"	"	0.0436	0.1962	"
	1383	"	212956	0.0152	0.0683	1.4760
	1524	"	"	0.0272	0.1224	"
	1592	"	"	0.0362	0.1629	"
	1524	"	2.6782	0.0233	0.1049	1.7220
	1592	"	"	0.0313	0.1408	"
	1524	"	3.0608	0.0199	0.0895	1.9680
	1592	"	"	0.0264	0.1186	"
	1524	"	3.4434	0.0175	0.0787	2.214
	1592	"	"	0.0215	0.0967	"
	1524	"	4.2086	0.0127	0.0571	2.706
	1592	"	"	0.0167	0.0751	"
	1592	"	5.7390	0.0196	0.0881	3.686
16	1592	4.4453	4.9085	0.0168	0.0755	3.16
17	1592	4.4453	3.8420	0.0203	0.0915	2.472
15	1592	4.4453	6.5775	0.0163	0.0740	4.23

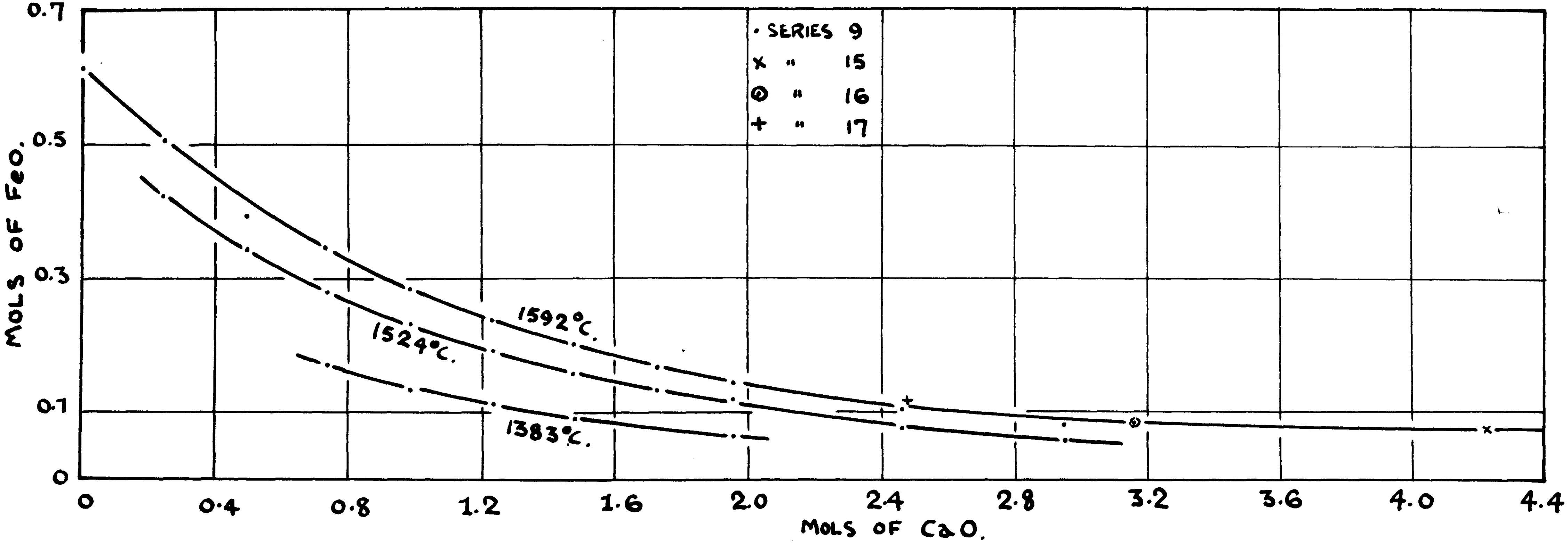


FIG. 21. EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

CONSTANT SiO_2 CONTENT = 0.2400 MOLS PER MOL Fe_2O_3.

TABLE XVII.- EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Constant SiO_2 Content = 0.4000 gm. i.e. 0.2400 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Initial Fe_2O_3 gm.	CaO gm.	Loss in weight. gm.	Mols of FeO.	Mols of CaO.
9	1592	4.4450	0	0.1375	0.6190	0
	1524	"	0.3826	0.0946	0.426	0.246
	1592	"	"	0.1126	0.507	"
	1524	"	0.7652	0.0772	0.3472	0.492
	1592	"	0."	0.0877	0.3945	"
	1383	"	1.1478	0.0378	0.1700	0.728
	1524	"	"	0.0628	0.2380	"
	1592	"	"	0.0773	0.3480	"
	1383	"	1.5304	0.0299	0.1345	0.984
	1524	"	"	0.0519	0.2336	"
	1592	"	"	0.0636	0.2861	"
	1383	"	1.9130	0.0245	0.1103	1.230
	1524	"	"	0.0425	0.1912	"
	1592	"	"	0.0532	0.2390	"
	1383	"	2.2956	0.0201	0.0903	1.476
	1524	"	"	0.0351	0.1579	"
	1592	"	"	0.0451	0.2028	"
	1524	"	2.6782	0.0292	0.1314	1.722
	1592	"	"	0.0377	0.1695	"
	1383	"	3.0608	0.0138	0.062	1.968
	1524	"	"	0.0248	0.1215	"
	1592	"	"	0.0323	0.1453	"
	1524	"	3.8260	0.0170	0.0764	2.460
	1592	"	"	0.0230	0.1036	"
	1524	"	4.5912	0.0132	0.0595	2.952
	1592	"	"	0.0177	0.0796	"
	1524	"	5.3564	0.0154	0.0693	3.444
	1592	"	"	0.0194	0.0873	"
16	1592	4.4453	4.9085	0.0188	0.0845	3.160
17	1592	4.4453	3.8420	0.0253	0.1140	2.472
15.	1592	4.4453	6.5775	0.0163	0.073	4.23

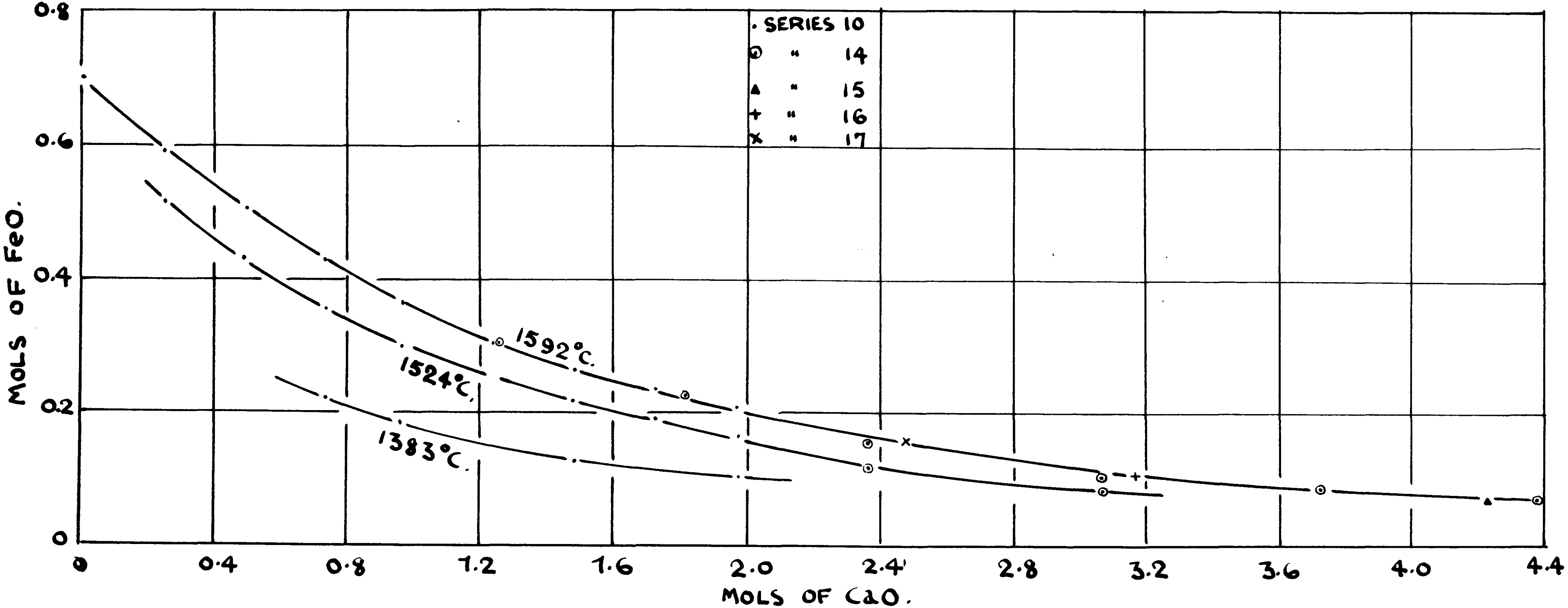


FIG. 22. EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

CONSTANT SiO_2 CONTENT = 0.4980 MOLS PER MOL Fe_2O_3.

TABLE XVIII.- EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Constant SiO_2 Content = 0.8288 gm. i.e. 0.4980 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO gm.	Loss in weight. gm.	Mols of FeO.	Mols of CaO.
10	1592	4.4387	0	0.1560	0.7040	0
	1524	"	0.3826	0.1146	0.516	0.2460
	1592	"	"	0.1316	0.593	"
	1524	"	0.7652	0.0952	0.4290	00.4920
	1592	"	"	0.1127	0.5080	"
	1383	"	1.1478	0.0488	0.2200	0.7380
	1524	"	"	0.0793	0.3575	"
	1592	"	"	0.0948	0.4270	"
	1383	"	1.5304	0.0414	0.1865	0.9840
	1524	"	"	0.0664	0.2992	"
	1592	"	"	0.0809	0.3646	"
	1524	"	1.9130	0.0565	0.2545	1.2300
	1592	"	"	0.0675	0.3042	"
	1383	"	2.2956	0.0286	0.1290	1.4760
	1524	"	"	0.0481	0.2170	"
	1592	"	"	0.0586	0.2640	"
	1524	"	2.6782	0.0422	0.1902	1.7220
	1592	"	"	0.0522	0.2356	"
	1383	"	3.0608	0.0231	0.1041	1.9680
	1524	"	"	0.0363	0.1646	"
	1592	"	"	0.0458	0.2063	"
14	1592	4.4455	1.9400	0.0678	0.3055	1.246
	1592	"	2.8090	0.0498	0.2246	1.808
	1524	"	3.6700	0.0258	0.1161	2.360
	1592	"	"	0.0338	0.1521	"
	1524	"	4.7620	0.0178	0.0800	3.066
	1592	"	"	0.0222	0.1000	"
	1592	"	5.7820	0.0183	0.0813	3.719
	1592	"	6.8320	0.0153	0.0689	4.395
16	1592	"	4.9085	0.0226	0.1015	3.160
17	1592	4.4453	3.8420	0.0356	0.1600	2.472
15	1592	4.4453	6.5775	0.0151	0.0680	4.23

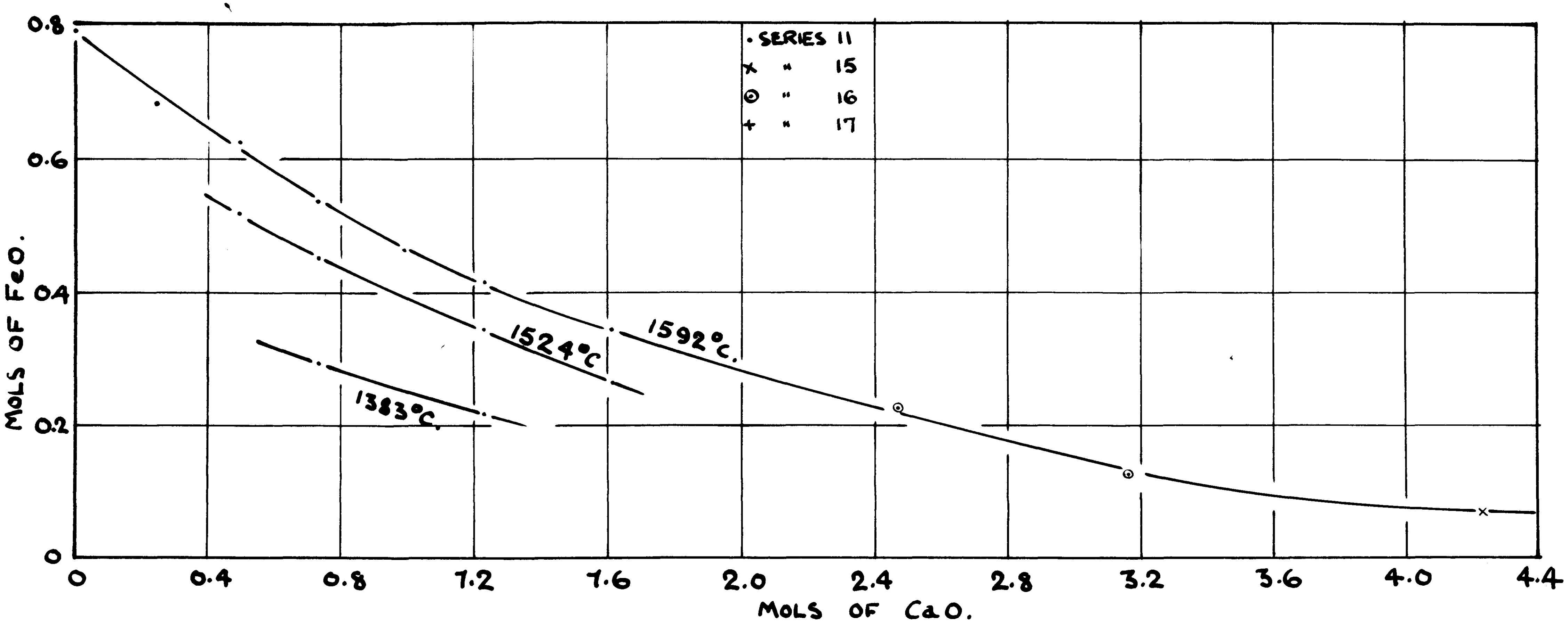


FIG. 23. EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

CONSTANT SiO_2 CONTENT = 0.7630 MOLS PER MOL OF Fe_2O_3.

TABLE XIX.- EQUILIBRIUM IN LIME/SILICA/ FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Constant SiO_2 Content = 1.2700 gm. i.e. 0.7630 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO gm.	Loss in weight. gm.	Mols of FeO.	Mols of CaO.
11	1592	4.4453	0	0.1763	0.8940	0
	1592	"	0.3826	0.1592	0.688	0.2460
	1524	"	0.7652	0.1155	0.520	0.4920
	1592	"	0 "	0.1380	0.621	"
	1383	"	1.1478	0.0651	0.2935	0.7380
	1524	"	"	0.1001	0.451	"
	1592	"	"	0.1196	0.538	"
	1592	"	1.5304	0.1032	0.465	0.984
	1383	"	1.9130	0.0483	0.2176	1.2300
	1524	"	"	0.0763	0.344	"
	1592	"	"	0.0918	0.413	"
	1524	"	2.5158	0.0586	0.2640	1.616
	1592	"	"	0.0756	0.3405	"
16	1592	4.4453	4.9085	0.0288	0.1296	3.160
17	1592	4.4453	3.8420	0.0491	0.2210	2.472
15	1592	4.4453	6.5775	0.0118	0.0530	4.23

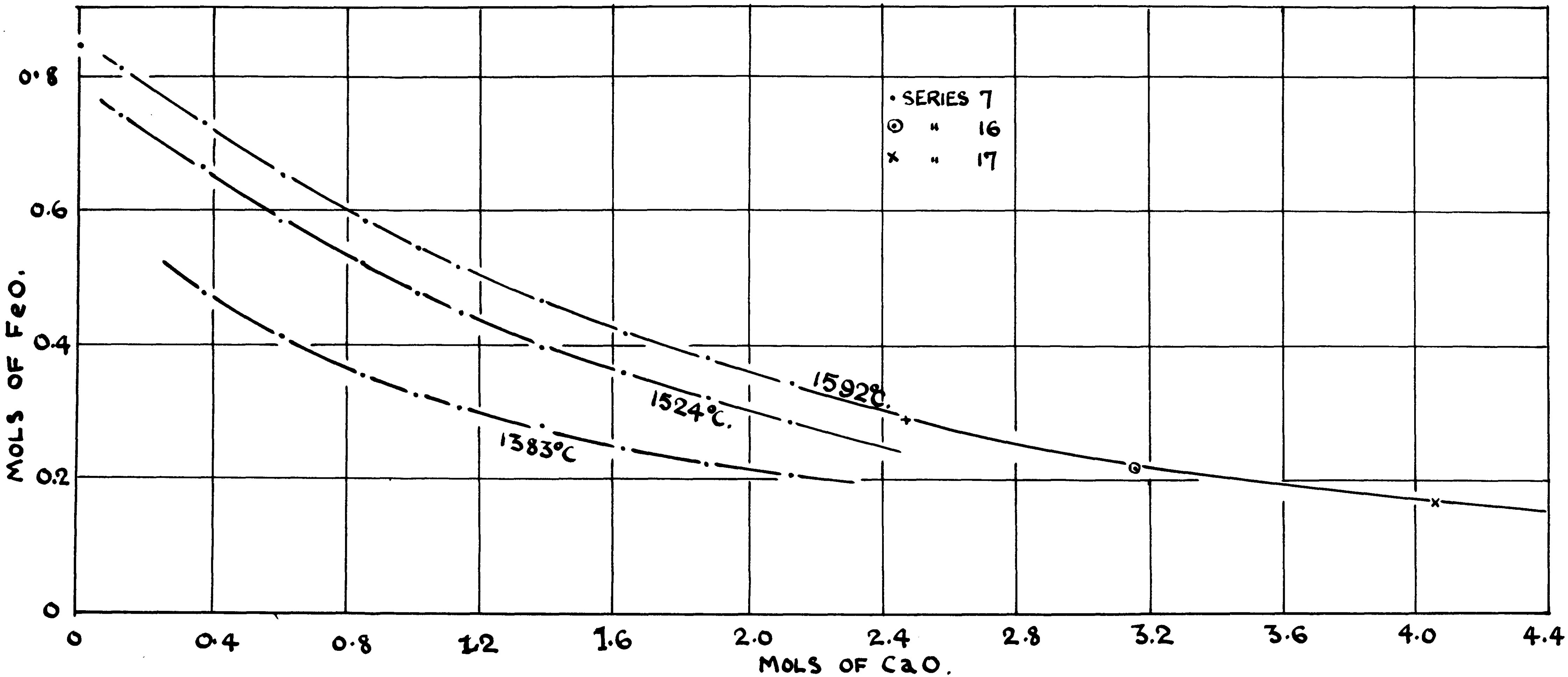


FIG. 24. EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

CONSTANT SiO_2 CONTENT = 1.000 MOLS PER MOL OF Fe_2O_3.

TABLE XX.- EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Constant SiO_2 Content = 1.6670 gm. i.e. 1.000 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO gm.	Loss in weight. gm.	Mols of FeO.	Mols of CaO.
7	1592	4.4455	0	0.1882	0.8450	0
	1524	"	0.1913	0.1655	0.7430	0.1230
	1592	"	"	0.1805	0.812	"
	1383	"	0.5739	0.1061	0.477	0.369
	1524	"	0 "	0.1481	0.667	" "
	1592	"	"	0.1626	0.732	"
	1383	"	0.9565	0.0912	0.411	0.615
	1524	"	"	0.1297	0.583	"
	1592	"	"	0.1447	0.651	"
	1383	"	1.3391	0.0783	0.352	0.860
	1524	"	"	0.1148	0.517	"
	1592	"	"	0.1303	0.586	"
	1383	"	1.5879	0.0721	0.324	1.020
	1524	"	"	0.1051	0.473	"
	1592	"	"	0.1211	0.545	"
	1383	"	1.7792	0.0684	0.308	1.142
	1524	"	"	0.0989	0.455	"
	1592	"	"	0.1144	0.514	"
	1383	"	2.1618	0.0615	0.277	1.392
	1524	"	"	0.0885	0.3978	"
	1592	"	"	0.1035	0.466	"
	1383	"	2.5444	0.0544	0.2444	1.639
	1524	"	"	0.0791	0.3561	"
	1592	"	"	0.0926	0.416	"
	1383	"	2.9270	0.0487	0.2192	1.882
	1524	"	"	0.0712	0.3203	"
	1592	"	"	0.0847	0.3808	"
	1383	"	3.3096	0.0453	002040	2.129
	1524	"	"	0.0628	0.283	"
	1592	"	""	0.0763	0.344	"
16	1592	4.4453	4.9085	0.0483	0.2170	3.160
17	1592	4.4453	3.8420	0.0641	0.2890	2.472
	1592	"	6.3170	0.0366	0.1646	4.06

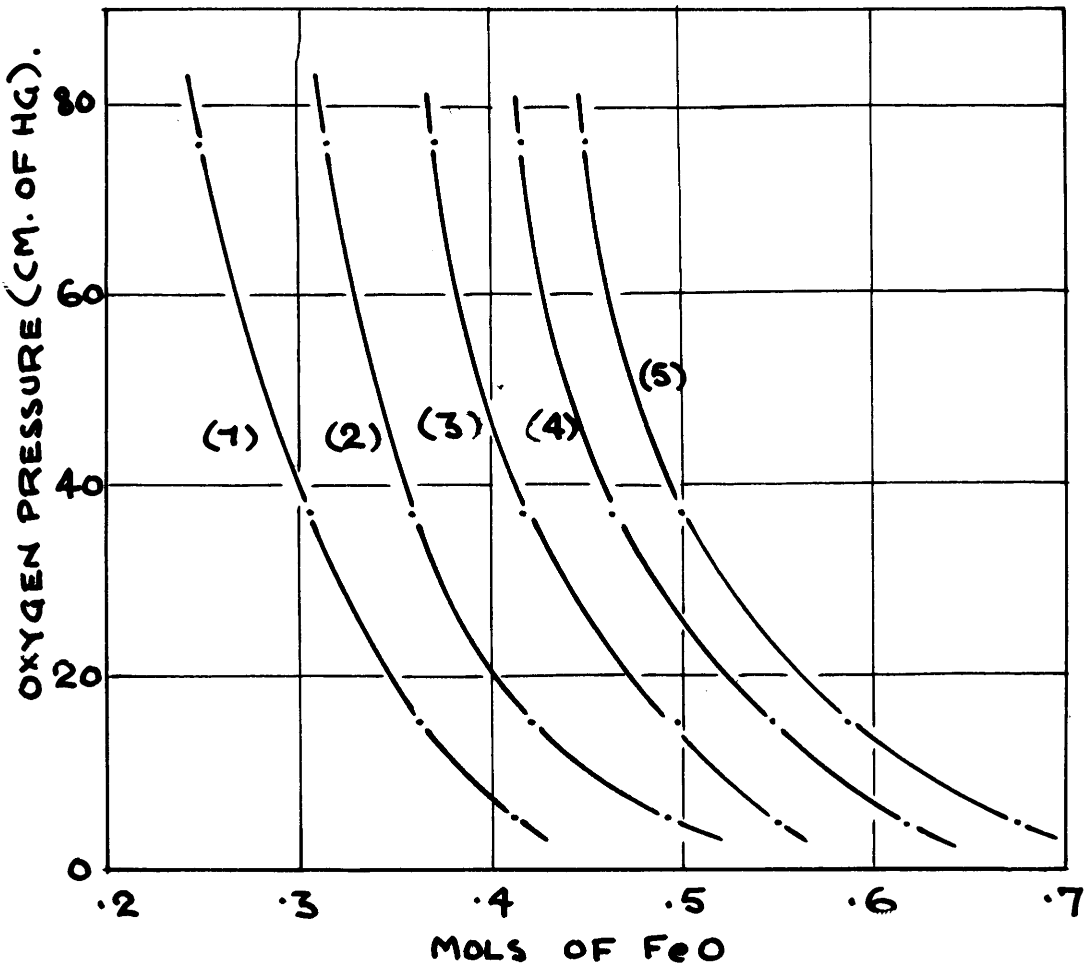


FIG. 25. EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.
OXYGEN-PRESSURE/FERROUS-OXIDE ISOTHERMS.

(1) 1·739 CaO : 1.000 SiO_2 : 1.000 Fe_2O_3 AT 1544°C.
(2) " " " " " " " 1619°C.
(3) 1·000 CaO : 1.000 SiO_2 : 1·000 Fe_2O_3 AT 1544°C.
(4) " " " " " " " 1592°C.
(5) " " " " " " " 1619°C.

TABLE XXI. - EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure Varying.

Constant CaO Content = 1.5534 gm. i.e. 1.000 mol per mol of Fe_2O_3.

Constant SiO_2 Content = 1.6667 gm. i.e. 1.000 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols of FeO.
30	1544	76.0	4.4453	0.0821	0.3700
	1592	"	"	0.0921	0.4155
	1619	"	"	0.0995	0.4485
	1544	27.0	"	0.0921	0.4150
	1592	"	"	0.1030	0.4640
	1619	"	"	0.1108	0.4990
	1544	15.2	"	0.1105	0.4980
	1592	"	"	0.1210	0.5455
	1619	"	"	0.1300	0.5860
	1544	4.5	"	0.1218	0.5485
	1592	"	"	0.1370	0.6170
	1619	"	"	0.1500	0.6755

TABLE XXII.- EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure Varying.

Constant CaO Content = 2.7024 gm. i.e.1.739 mol per mol of Fe_2O_3.

Constant SiO_2 Content = 1.6667 gm. i.e. 1.000 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Oxygen Pressure cm. of Hg.	Initial Fe_2O_3. gm.	Loss in weight. gm.	Mols of FeO.
30	1544	76.0	4.4453	0.0545	0.2456
	1619	"	"	0.0695	0.3136
	1544	37.0	"	0.0675	0.3041
	1619	"	"	0.0793	0.3575
	1544	15.2	"	0.0802	0.3612
	1619	"	"	0.0936	0.4213
	1544	4.5	"	0.0912	0.4110
	1619	"	"	0.1090	0.4910

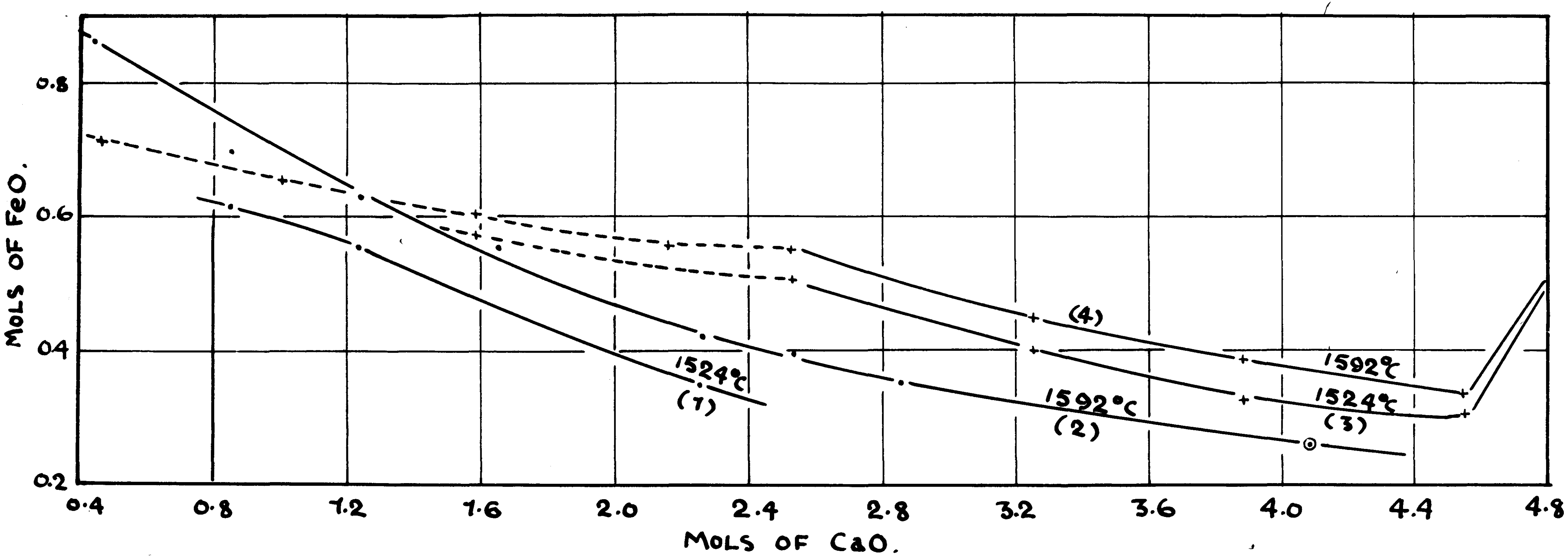


FIG.26. EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS AT AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY.

(1) AND (2): CONSTANT SiO_2 CONTENT = 1.746 MOLS PER MOL Fe_2O_3.

(3) AND (4): " " " = 2.478 " " " " .

TABLE XXIII.-EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Constant SiO_2 Content = 2.9075 gm. i.e. 1.746 mol per mol of Fe_2O_3.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO gm.	Loss in weight. gm.	Mols of FeO.	Mols of CaO.
12	1592	4.4453	0.6824	0.1917	0.862	0.4380
	1524	"	1.3194	0.1362	0.614	0.8480
	1592	"	"	0.1552	0.699	"
	1524	"	1.9204	0.1232	0.555	1.235
	1592	"	"	0.1402	0.631	"
	1592	"	2.5794	0.1227	0.552	1.656
	1524	"	3.5104	0.0767	0.3455	2.259
	1592	"	"	0.0927	0.4170	"
	1592	"	4.4304	0.0780	0.3514	2.853
	1592	"	5.3904	0.0805	0.3625	3.465
16	1592	4.4453	5.9085	0.0873	0.3930	3.160
17	1592	4.4453	6.3170	0.0606	0.2724	4.06

TABLE XXIV.- EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS.

Oxygen Pressure = 15.2 cm. of mercury.

Constant SiO_2 Content = 4.1243 gm. i.e. 2.478 mols per mol of Fe_2O_3.

Series No.	Temp. °C.	Initial Fe_2O_3. gm.	CaO gm.	Loss in weight. gm.	Mols of FeO.	Mols of CaO.
13	1592	4.4453	0.6905	0.1596	0.7180	2.478
	1592	"	1.5550	0.1446	0.6510	1.000
	1524	"	2.4600	0.1271	0.5725	1.581
	1592	"	"	0.1351	0.6090	"
	1592	"	3.3590	0.1236	0.5560	2.160
	1524	"	4.2340	0.1116	0.5022	2.722
	1592	"	"	0.1221	0.5500	"
	1524	"	5.0620	0.0891	0.4010	3.256
	1592	"	"	0.1001	0.4500	"
	1524	"	6.0350	0.0731	0.3295	3.880
	1592	"	"	0.0861	0.3880	"
	1524	"	7.0780	0.0681	0.3070	4.550
	1592	"	"	0.0721	0.3245	"
	1524	"	8.1230	0.1706	0.7675	5.225
	1592	"	"	0.1721	0.7750	"
	1592	"	9.0230	0.1731	0.7800	5.810
	1592	"	9.9094	0.1751	0.7880	6.375

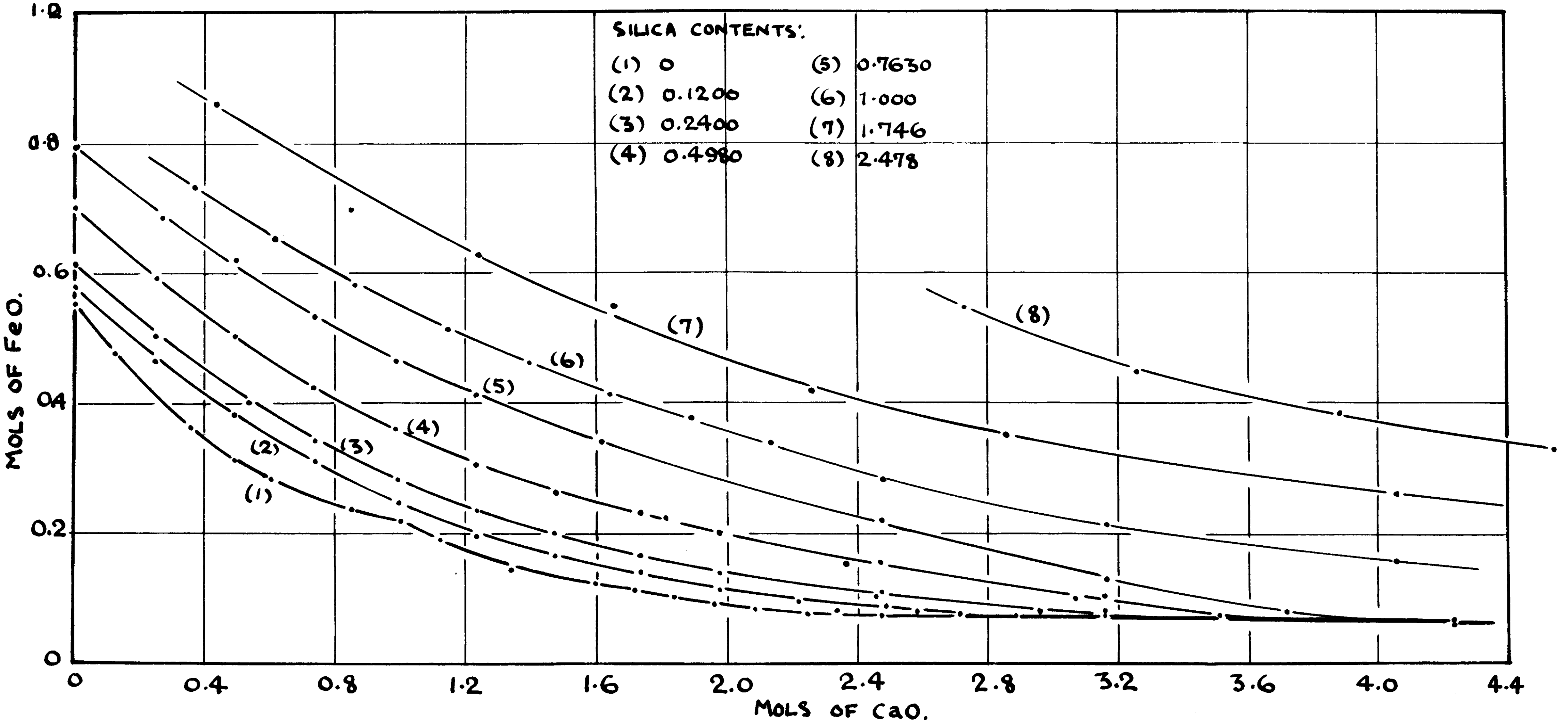


FIG. 27. EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS AT 1592°C AND AN OXYGEN PRESSURE OF 15.2 CM. OF MERCURY. CURVES OF CONSTANT SiO_2 CONTENT.

It will be noticed that all of the curves obtained in this fashion (i.e. by keeping the silica content constant and increasing the lime content) follow the same general trend. They run, in fact, roughly parallel to each other and to the curve obtained by simple lime addition to ferric oxide in the absence of silica. This can be seen clearly by referring to Figure 27. At high lime concentrations several of the lower-silica-content curves converge on this basal zero-silica-content curve. The lime content at which this takes place increases progressively as the silica content increases. It seems reasonable to suppose, from their general trend, that the other curves will also approach the zero silica curve ultimately.

GENERAL SURVEY OF THE EXPERIMENTAL RESULTS.

The findings of the preceding sections can be briefly summarized as follows.

(a) In liquid (as in solid) systems containing iron oxides there exists, at high temperatures, an equilibrium between the ferrous and ferric oxide contents of the system.

(b) The equilibrium relationship is determined by the temperature and oxygen pressure of the system. The proportion of ferric oxide to ferrous oxide decreases as the temperature is increased, and increases as the oxygen pressure is increased.

(c) The presence of lime alters the equilibrium relationship. The higher the lime content, the lower is the proportion of ferrous oxide to ferric oxide at equilibrium.

(d) Silica also causes a displacement of the equilibrium, but in the opposite sense. The higher the silica content, the higher is the proportion of ferrous oxide to ferric oxide at equilibrium.

(e) When lime and silica are present simultaneously, each tends to shift the equilibrium in the sense characteristic of it. Hence the proportion of ferrous oxide to ferric oxide at equilibrium depends on the relative proportions of lime and silica. It does not depend solely on that, however, as, even when the proportions are kept constant, a variation in the amounts of these additions causes a variation in the equilibrium relationship. There is a continuous variation in the relationship as the ratio of lime to silica is varied over the entire range of compositions covered by the investigations.

The data thus summarised are given quantitatively by the Tables and Curves. From these the equilibrium composition of any lime/silica/iron-oxide slag under any condition of temperature, and oxygen pressure (in the range covered by the investigations, of course) is obtainable.

APPLICATION TO OPEN HEARTH FURNACE SLAGS.

The results obtained throw considerable light on the relationship between acid and basic furnace slags as regards their reaction to the influence of the furnace atmosphere. In slags of the former type the ratio of ferrous- to ferric-oxide will be much larger at equilibrium than in those of the latter. The effect of this on gas-oxidation is easy to foresee. In contact with liquid iron only ferrous oxide is stable (or at least a combination of iron and oxygen approaching the composition FeO as can be seen from a consideration of the immiscible liquid region of the iron-oxygen thermal equilibrium diagram.[21]). Hence at the slag/metal interface the slag is tending to an equilibrium state in which only ferrous oxide is present in it, while in the upper regions it is tending to pick up oxygen from the furnace atmosphere to reach an equilibrium state at which a definite proportion of ferric oxide, depending on the constitution of the slag, the temperature and the furnace atmosphere, will be present. The two conditions are, of course, incompatible, and hence a cycle of reactions is set up which results, as previously noted, in gas oxidation. In a basic slag the difference between the equilibrium conditions in the two regions of the slag is much more marked than in an acid slag, and hence, it might be expected that, in the absence of complicating factors, gas oxidation would take place to a greater extent in the basic process than in the acid process, which, in actual fact, is the case. It is, however, necessary to make allowance for the fact that the increased ferric oxide content of basic slags is, in all probability, due to compound formation, and that the increased amount of ferric oxide is consequently not free but combined as ferrite. In this connection it has been suggested that the presence of lime should actually decrease gas oxidation since it forms stable compounds with the ferric oxide of the slag. This need not necessarily be the case, however. For one thing the present experimental results indicate that the ferrites are not completely stable in the liquid state, but that they undergo partial dissociation od melting. Hence, even in the presence of lime the ferric oxide cannot be considered as being stably combined. On the contrary there will always be a certain proportion of free iron oxide in the slag. The equilibrium condition in slags containing ferrites can probably be represented by the following reversible reactions -

$$CaO.Fe_2O_3 = CaO + Fe_2O_3$$

and

$$Fe_2O_3 = 2FeO + \tfrac{1}{2}O_2$$

In all cases dissociation will proceed till equilibrium is reached. It will be observed that at equilibrium a certain content of free ferric oxide is to be expected in the slag, in addition to the ferrous oxide formed by dissociation. The experimental results, as they stand, do not, however, give any information as to the amount of this oxide or of any of the other molecular species in the liquid melts, nor is it possible to say whether the two oxides of iron are actually chemically free or combined to give Fe_3O_4, as takes place in the solid state.

It was with the object of throwing light on these points, and on others of a similar nature, that the theoretical investigations described in the succeeding sections were undertaken.

NOTE ON VOLATILITY OF Fe_2O_3 (see footnote to page 40).

More recent experiments have shown, however, that Fe_2O_3 can apparently volatilize under certain conditions. A current of air, passed over the molten oxide at 1600°C., carries with it appreciable amounts of oxide which appears to be mainly in the ferric state. Hence it would appear that molten iron oxide has an appreciable vapour pressure at this temperature. This suggests a possible reason why the rate of loss of weight was accelerated by a rising temperature (see remarks near foot of page 40). The bubbles of oxygen escaping from the melt as the temperature rose would tend to be saturated with iron-oxide vapour, thus contributing to the permanent loss in weight observed.

SECTION II.

INTERPRETATION OF THE PRESENT EXPERIMENTAL DATA IN TERMS OF THE LAW OF MASS ACTION. DEDUCTION OF THE MOLECULAR CONSTITUTION OF THE MELTS.

NOTE ON CALCULATIONS IN THIS SECTION: The calculations carried out during the theoretical investigations described in the following section were very lengthy, and depended very largely on methods of trial and error, and on successive approximations. It has been found practically impossible to reduce them to a form of reasonable length suitable for reproduction, and hence only a very brief indication of the methods employed is given. The results obtained are, however, given in full, since, in addition to their intrinsic significance, they provide evidence that the various theoretical curves deduced are actually Mass Action curves.

INTERPRETATION OF THE PRESENT DATA IN TERMS OF MOLECULAR CONSTITUTION OF THE MELTS.

The experimental results, as they stand, give no information concerning the actual molecular constitution of the liquid melts, since only the total amounts of the various constituents are recorded. In this respect the liquid state is more difficult to study than the solid state, in which the crystalline compounds present can usually be identified. Similar knowledge of liquid systems can only be obtained indirectly e.g. by examination of data of the kind now under discussion in the light of established chemical laws. The study of the chemical kinetics of high temperature systems is still, comparatively speaking, in its infancy. It is known, however, that the laws of ideal solutions are obeyed at least approximately. It is hardly to be expected that they will be obeyed exactly, since many of the reactants are highly concentrated (at least in systems of the kind now under consideration). Nevertheless, much useful information can often be derived by applying the ideal laws in such cases, even though only approximate agreement may be obtained.

CALCULATIONS BASED ON THE LAW OF MASS ACTION.

EQUILIBRIUM IN IRON OXIDE MELTS.

It is convenient to consider this simpler case first. The calculations are based on the data in Figures 5, 6, 7, 8 and 9.

Three oxides of iron with definite chemical identities are known to exist, and so long as no evidence to the contrary arises we are justified in assuming that only these three are liable to occur in the liquid melts. It is not, of course, known to what extent Fe_3O_4 may be dissociated into FeO and Fe_2O_3 under these conditions. (It should be noted that FeO itself is, according to the iron-oxygen thermal equilibrium diagram, subject to dissociation on melting, but at the oxygen pressures now under review this will be very much suppressed and can almost certainly be neglected.) Assuming an equilibrium to exist between the three oxides and the oxygen pressure over them, it can be completely defined by the two reversible equilibria:

$$Fe_2O_3 \;=\; 2FeO + \tfrac{1}{2}O_2, \quad \text{whence } k_1 = \frac{(FeO)^2 \times \sqrt{P}}{(Fe_2O_3)},$$

$$\text{and } Fe_3O_4 \;=\; FeO + Fe_2O_3, \quad \text{whence } k_2 = \frac{(FeO)(Fe_2O_3)}{(Fe_3O_4)},$$

where (FeO), (Fe_2O_3) and (Fe_3O_4) are the activities of these oxides and P is the pressure of diatomic oxygen over the melt.

Assume that one gram-molecule of ferric oxide was taken initially.

Let the total ferrous oxide formed from it at equilibrium be 2A (expressed in gram-molecules, as are all the other quantities in the discussion). Then the total ferric oxide left at equilibrium = 1 - A.

Let the free FeO = x.

Then $Fe_3O_4 = 2A - x$.

and $Fe_2O_3 = (1 - A) - (2A - x) = 1 - 3A + x$,

where Fe_3O_4 and Fe_2O_3 denote the amounts of these substances actually present in the free state in the melts.

Also if M denotes the total number of gram-molecules of all molecular species present in the system, then

$$M = 1 - A + x.$$

Hence, assuming the activities of the oxides to be proportional to their concentrations expressed as molar fractions,

$$k_1 = \frac{x^2 \times \sqrt{P}}{(1 - A + x)(1 - 3A + x)},$$

and $$k_2 = \frac{x\ (\ 1 - 3A + x\ )}{(\ 1 - A + x\ )\ (\ 2A - x\ )},.$$

If, at any temperature, the value of A is known for two values of P, k_1 and k_2 can be evaluated. Sufficient experimental data on the iron oxide melts had been obtained to make it possible to draw oxygen-pressure/ferrous-oxide isotherms at various temperatures. Use was also made of the data from the silica/iron-oxide melts to obtain confirmation of these as far as possible. Since the silica/iron-oxide isobars were almost linear, they could readily be be produced to zero silica content, and the values thus obtained used to check the iron oxide data. Figure 28 shows the experimental values which were utilised in evaluating these constants.* From the isotherm at 1619°C the values calculated were $k_1 = 0.4926$ and $k_2 = 0.2432$ (the oxygen pressure being expressed in centimetres of mercury). Using these constants it is possible to calculate a theoretical isotherm at this temperature (passing, of course, through the points selected to evaluate k_1 and k_2), as shown in the following table:

Theoretical data on isotherm at 1619°C. calculated on the basis of $k_1 = 0.4926$, $k_2 = 0.2432$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	M	Oxygen Pressure. Cm. of Hg.
0.4600	0.1503	0.3097	0.4603	0.9203	85.9
0.5000	0.1735	0.3265	0.4235	0.9235	40.9
0.5570	0.2100	0.3470	0.3745	0.9315	15.2
0.6000	0.2410	0.3590	0.3410	0.9410	7.4
0.6600	0.2888	0.3710	0.2988	0.9588	2.9

Similarly, from the data for 1592°C. the values of the constants calculated were $k_1 = 0.3845$, $k_2 = 0.2387$, which gave the following figures:

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* See also Figure 11.

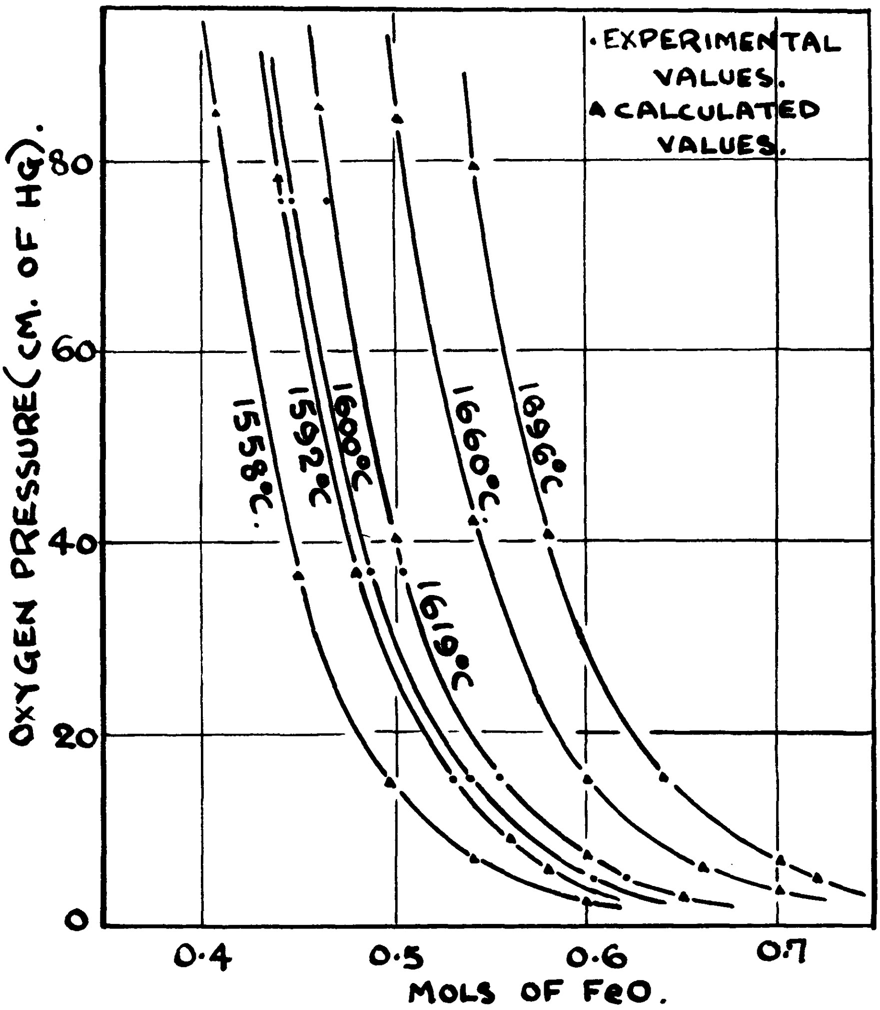

FIG. 28. CALCULATED DATA ON IRON-OXIDE EQUILIBRIA.

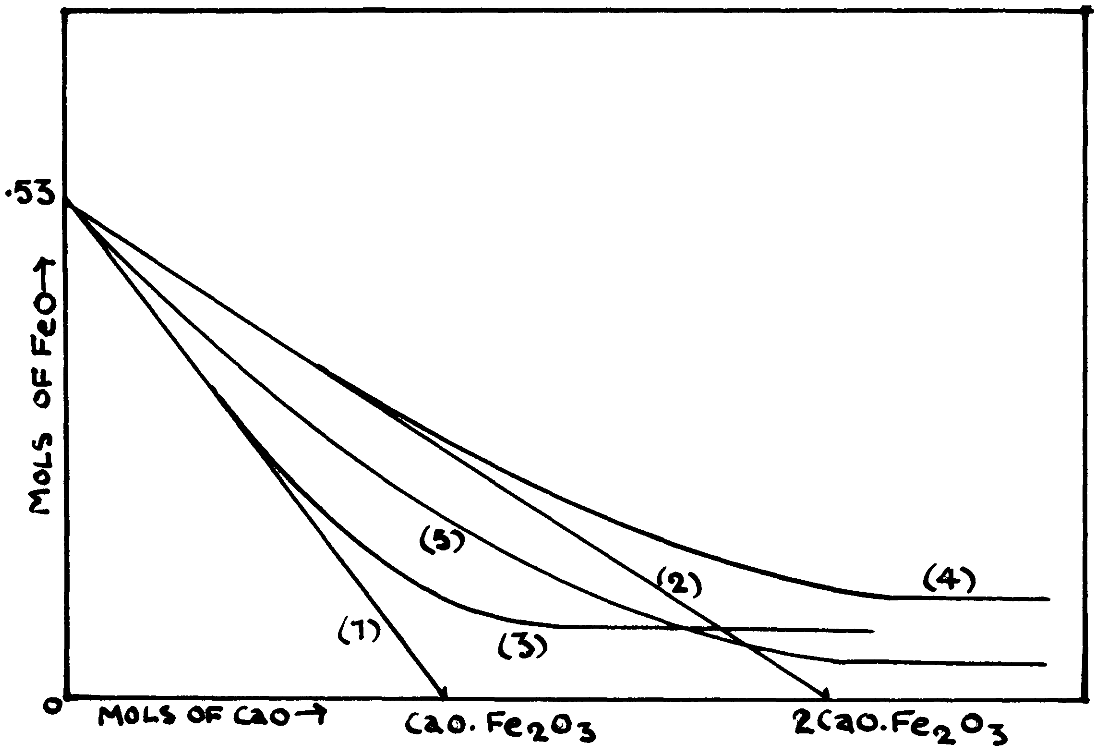

FIG. 29. EFFECT OF CaO ON THE DISSOCIATION OF FERRIC OXIDE — DEPENDENCE ON STABILITY OF CALCIUM FERRITES.

(1) $CaO.Fe_2O_3$ COMPLETELY STABLE.
(2) $2CaO.Fe_2O_3$ ALONE COMPLETELY STABLE.
(3) $CaO.Fe_2O_3$ " PARTLY STABLE.
(4) $2CaO.Fe_2O_3$ " " "
(5) BOTH FERRITES PARTLY STABLE.

Theoretical data on the isotherm at 1592°C. calculated on the basis of $k_1 = 0.3845$, $k_2 = 0.2387$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	M.	Oxygen Pressure. cm. of Hg.
0.4400	0.1380	0.3020	0.4780	0.9180	78.5
0.4800	0.1600	0.3200	0.4400	0.9200	37.0
0.5300	0.1900	0.3400	0.3950	0.9250	15.2
0.5600	0.2100	0.3500	0.3700	0.9300	9.0
0.5800	0.2240	0.3560	0.3540	0.9340	5.0

It can be seen (see Figure 28) that these figures reproduce the characteristic form of the isotherms very closely.

By assuming logarithmic variation of the constants with the reciprocal of the absolute temperature, it was possible to calculate values of k_1 and k_2 at other temperatures, and hence to calculate the approximate form of the isotherms at these temperatures. The results of these calculations are given below and (graphically) in Figure 28.

Equilibrium values at 1558°C. on the basis of $k_1 = 0.2793$, $k_2 = 0.2310$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	M	Oxygen Pressure. cm. of Hg.
0.4060	0.1190	0.2870	0.5100	0.9160	85.0
0.4500	0.1404	0.3096	0.4654	0.9154	36.5
0.4970	0.1665	0.3305	0.4210	0.9180	15.2
0.5400	0.1930	0.3470	0.3830	0.9230	7.0
0.6000	0.2352	0.3648	0.3352	0.9352	2.5

Equilibrium values at 1660°C. on the basis of $k_1 = 0.7170$, $k_2 = 0.2468$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	M	Oxygen Pressure. cm. of Hg.
0.5000	0.1750	0.3250	0.4250	0.9250	84.7
0.5400	0.2002	0.3398	0.3902	0.9302	42.1
0.6010	0.2435	0.3575	0.3420	0.9430	15.2
0.6600	0.2910	0.3690	0.3010	0.9610	6.0
0.7000	0.3260	0.3740	0.2760	0.9760	3.3

Equilibrium values at 1696°C. on the basis of $k_1 = 0.9920$, $k_2 = 0.2506$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	M	Oxygen Pressure. cm. of Hg.
0.5400	0.2018	0.3382	0.3918	0.9318	79.3
0.5800	0.2296	0.3504	0.3596	0.9396	40.5
0.6410	0.2770	0.3640	0.3155	0.9565	15.2
0.7000	0.3280	0.3720	0.2780	0.9780	6.3
0.7200	0.3462	0.3738	0.2662	0.9862	4.7

The isotherms thus obtained agree well with the experimental data, as can be seen from Figures 5a, 6a, 7a and 8a, in which theferrous oxide values obtained from them at the appropriate oxygen pressures have been plotted against temperature. This seems to justify the assumptions made.

From the variation in k_1 and k_2 with temperature, indicated by the above calculations, the heats of reaction of the corresponding reactions are as follows :

$$Fe_2O_3 = 2FeO + \tfrac{1}{2}O_2 - 65.1 \text{ Cal.}$$

$$Fe_3O_4 = FeO + Fe_2O_3 - 4.9 \text{ Cal.}$$

The first of these values agrees closely with that usually accepted, which was, of course, determined at much lower temperatures, and with the solid oxides. The figures for the second reaction is considerably greater than the accepted value, which is usually given as 1.9 Cal. The latent heats of fusion of the oxides have, however, to be allowed for. Further, the values given above can only be accepted as approximate, as comparatively small changes in the values of the constants at the various temperatures produce considerable changes in the calculated values of the heats of reaction.

EQUILIBRIUM IN LIME/IRON-OXIDE MELTS.

On general chemical grounds it is to be expected that the effect produced by lime on the iron oxide equilibrium will be due to compound formation in the liquid state, involving presumably the free Fe_2O_3 of the melts and the added lime. In the solid state two calcium ferrites are known to exist[8], monocalcium and dicalcium ferrite. Assuming that both of these can occur in the liquid melts, and that they are then at least partially dissociated (since, in view of the experimental data, it is impossible that either should be completely stable), the equilibrium in these melts is defined by the two iron-oxide equilibria already considered and the following equilibria:

$$CaO.Fe_2O_3 = CaO + Fe_2O_3, \text{ whereby } k_3 = \frac{(CaO)\ (Fe_2O_3)}{(CaO.Fe_2O_3)},$$

and $2(\ CaO.Fe_2O_3\ ) = 2CaO.Fe_2O_3 + Fe_2O_3,$

$$\text{whereby } k_4 = \frac{(2CaO.Fe_2O_3)(Fe_2O_3)}{(CaO.Fe_2O_3)^2}.$$

As before the quantities in brackets are the activities of the substances indicated, and are assumed to be proportional to the molecular concentrations expressed as molar fractions.

The conditions to be investigated are somewhat more complex than in the case of the simple iron oxide equilibria, and no fewer than six molecular species are involved. Matters are, however, somewhat simplified if k_1 and k_2 are known at the temperature under investigation. Then, provided that the total ferrous oxide content and the corresponding oxygen pressure are known at two different lime contents, k_3 and k_4 can be evaluated. Hence it is possible to calculate the equilibrium concentrations of the various reactants at any desired lime content and oxygen pressure. The total ferrous oxide content can also be be derived and compared with the value determined experimentally under the same conditions. The calculations required are somewhat involved but present nothing novel in a mathematical sense, so they are not reproduced.

Below are given some of the results obtained on investigating the lime/iron-oxide equilibria in this way:

Equilibrium in Lime/Iron Oxide Melts at 1592°C. and Oxygen Pressure of 15.2 cm. of Mercury.

Lime Content Varying.

Constants: $k_1 = 0.3845$, $k_2 = 0.2387$, $k_3 = 0.0422$, $k_4 = 0.1417$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	CaO.- Fe_2O_3	2CaO.- Fe_2O_3	CaO	M.	Total Lime.
0.530	0.1900	0.3400	0.3950	0.0000	0.0000	0.0000	0.925	0.0000
0.341	0.1656	0.1758	0.2660	0.3305	0.0580	0.0548	1.051	0.501
0.210	0.1350	0.0750	0.1570	0.4655	0.1960	0.1469	1.175	1.004
0.174	0.1227	0.0513	0.1234	0.4773	0.2610	0.2017	1.237	1.200
0.132	0.1051	0.0269	0.0830	0.4563	0.3610	0.3145	1.347	1.493
0.096	0.0860	0.0100	0.0457	0.4003	0.4960	0.6076	1.645	2.000
0.081	0.0765	0.0045	0.0290	0.3451	0.5835	1.0100	2.049	2.520
0.078	0.0744	0.0031	0.0235	0.3190	0.6165	1.3690	2.406	2.920

When the values for the total lime content and total ferrous oxide content thus obtained are plotted against each other, as shown in Figure 12, a smooth curve is obtained. The actual experimental curve shows breaks, however, a quite definite one at one gram-molecule of lime (the composition of the monocalcium ferrite) and a very slight one at two gram- molecules of lime. Such breaks are usually assumed to constitute evidence of compound formation. It should be realised, however, that the ideal laws assumed in the calculations above cannot account for such breaks, which are due to influences which constitute deviations from the simple laws. Hence exact agreement is not to be looked for. The values of k_3 and k_4 given above are those which, on the basis of the ideal laws only, reproduce the general trend of the experimental curve most closely.

It will be as well to make clear at this stage the principal factors governing the shape of the calculated curve. The greater the stability of the ferrites the more will the curve be depressed and the nearer will it approach to the horizontal axis of reference i.e the axis of zero ferrous oxide content on Figure 12. The slope of the curve depends on which of the ferrites is most stable. Several examples to illustrate these points are given in Figure 29. If monocalcium ferrite were completely stable the curve would be practically a straight line intercepting the horizontal axis at one gram-molecule of lime (see Curve 1). If the dicalcium compound alone were stable in the liquid state, an approximately straight line meeting the horizontal axis at a lime content of two gram-molecules would be obtained. (Curve 2). On the other hand, if only the monocalcium ferrite existed but in a partially dissociated state in the liquid, the curve obtained would be of the type shown by Curve 3. This curve slopes downwards till it approaches a lime content of one gram-molecule when it flattens out rapidly so that, for higher lime contents it is almost horizontal. The greater the stability of the ferrite, the nearer will it be to the horizontal axis when this occurs. Curve 4 shows the type obtained when only dicalcium ferrite has appreciable stability in the liquid melts. It is similar to Curve 3 in general form but the flattening-out is confined mainly to the region of two gram-molecules of lime. Below this lime content the curve shows only slight convexity towards the horizontal axis. At higher lime contents it is practically horizontal. When both ferrites are present the form of the curve depends on the relative stability of the two. The greater the stability of the monocalcium compound, the greater will be the convexity of the curve towards the horizontal axis in the range zero to two gram-molecules of lime, while the greater the stability of the dicalcium ferrite, the more pronounced will be the slope of the curve in the range one to two gram-molecules of lime. Bearing these considerations in mind, and neglecting the breaks previously mentioned, it will be seen that the general form of the experimental curve indicates that both ferrites must have appreciable stability in the liquid state.

The discrepancy between the experimental and the calculated curves is greatest at low lime concentrations, and at first sight it might be expected that the agreement between theory and fact should be closest here. The analogy with aqueous solutions does not necessarily hold, however, since even at low lime contents a system containing concentrated reactants is being dealt with. If only the initial part of the experimental curve is considered in evaluating the constants the calculated curve deviates widely from the experimental curve at higher concentrations.

(It will be noticed, of course, that the total ferrous oxide content at zero lime content has, for the purposes of the calculations, been obtained by extrapolation of the experimental data for the liquid state of the iron oxide samples investigated at 15.2 cm. of oxygen. (See Figure 5a and also the experimental points on Figure 28.) This is necessary since the actual experimental value got at 1592°C. and 15.2 cm. pressure is for a system that is only partly liquified. Even allowing for this, however, the deviations are still as stated.)

The lack of complete agreement between theory and fact indicates (as might be expected) that the laws of ideal solutions assumed are not completely valid. In particular, it is probable that the assumption that the activity of the reactants is directly proportional to their molecular concentrations is only approximately true. It can be shown that the break in the experimental curve at the composition $CaO.Fe_2O_3$ can be reproduced if the proportionality factor connecting the activity and the molecular concentration of this reactant is itself a decreasing function of its concentration, i.e. if the now current concept of "activity coefficients" is utilised. (It may be noted in this connection that the molar concentration of monocalcium ferrite reaches a

maximum in the melt having a lime content of one gram-molecule, i.e. in the melt which was originally of the composition of monocalcium ferrite. Similarly the concentration of dicalcium ferrite is a maximum in the melt having a lime content of two gram-molecules. This can readily be seen by referring to the table of figures given above.)
The rapid dip of the initial part of the experimental curve could be reproduced in similar fashion, by attributing a similar variation to the activity coefficients of some of the other reactants. These are the usual methods employed in the study of aqueous solutions at higher concentrations. In the present instance, however, such devices would be arbitrary in nature, especially when it is remembered that no fewer than six molecular species are involved, each of which is liable to show similar deviation from the ideal law. At the present stage it is probably more useful and instructive to consider only the approximate agreement provided by the simple theory.

The constants obtained above were used to calculate theoretical oxygen-pressure/ferrous-oxide isotherms at 1592°C with various lime contents.

Equilibrium in Lime/Iron Oxide Melts at 1592°C. Oxygen Pressure Varying.

Constants: $k_1 = 0.3845$, $k_2 = 0.2387$, $k_3 = 0.0422$, $k_4 = 0.1417$.

(1) Total Lime = 0.5000.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	CaO.- Fe_2O_3	2CaO.- Fe_2O_3	CaO	M.	Oxygen Pressure cm. of Hg
0.292	0.1323	0.1599	0.3000	0.3405	0.0545	0.0495	1.037	47.0
0.336	0.1615	0.1740	0.2700	0.3315	0.0590	0.0539	1.050	17.4
0.352	0.1720	0.1796	0.2600	0.3275	0.0580	0.0552	1.052	12.4
0.368	0.1845	0.1832	0.2500	0.3235	0.0590	0.0573	1.056	8.9

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	CaO.- Fe_2O_3	2CaO.- Fe_2O_3	CaO	M.	Oxygen Pressure. cm. of Hg.
(2) Total Lime = 1.000.								
0.145	0.0872	0.0580	0.1800	0.4950	0.1925	0.1325	1.145	104.5
0.182	0.1129	0.0695	0.1700	0.4790	0.1900	0.1367	1.158	35.0
0.205	0.1302	0.0746	0.1600	0.4680	0.1955	0.1442	1.172	18.1
0.260	0.1711	0.0889	0.1500	0.4550	0.1980	0.1540	1.217	5.7
(3) Total Lime = 1.500								
0.0834	0.0639	0.0195	0.0915	0.4843	0.3620	0.2936	1.315	129.5
0.0997	0.0778	0.0219	0.0900	0.4793	0.3610	0.2995	1.330	58.6
0.1256	0.0995	0.0261	0.0850	0.4650	0.3620	0.3182	1.350	20.0
0.1580	0.1272	0.0308	0.0800	0.4511	0.3605	0.3278	1.377	6.98
(4) Total Lime = 2.000.								
0.080	0.0716	0.0086	0.0465	0.4053	0.5000	0.5890	1.621	31.8
0.092	0.0820	0.0096	0.0455	0.4000	0.5000	0.6050	1.643	18.6
0.149	0.1360	0.0140	0.0420	0.3795	0.4860	0.6440	1.700	2.2
(5) Total Lime = 2.500.								
0.059	0.0552	0.0035	0.0305	0.3544	0.5810	0.9760	2.001	59.0
0.076	0.0713	0.0044	0.0300	0.3496	0.5760	0.9945	2.026	21.1
0.103	0.0975	0.0058	0.0200	0.3410	0.5700	1.0180	2.062	5.8

The figures for total lime and total ferrous oxide contents indicated in these tabulations have been plotted on the appropriate diagrams for comparison purposes (see Figures 13 to 17). As no experimental determinations of the isotherms were actually carried out at 1592°C., it is necessary to interpolate the experimental results at this temperature to obtain a direct comparison. This can readily be done because of the regular fashion in which the ferrous oxide content of the melts varies with the temperature at any oxygen pressure. The interpolated values are also indicated on the diagrams. The calculated curves are indicated in the figures by broken lines.

In comparing the calculated curves with the experimental ones allowance must be made for the divergence which, as already noted, occurs at certain lime contents. For instance because of the discrepancy between the calculated and the experimental isobar at low lime contents, the calculated isotherms for a lime content of 0.5000 gram-molecules are necessarily displaced relative to the corresponding isotherms experimentally obtained. In this case it is only possible to compare the two for general form, and for parallelism.

In comparing the experimental results with the calculated ones, the following points will be noted. Theory is able to predict curves of the same type as are obtained by experiment. Theory predicts that the steepness of the curves should increase as the lime content increases, and this also is found in actual fact. The chief discrepancy is that for most of the compositions the calculated curves are noticeably steeper than the experimental curves. It was thought at first, in view of the difficulties encountered in establishing the simple iron oxide equilibria and the form of the iron oxide isotherms, that this might be due to errors in k_1 and k_2. It has been found, however, that as the lime content increases the part played by these two constants in determining the slope of the calculated curves decreases markedly. It is much more probable that the discrepancy is due to the shortcomings of the simple laws previously discussed, and calculation has indicated that the use of fractional activity coefficients in arriving at the activities of the ferrites would introduce a correction in the right direction.

Extrapolation of the iron oxide data to the appropriate temperatures made it possible to evaluate the constants for the ferrite equilibria at the other temperatures at which experimental determinations had been carried out:

Equilibrium in Lime/Iron-Oxide Melts at 1524°C.and Oxygen Pressure of 15.2 cm. of Mercury. Lime Content Varying.
Constants: $k_1 = 0.1950$, $k_2 = 0.2263$, $k_3 = 0.0451$, $k_4 = 0.0940$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	CaO.-Fe_2O_3	2CaO.-Fe_2O_3	CaO	M.	Total Lime.
0.460	0.1440	0.3160	0.4540	0	0	0	0.9140	0
0.272	0.1230	0.1490	0.2880	0.3790	0.0465	0.0623	1.048	0.535
0.134	0.0911	0.0429	0.1328	0.5473	0.2100	0.2327	1.250	1.20
0.078	0.0684	0.0096	0.0546	0.4868	0.4100	0.6932	1.716	2.00
0.065	0.0623	0.0024	0.0260	0.3840	0.5330	2.000	3.008	3.45

These values have been used to give the theoretical curve at 1524°C in Figure 12.

The following figures have also been calculated for the oxygen-pressure/ferrous-oxide isotherm at 1524°C with a lime content of 1.000 gram- molecule:

Equilibrium in Lime/Iron-Oxide Melts at 1524°C.

Oxygen Pressure Varying.

Constants: $k_1 = 0.1950$, $k_2 = 0.2263$, $k_3 = 0.0451$, $k_4 = 0.0940$.

Total Ferrous Oxide.	Lime Content = 1.000. FeO	Fe_3O_4	Fe_2O_3	Fe_2O_3	Fe_2O_3	CaO	M.	Oxygen Pressure. cm. of Hg.
0.1671	0.1021	0.0650	0.1700	0.5260	0.1540	0.1652	1.182	14.1
0.1501	0.0904	0.0597	0.1750	0.5350	0.1520	0.1620	1.174	23.8
0.1272	0.0747	0.0525	0.1850	0.5445	0.1500	0.1545	1.161	48.9

The calculated isotherm at 1524°C (see Figure 14) is of the same form and runs practically parallel to that calculated at 1592°C. This also is in agreement with the experimental observations. It is, however, rather steeper than the experimental curve.

Equilibrium in Lime/Iron-Oxide Melts at 1383°C. and Oxygen

Pressure of 15.2 cm. of Mercury.

Lime content Increasing.

Constants: $k_1 = 0.0394$, $k_2 = 0.2127$, $k_3 = 0.0600$, $k_4 = 0.0400$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	CaO.-Fe_2O_3	2CaO.-Fe_2O_3	CaO	M.	Total Lime.
0.310	0.0753	0.2347	0.6103	0	0	0	0.920	0
0.092	0.0514	0.0406	0.2060	0.6470	0.0600	0.2330	1.238	1.000
0.063	0.0440	0.0190	0.1330	0.6766	0.1400	0.4434	1.456	1.400

Equilibrium in Lime/Iron-Oxide Melts at 1274°C. and Oxygen Pressure of 15.2 cm. of Mercury.

Lime Content Increasing.

Constants : $k_1 = 0.00946$, $k_2 = 0.2043$, $k_3 = 0.0780$, $k_4 = 0.038$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	$CaO.-Fe_2O_3$	$2CaO.-Fe_2O_3$	CaO	M.	Total Lime.
0.202	0.0412	0.1588	0.7412	0	0	0	0.9412	0
0.062	0.0286	0.0334	0.2834	0.6022	0.0500	0.1978	1.1850	0.900
0.038	0.0244	0.0136	0.1641	0.6933	0.1100	0.4867	1.4920	1.400

The data in the above tables is also plotted in Figure 12.

On examination of the values of k_3 and k_4 obtained by calculation it can be seen that there is a regular variation with temperature. Actually it is found that the logarithms of the values of the constants vary almost linearly with the reciprocal of the absolute temperature, the only exception being in the case of the calculated value of k_4 at 1272°C, which is high. Neglecting this latter point, the thermal values for the various reactions are:

$$CaO.Fe_2O_3 = CaO + Fe_2O_3 + 11.1 \text{ Cal.}$$

$$2(CaO.Fe_2O_3) = 2CaO.Fe_2O_3 + Fe_2O_3 - 37.2 \text{ Cal.}$$

$$2CaO.Fe_2O_3 = 2CaO + Fe_2O_3 + 57.9 \text{ Cal.}$$

It is rather surprising to find that (if reliance is to be placed on the values thus obtained) the stability of the ferrites increases as the temperature rises, and that the increased dissociation found in ferrite melts as the temperature is increased is due solely to the increased instability of ferric oxide. On looking over the thermal curves determined a few years ago during the investigation of the system $CaO-Fe_2O_3$[8], it was found that there was usually no sign of a heat evolution on the first heating curves, which were always taken on the initial mixture of the two constituents. This lends a measure of support to the above findings. In two cases small heat evolutions were observed, both with compositions intermediate between $CaO.Fe_2O_3$

and $2CaO.Fe_2O_3$. These occurred above the temperatures of first liquid formation, and might have been due to the second of the above reactions. The question arises as to whether the heat of dissociation of the ferrites liberated at melting would not have tended to mask the the heat absorptions due to the melting process. In actual fact large and well-marked thermal arrests were obtained with most of the compositions. It is known now, however, that the heat changes measured were not simply due to fusion but involved the heat changes due to the dissociation (and association on cooling) of the ferric oxide liberated by the dissociation of the ferrites. The thermal changes measured are thus the sum of several effects.

EQUILIBRIUM IN SILICA/IRON OXIDE MELTS.

The equilibrium in silica/iron oxide melts can be studied by methods similar to those used for the melts containing lime. It can be assumed that two compounds are capable of existence in the melts in addition to the oxides of iron, these being $2FeO.SiO_2$ and $FeO.SiO_2$. Hence the following equilibria must be considered in addition to those between the oxides of iron:

$$FeO.SiO_2 = FeO + SiO_2, \text{ whereby } k_5 = \frac{(FeO)\,(SiO_2)}{(FeO.SiO_2)},$$

$$2FeO.SiO_2 = 2FeO + SiO_2, \text{ whereby } k_6 = \frac{(FeO)^2(SiO_2)}{(2FeO.SiO_2)}.$$

The methods employed in elucidating these equilibria were the same as those already outlined. The activities of the reactants were once more assumed proportional to their concentrations expressed as molar fractions, and the silica/ferrous- oxide isobars of Figure 18 were first investigated using the values of k_1 and k_2 previously established for the appropriate temperatures.

For the isobar at 1592°C and 15.2 cm. pressure the following figures were obtained:

Equilibrium in Silica/Iron-Oxide Melts at 1592°C. and Oxygen Pressure of 15.2cm. of Mercury.

Silica Content Increasing.

Constants: $k_1 = 0.3845$, $k_2 = 0.2387$, $k_5 = 0.2320$, $k_6 = 1.180$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	FeO.-SiO_2	2FeO.-SiO_2	SiO_2	M.	Total Silica.
0.530	0.1900	0.3400	0.3950	0	0	0	0.925	0
0.623	0.2080	0.2998	0.3885	0.1079	0.0039	0,1372	1.145	0.249
0.710	0.2270	0.2640	0.3810	0.2056	0.0067	0.2877	1.372	0.500
0.810	0.2457	0.2270	0.3680	0.3188	0.0096	0.5035	1.673	0.832
0.830	0.2493	0.2200	0.3650	0.3413	0.0097	0.5490	1.734	0.900
1.067	0.2891	0.1465	0.3200	0.6060	0.0130	1.297	2.672	1.916

Below are given the data similarly calculated for the isobars at 1619°C. and 1558°C. (Figure 18).

Equilibrium in Silica/Iron-Oxide Melts at 1619°C. and Oxygen Pressure of 15.2 cm. of Mercury.

Silica Content Increasing.

Constants: $k_1 = 0.4926$, $k_2 = 0.2342$, $k_5 = 0.2260$, k_6 = very large.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	FeO.-SiO_2	2FeO.-SiO_2	SiO_2	M.	Total Silica.
0.557	0.2100	0.3470	0.3745	0	0	0	0.9315	0
0.742	0.2502	0.2691	0.3599	0.2227	0	0.2773	1.379	0.500
0.871	0.2742	0.2221	0.3424	0.3747	0	0.5253	1.739	0.910

Equilibrium in Silica/Iron-Oxide Melts at 1558°C. and Oxygen Pressure of 15.2 cm. of Mercury.

Silica Content Increasing.

Constants: $k_1 = 0.2793$, $k_2 = 0.2310$, $k_5 = 0.2030$, $k_6 = 0.6300$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	FeO.-SiO_2	2FeO.-SiO_2	SiO_2	M.	Total Silica.
0.497	0.1665	0.3305	0.4210	0	0	0	0.9180	0
0.653	0.1935	0.2675	0.4060	0.1740	0.0009	0.2370	1.287	0.420
0.730	0.2061	0.2389	0.3961	0.2610	0.0120	0.3870	1.501	0.660

The following theoretical data were also calculated for the oxygen-pressure/ferrous-oxide isotherms of the melts containing 0.2400 and 0.8400 gram-molecules of silica respectively (Figure 19), assuming the values of the constants already found from consideration of the ferrous-oxide/silica isobar at 1592°C.

Equilibrium in Silica/Iron-Oxide Melts at 1592°C. Oxygen Pressure Varying.

Constants: $k_1 = 0.3845$, $k_2 = 0.2387$, $k_5 = 0.2320$, $k_6 = 1.180$.

Total Ferrous Oxide.	FeO	Fe_3O_4	Fe_2O_3	FeO.-SiO_2	2FeO.-SiO_2	SiO_2	M.	Oxygen Pressure. cm. of Hg.
(1) Total Silica Content = 0.240.								
0.529	0.1600	0.2740	0.4625	0.0898	0.0025	0.1479	1.137	62.1
0.567	0.1800	0.2853	0.4315	0.0961	0.0030	0.1410	1.137	33.8
0.606	0.2000	0.2967	0.4020	0.1019	0.0035	0.1345	1.139	19.3
0.639	0.2200	0.3042	0.3758	0.1070	0.0041	0.1289	1.140	11.6
(2) Total Silica Content = 0.840.								
0.712	0.2000	0.2150	0.4280	0.2835	0.0067	0.5498	1.684	47.2
0.779	0.2300	0.2232	0.3980	0.3090	0.0083	0.5225	1.690	22.3
0.812	0.2460	0.2262	0.3679	0.3215	0.0093	0.5095	1.680	15.4

The following points may be noted in connection with the theoretical data thus calculated. From the isobars it would appear that 2FeO.SiO_2 is almost completely dissociated in these melts. The almost linear nature of the curves over the range of silica contents covered indicates that this should be so. The greater the content of 2FeO.SiO_2 in the melts, the greater would be the tendency of the curves to flatten out in this range, i.e. the greater would be their convexity towards the top of the diagram (Figure 18). It is of interest that the most stable silicate of iron in the liquid state appears to be the metasilicate, if the evidence of the isobars is accepted. There is good reason to believe that, under normal circumstances, this compound does not crystallize out from simple FeO-SiO_2 melts[7] on freezing.

The calculated pressure/ferrous-oxide isotherms are again of the same form as those obtained experimentally. Further, the calculated values indicate that they should become less steep as the silica content increases, and this is found to be the case. Using the values of the constants obtained from the isobars, however, there is, as in the case of the ferrite isotherms, a discrepancy in that the calculated curves are steeper than the experimental ones for the same silica content. It is of interest that the slope of the experimental isotherms can be very nearly reproduced if the assumption is made that only $2FeO.SiO_2$ exists in the liquid state. This does not agree with the evidence of the isobars, however, since they would then be markedly curved in the range of silica contents studied. The discrepancy can probably be attributed to a departure from the ideal laws similar to that previously discussed.

From the figures given it is probable that the dissociation of both silicates increases as the temperature rises, though the variation of k_5 with temperature is rather irregular. If this is so, the formation of both of these compounds will be accompanied by heat evolutions. From the figures it appears that the heat of formation of $FeO.SiO_2$ will be small, and that of $2FeO.SiO_2$ much larger, since the dissociation constant of the former appears to be much less affected by temperature than that of the latter. In this connection it may be pointed out that, on the evidence provided by the constants, the stability of $2FeO.SiO_2$ should increase rapidly as the temperature drops below 1600°C, while that of $FeO.SiO_2$ will be affected to a much less extent. This may explain why $2FeO.SiO_2$ can separate out from simple $FeO-SiO_2$ melts (which it does as the crystalline compound Fayalite) while $FeO.SiO_2$ apparently does not, primary silica and fayalite alone appearing from melts of

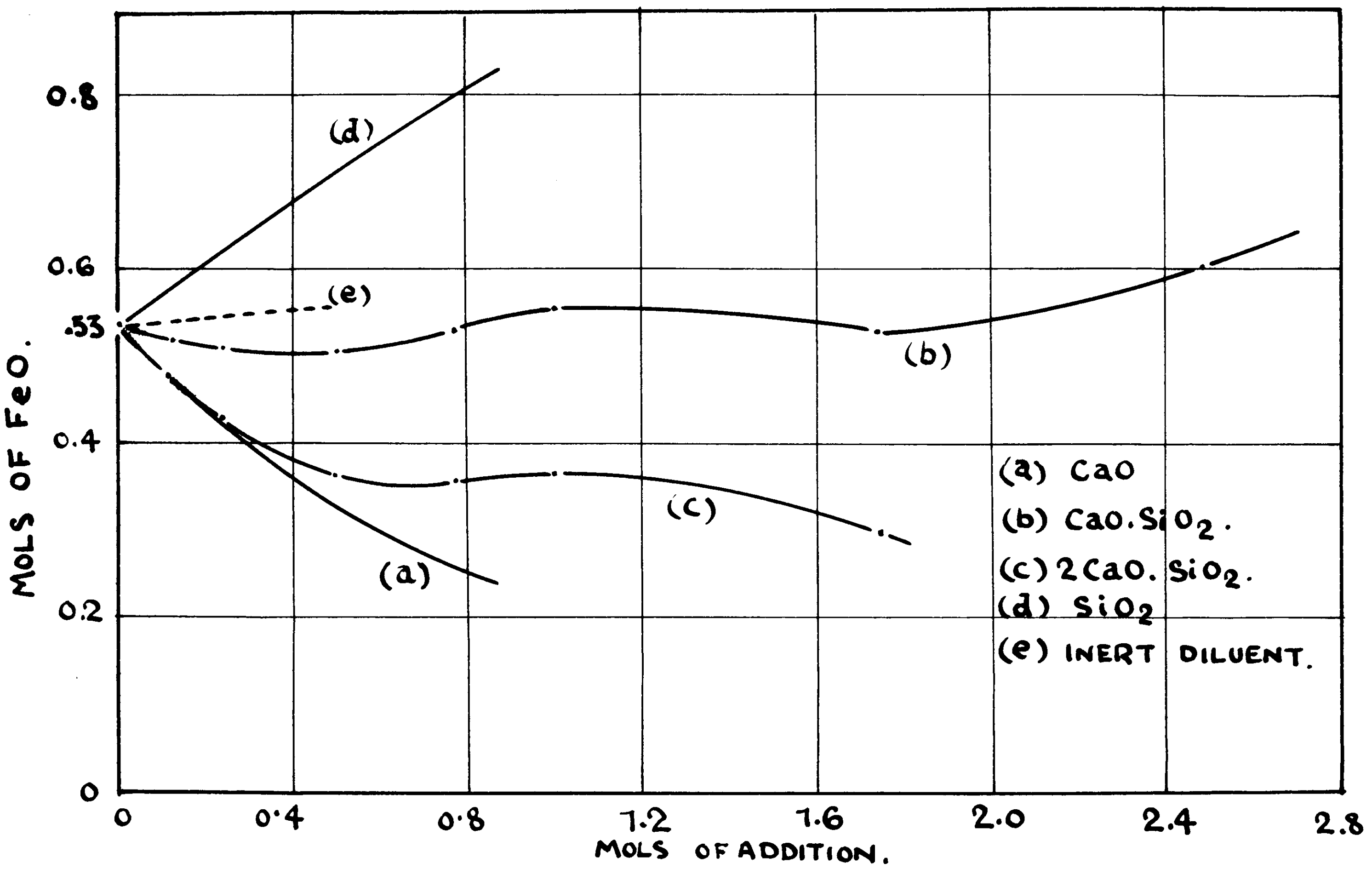

FIG. 30. EFFECT OF VARIOUS ADDITIONS ON DISSOCIATION OF FERRIC OXIDE AT 1592°C AND OXYGEN PRESSURE = 15.2 CM. OF MERCURY.

the composition $FeO.SiO_2$ on freezing. It is, however, known that certain basic metasilicate-forming oxides have the effect of stabilizing, or at any rate of promoting, the separation of $FeO.SiO_2$ from silicate melts. The substance grunerite, for instance, which occurs naturally, is essentially a metasilicate of iron in which some of the FeO has been replaced by other basic oxides, notably by MgO. There are also indications that rhodonite ($MnO.SiO_2$), the metasilicate of manganese, can exist when well over fifty per cent of the MnO has been replaced by FeO[9].

EQUILIBRIUM IN LIME/SILICA/IRON-OXIDE MELTS.

The equilibria possible in lime/silica/iron-oxide melts are very complex, as a large number of reactants are possible. In addition to the compounds mentioned in the previous discussions, several compounds between lime and silica might exist in the liquid melts; several ternary compounds are also possible. Concerning these latter there is a certain amount of justification for the assumption that they will be largely dissociated in the liquid state, and it was found convenient to assume this, a priori, as a working hypothesis on which to base the theoretical treatment. It is in fact known that the ternary combination $CaO-FeO-SiO_2$, which is probably the most important combination of those involved from the point of view of compound formation forms only one compound which is stable up to its melting point - the compound $CaO.FeO.SiO_2$[23]. Examination of the experimental data suggests that this compound is probably not very stable in the liquid melts.

Figure 30 contains a series of curves derived from the experimental data already given. These curves show the variation in the ferrous oxide content of iron-oxide melts at 1592°C. and 15.2 cm. oxygen pressure when (a) CaO, (b) $CaO.SiO_2$, (c) $2CaO.SiO_2$, (d) SiO_2 are added in progressively increasing amounts. The two latter are of peculiar form and appear to indicate the operation of several conflicting influences in the melts. On the same diagram (curve (e)) is shown the effect of an inert diluent on the dissociation of ferric oxide, as found by calculation. It will be seen that neither $CaO.SiO_2$ nor $2CaO.SiO_2$ can be regarded as inert diluents. Both must, therefore, be at least in part dissociated in the liquid state. Further the effect of $2CaO.SiO_2$ is at low concentrations practically the same as the effect of CaO added in the same molecular amounts. This can be taken as an approximate indication that, neglecting the effect of dilution by the $CaO.SiO_2$, $2CaO.SiO_2$ behaves as a mixture of CaO and stable $CaO.SiO_2$. The $CaO.SiO_2$, by diluting the reactants, would of course cause increased dissociation of the ferric oxide. Hence even in the presence of the free lime liberated by the dissociation of $2CaO.SiO_2$, $CaO.SiO_2$ must be sufficiently dissociated to counteract the effect of this dilution. It was, therefore, concluded that,as far as could be ascertained from such an examination, $2CaO.SiO_2$ is probably practically completely dissociated in the liquid state, while $CaO.SiO_2$ is at least partly dissociated. It is of interest that Krings and Schackmann[24] conclude from their studies of slag-metal relationships that $2CaO.SiO_2$ is completely dissociated in liquid slags into $CaO.SiO_2$ which is completely stable and free lime.

Because of the complexity of the iron-oxide/lime/ silica melts exact mathematical investigation of the equilibrium conditions is necessarily somewhat involved. In attempting to represent the experimental results the following equilibria were first considered.

$$2Fe_2O_3 = 2FeO + \tfrac{1}{2}O_2 \qquad (k_1)$$

$$Fe_3O_4 = FeO + Fe_2O_3 \qquad (k_2)$$

$$CaO.Fe_2O_3 = CaO + Fe_2O_3 \qquad (k_3)$$

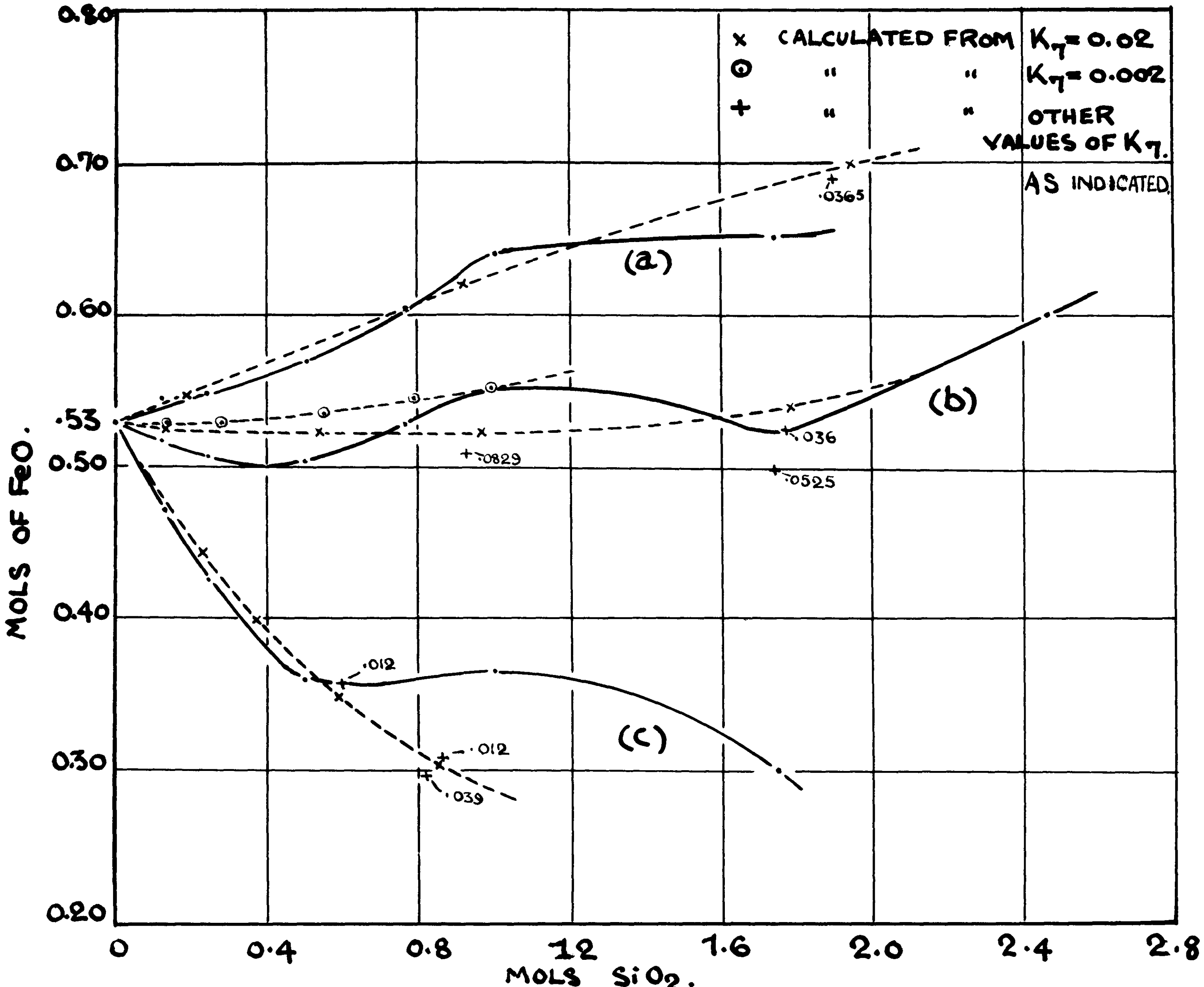

FIG.30a. EFFECT OF ADDITION OF LIME-SILICA MIXTURES TO FERRIC OXIDE – EXPERIMENTAL AND CALCULATED CURVES.

$$2(CaO.Fe_2O_3) = 2CaO.Fe_2O_3 + Fe_2O_3, \qquad (k_4)$$
$$FeO.SiO_2 = FeO + SiO_2, \qquad (k_5)$$
$$2FeO.SiO_2 = 2FeO + SiO_2, \qquad (k_6)$$
$$CaO.SiO_2 = CaO + SiO_2, \qquad (k_7)$$
$$2(CaO.SiO_2) = 2CaO.SiO_2 + SiO_2. \qquad (k_8)$$

Because of the high degree of dissociation of $2FeO.SiO_2$ found previously k_6 could be neglected in the discussion so that a slight simplification was introduced. Of the other constants all had been previously determined except those relating to the calcium silicates. The method of analysis adopted was, as before, to find the values of the unknown constants which would most nearly reproduce the experimental curves. For the purposes of a preliminary investigation it was found convenient to work from curves of constant lime to silica ratio (i.e. curves of the type of curve (b) and curve (c) of Figure 30) rather than with the curves as determined experimentally. Such curves were, of course, readily derived from the experimental curves. Figure 30a shows the effects of adding to ferric oxide, in progressively increasing amounts, lime and silica in the constant ratios of (a) 1:1.5, (b) 1:1, and (c) 2:1, all at 1592°C. To facilitate the examination of the curves, and to enable more accurate comparisons to be made the vertical scale has been doubled in this diagram. For the purpose of this preliminary investigation it was assumed that the value of k_8 was small so that the presence of $2CaO.SiO_2$ could be neglected. The value of k_7 giving the best agreement with experiment was 0.02.

The following points emerged as a result of the mathematical investigation of the curves. As in previous cases only smooth curves were obtained by application of the simple law of mass action. Secondary influences must, therefore, have been operating in the melts. The path followed by the calculated curves is dependent on the amount of dissociation of the $CaO.SiO_2$ i.e. on the value of k_7. For example in the case of the curve relating to the addition of $CaO.SiO_2$ to ferric oxide, if the value of k_7 were zero, indicating complete stability of $CaO.SiO_2$, the curve of inert dilution (see Figure 30) would be obtained. As k_7 is increased from zero the calculated curve is displaced progressively downwards. This is illustrated by inclusion in the diagram (Figure 30a) of the curve corresponding to $k_7 = 0.002$ alongside that got with $k_7 = 0.02$. At still higher values of k_7 than these the curve is displaced still further, but the rate of displacement falls off, and a limit would be reached at complete dissociation of $CaO.SiO_2$, the path of the curve being then determined solely by the relative values of the dissociation constants of the calcium ferrites and of the ferrous silicates respectively. Several calculated points, obtained in the course of the mathematical investigation, are reproduced in Figure 30a, with the corresponding values of k_7 alongside them so that the significance of the value of the constant can readily be seen. It will be noticed that variation in the value of k_7 is not particularly critical in its effect on the path of the curve. Variations ranging from $k_7 = 0.015$ to $k_7 = 0.025$ do not, over most of the range, cause very much displacement of the curve. Hence allowance must be made for a fairly wide degree of tolerance in attributing the value of 0.02 to the constant.

The calculated data based on $k_7 = 0.02$ is given in the following tables:

EQUILIBRIUM IN LIME/SILICA/IRON-OXIDE MELTS AT 1592°C, AND OXYGEN PRESSURE = 15.2 CM. OF MERCURY.

Constants: $k_1 = 0.3845$, $k_2 = 0.2387$, $k_3 = 0.0422$, $k_4 = 0.1417$,
$k_5 = 0.232$, $k_7 = 0.02$.

(a) $CaO : SiO_2 = 1 : 1.5$.

		(1)	(2)	(3)
FeO	(mols.)	0.2039	0.2478	0.2933
Fe_2O_3	"	0.3710	0.3260	0.2940
Fe_3O_4	"	0.2780	0.1770	0.1216
$FeO.SiO_2$	"	0.0699	0.1970	0.2945
SiO_2	"	0.0905	0.3510	0.6915
$CaO.SiO_2$	"	0.0314	0.3800	0.9495
$CaO.Fe_2O_3$	"	0.0605	0.1705	0.2095
$2CaO.Fe_2O_3$	"	0.0141	0.0158	0.0212
CaO	"	0.0079	0.0421	0.0890
M.	"	1.1272	1.907	2.954
Total FeO	"	0.5518	0.622	0.709
Total CaO	"	0.128	0.624	1.290
Total SiO_2	"	0.192	0.928	1.936
k_7	"	0.020	0.020	0.022
$\frac{FeO.SiO_2}{M}$		0.0803	0.1842	0.2340
$\frac{CaO.Fe_2O_3}{M}$		0.0537	0.0895	0.0708

(b) $CaO : SiO_2 = 1 : 1$.

		(1)	(2)	(3)	(4)
FeO	(mols.)	0.1966	0.2200	0.2390	0.2719
Fe_2O_3	"	0.3675	0.3208	0.2885	0.2521
Fe_3O_4	"	0.2870	0.1935	0.1436	0.0970
$FeO.SiO_2$	"	0.0426	0.1081	0.1430	0.1697
SiO_2	"	0.0535	0.1750	0.2780	0.4295
$CaO.SiO_2$	"	0.0256	0.2386	0.5350	1.1980
$CaO.Fe_2O_3$	"	0.0812	0.2048	0.2696	0.3230
$2CaO.Fe_2O_3$	"	0.0025	0.0186	0.0358	0.0580
CaO	"	0.0100	0.0413	0.0796	0.1605
M.	"	1.066	1.521	2.012	2.970
Total FeO	"	0.526	0.522	0.526	0.539
Total CaO	"	0.122	0.522	0.956	1.797
Total SiO_2	"	0.122	0.522	0.956	1.797
k_7	"	0.020	0.020	0.021	0.020
$\frac{FeO.SiO_2}{M}$		0.0501	0.0712	0.0712	0.0571
$\frac{CaO.Fe_2O_3}{M}$		0.0761	0.1347	0.1340	0.1083

EQUILIBRIUM IN LIME/SILICA/IRON-OXIDE MELTS AT 1592°C. AND OXYGEN PRESSURE = 15.2 CM. OF MERCURY. (CONTINUED).

(c) $CaO : SiO_2 = 2 : 1$.

		(1)	(2)	(3)	(4)
FeO	(Mols.)	0.1960	0.1941	0.1921	0.1897
Fe_2O_3	"	0.3138	0.2670	0.2165	0.1718
Fe_3O_4	"	0.2060	0.1515	0.1006	0.0646
$FeO.SiO_2$	"	0.0437	0.0545	0.0550	0.0479
SiO_2	"	0.0645	0.0932	0.1149	0.1239
$CaO.SiO_2$	"	0.1150	0.2161	0.4096	0.6680
$CaO.Fe_2O_3$	"	0.2410	0.3250	0.4027	0.4480
$2CaO.Fe_2O_3$	"	0.0262	0.0570	0.1063	0.1649
CaO	"	0.0410	0.0735	0.1355	0.2340
M.	"	1.247	1.432	1.733	2.113
Total FeO	"	0.446	0.400	0.348	0.302
Total CaO	"	0.449	0.728	1.160	1.680
Total SiO_2	"	0.224	0.364	0.579	0.840
k_7		0.019	0.022	0.022	0.021
$\frac{FeO.SiO_2}{M}$		0.0518	0.0657	0.0664	0.0587
$\frac{CaO.Fe_2O_3}{M}$		0.1935	0.2270	0.2330	0.2120

These results when plotted in the form "Total FeO" against "Total SiO_2" give the calculated curves of Figure 30a. As previously mentioned these curves are smooth and do not follow the irregular path of the experimental curves. It will be noticed that all of the latter show a maximum deviation from the theoretical curves at a silica content in the melts of 1.000 gram-molecules. A study of the calculated data (see the last two lines of each table) shows that the molecular concentrations of both $FeO.SiO_2$ and $CaO.Fe_2O_3$, expressed as molar fractions, appear to reach a maximum in the melts at roughly this composition. This supports the view that the deviations are due to secondary influences resulting in a variation in the activities of the reactants with their concentrations.

When an attempt was made to reproduce the experimental curves of Figure 27 using the value of k_7 thus arrived at, and assuming that $2CaO.SiO_2$ had negligible stability in the liquid melts, it was found that the calculated curves, though they agreed quite well with the experimental curves at low lime concentrations, indicated too low ferrous oxide contents at higher lime concentrations. It was necessary to assume, therefore, that $2CaO.SiO_2$ also had some degree of stability in the liquid melts. (At least it was found that better agreement over the whole length of the experimental curves could be got by assuming that k_8 as well as k_7 was of measurable dimensions.) k_7 had already been fixed by investigating melts of low lime and silica content when the effect of k_8 was likely to be slight. It could, therefore, be assumed that the value then arrived at would be at least approximately correct. This was borne out by the results of the calculations now made. It was found that the values of the two constants giving best all-round agreement with the experimental curves were $k_7 = 0.02$ and $k_8 = 0.10$, where

$$k_7 = \frac{(CaO)(SiO_2)}{(CaO.SiO_2)} \quad \text{and} \quad k_8 = \frac{(2CaO.SiO_2)(SiO_2)}{(CaO.SiO_2)^2} ,$$

the reactants being expressed in molar fractions as previously. k_6 was again neglected since $2FeO.SiO_2$ was previously found to be highly dissociated in the liquid melts. The following table shows the calculated data for melts of various lime and silica contents. As in earlier tables the amounts of the various reactants are based on an initial ferric oxide content of 1 gram-molecule so as to be directly comparable with the experimental results. The number of gram-molecules of each reactant in this amount of melt is given. M denotes the total number of gram-molecules of all the molecular species present. The total lime, silica and ferrous oxide are also expressed as gram-molecules.

EQUILIBRIUM IN LIME/SILICA/IRON-OXIDE MELTS AT 1592°C. AND OXYGEN PRESSURE = 15.2 CM. OF MERCURY.

Constants: $k_1 = 0.3845$, $k_2 = 0.2387$, $k_3 = 0.0422$, $k_4 = 0.1417$,
$k_5 = 0.232$, k_6 neglected, $k_7 = 0.02$, $k_8 = 0.10$.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
FeO	0.1828	0.1400	0.0825	0.1936	0.1293	0.0922	0.0840
Fe_2O_3	0.2958	0.1490	0.0315	0.3020	0.1108	0.0398	0.0237
Fe_3O_4	0.1966	0.0660	0.0050	0.1941	0.0390	0.0071	0.0028
$FeO.SiO_2$	0.0206	0.0045	0.0003	0.0423	0.0417	0.0007	0.0003
SiO_2	0.0300	0.0100	0.0015	0.0639	0.0115	0.0038	0.0022
$CaO.SiO_2$	0.0581	0.0645	0.0352	0.1137	0.1000	0.0775	0.0617
$2CaO.SiO_2$	0.0113	0.0410	0.0828	0.0202	0.0868	0.1580	0.1759
$CaO.Fe_2O_3$	0.2721	0.4700	0.3548	0.2579	0.4664	0.3826	0.3200
$2CaO.Fe_2O_3$	0.0355	0.2097	0.5647	0.0312	0.2790	0.5205	0.6100
CaO	0.0446	0.1755	1.0450	0.0455	0.2728	0.8780	1.7200
M.	1.148	1.332	2.200	1.265	1.539	2.162	3.000
Total FeO	0.400	0.210	0.087	0.430	0.210	0.100	0.087
Total CaO	0.468	1.211	2.729	0.520	1.572	2.695	3.674
Total SiO_2	0.120	0.120	0.120	0.240	0.240	0.240	0.240

	(8)	(9)	(10)	(11)	(12)	(13)	(14)
FeO	0.2170	0.1866	0.1489	0.1082	0.0953	0.2397	0.2020
Fe_2O_3	0.3168	0.2132	0.1210	0.0504	0.0300	0.3350	0.2109
Fe_3O_4	0.1896	0.1000	0.0407	0.0097	0.0039	0.1940	0.0906
$FeO.SiO_2$	0.0924	0.0334	0.0104	0.0021	0.0008	0.1663	0.0474
SiO_2	0.1490	0.0690	0.0300	0.0107	0.0059	0.2782	0.1069
$CaO.SiO_2$	0.2235	0.2813	0.2498	0.1806	0.1436	0.2883	0.4332
$2CaO.SiO_2$	0.0335	0.1144	0.2078	0.3042	0.3484	0.0299	0.1753
$CaO.Fe_2O_3$	0.2215	0.4134	0.4747	0.4092	0.3477	0.1600	0.4130
$2CaO.Fe_2O_3$	0.0219	0.1134	0.2636	0.4707	0.5685	0.0109	0.1156
CaO	0.0447	0.1359	0.3080	0.8110	1.4920	0.0349	0.1628
M.	1.512	1.661	1.855	2.357	3.036	1.737	1.958
Total FeO	0.500	0.320	0.200	0.120	0.100	0.600	0.340
Total CaO	0.600	1.286	1.855	2.951	3.817	0.565	1.591
Total SiO_2	0.498	0.498	0.498	0.498	0.498	0.763	0.763

	(15)	(16)	(17)	(18)	(19)	(20)
FeO	0.1355	0.1113	0.2565	0.2410	0.1990	0.1600
Fe_2O_3	0.0773	0.0424	0.3455	0.2830	0.1740	0.1012
Fe_3O_4	0.0182	0.0066	0.1920	0.1370	0.0628	0.0265
$FeO.SiO_2$	0.0064	0.0021	0.2514	0.1220	0.0382	0.0135
SiO_2	0.0262	0.0131	0.4395	0.2441	0.1027	0.0501
$CaO.SiO_2$	0.3261	0.2541	0.2900	0.5217	0.5562	0.4798
$2CaO.SiO_2$	0.4041	0.4939	0.0191	0.1115	0.3020	0.4570
$CaO.Fe_2O_3$	0.4507	0.3885	0.1078	0.2880	0.4493	0.4664
$2CaO.Fe_2O_3$	0.3740	0.5030	0.0047	0.0416	0.1643	0.3050
CaO	0.5930	1.1500	0.0255	0.0895	0.2519	0.4996
M.	2.412	2.965	1.934	2.080	2.300	2.562
Total FeO	0.160	0.120	0.700	0.500	0.300	0.200
Total CaO	2.926	3.786	0.471	1.205	2.190	2.970
Total SiO_2	0.763	0.763	1.000	1.000	1.000	1.000

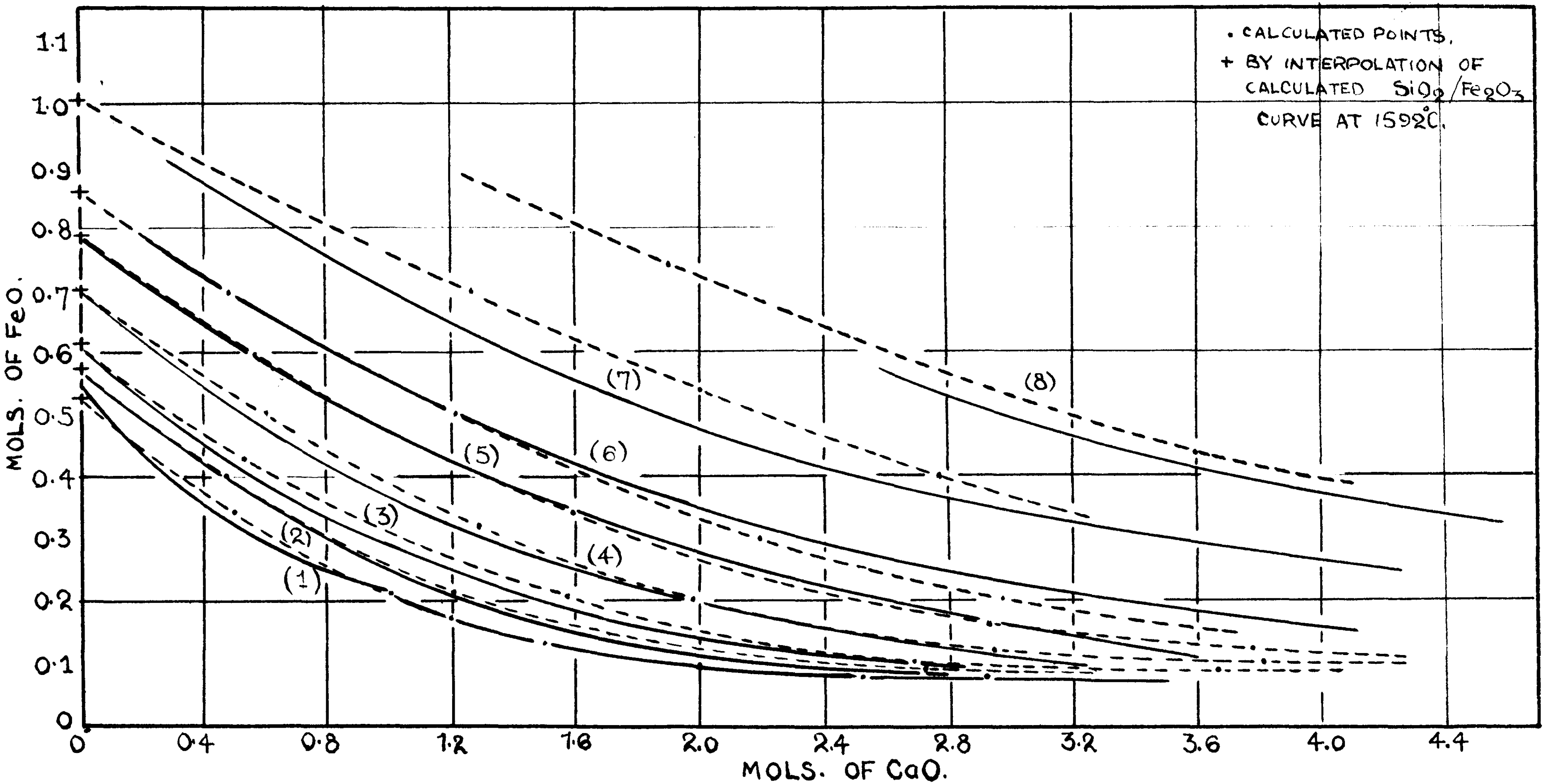

FIG. 30b: EQUILIBRIUM IN LIME/SILICA/FERRIC-OXIDE MELTS AT 1592°C. AND OXYGEN PRESSURE OF 15·2 CM. OF MERCURY.
CURVES OF CONSTANT SILICA CONTENT.
SOLID LINES — EXPERIMENTAL CURVES. BROKEN LINES — BY CALCULATION.

(1) $SiO_2 = 0$
(2) $SiO_2 = 0·120$ MOLS.
(3) $SiO_2 = 0·240$ " .
(4) $SiO_2 = 0·498$ MOLS.
(5) $SiO_2 = 0·763$ " .
(6) $SiO_2 = 1·000$ "
(7) $SiO_2 = 1·746$ MOLS.
(8) $SiO_2 = 2·478$ " .

EQUILIBRIUM IN LIME/SILICA/IRON-OXIDE MELTS AT 1592°C. AND OXYGEN PRESSURE = 15.2 CM. OF MERCURY (CONTINUED).

	(21)	(22)	(23)	(24)	(25)
FeO	0.2900	0.2750	0.2490	0.3190	0.2756
Fe_2O_3	0.3098	0.2659	0.2055	0.2920	0.1994
Fe_3O_4	0.1360	0.1057	0.0696	0.1098	0.0595
$FeO.SiO_2$	0.2740	0.1593	0.0814	0.3112	0.1049
SiO_2	0.6040	0.3880	0.2320	0.8010	0.3418
$CaO.SiO_2$	0.7700	0.9606	1.0010	1.1898	1.4318
$2CaO.SiO_2$	0.0980	0.2381	0.4316	0.1763	0.5997
$CaO.Fe_2O_3$	0.1880	0.3062	0.4095	0.2078	0.4045
$2CaO.Fe_2O_3$	0.0162	0.0522	0.1154	0.0209	0.1167
CaO	0.0706	0.1407	0.2578	0.1066	0.3320
M.	2.757	2.892	3.053	3.536	3.868
Total FeO	0.700	0.540	0.400	0.740	0.440
Total CaO	1.257	1.998	2.762	1.899	3.601
Total SiO_2	1.746	1.746	1.746	2.478	2.478

By plotting total ferrous oxide against total lime for the various silica contents the broken curves shown in Figure 30b were obtained. They are shown alongside the experimental curves (unbroken lines) for comparison. It will be seen that the ideal laws can account for the experimental data with considerable success - to a first approximation at least.

CONCLUSIONS WITH REGARD TO THEORETICAL INTERPRETATION OF EXPERIMENTAL DATA : The constants arrived at by the above methods do not necessarily represent finality. It is evident that other influences than can be accounted for by the ideal laws assumed are operative in the melts. It is hoped, however, that the values obtained may be at least approximately true and that they will hence contribute in some measure to our knowledge of the chemistry of liquid slags.

Some interesting points arise from the calculated figures. One way of regarding the action of lime on the iron-oxide equilibrium is that it displaces FeO, a weaker base, from combination in Fe_3O_4, the liberated FeO undergoing partial oxidation which results in a drop in the total ferrous oxide of the system. Similarly, silica displaces Fe_2O_3 from combination in Fe_3O_4, the liberated Fe_2O_3 undergoing partial dissociation, with a resulting increase in the ferrous oxide content of the melt. When both lime and silica are present calcium metasilicate and calcium orthosilicate form in the melts tending to cause decomposition of the calcium ferrites on the one hand, and of the ferrous silicates on the other. They are not, however, completely stable but are considerably dissociated, and an equilibrium condition is reached in the melts when both calcium ferrites and ferrous silicates are present as well as the calcium silicates.

The present investigation was undertaken primarily from the point of view of oxygen transfer through the slag in the open hearth furnace. The calculated data is of special interest in this connection because of the light which it throws on the mechanism involved. It appears that in the liquid slag, whether acid or basic, there is always an appreciable proportion of the iron oxides in the free condition, which are thus able to take part in the reactions involved in gas-oxidation. Further, even in acid slags, the ferric oxide, the active agent for the oxidation of the metal of the bath, is not entirely free, but is partly combined as Fe_3O_4. In basic slags the principal mode of combination of the Fe_2O_3 is as the calcium ferrites, but there is still an appreciable amount of free ferric oxide present. The velocity of gas oxidation will depend very much on the velocity of dissociation of the Fe_3O_4 and of the ferrites which will take place as the free Fe_2O_3 is used up in the vicinity of the metal surface. Similarly at the gas/slag surface free FeO will be continually tending to undergo oxidation to reach equilibrium with the atmosphere of the furnace, the decrease in the free FeO which thus occurs causing a readjustment among the other molecular species present to take place. Hence gas-oxidation will depend closely on the velocities of dissociation of the various combinations containing the iron oxides. At the moment little is known of these velocities. It is, however, known that the ferrites are readily reduced by metallic iron which supports the view that they must dissociate with considerable rapidity. The present investigation was concerned with the study of equilibrium conditions only, and hence , though the data obtained can be used as a criterion of the tendency which a slag of any composition has to undergo change, gives no direct quantitative information on the velocities of the reactions involved. In this connection it was noticed, with most of the melts that the rates of oxygen evolution and pick-up were very rapid. For example, on cooling the sample, a gain in weight occurred practically simultaneously with the fall in temperature as registered by the thermocouple. The only exception to this was in the case of melts approaching saturation with silica and , to a less extent, with lime. These were noticeably more sluggish and took longer to come to equilibrium. They were also noticeably more viscous.

SECTION III.

INTERPRETATION OF SLAG/METAL RELATIONSHIPS IN TERMS OF SLAG CONSTITUTION.

INTRODUCTORY.

This part of the work constitutes an attempt to apply the data on the molecular constitution of liquid slags obtained in the previous section to certain other known, and fairly well established data on the physical chemistry of slags. The object of this was twofold - (1) to test the applicability of the constants to established quantitative data, and to test their feasibility by examination of the conclusions to which their applications may lead, and (2) to establish constants for certain other slag equilibria, for example, the dissociation constants of the manganese silicates in the slag.

During the past ten years a considerable amount of quantitative data has been accumulated, particularly in Germany, on the relationships that exist between the composition of molten iron and that of liquid slags in contact with it. When the two phase system consisting of liquid slag and metal is allowed to come to equilibrium, it is found that the composition of the metal, as regards the elements which it picks up from the slag, and the composition of the slag bear a definite relationship to one another. This is due to the fact that, at high temperatures, and in contact with the molten metal, the component oxides of the slag are not completely stable , but may be considered as being in part dissociated or reduced by the iron, the metal or metalloid liberated entering the metallic layer in solution.

The system consisting of two immiscible liquid phases in contact, and each containing substances in solution, is a well-known one in physical chemistry. Each solute is partitioned between the two phases according to a definite partition coefficient which is a characteristic of the solute and the two solvents. If a compound dissolved in one of the solvents undergoes dissociation till an equilibrium condition is reached, then, since the compound and each of the products of its dissociation are partitioned in this way between both liquids, it can be shown that equilibrium between the compound and its products must exist in each of the liquids.

The molten chlorides of tin and lead in ~~the~~ contact with the molten metals is an example of such a system which has been fairly thoroughly investigated[25]. At high temperatures a definite relationship exists between the composition of the chloride layer and that of the metal layer. The equilibrium involved is -

$$PbCl_2 + Sn = SnCl_2 + Pb.$$

This equilibrium can be considered to exist in either the chloride layer or the metal layer. In the chloride layer at equilibrium

$$K = \frac{(SnCl_2)\ (Pb)}{(PbCl_2)\ (Sn)}$$, where the brackets "()" indicated concentrations measured in the chloride layer. Similarly in the metal layer at equilibrium

$$K' = \frac{[SnCl_2]\ [Pb]}{[PbCl_2]\ [Sn]}$$, where the brackets "[]" indicate concentrations measured in the metal layer.

In practice it is more convenient to represent this equilibrium in yet another way. Because of the direct proportionality between the concentrations of each of the reactants in the two media, it is possible to substitute in the above formulae concentrations in the metal for concentrations in the chloride layer or vice versa, so long as it is understood that the values of the partition coefficients involved in the operation become embodied in the equilibrium constant for the reaction. In this particular case, the concentrations of the chlorides in the metal phase, and of the metals in the chloride phase are negligible. Hence it is convenient to express the equilibrium in the form

$$K'' = \frac{(SnCl_2)\ [Pb]}{(PbCl_2)\ [Sn]},$$ where the

concentrations of the chlorides are measured (by analysis) in the chloride layer, and the concentrations of the metals (obtained similarly) in the metal layer.

Considerable theoretical signifance was attached to the experimental investigation of this equilibrium (and of the exactly similar one involving the chlorides of lead and cadmium in contact with the metals) because of the opportunity afforded for testing the applicability of the ideal solution laws to high temperature systems of this type. It was ultimately concluded by Korber and Olsen[25] that, to a sufficiently close approximation , the simple laws were applicable.

The case of molten iron in contact with ferrous slags constitutes a system which is essentially similar in nature, though conditions may be complicated in some cases by compound formation between the constituents of the slag. When the slag layer is composed of only ferrous and manganous oxides the system is exactly similar. In this case the equilibrium involved is

$$FeO + Mn = MnO + Fe$$

whereby, at equilibrium, $K_{Mn} = \frac{(FeO)\ [Mn]}{(MnO)\ [Fe]}$.

In this case the metals are sparingly soluble in the oxide layer, and the oxides are sparingly soluble in the metallic layer, so it is convenient to express the constant as shown, where the brackets "()" indicate concentrations in the slag layer, and the brackets "[]" indicate concentrations in the metal, this being the usual convention adopted.

This system has been studied by several investigators[26] at temperatures from 1550°C upwards and there seems little reason to doubt from the degree of constansy observed in the value of K_{Mn} that the solution laws hold. Of the reactants involved, only ferrous oxide appears to be appreciably soluble in both liquid phases, and its partition coefficient has been measured over a fairly wide range of temperatures and concentrations. At any temperature it appears to be a true constant, and independent of the dilution of the ferrous oxide in the slag layer by manganous oxide or by lime.

When silica is present in the slag it may be expected that different relationships will prevail in view of the fact that silica is capable of forming silicates with the ferrous oxide and manganous oxide of the slag. In silicate slags it is found that the partition coefficient of ferrous oxide between slag and metal is materially altered. Korber[27, 28.] found a value for the ratio [FeO]/(FeO) with silicate slags at 1600°C which is decidedly lower than the value obtained with simple oxide slags at this temperature. Since the term (FeO) in the ratio represents the total ferrous oxide concentration in the slag as got by chemical analysis, the natural conclusion is that all of the ferrous oxide in silicate slags cannot be regarded as being chemically free. If this is so, the ratio measured with these slags cannot be regarded as the "true" partition coefficient, but rather as the "apparent" partition coefficient since it is based on measurement of the total ferrous oxide of the slag. The "true" coefficient would take into account only the free ferrous oxide content, and it would presumably, if no complicating factors are involved, be the same as the coefficient measured with simple oxide slags. Up to the present there has been no way of estimating the free ferrous oxide of silicate slags to test the validity of this assumption.

With silicate slags the experimentally determined values of K_{Mn} likewise differ from the values determined with simple oxide slags. This, of course, is to be expected from the alteration in the "apparent" partition coefficients produced by the action of the silica on the ferrous and manganous oxides. (This holds only so long as the coefficients for FeO and MnO are not altered in the same proportion i.e. so long as the silicates of iron and manganese have not the same degree of stability.) The investigations of Krings and Schackmann[24] indicate that the value of K_{Mn} is altered progressively as the silica content of the slag is increased. Korber and Oelsen[29] have made a systematic investigation of slag/metal relationships with a ferrous-oxide-manganous-oxide-silica slag saturated with silica, at temperatures ranging from 1550 to 1700°C. They found that, in slags of this type, the silica content at saturation is practically independent of the relative proportions of ferrous oxide to manganous oxide, and is, furthermore, little affected by temperature over the range of temperatures investigated. It remained constant in their slags at approximately 50 per cent of the slag by weight. (This is a consequence of the form of the liquidus surface of the ternary thermal equilibrium diagram of the system $FeO-MnO-SiO_2$, and follows naturally from the form of the diagram proposed by Hay, White and McIntosh[9].) The relationships between slag and metal were investigated by the usual method employed for such studies, namely, chemical analysis of the two layers in specimens which had been cooled rapidly from high temperatures by quenching after equilibrium had been reached. It was found that over the entire range of compositions studied the "apparent" partition coefficient of FeO, and the "apparent" value of K_{Mn} remained appreciably constant. It should be pointed out that this is not a necessary consequence of the applicability of the law of mass action to the system, because, owing to the presence of ferrous and manganous silicates in the slag as indicated by the changed values of the constants, the case presented by such a slag/metal system is not strictly analogous to the simple metal/metallic-chlorides system, or to the simple iron-manganese/ferrous-oxide-manganous-oxide system. The observed constancy in these relationships is not a necessary consequence of the simple laws, and hence, from the point of view of the underlying theory, must be taken as constituting a special case.

In the following sections an attempt is made to interpret these and similar observations in terms of slag constitution, using as a starting point the values of the constants already derived earlier in this work.

EQUILIBRIUM IN FERROUS-OXIDE/MANGANOUS-OXIDE/SILICA SLAGS.

The most comprehensive and consistent data on slags of this type are undoubtedly those provided by the investigations of Korber and Oelsen[29] to which reference has already been made. Figure 31 summarizes the results of their investigations with silica-saturated slags at 1550°C. and 1600°C. The curves reproduced show the variation of the concentrations of the various constituents in the slag and metal layers that takes place as the manganese in the metal is varied, this being a convenient method of representing the relationships observed. They are mean curves drawn through the experimental points obtained. They are also "ideal" curves in the sense that they were drawn by these authors on the assumption that the various "apparent" constants are truly constant and independent of the slag and metal compositions at any temperature, i.e. that the following expressions should be constant -

$$L_{FeO} \text{ (partition coefficient)} = \frac{[s.FeO]}{(s.FeO)}$$

$$K_{Mn} = \frac{(s.FeO)[s.Mn]}{(s.MnO)}$$

$$K_{Si} = \frac{(s.FeO)^2[s.Si]}{(s.SiO_2)^2},$$

where (s.FeO), (s.MnO), $(s.SiO_2)$ are the total concentrations of these reactants in the slag, and [s.Mn], [s.Si] are total concentrations in the metal. There is a considerable amount of scattering of the experimental points about the curves thus drawn, but, considering the difficulties involved in the investigation, the agreement is reasonably good, and the assumption made by the authors, that the experimental points should fall on the ideal curves, is justifiable.

In the following discussion it is shown that the observations of these authors can be interpreted in terms of the general law of mass action with a fair degree of accuracy. Incidentally values are obtained for the stabilities of the manganese silicates in the liquid slag.

In a slag consisting of FeO, MnO and SiO_2 the following equilibria have to be considered:

$$FeO.SiO_2 = FeO + SiO_2, \qquad \text{whence } k_5 = \frac{(FeO)\ (SiO_2)}{(FeO.SiO_2)}$$

$$2FeO.SiO_2 = 2FeO + SiO_2, \qquad \text{"} \quad k_6 = \frac{(FeO)^2\ (SiO_2)}{(2FeO.SiO_2)}$$

$$MnO.SiO_2 = MnO + SiO_2, \qquad \text{"} \quad k_9 = \frac{(MnO)\ (SiO_2)}{(MnO.SiO_2)}$$

$$2MnO.SiO_2 = 2MnO + SiO_2, \qquad \text{"} \quad k_{10} = \frac{(MnO)^2\ (SiO_2)}{(2MnO.SiO_2)}$$

Of these constants k_5 and k_6 have been established at certain temperatures.

The discussion is based on the following considerations. If the law of mass action holds strictly in these slags, it should be possible to interpret the observations on the slag/metal relationships in terms of these constants, and of the "true" values of K_{Mn} and L_{FeO} i.e. the values of these constants that involve the concentrations of the free reactants only, and these values should, theoretically, be the same as the values obtained for these constants with simple oxide slags in the absence of silica. It is understood that all concentrations must be expressed as molar fractions, not as weight percentages. (In the metallic layer this is not necessary, however, owing to the smallness of the concentrations involved.)

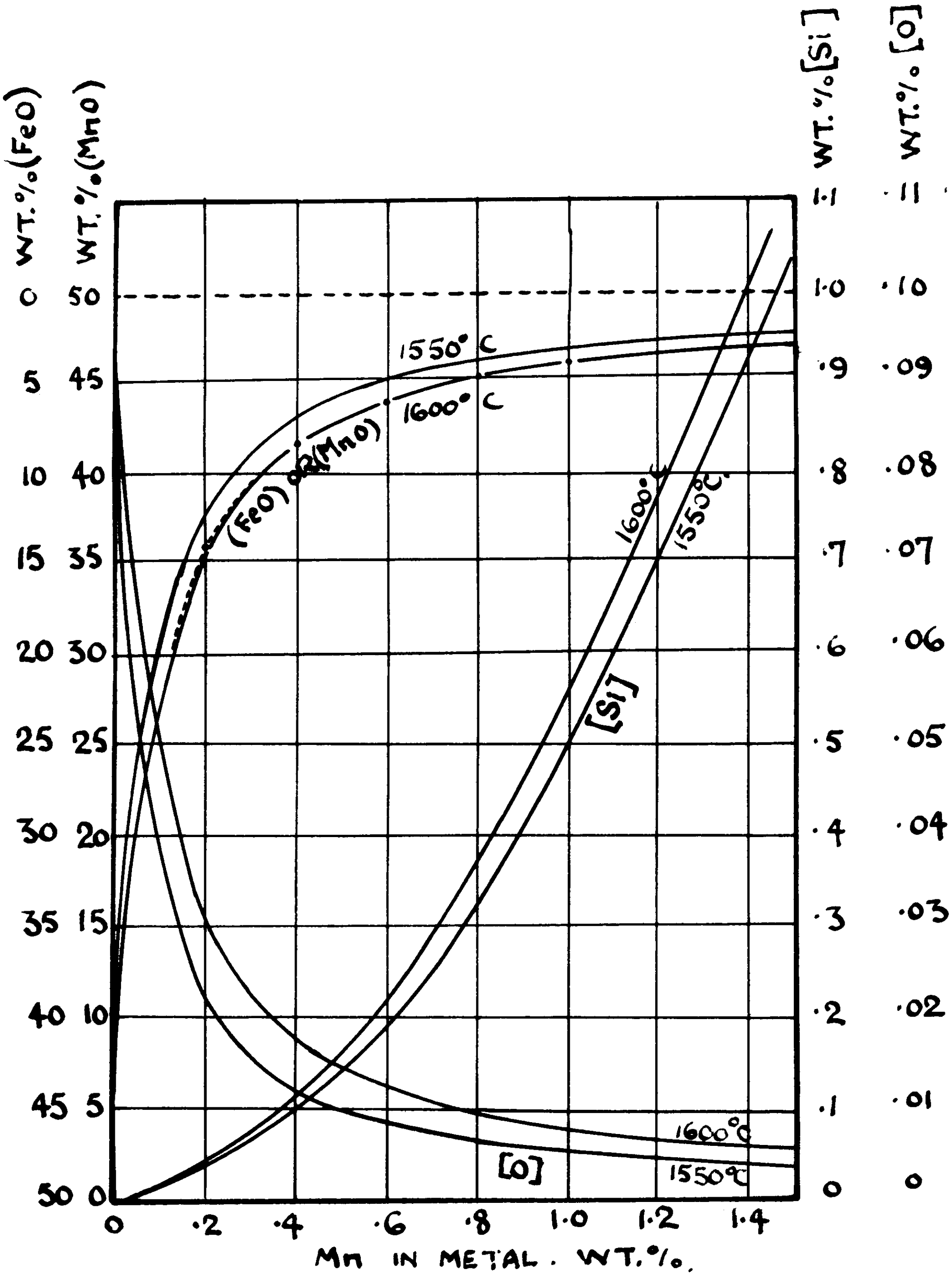

FIG. 31. THE EQUILIBRIA BETWEEN MOLTEN Fe AND FeO, MnO, SiO_2, SATURATED WITH SiO_2 AT DIFFERENT TEMPERATURES. (KÖRBER AND OELSEN).
• VALUES CALCULATED ON THE BASIS OF $K_9 = 0.0205$ AT 1600°C.

Equilibrium at 1600°C:

In the following table is given a list of equilibrium slag and metal compositions as given by Korber and Oelsen (see Figure 31). The list covers practically the entire range of manganese concentrations studied by them. Their original curves are for weight percentages of the constituents. In the table the concentrations of the slag constituents are given on this basis, and also as molecular concentrations, the figures given being the number of gram-molecules of the various constituents in 100 grams of the slag.

Slag/Metal Equilibrium Compositions at 1600°C.

	SLAG.						METAL.		
	Weight per cent.			Gram-molecules.			Weight per cent.		
	MnO	FeO	SiO_2	MnO	FeO	SiO_2	Mn	Si	O
)	35.5	14.5	50.0	.500	.202	.834	.200	.038	.0304
)	41.5	8.5	50.0	.585	.118	.834	.400	.110	.0178
)	44.0	6.0	50.0	.620	.083	.834	.600	.221	.0126
)	45.46	4.54	50.0	.6395	.063	.834	.800	.366	.0095
)	46.3	3.7	50.0	.652	.0514	.834	1.00	.561	.0078

These correspond to the following constant values of the "apparent" constants, i.e. the constants calculated on the basis of the total concentrations of the various constituents (as weight fractions).

$K_{Mn} = 0.00082$,

$L_{FeO} = 0.0021$ (expressed as $[O]/(FeO)$)), $K_{Si} = 0.159 \times 10^{-4}$.

The following data has been used in interpreting these results in terms of the law of mass action:

At 1592°C.(the difference between this and 1600°C, can be neglected.) $k_5 = 0.23$, $k_6 = 1.18$.

K_{Mn} for simple oxide slags has been measured by several workers at 1600°C.[26] There is reasonable agreement between most of the recent determinations, and the value given by Korber and Oelsen[30] can probably be accepted as reasonably correct. According to them

$$K_{Mn} = \frac{(s.FeO)\,[Mn]}{(s.MnO)} = 0.005$$

when the concentrations are expressed as weight fractions.

$$= 0.5$$

when the concentrations are expressed directly as weight percentages.

This is equivalent to 0.494 when the concentrations of FeO and MnO in the slag are expressed as molar fractions but the difference is probably negligible.

For the present purpose all slag concentrations are expressed as molar fractions. Concentrations in the metal are left as weight percentages as the concentrations are small, and the changes occurring in the total number of gram-molecules in the metal phase are negligible.

The methods employed in the mathematical investigation were similar to those used in previous sections. k_5, k_6 and K_{Mn} being assumed known, constant values of k_9 and k_{10} were sought to fit the experimental results.

Examination of the figures for the ferrous silicate equilibria discussed in a previous section showed that the concentration of $2FeO.SiO_2$ in the slags was always very small, and so it was possible to neglect the presence of this compound in the case under consideration, and hence k_6 could be omitted from the discussion, thus introducing a simplification. The results of the investigation are shown in the following table. The compositions taken are those from the previous table and appear in the same order as indicated by the tabulation numbers.

	SLAG CONSTITUTION..						CONSTANTS.		
	Gm.-Mols. per 100 gm. of slag.						"True" Values.		
	FeO	$FeO.SiO_2$	MnO	$MnO.SiO_2$	SiO_2	M.	k_9	L_{FeO}	$K_{Si} \times 10^2$.
(1)	0.092	0.109	0.037	0.463	0.262	0.963	0.0216	0.00315	0.00129
(2)	0.057	0.061	0.046	0.539	0.233	0.936	0.0210	0.00293	0.00164
(3)	0.041	0.042	0.049	0.571	0.221	0.924	0.0204	0.00284	0.00181
(4)	0.031	0.032	0.050	0.589	0.213	0.916	0.0199	0.00278	0.00185
(5)	0.026	0.026	0.052	0.600	0.208	0.910	0.0197	0.00280	0.00197

The first five columns give the various molecular species present in the form of gram-molecules per 100 grams of the slag. M is the total number of gram-molecules of all the molecular species in the slag. k_9 is the dissociation constant of $MnO.SiO_2$ in the slag. L_{FeO} is the partition coefficient of FeO between slag and metal, and is got by dividing the concentration of oxygen in the metal, expressed as a weight fraction, by the concentration of free FeO in the slag, expressed as a molar fraction. K_{Si} is got similarly from the free FeO in the slag, the free SiO_2 in the slag and the Si of the metal expressed as a weight fraction.

The following points will be noted. k_9, L_{FeO}, and K_{Si} show only a slight variation, and might, to a first approximation, be considered as reasonably constant. The variation is, however, systematic not haphazard, indicating that the figures arrived at are not completely satisfactory. In this connection it must be remembered that the influence of the orthosilicates of FeO and MnO has been neglected. The accuracy of the experimental results, however, probably does not warrant any closer analysis. For one thing the assumption that the SiO_2 content at saturation is constant at 50 per cent by weight as stated by Korber and Oelsen is at best only an approximation. A variation of 1-2 per cent is actually liable to occur. Further the scattering of the experimental points obtained by these workers does not allow the mean curves to be fixed with absolute exactness. A slight displacement either way would be possible without seriously detracting from the probability of the curves. Hence it is felt that a more rigid analysis would not be justified. To illustrate this point similar composition curves were calculated on the basis of a mean constant value of 0.0205 for k_9. The FeO/MnO isotherm obtained in this way is plotted in Figure 31. The curve obtained is similar in form to, and is only slightly displaced from, the experimental curve. Hence it seems legitimate to assume that k_9 is a true constant and that it has been evaluated at least approximately.

The values got for L_{FeO} are of special interest. They indicate a mean value of about 0.0029. This agrees very well with the experimentally determined values for the partition coefficient with simple oxide slags, and for the values given for the solubility of FeO in liquid iron at 1600°C. Some of these values are

Partition coefficient-	0.0033	Korber[31]
	0.003	Sauerwald and Hummitzsch[32].
Solubility -	0.304 % Oxygen by weight.	Herty and coworkers[33].
	0.31 % Oxygen by weight.	Schenck[34].

Equilibrium at 1550°C.

A similar examination has been made of the data provided by Korber and Oelsen's curves at 1550°C.

Slag/Metal Equilibrium Compositions at 1550°C.

	SLAG.						METAL		
	Weight per cent.			Gram-molecules.			Weight per cent.		
	MnO	FeO	SiO_2	MnO	FeO	SiO_2	Mn	Si	O.
(1)	37.85	12.15	50.0	0.533	0.169	0.834	0.200	0.031	0.0210
(2)	43.1	6.9	50.0	0.608	0.096	0.834	0.400	0.094	0.0119
(3)	45.18	4.82	50.0	0.636	0.067	0.834	0.600	0.190	0.0083
(4)	46.28	3.72	50.0	0.652	0.0517	.834	0.800	0.324	0.0064
(5)	46.98	3.02	50.0	0.661	0.042	0.834	1.000	0.493	0.0052
(6)	47.46	2.54	50.0	0.668	0.035	0.834	1.200	0.692	0.0044

These figures correspond to the following "apparent" values of the constants-

$K_{Mn} = 0.00064$, $L_{FeO} = 0.0017$, $K_{Si} = 0.09 \times 10^{-4}$.
(all on the basis of weight fractions in slag and metal).

The constants used in analysis of this data were-

$k_5 = 0.203$, k_6 = assumed large. (both established at 1558°C.).

$K_{Mn} = 0.004$ (weight fractions) in simple oxide slags.
$= 0.00394$ (molar fractions in slag).
(Korber and Oelsen[30]).

The results of the analysis are shown in the following table.

	SLAG CONSTITUTION.						Constants.		
	Gm.-Mols. per 100 gm. of slag.						"True" Values.		
	FeO	FeO. SiO_2	MnO	MnO. SiO_2	SiO_2	M.	k_9	L_{FeO}	$K_{Si} \times 10^2$
(1)	0.074	0.095	0.038	0.495	0.244	0.945	0.0196	0.00268	0.00078
(2)	0.044	0.052	0.045	0.563	0.219	0.922	0.0190	0.00248	0.00091
(3)	0.031	0.036	0.048	0.588	0.210	0.912	0.0187	0.00240	0.00098
(4)	0.025	0.027	0.050	0.602	0.205	0.908	0.0187	0.00240	0.00105
(5)	0.020	0.022	0.051	0.610	0.201	0.904	0.0186	0.00233	0.00104
(6)	0.017	0.018	0.052	0.617	0.198	0.902	0.0184	0.00235	0.0011

An approximately constant value for k_9 is again obtained. L_{FeO}

(mean value about 0.0024) again agrees well with the results of experiment as shown by the following figures-

Partition coefficient of FeO-	0.0027	Korber[31].
Solubility of FeO in liquid iron-	0.233	Herty and coworkers[33]
	0.25	Schenck[34].

Both at 1600°C and 1550°C the results obtained indicate that $MnO.SiO_2$ is much more stable in liquid slags than $FeO.SiO_2$. Incidentally the reason for the approximate constancy of the "apparent" value of L_{FeO} with silica-saturated slags is made clear, since it will be seen from the data on slag constitution in the tables above that at each of the temperatures studied the proportion of the total FeO that is chemically free is fairly constant over the entire range of slag compositions considered. At 1600°C the free FeO is very nearly one half of the total FeO in all the cases dealt with.

EFFECT OF INCREASING SILICA CONTENT ON THE APPARENT VALUE OF K_{Mn} WITH $FeO-MnO-SiO_2$ SLAGS.

From the values obtained for k_5, k_9 and K_{Mn} for simple oxide slags it is possible to work out the effect of progressive silica additions on the "apparent" value of K_{Mn}. This has been done at 1600°C and 1550°C as shown in the following tables. Mean values of k_9 have been assumed as indicated.

Effect of SiO_2 Addition on "Apparent" K_{Mn} at 1600°C.

Constants: $k_5 = 0.23$, $k_9 = 0.0205$, K_{Mn} ("true") = 0.00494.

Gm.-Mols. per 100 gm. of Slag.						Slag Composition Weight %.			"Apparent"
FeO	$FeO.SiO_2$	MnO	$MnO.SiO_2$	SiO_2		FeO	MnO	SiO_2	K_{Mn}
Mn in metal = 0.1 % by weight.									
.9100	.0479	.1842	.1087	.0153	1.266	69.0	20.75	10.35	.0033
.6625	.0946	.1341	.2146	.0375	1.143	54.45	24.75	20.8	.0022
.4150	.1383	.0839	.3145	.0790	1.030	39.8	28.4	31.8	.0014
.1677	.1677	.0339	.3803	.2240	.974	24.15	29.45	46.4	.00082
.0944	.1575	.0191	.3583	.3925	1.023	18.15	26.8	55.05	.00068
.0351	.1052	.0071	.2395	.8605	1.247	10.1	17.5	72.4	.00058

Effect of SiO_2 Addition on "Apparent" K_{Mn} at 1600°C.(continued).

Gm.-Mols. per 100 gm. of Slag						Slag Composition. Weight %.			"Apparent"
FeO	FeO-SiO_2	MnO	MnO-SiO_2	SiO_2	M.	FeO	MnO	SiO_2	K_{Mn}
Mn in metal = 0.5% by weight.									
.4320	.0228	.4386	.2586	.0141	1.166	32.78	49.5	17.72	.0033
.2610	.0373	.2646	.4240	.0334	1.020	21.48	48.87	29.65	.0022
.1396	.0465	.1416	.5300	.0713	.929	13.4	47.7	38.9	.0014
.0495	.0495	.0501	.5615	.2141	.925	7.12	43.45	49.45	.00082
.0271	.0451	.0274	.5140	.3820	.996	5.2	38.4	56.4	.00068
.0098	.0294	.0099	.3335	.8510	1.234	2.85	24.35	72.8	.00058
Mn in metal = 1.0 % by weight.									
.3370	.0086	.6820	.1968	.0073	1.232	24.9	62.3	12.8	.0040
.2615	.0138	.5300	.3124	.0137	1.131	19.8	59.8	20.4	.0033
.1489	.0213	.3016	.4820	.0324	.986	12.25	55.6	32.15	.0022
.0765	.0255	.1549	.5800	.0695	.906	7.4	52.1	40.5	.0014
.0263	.0263	.0533	.5970	.2102	.913	3.89	46.2	50.0	.00082
00143	.0238	.0290	.5415	.3790	.988	2.75	40.5	56.75	.00068
.0051	.0153	.0103	.3465	.8400	1.217	1.45	25.35	73.2	.00058

(K_{Mn} is calculated on the basis of weight fractions.)

Effect of SiO_2 Addition on "Apparent" K_{Mn} at 1550°C.

Constants: $k_5 = 0.203$, $k_9 = 0.0185$, K_{Mn}("true") = 0.00394.

Gm.-Mols. per 100 gm. of Slag.						Slag Composition. Weight %.			"Apparent"
FeO	FeO-SiO_2	MnO	MnO-SiO_2	SiO_2	M.	FeO	MnO	SiO_2	K_{Mn}
Mn in metal = 0.1 % by weight.									
.8570	.0451	.2179	.1257	.0134	1.259	64.55	24.4	11.05	.0027
.6095	.0870	.1547	.2423	.0327	1.126	50.1	28.2	21.7	.0018
.3752	.1250	.0952	.3483	.0685	1.012	36.0	31.5	32.5	.0011
.1483	.1483	.0382	.4235	.1935	.952	21.35	32.75	45.9	.00065
.0861	.1433	.0227	.4155	.3420	1.010	16.5	31.1	52.4	.00053
.0363	.1088	.0092	.2993	.7110	1.165	10.5	22.2	67.3	.00047
Mn in metal = 0.2 % by weight.									
.6405	.0337	.3255	.1879	.0128	1.200	48.53	36.4	15.07	.0027
.4250	.0607	.2160	.3383	.0311	1.071	34.8	39.4	25.8	.0018
.2405	.0802	.1222	.4552	.0652	.963	23.1	41.0	35.9	.0011
.0915	.0915	.0465	.5104	.1888	.929	13.15	39.4	47.45	.00067
.0518	.0863	.0263	.4815	.3300	.976	9.95	36.1	53.95	.00055
.0214	.0642	.0109	.3575	.7070	1.161	6.15	26.15	67.7	.00047
Mn in metal = 0.5 % by weight.									
.3740	.0197	.4755	.2743	.0124	1.156	28.34	53.3	18.36	.0027
.2226	.0318	.2822	.4415	.0293	1.007	18.3	51.5	30.2	.0018
.1183	.0394	.1502	.5500	.0622	.920	11.35	49.65	39.0	.0011
.0700	.0420	.0889	.5850	.1090	.895	8.05	47.85	44.1	.00084
.0416	.0416	.0529	.5850	.1839	.905	6.0	45.4	48.6	.00066
.0235	.0391	.0298	.5455	.3261	.964	4.5	40.8	54.7	.00055
.0099	.0296	.0125	.4000	.7020	1.154	2.85	29.25	67.9	.00049

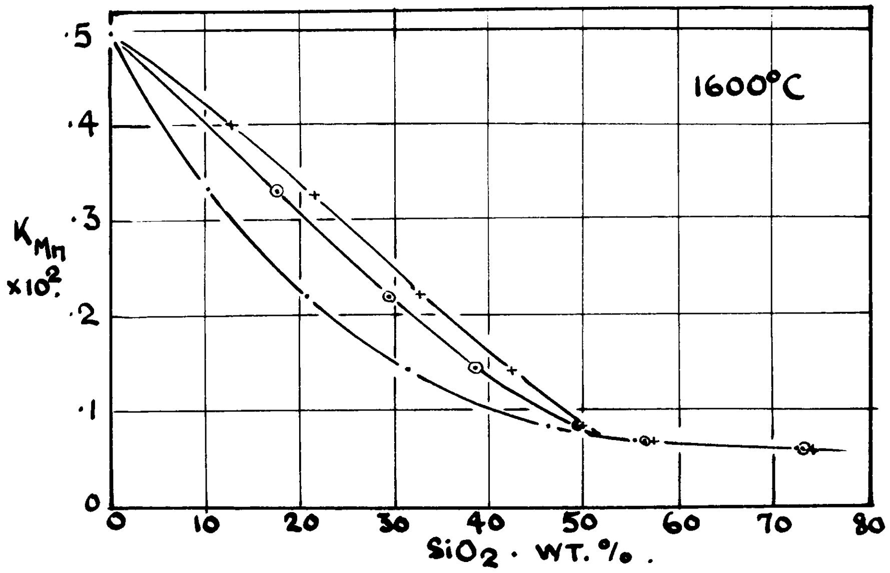

FIG. 32a.

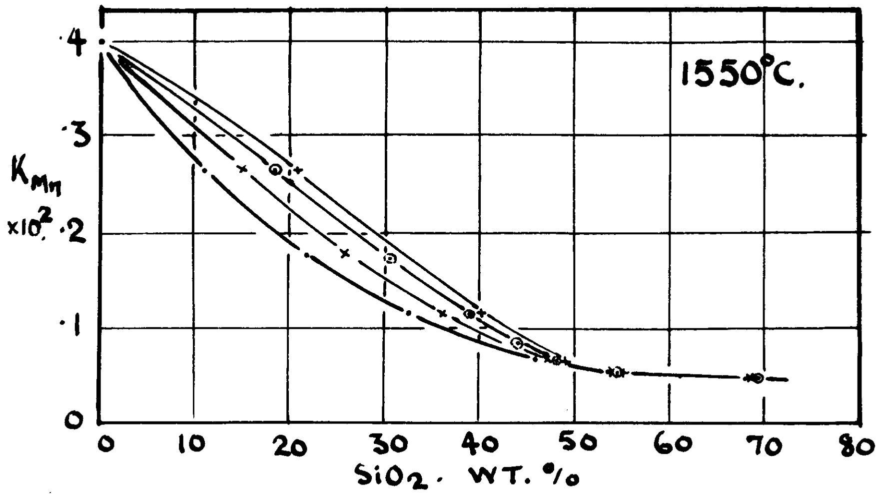

FIG. 32b.

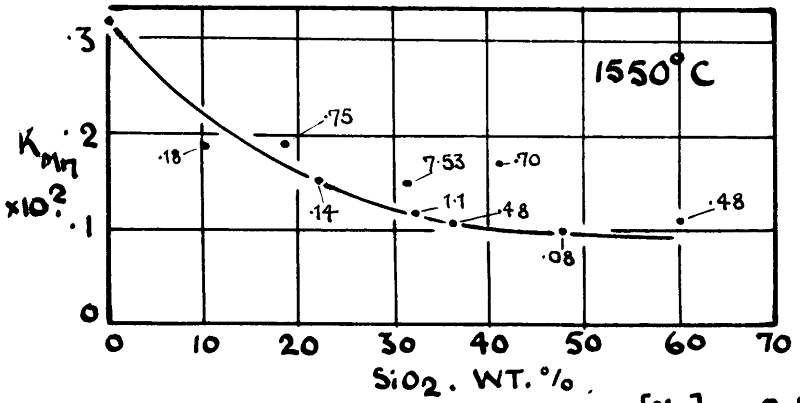

FIG. 32c.

FIG. 32a: CALCULATED DATA AT 1600°C.

FIG. 32b: " " " 1550°C.

· [Mn] = 0.1 + [Mn] = 1.0.
x [Mn] = 0.2
⊙ [Mn] = 0.5

FIG. 32c: KRINGS AND SCHACKMANN'S EXPERIMENTAL DATA AT 1550°C.

Effect of SiO_2 Addition on "Apparent" K_{Mn} at 1550°C. (continued).

Gm.-Mols. per 100 gm. of slag.						Slag Composition. Weight %.			"Apparent" K_{Mn}
FeO	$FeO.SiO_2$	MnO	$MnO.SiO_2$	SiO_2	M.	FeO	MnO	SiO_2	
Mn in metal = 1.0 % by weight.									
.2200	.0116	.5590	.3224	.0120	1.125	16.7	62.55	20.75	.0027
.0636	.0212	.1612	.5910	.0609	.898	6.1	53.5	40.4	.0011
.0221	.0221	.0561	.6152	.1824	.899	3.2	47.6	49.2	.00067
.0123	.0215	.0312	.5710	.3255	.961	2.36	42.74	54.9	.00055

("Apparent" K_{Mn} is based on weight fractions in slag and metal.)

The data thus obtained is plotted graphically in Figure 32 A and B, the "apparent" value of K_{Mn} being plotted as a function of the total weight percentage of SiO_2 in the slag for the various contents of manganese in the metal. It will be noticed that the value of K_{Mn} should, over a wide range of SiO_2-contents of the slag, depend on the Mn content of the metal as well as the silica content of the slag. From 50 per cent of silica upwards, however, the value of the constant is practically independent of the Mn in the metal. This explains the observed constancy of the "apparent" K_{Mn} in silica-saturated slags as found by Korber and Oelsen. (Note: It is understood, of course, that some of the slag compositions given in the above tables would not actually be liquid at the temperatures quoted.)

Many writers appear to have assumed that "apparent" K_{Mn} would depend on SiO_2 concentration only for all ranges of composition. If the reasoning by which the present conception of slag constitution has been arrived at is correct, this should not actually be the case. Krings and Schackmann[24] investigated the effect of progressive SiO_2 addition on the value of K_{Mn}, and drew a single smooth curve through their somewhat scattered experimental points, assuming the value of the constant to be independent of the manganese content of the metal. Figure 32 C is a reproduction of their curve at 1550°C and the experimental points from which it is derived. (The points shown were obtained using alumina crucibles. Those obtained with magnesia crucibles were consistently high and were not considered when drawing the curve, so they have been omitted from the diagram. With both types of crucible considerable contamination of the slags occurred.) Alongside the experimental points the manganese content of the metal at which the equilibrium was determined is indicated. It will be seen that there is a distinct tendency to higher values of K_{Mn} as the manganese of the metal increases.

The general form of the curve indicated by Krings and Schackmann is similar to that of the theoretical curves when allowance is made for the fact that the value of K_{Mn} for simple oxide slags as obtained by them (0.0032 at 1550°C.) differs somewhat from the value obtained by Korber and Oelsen (0.0040) which was assumed in making the theoretical calculations.

Equilibrium in Lime/Ferrous-Oxide/Manganous-Oxide/Silica Slags.

The previous investigations have shown that in slags consisting of these four components, four equilibria within the slag must be considered:

$$FeO.SiO_2 = FeO + SiO_2,$$
$$CaO.SiO_2 = CaO + SiO_2,$$
$$2(CaO.SiO_2) = 2CaO.SiO_2 + SiO_2,$$
$$MnO.SiO_2 = MnO + SiO_2,$$

(assuming the orthosilicates of FeO and MnO to have negligible stability). The corresponding constants, k_5, k_7, k_8 and k_9, have all been evaluated at 1600°C. Hence it is possible to work out the molecular constitution of any quaternary slag of these components, and, in the case of such a slag in contact with molten iron, to calculate what the "apparent" value of K_{Mn} will be at this temperature, provided that the "true" value of K_{Mn} as got with simple oxide slags is known.

With four component slags of this type it was found that "apparent" K_{Mn} was dependent on three variables, these being (1) the ratio of lime to silica in the slag, (2) the percentage of lime plus silica, or, conversely, of FeO plus MnO, in the slag, and (3) the content of manganese in the metal. In the following tables the variation of "apparent" K_{Mn} is shown as a function of the lime/silica ratio, the sum of the FeO and MnO contents being kept at approximately 25 per cent of the slag by weight. Two cases were considered, viz. (1) 0.1 % by weight of manganese in the metal, and (2) 0.5 % by weight of manganese in the metal, and the results of the calculations are shown in the tables below. In the lower table ΣCaO, ΣSiO_2, ΣFeO and ΣMnO denote the total amounts of these constituents by weight in 100 grams of the slag.

Equilibrium in Slag/Metal System at 1600°C. $CaO/FeO/MnO/SiO_2$-Slag:

Constants: $k_5 = 0.23$, $k_7 = 0.02$, $k_8 = 0.10$, $k_9 = 0.0205$,
"true" $K_{Mn} = 0.00494$.

SLAG CONSTITUTION (Gram-molecules per 100 grams of slag).

Mn in metal = 0.10 % by weight.

	FeO	FeO. SiO_2	MnO	MnO. SiO_2	CaO	CaO. SiO_2	2CaO. SiO_2	SiO_2	M.
(1)	0.0322	0.0958	0.0065	0.2179	0.0012	0.0410	0.0002	0.8530	1.248
(2)	0.0378	0.0935	0.0077	0.2103	0.0055	0.1412	0.0030	0.6600	1.159
(3)	0.0630	0.0830	0.0128	0.1887	0.0197	0.2988	0.0296	0.3023	0.998
(4)	0.1438	0.0561	0.0292	0.1274	0.0680	0.3055	0.1122	0.0827	0.925
(5)	0.2415	0.0167	0.0490	0.0381	0.2303	0.1836	0.2139	0.0158	0.989
(6)	0.2710	0.0080	0.0549	0.0182	0.3708	0.1262	0.2175	0.0073	1.074
(7)	0.2821	0.0020	0.0572	0.0047	0.7070	0.0591	0.1634	0.0021	1.278

Mn in metal = 0.50 % by weight.

	FeO	FeO. SiO_2	MnO	MnO. SiO_2	CaO	CaO. SiO_2	2CaO. SiO_2	SiO_2	M.
(8)	0.0090	0.0257	0.0091	0.3039	0.0012	0.0404	0.0002	0.8460	1.233
(9)	0.0196	0.0258	0.0198	0.2940	0.0171	0.2596	0.0236	0.2861	0.945
(10)	0.0318	0.0235	0.0322	0.2660	0.0360	0.3062	0.0605	0.1551	0.911
(11)	0.0525	0.0205	0.0533	0.2330	0.0631	0.2862	0.1024	0.0798	0.890
(12)	0.1245	0.0086	0.1245	0.0967	0.2202	0.1753	0.1992	0.0154	0.965
(13)	0.1693	0.0012	0.1693	0.0138	0.7030	0.0585	0.1606	0.0021	1.278
(14)	0.1492	0.0044	0.1560	0.0509	0.3526	0.1236	0.2113	0.0072	1.055

(For second table see overleaf.)

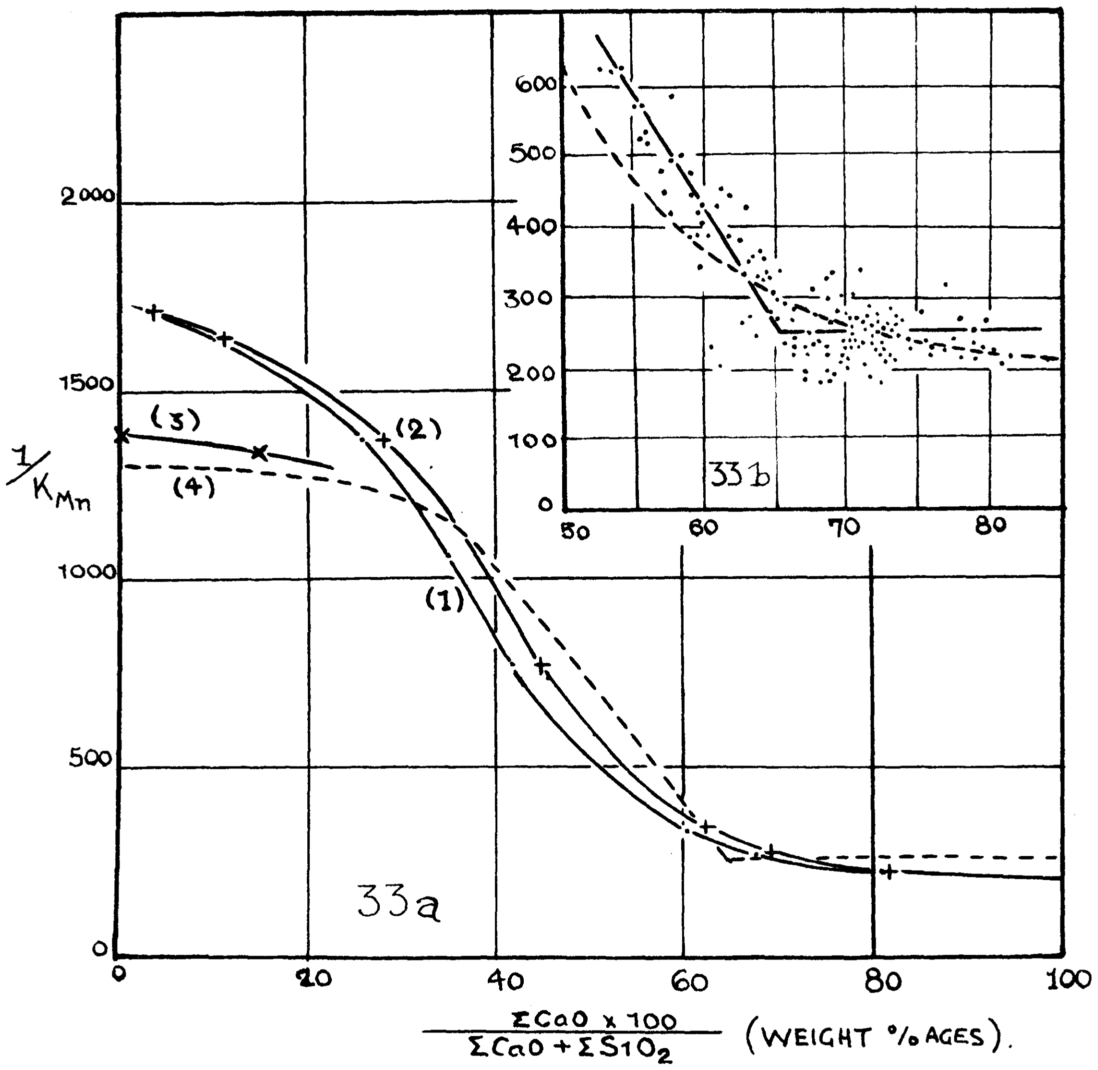

FIG.33a: DEPENDENCE OF $1/K_{Mn}$ ON $\frac{\Sigma CaO}{\Sigma CaO + \Sigma SiO_2}$ AT 1600°C. $CaO-FeO-MnO-SiO_2$ SLAGS.

(1). $\Sigma FeO + \Sigma MnO = 25\%$, $[Mn] = 0{\cdot}5\%$.
(2). $\Sigma FeO + \Sigma MnO = 25\%$, $[Mn] = 0{\cdot}1\%$. } BY CALCULATION.
(3) $\Sigma FeO + \Sigma MnO = 50\%$, $[Mn] = 0{\cdot}1\%$.
(4) CURVE OF TAMMAN AND OELSEN SHOWING RELATIONSHIP BETWEEN ACID AND BASIC SLAGS. ARCHIV FUR DAS EISENHUTTENWESEN, 5, 1931-32, p.77, FIG. 2.

FIG.33b: DATA FROM FURNACE SLAGS – TAMMAN AND OELSEN, ARCHIV FUR DAS EISENHÜTTENWESEN, 5, 1931-32, p77, FIG. 1. BROKEN CURVE SHOWS CURVE (2) FIG. 33a.

ULTIMATE COMPOSITION OF SLAGS IN ABOVE TABLE.

Weight percentages of constituents.

	ΣCaO	ΣFeO	ΣMnO	ΣSiO_2	$\frac{\Sigma CaO \times 100}{\Sigma CaO + \Sigma SiO_2}$	$\Sigma FeO + \Sigma MnO$	$\frac{1}{K_{Mn}}$ (apparent
			Mn in metal = 0.10 % by weight.				
(1)	2.38	9.22	15.9	72.5	3.3	25.1	1725
(2)	8.51	9.43	15.46	66.6	11.36	24.9	1640
(3)	21.2	10.5	14.3	54.0	28.2	24.8	1362
(4)	33.5	14.4	11.1	41.0	45.0	25.4	773
(5)	47.1	18.56	6.16	28.18	62.75	24.8	331
(6)	52.10	20.05	5.20	22.65	69.8	25.25	257
(7)	61.3	20.45	4.39	13.86	81.5	24.90	215
			Mn in metal = 0.50 % by weight				
(8)	2.35	2.52	22.13	73.0	3.12	24.7	1718
(9)	19.43	3.27	22.23	55.07	26.0	25.4	1360
(10)	25.96	3.98	21.24	48.82	34.8	25.2	1063
(11)	31.12	5.25	20.31	43.32	41.8	25.5	775
(12)	44.97	9.57	15.70	29.76	60.1	25.2	328
(13)	60.59	12.29	12.97	14.15	81.2	25.2	214
(14)	50.9	11.04	14.26	23.8	68.0	25.3	257

("Apparent" K_{Mn} is as usual calculated on the basis of weight fractions of FeO, MnO and Mn in slag and metal.)

Curves (1) and (2) of Figure 33a show the variation of the reciprocal of "apparent" K_{Mn} with the value of the fraction $\frac{\Sigma CaO}{\Sigma CaO + \Sigma SiO_2} \times 100$ for the two cases considered. Curve (4) is a similar curve proposed by Tamman and Oelsen[35] which purports to show the relationship between acid and basic slags as regards the value of K_{Mn}. These authors studied the dependence of K_{Mn} on slag composition from actual steel furnace data. Figure 33b shows the results of their study of basic slags, the unbroken curve being the form proposed by them while the broken curve is a reproduction of curve (2) of Figure 33a for comparison. In calculating $\frac{\Sigma CaO}{\Sigma CaO + \Sigma SiO_2}$ they assumed arbitrarily the effective lime content to be the total lime diminished by the amount necessary to form $3CaO.P_2O_5$ with the P_2O_5 content of the slag. The ($\Sigma FeO + \Sigma MnO$) content of these slags was throughout 20 to 30 per cent by weight, and their results for these slags are, therefore, directly comparable with the present data. Their results for acid slags are not directly comparable with curves (1) and (2) of Figure 33a, however, since the latter are for a ($\Sigma FeO + \Sigma MnO$) content of 25 per cent throughout, whereas the acid slags studied by them would have a considerably higher content of these oxides. Curve (3) of Figure 33a was calculated for (ΣFeO + ΣMnO) = 50 per cent by weight and can be compared directly with their curve in this range. Their curve can be regarded as a composite one since the content of these two oxides does not remain constant throughout its entire range.

The agreement between Tamman and Oelsen's curve and the present curves is only fair. The form proposed by them, having a sharp break at the composition corresponding to the compound $2CaO.SiO_2$ would indicate that this compound had complete stability in the liquid melts, while $CaO.SiO_2$ would presumably have negligible stability. It is doubtful, however, whether the sharp break in their curve is completely justified on the evidence shown (Figure 33b). It should also be remembered that their data is necessarily somewhat "rough" in character, being derived from analytical data on slag and metal by the rather arbitrary method mentioned above. On the other hand, as regards the present curves, the probable shortcomings of the ideal laws must be borne in mind. Another point is, of course, that while the present data is for a temperature of 1600°C., there is no record of the temperature in the furnaces involved in their study.

CONCLUSION.

The earliest conception of fused slags and magmas was that they were to be regarded as solutions of the component oxides in each other. As data concerning the physical chemistry of slags was accumulated, however, it was seen that this simple view of slag constitution was hardly tenable. Field and Royster's[36] investigations of slag-viscosity/composition relationships showed that decided constitutional influences were operative in their slags. The stabilizing effect of lime on ferric oxide, and of silica on ferrous oxide in steel furnace slags points to the same conclusion, as does the dependence of K_{Mn} in slag/metal systems on the composition of the slag.

Many attempts have been made to throw light on this aspect of slag chemistry. Several workers have tried to group the component oxides present in furnace slags into supposedly stable combinations in such a way that an explanation of the observed slag/metal relationships would be obtained[37]. Such attempts have usually been based on somewhat arbitrary assumptions, however. In the present instance an attempt has been made to apply in systematic fashion the ideal solution laws to reactions occurring within the slag, and the conclusions arrived at have been tested in the light of experimentally-established slag/metal relationships. As regards the results obtained, their primary significance, in the opinion of the writer, lies not so much in the values of the constants which were arrived at, as in the fact that so many of the experimental curves have been shown to be of a form which naturally follows from the applicability of the ideal solution laws. In most cases the numerical agreement between the theoretical and experimental values is only approximate, but this was to be expected. In concentrated systems of the type dealt with it is hardly likely that the activity coefficients of the reactants should be independent of their concentrations. Nevertheless the results of the investigation appear to indicate that variations in the activity coefficients are of secondary importance only in the slags considered. It should be noted in this connection, however, that in the case of the slag and metal systems dealt with only low concentrations of the reactants in the metal layer were considered. At higher concentrations of manganese and silicon in the metal layer Korber and Oelsen[29] have found marked departure from the ideal slag/metal relationships found to hold at lower concentrations in the metal layer, this being attributed to the fact that with such concentrations the simple laws are no longer applicable to the reactants in the metal layer. This finding is confirmed by the present investigation since the experimental data for these melts does not agree with the constants now given.

In his most recent paper (presented to the Iron and Steel Institute in May 1938) McCance[38] appears to favour the view that the real cause of the variation with slag composition of the constants for the slag/metal equilibria is to be found in the variation of the activity coefficients of the reactants involved. In view of the success of the simpler laws in accounting for the observed phenomena such an assumption seems hardly justified. It would appear that variations in the activity coefficients play only a secondary part in determining the slag/metal relationships at normal concentrations of the reactants in the metal layer.

The possibility of an ionic type of dissociation in liquid slags[39] has also been suggested. At the moment it would appear that the non-ionic type of dissociation postulated in the present work is capable of furnishing a more complete explanation of the observed phenomena.

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39. See contribution by Herasymenko to Discussion of McCance's paper as in reference 38.