EQUILIBRIA OF LIQUID IRON AND SLAGS OF THE SYSTEM CaO-MgO-FeO-SiO_2

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by

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SYNOPSIS

A. Statement of the Problem

This experimental investigation deals with the establishment and measurement of the equilibria between a slag and molten iron. The slags used are those which have a direct bearing on the reactions which take place in an open-hearth furnace, and are a necessary preliminary to the study of reaction rates in the open hearth process.

This investigation is concerned specifically with the development of an adequate experimental method, the use of this method to determine the distribution of FeO between the slag and the metal, and the effect of various additions on this distribution. This was accomplished by placing a slag on the surface of the molten metal, allowing sufficient time for equilibrium to take place, and taking temperatures, and slag and metal samples. The slags were then analysed for CaO, SiO_2, FeO, Fe_2O_3, Al_2O_3, MgO, and the metal for oxygen and nitrogen. The metal was held molten for seven or eight hours, while various slags were placed on it, and their effects noted. The atmosphere was pure dry nitrogen to eliminate the variable of gaseous oxidation.

The experimental arrangement embodied a combination of techniques not here-to-fore reported.

1) Rotation of the crucible to produce a liquid metal cup.

(a) The rotation forms a cup in which the slag is held, preventing contamination of the slag by the walls of the crucible. This method allows the use of relatively pure $CaO - SiO_2 - FeO$ slags.

(b) The interfacial area of the slag and metal is increased, promoting the rate of attainment of equilibrium.

2) Development of an accurate and reproducible sampling method for oxygen in liquid iron.

3) The use of thermo electric elements for the measurement of molten metal temperatures.

B. Scope of the Study

The scope of the study was limited by three considerations:

1) The temperature range was limited on the lower end by the melting point of iron, 1530° C, and on the upper end by the power available for melting. This latter condition restricted the upper limit to 1700° C.

2) Only those compositions of FeO, SiO_2, CaO, could be studied, which were molten in the above temperature range.

3) The slag compositions were limited for the most part to those not studied by Fetters and Chipman (72).

C. Statement of Results

1) The development of an adequate technique for the study of slag-metal relationships.
2) The determination of the solubility of FeO in the molten iron under pure iron oxide slags.
3) Determination of the distribution of FeO between liquid iron and slags of the system CaO - FeO - SiO_2.
4) The determination of the activity of FeO in the slag as affected by the composition of the slag.
5) The redetermination of the solubility of nitrogen in liquid iron.

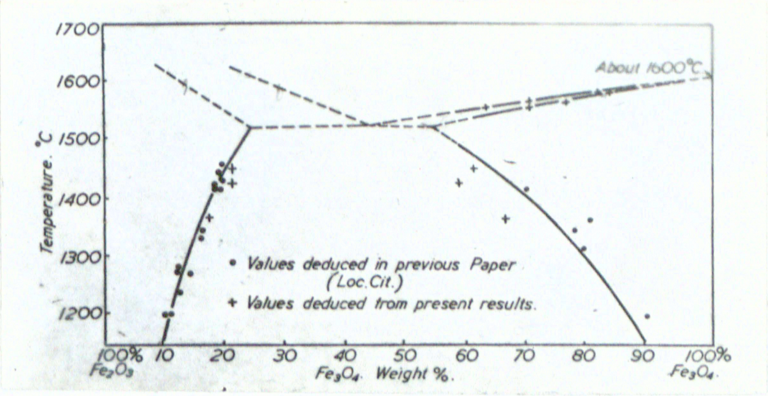


Fig. 1. Thermal equilibrium diagram for the system Fe_2O_3 - Fe_3O_4 (1, 29)

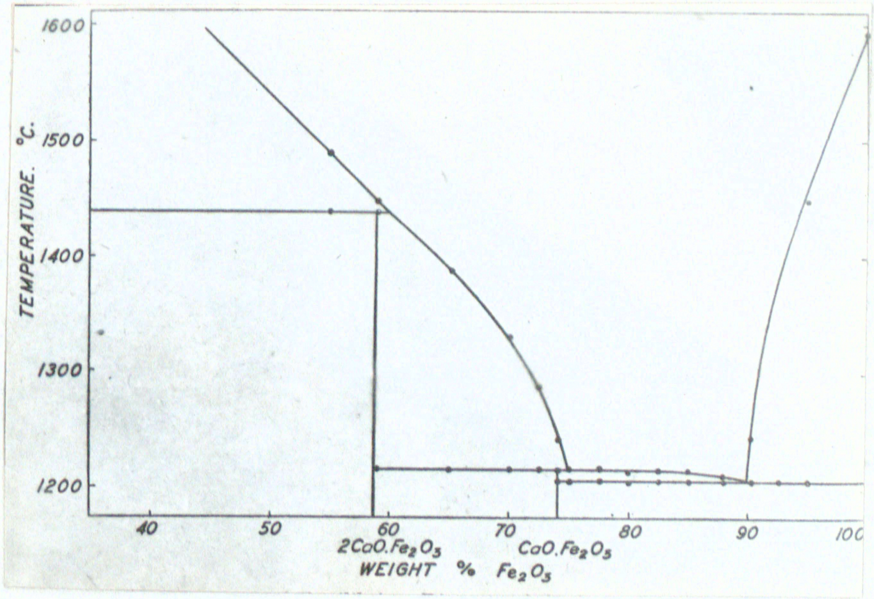


Fig. 2. Thermal equilibrium diagram of the system CaO-Fe_2O_3 (1)

LITERATURE SURVEY

A. Slags in the Absence of Liquid Iron

Since the system $CaO-SiO_2-FeO$ is of importance in the ceramic and glass industries as well as the steel-making industries, there has been a lot of research work done on the system in the absence of liquid iron. Most of this work has been done towards establishing the constitutional diagram of the binary and ternary systems. The emphasis has been placed on the identification of phases and their optical constants. Such work is of great value in determining the composition and manner of formation of oxide inclusions in solid iron. For molten slags, however, their greatest value lies in suggesting the possibilities of compound formation. They cannot be used to determine the degree of association of these compounds in the liquid phase. This is especially true, since these slags are used in steel making several hundred degrees above their melting points. Their value is sufficient, however, to warrant at least an inspection of the more exact data assembled by the various workers.

The System $Fe_3O_4-Fe_2O_3$

White, Graham, and Hay (1) have reported the binary system $Fe_2O_3-Fe_3O_4$. Their diagram is given in Fig. 1. The melting ranges are qualitative since the oxygen pressure of these oxides becomes quite large as the temperature goes up, being 10,000 atmospheres for Fe_2O_3 at 1575° C., as reported by Krings and Schakmann (2). They give a melting point of 1595° C. for Fe_2O_3 and determined the oxygen pressure curve of Fe_2O_3 versus temperature. White (29) has obtained liquidus and solidus points which point to a eutectic type of diagram rather than a peretectic.

The System $CaO-Fe_2O_3$

White, Graham, and Hay (1) used cooling curves to investigate the system $CaO-Fe_2O_3$ (Fig. 2). They prepared $CaO \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ and determined optical properties. Their opinion was that the dicalciumferrite is the more stable of the two. Sosman and Merwin (3) have also investigated the system and reported these compounds. Their diagram is in substantial agreement with that of White, Graham, and Hay. They feel that both of the compounds $CaO \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ decompose at the melting point. Since the Fe_2O_3 has an appreciable oxygen pressure in these melts, this should be written as a binary system, since there is an appreciable amount of FeO formed.

Singewald (4) claims that a large excess of CaO gives $3CaO \cdot Fe_2O_3$, but that the $2CaO \cdot Fe_2O_3$ and free lime are the usual phases found in petrographic investigation. Martin and R. Vogel (5) claim the existence of a compound $CaO \cdot (FeO)_9$ and $(CaO)_4\ (Fe_3O_4)_3$. However, the last one is quite close to $CaO \cdot Fe_3O_4$ and may have been erroneously reported, since it is very difficult to prepare these compounds pure.

Konarzewsky (6) reports melting points of 1440° C for $2CaO{\cdot}Fe_2O_3$ and 1215° C for $CaO{\cdot}Fe_2O_3$. Klarding (7) in reporting on the ease of reduction of iron ores says that when the molecular ratio CaO/SiO_2 is 2, all the iron is free to be reduced, and that any excess CaO ties up the Fe_2O_3 in the compound $CaO{\cdot}Fe_2O_3$. His reductions were carried out at 900 - 1000° C.

Hay, McIntosh, Rait and White (8) used a weight loss method. They found that CaO decreased the FeO/Fe_2O_3 ratio. In their viscosity measurements, they did not find any evidence for the existance of $CaO{\cdot}Fe_2O_3$ at 1600° C. Hay and White (9) using oxygen loss as a criterion, report that $CaO{\cdot}Fe_2O_3$ and $2CaO{\cdot}Fe_2O_3$ are only slightly dissociated "above the melting point," and that this dissociation was reversible if the melts were cooled slowly enough in the presence of oxygen. CaO-FeO does not exist, since the formation of $2CaO{\cdot}Fe_2O_3$ takes place with sufficient energy to liberate iron. They write the reaction:

$$2CaO + 3FeO \rightarrow 2CaO{\cdot}Fe_2O_3 + Fe$$

They got globules of iron in all their melts. The system to be correctly interpreted must be written $CaO\text{-}Fe\text{-}Fe_2O_3$.

Crook (10) melted lime- iron oxide mixtures in an oxidizing atmosphere in a gas fired furnace and examined the solidified melts microscopically. He found metalic iron in all his melts, and reported his results on a ternary diagram $CaO\text{-}FeO\text{-}Fe_2O_3$. He reports a eutectic between $FeO\text{-}3CaO{\cdot}Fe_2O_3$.

Table 1, contains a summary of the opinion of various authors on the stability and existence of these compounds.

TABLE 1

Compound	Reference	Remarks
$CaO \cdot FeO$	9, 10	Does not exist in a stable form.
$CaO \cdot Fe_2O_3$	11	Considers Fe_2O_3 an acid in B.O.H. slags.
	3	Dissociates at melting point.
	6	Melting point - 1215° C.
	8	No evidence of existence at 1600° C by viscosity measurements.
$2CaO \cdot Fe_2O_3$	12	Claims this to be the stable compound at high temperatures.
	3	Decomposes at melting point.
	6	Melting point at 1440° C.
	13	The stable compound at steel making temperature.
	5	Obtained by sintering $CaO-Fe_2O_3$ just below the melting point.
$3CaO \cdot Fe_2O_3$	14	Found petrographically in large masses of B.O.H. slags.
	10	Reports eutectic $FeO-3CaO \cdot Fe_2O_3$
$CaO \cdot (FeO)_9$ $(CaO)_4(Fe_3O_4)_3$	5	Claimed to have obtained these compounds.

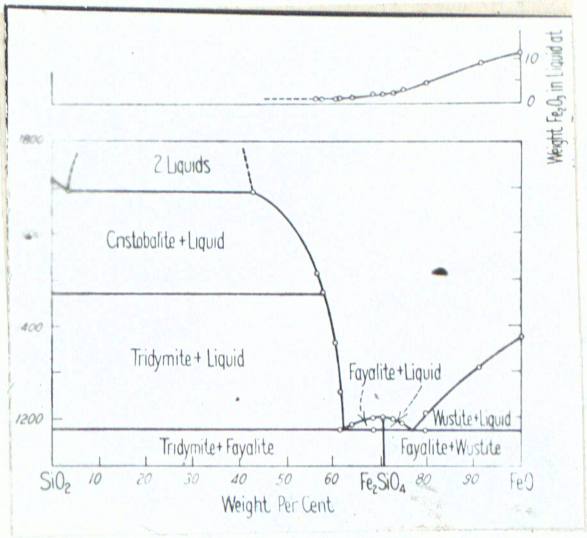


Fig. 3. The system FeO - SiO_2

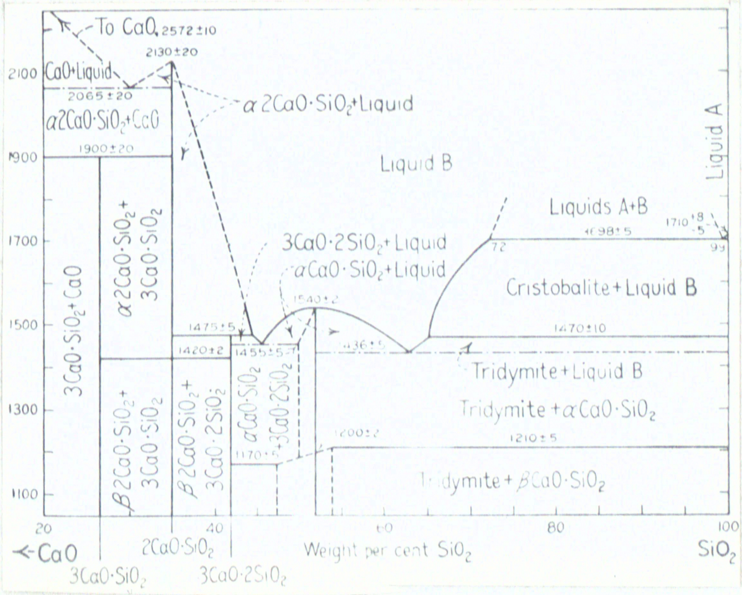


Fig. 4. The system CaO-SiO_2
(19, 20, 21, 22)

The System $FeO-SiO_2$

This system has been investigated by Bowen and Schairer (15) and the constitutional diagram is reproduced in Fig. 3.

Klarding (7) reports, based on reduction characteristics, that an excess SiO_2 over the mol ratio of CaO/SiO_2 of 2/1 combines with the FeO to form $FeO \cdot SiO_2$. At 900-1000° C, Hay McIntosh, Rait & White (8) claim that increase in SiO_2 decreases the FeO/Fe_2O_3 ratio and explains it on the basis of compound formation. Hay, White and McIntosh (16) could not find the compound $FeO \cdot SiO_2$ but confirmed the existence of the autectic of Bowen and Schairer, at $FeO-2SiO_2 \cdot FeO$. They estimated the activity of FeO in several silicon slags by the rate at which they decarburized a carbon steel at 1100° C. They agree with Korber that above 1660° C, all the FeO is free - none combined with SiO_2.

Crook (18) found that he got a somewhat different effect when he melted his oxides in a silica crucible and an iron one. He believes, however, that $2FeO \cdot SiO_2$ is the most stable compound. All of his slags contained magnetite when the FeO content was in excess of this compound. There was also some metalic iron in the melts. These observations have been compiled in Table 2.

TABLE 2

Compound	Reference	Remarks
$FeO \cdot SiO_2$	7	Evidence of combination based on ease of reduction.
	8	Change of FeO/Fe_2O_3 ratio as evidence of the existence.
$2FeO \cdot SiO_2$	16,17	Estimate that the compound is completely dissociated at 1660°C.
	18	Believe to be most stable compound.

The System $CaO-SiO_2$

This binary system has been investigated by a number of workers. The best of these (19,20,21,22) have been compiled to get the constitutional diagram given in Fig. 4.

Anderson (23) reported on the optical properties of $3CaO \cdot SiO_2$ in large masses of slags which cooled slowly. Crystalizes in trigonal system. Hay, McIntosh, Rait & White (8) have made viscosity measurements. They show no evidence of $CaO \cdot SiO_2$ existing in the liquid. Hartmann (24) also found no relationship between viscosity and basicity.

The System $CaO-Fe-Fe_2O_3$

Hay and White (9) have claimed that the lime-oxides should be represented as a ternary, $CaO-Fe-Fe_2O_3$. On the basis of this diagram they have explained several anomalies of other investigators. The ternary is reproduced in Fig. 5.

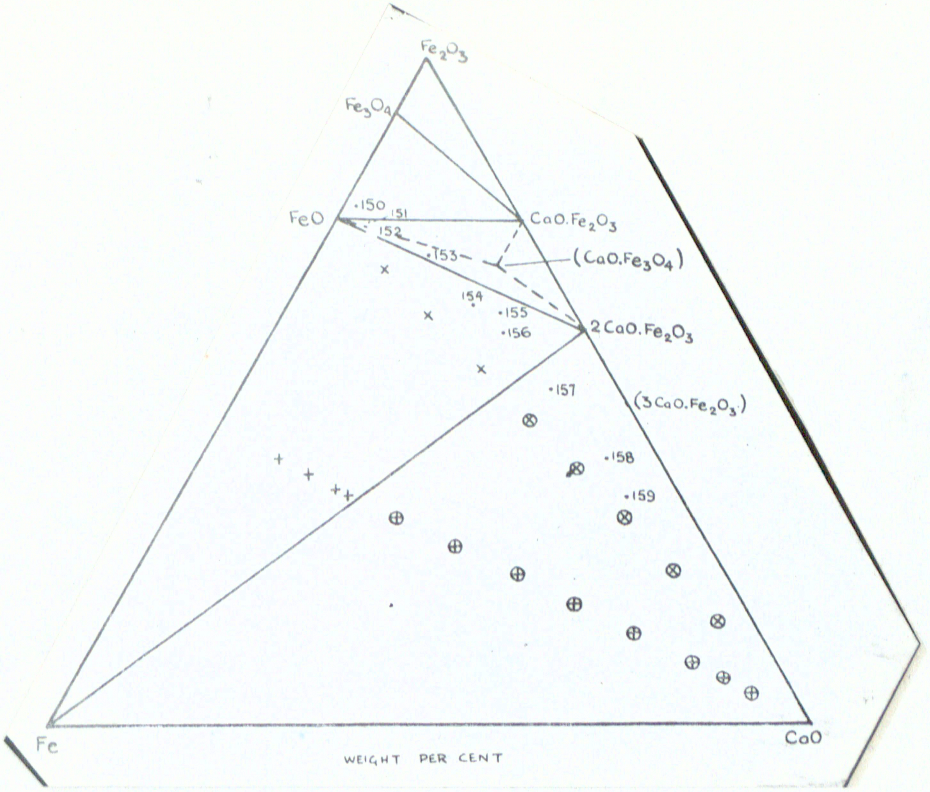


Fig. 5. The Ternary System
CaO-Fe-Fe_2O_3 (9)

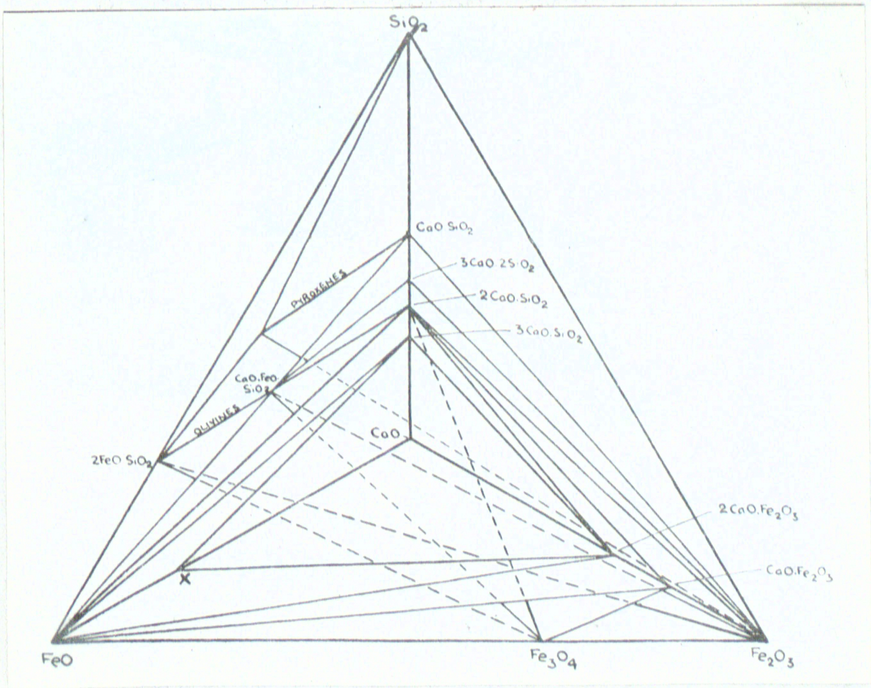


Fig. 6. The Quaternary System
CaO-FeO-Fe_2O_3-SiO_2 (9)

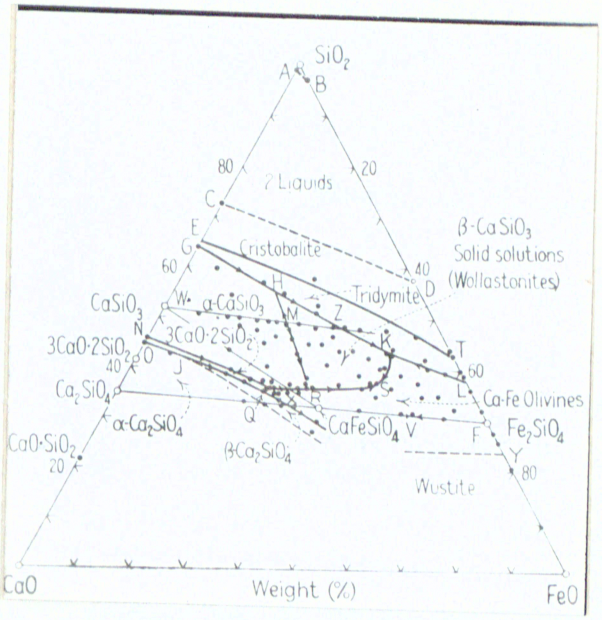


Fig. 7. Equilibrium diagram of part of the System CaO-FeO-SiO$_2$, showing fields of stability of crystaline phases in contact with liquid (Small amount of Fe$_2$O$_3$ in all liquids) (25)

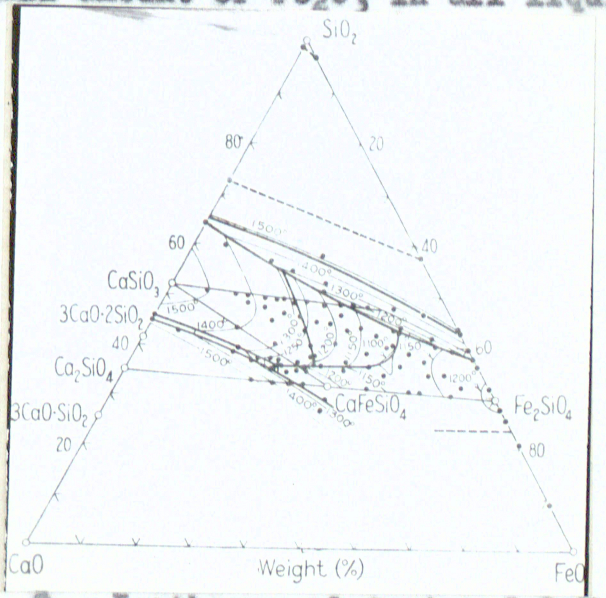


Fig. 8. Isotherms of System CaO-FeO-SiO$_2$ (25)

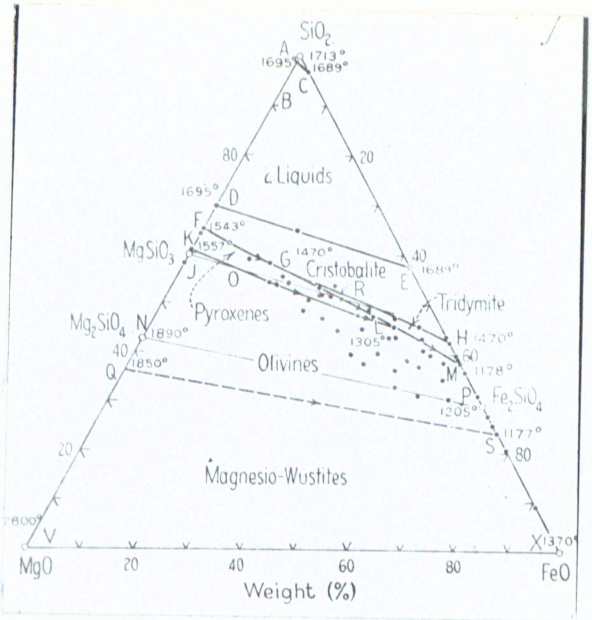


Fig. 9. Equilibrium diagram of system MgO-FeO-SiO_2 showing fields of stability of crystaline phases in contact with liquid (small amount of Fe_2O_3 in all liquids) (28)

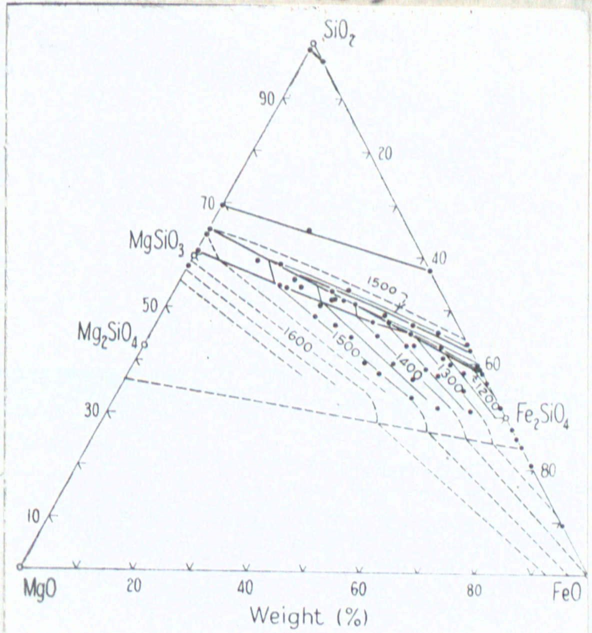


Fig. 10. Isotherms of the system CaO-FeO-SiO_2 (28)

The System $CaO-Fe_2O_3-FeO-SiO_2$

Fig. 6 gives the quaternary diagram of $CaO-Fe_2O_3-FeO-SiO_2$ from Hay and White (9). They observed the decrepitation of ortho silicate ($2CaO \cdot SiO_2$) at 674° C. because of a volume change. Negresco and Crook (74) have also investigated this system and identified a number of the complex lime-iron-silicate, etc., in the solidified melts. They claim that Fe_2O_3 is acidic, but weaker than silica, and CaO will displace FeO.

They claim that a simple relationship holds for the slags studied. That the per cent Fe_2O_3 in a slag may be calculated to ± 1.19 per cent Fe_2O_3 by the relationship,

$$Fe_2O_3 = 1/2\ (4FeO - SiO_2)$$

This relationship is independent of the CaO content.

The System $CaO-SiO_2-FeO$

The outstanding work on this system has been done by Bowen, Schairer, and Posnjak (25). Their work has been confirmed by Morey (26) and Sitz (27).

The diagrams of Bowen, Schairer, and Posnjak for the ternary system are reproduced in Figs. 7 and 8.

The System $MgO-SiO_2-FeO$

This work has also been done by Bowen and Schairer (28), and is reproduced in Figs. 9 and 10 to show the differences and similarities between the $MgO-SiO_2-FeO$ system and the $CaO-SiO_2-FeO$ system.

By far the most exact work which has been done to date on the molecular constitutions of slags above their melting points was done by J. White (29). He has investigated the $FeO-CaO-SiO_2$ slags systematically. The method he used was a weight loss method. He suspended a platinum crucible from the arm of a sensitive assay balance into his high temperature furnace. The composition of the gas was adjusted and equilibrium was followed by weight changes in the oxides in the crucible.

The reactions studied and the equilibrium constants determined are given in Table III.

It is well to note that k_7 and k_8 of his work are apparently more or less empirically arrived at. He is not specific as to how they are calculated, although presumably they are calculated from the oxide equilibrium measured in the earlier part of the study. Also k_9 and k_{10} are calculated from Korber's data, and parts at least of this have been shown to be in error.

TABLE III

SUMMARY OF RESULTS OBTAINED BY J. WHITE (29)

Reaction	Equilibrium Constant	Constant at 1592° C.	F at 1592° C.	Temperature Dependence
$Fe_2O_3 \rightleftarrows 2FeO + 1/2\ O_2$	$k_1 = (FeO)^2\sqrt{P}/(Fe_2O_3)$	.3845	3543	$\log k_1 = -14490/T + 7.357$
$Fe_3O_4 \rightleftarrows FeO + Fe_2O_3$	$k_2 = (FeO)(Fe_2O_3)/(Fe_3O_4)$	.2387	5309	$\log k_2 = -926/T - .128$
$CaO\cdot Fe_2O_3 \rightleftarrows CaO + Fe_2O_3$	$k_3 = (CaO)(Fe_2O_3)/(CaO\cdot Fe_2O_3)$	.0422	11730	$\log k_3 = 2489/T - 2.721$
$2(CaO\cdot Fe_2O_3) \rightleftarrows 2CaO\cdot Fe_2O_3 + Fe_2O_3$	$k_4 = (2CaO\cdot Fe_2O_3)(Fe_2O_3)/(2CaO\cdot Fe_2O_3)^2$	.1417	7243	$\log k_4 = -6044/T + 2.367$
$FeO\cdot SiO_2 \rightleftarrows FeO + SiO_2$	$k_5 = (FeO)(SiO_2)/(FeO\cdot SiO_2)$	.232	5415	$\log k_5$ = data erratic
$2FeO\cdot SiO_2 \rightleftarrows 2FeO + SiO_2$	$k_6 = (FeO)^2\ (SiO_2)/(2FeO\cdot SiO_2)$	1.180	-614	$\log k_6$ = very nearly completely dissociated.
$(CaO\cdot SiO_2) \rightleftarrows CaO + SiO_2$	$k_7 = (CaO)(SiO_2)/(CaO\cdot SiO_2)$	.020	14500	$\log k_7$ = no temperature data.
$2(CaO\cdot SiO_2) \rightleftarrows 2CaO\cdot SiO_2 + SiO_2$	$k_8 = (2CaO\cdot SiO_2)(SiO_2)/(CaO\cdot SiO_2)^2$	.10	853	$\log k_8$ = " " "
$MnO + SiO_2 \rightleftarrows MnO\cdot SiO_2$	$k_9 = (MnO)(SiO_2)/(MnO\cdot SiO_2)$	.0205	14400	Calculated using Korber and Oelsen's data for K_{Mn}.
$2MnO + SiO_2 \rightleftarrows 2MnO\cdot SiO_2$	$k_{10} = (MnO)^2\ (SiO_2)/(2MnO\cdot SiO_2)$	Almost completely dissociated.		(Calculated using Korber and Oelsen data)

B. Slag-metal Equilibria Studies

Steel makers have long realized the importance of oxygen in determining the quality of steel. As early as 1878, Krebs (30) analyzed Bessemer steel for oxygen, reporting .165, .162, .185, .171% oxygen. A sample of a burned rail gave .76% oxygen. This directed attention towards oxygen, and several methods of determination were developed. Tucker (31) melted his samples on charcoal. Then from a calculation of the loss in weight, after correcting for carbon pick-up, he arrived at an analysis of 2.88% FeO in burned steel. 3.09% FeO was found in blown Bessemer metal. Troilius (32) used a chlorine solution method, determining SiO_2 and FeO on the weighed residue. Ledebur (33, 34) used the chlorine method (volatilization of the iron as $FeCl_3$) and the hydrogen reduction method (weighed oxygen as H_2O) to determine oxygen. The first use of the so-called vacuum method (in graphite crucibles) was made by Oberhoffer and Hessenbruch (35). A critical study of the various methods for oxygen analysis has been made by Thompson, Vacher and Bright (36). They compared vacuum fusion, hydrogen reduction, chlorine volatilization, iodine methods (wet solution), electrolytic method, nitric acid, and hydrochloric acid solutions and concluded that the vacuum fusion method was the most reliable. This method has been used exclusively in this study.

The solubility of oxygen in liquid steel has been observed by a number of workers. Le Chatlier (37) reported the solubility of .244% oxygen at 1600° C. Austin (38) during an investigation of the effect of oxygen on the physical properties of iron reported a maximum value of .288% oxygen. No temperatures were recorded. Pickard (39) held iron under an oxidizing slag for many hours and got .092 oxygen. However, he had .022 carbon in the metal which would limit the solubility. He gave .405% FeO as the solubility in liquid steel. No temperatures were given. The Bureau of Standards (40) gives an oxygen content of .21% to iron melted in quiet air. Tritton and Hanson (41) determined the constitutional diagram of iron and oxygen. They gave a value of .21% oxygen at 1545°C. (platinum couple), and a solid solubility of .05%. They also reported the melting point of FeO at 1370°C. The melting point of iron saturated with FeO was reported as 1524°C. and that with .08 oxygen at 1535°C.

Burgess (42) reports .26% oxygen as the solubility of oxygen in liquid iron at 1600°C. Herty and co-worker (43) made the first large laboratory investigation to determine the solubility of oxygen in molten iron. They melted their charge in magnesia crucible, keeping liquid slag on the surface. The melts were sampled in steel spoons and poured into a steel mold. There was no difference in the oxygen analyses taken with the power on, and with the power off, indicating no entrapment of iron oxide droplets due to the stirring of the melt. The metal analyses varied somewhat as to carbon, from .003 to .011, which may have influenced their oxygen values. Since the samples were saturated with oxygen, pouring through air into a mold could not increase the dissolved oxygen, but there could easily be entrapped iron oxide due to film formation on the surface of the metal. All temperatures were taken with an optical pyrometer. The emissivity of the metal was determined by using a pig iron melt, and sighting alternately on the surface of the bath and into a tube immersed in the bath. An error may be involved here, since the emissivity of liquid iron is reported as .35, and that of pig iron as .45, (44).

They allowed fifteen minutes for the attainment of equilibrium. The FeO content of the slags was calculated as FeO + 1.35 Fe_2O_3, which assumes the reduction of Fe_2O_3 by the iron to FeO at the interface, and may or may not be justified. The Fe_2O_3 ran from 17% in oxide slags to 28% in lime bearing slags. They expressed the opinion that the lime compounds were completely dissociated in the slag and that the oxygen dissolved in the liquid iron was directly proportional to the mol fraction FeO in the slag.

Herty and Gaines (45) continued this work. They reported the following data for pure CaO - FeO and SiO_2 - FeO slags. These slags presumably had the same FeO content.

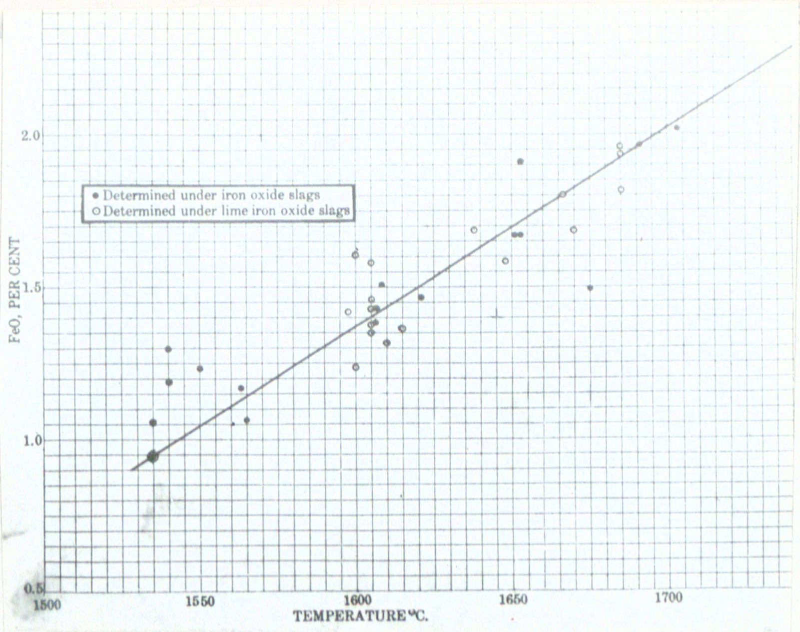


Fig. 11. Effect of temperature on the solubility of FeO in iron (45)

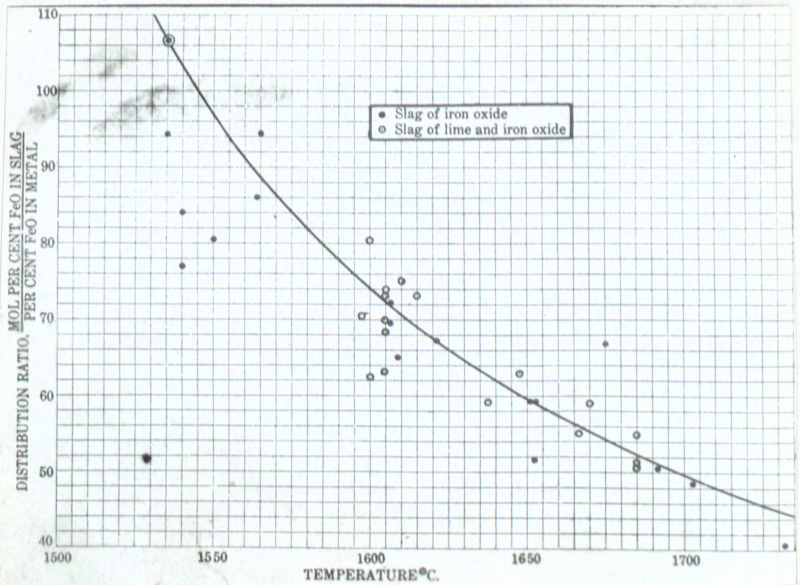


Fig. 12. Effect of temperature on the distribution ratio of FeO between slag and metal (45)

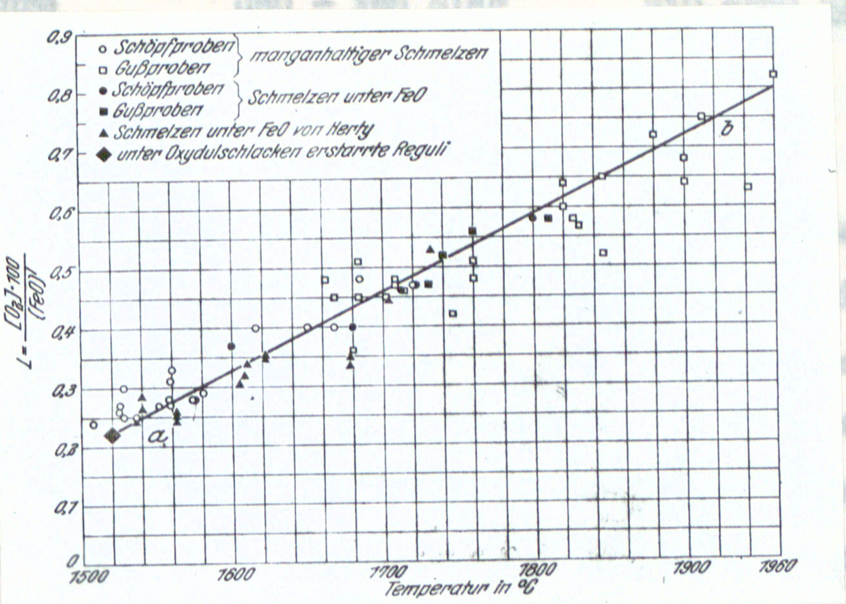


Fig. 13. Oxygen solubility in iron under oxidizing slags (46)

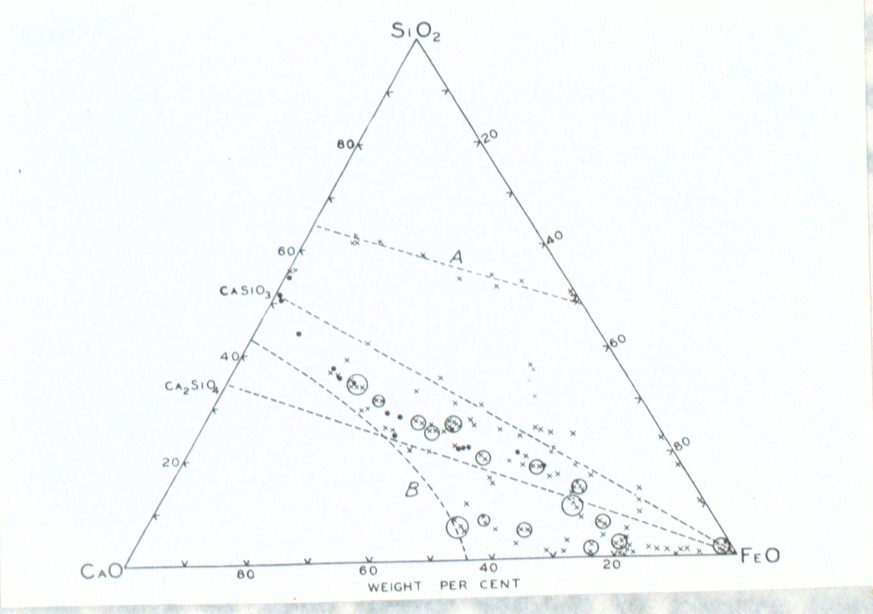


Fig. 14. The experimental ranges covered by Fetters and Chipman (72)

Temperature	CaO - FeO Slag	SiO_2-FeO Slag
1540°C.	.118	.056
1565°C.	.136	.102

Their results are shown in Figs. 11 and 12.

Korber and Oelsen (46) have also carried out an extensive investigation into the solubility of FeO in liquid iron. Their melts were made in magnesia crucibles. The slag was added in sufficient amount to keep a small bare spot in the center of the melt. Optical temperatures were measured on both the bright edge of the slag, and the bare surface of the metal. An emissivity constant of .40 was used for the metal and .65 for the slag. The slag samples were dipped out in an iron spoon, or, at higher temperatures, poured into a small copper mold. Here again entrapment of oxide film might account for the apparently high results. The distribution of FeO between the slag and metal was calculated to 100% FeO in the slag. A good many of his slags had 95% FeO. His data can be expressed by the equation:

$$\log \% \text{Ox} = \frac{-5883}{T} + 2.615$$

and is reproduced along with Herty's data in Fig. 13.

Chipman and Fetters (47) have made an investigation of the solubility of oxygen in liquid iron under oxidizing slags. They melted a 70# heat of iron under vacuum to remove carbon. Then they saturated the metal with FeO. The slag was kept molten by means of a graphite heater of special design. About 30 minutes was allowed for equilibrium. The temperature was measured by means of a tungsten-molybdenum thermocouple encased in a magnesia protection tube. Slag and metal samples were then taken. Their results were distinctly different from those obtained by Korber, Oelsen and Herty. According to them, the solubility of oxygen in liquid iron can be expressed by the equation

$$\log \% \ O = -4860/T + 1.935$$

Table 4 is a compilation of the work done to date on the solubility of FeO in liquid iron under oxidizing slags.

Jette, Ellis and Chipman (71) took slag samples directly from the open hearth furnace. They then placed these slags in an experimental furnace and attempted to determine the actual equilibria. The equilibria were so far displaced from that found in the open hearth furnace that the final analysis obtained in the slag bore little resemblance to the starting analysis. The results from these experiments are reported in their series A experiments (73). They used a graphite heater over the slag, but the temperature of the slag was so far below the actual temperature of the metal that temperatures were later calculated from a manganese constant (K_2), determined by another series of heats, Series B. They used a basicity measure

$$R = \frac{(CaO)}{2\ (SiO_2) + 3\ (P_2O_5)} = \frac{B}{A}$$

$K_1 = \frac{(MnO)}{(FeO)\ Mn}$ was displaced by varying R. Empirically

TABLE IV

Reference	Temp. Meas.	Crucible Material	Atmosphere	Power	Analytic Method	Sampling	Oxygen Analyses 1550°C.	1600°C.	Slags	Size of Heat
Herty & Co-workers (43)	Optical & Pt. Couple	MgO	Air	Ind.	Ledebur	dip and pour	.254	.327	FeO FeO-CaO	50 lb.
Korber (46)	Optical	MgO	Air	Ind.	Vac. Fus.	dip and pour	.260	.330	FeO	350 g.
Herty & Gaines (45) Same as (43)	Optical	MgO Zr_2O_3	Air	Ind.	Ledebur	Pour entire heat.	.254	.327	FeO	230 g.
Tritton & Hanson (41)	Pt. Couple	MgO	Air	C.Ring Ind.	Ledebur	Heat solid. in fce.	.21 at 1545°C.	---	FeO	10 g.
Fetters & Chipman (47)	W-Mo	MgO	N_2 Air (10% H_2) (90% N_2)	Ind.	Vac.Fus.	Dip - small chill mold.	.187	.219	FeO	50 kg.
Le Chatlier								.244		

they found that if they plotted log K_1 R vs T^{-1} they got a sensibly straight line. The same results were obtained for % 0 / (FeO_T) where FeO_T = FeO + 3 Fe_2O_3.

$$K_2 = \frac{(MnO)\ \ Fe}{O\ \ \ Mn}$$

$$\log K_2 = 10\ 478T^{-1} - 4.592$$

$$\log K_1 R = 5966T^{-1} - 2.685$$

$$K_3 = \frac{O}{(FeO)_T}$$

$$\log K_3 R = -4510T^{-1} + 1.901$$

Since the R appears only in those equations in which (FeO) appears in the denominator, it is concluded that it is the change in activity of (FeO) that makes this necessary and the $R^{1/2}$ may in a sense be regarded as the activity coefficient. Several units for (FeO) were tried, for instance $(FeO)_s$, and several measures of basicity such as B = (CaO) + (MgO), but the units described above seemed to make the most sense when applied to the data. The activity coefficient $R^{1/2}$ could not be used when applied to the acid slags of Korber and Oelsen, etc.

Krings and Schackmann (78) claimed that additions of $CaO \cdot SiO_2$ did not affect the manganese constant, but that 2 $CaO \cdot SiO_2$ show an increasing value with lime. They claimed that this showed that the other silicate dissociated.

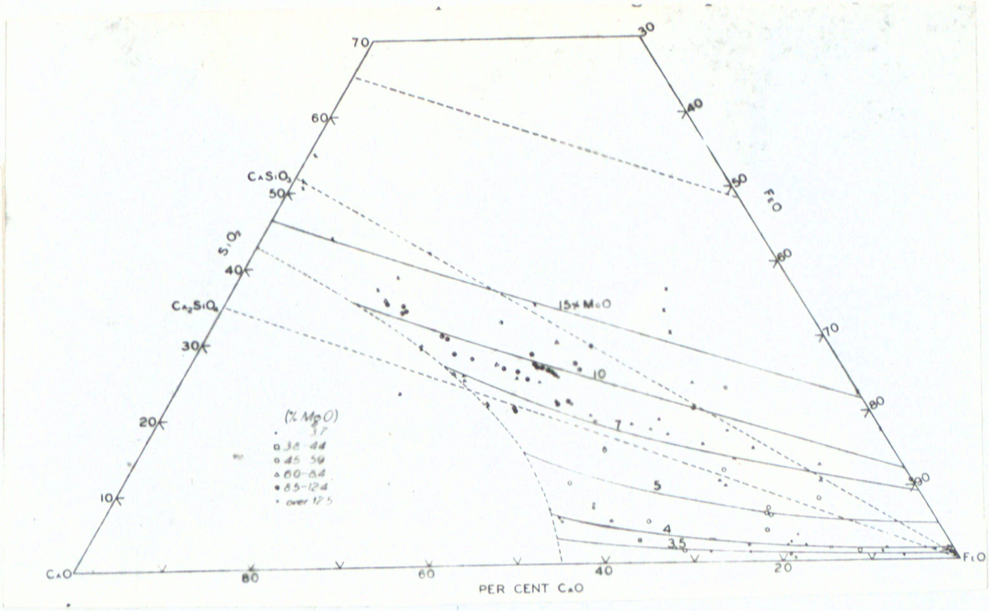


Fig. 19. Apparent solubility of MgO in slags in contact with solid magnesia at 1600° C (72)

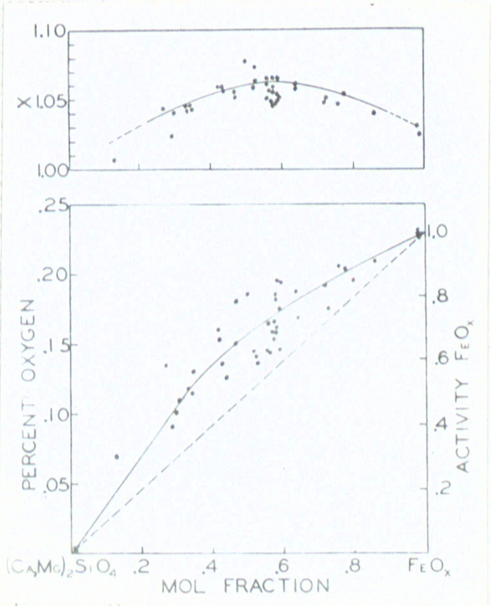


Fig. 20. Oxygen in metal as function of slag composition in system $FeO_t - Ca_2SiO_4$ (72)

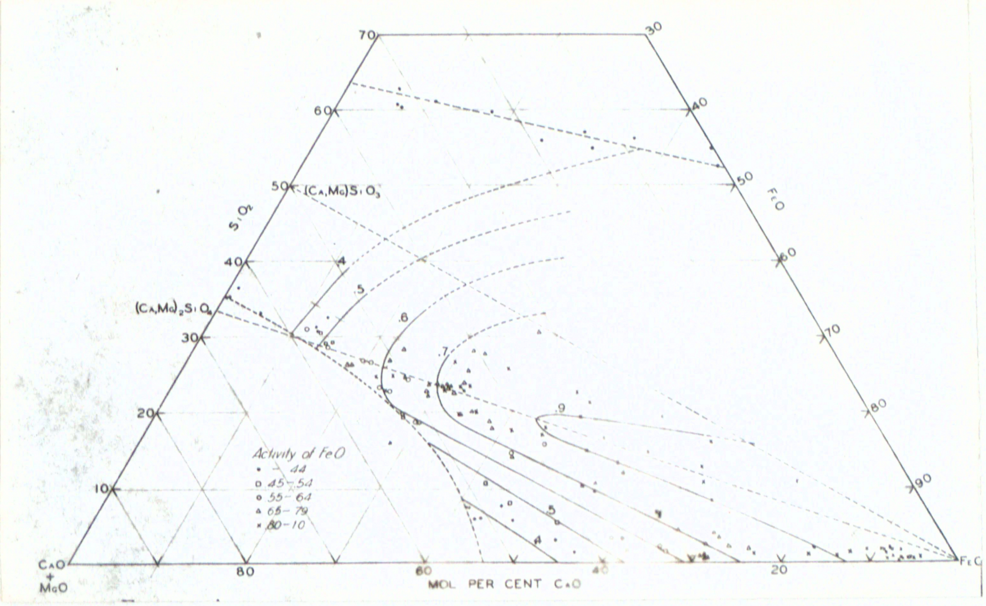


Fig. 17. Activity of iron oxide in slags plotted on a mol fraction basis (72)

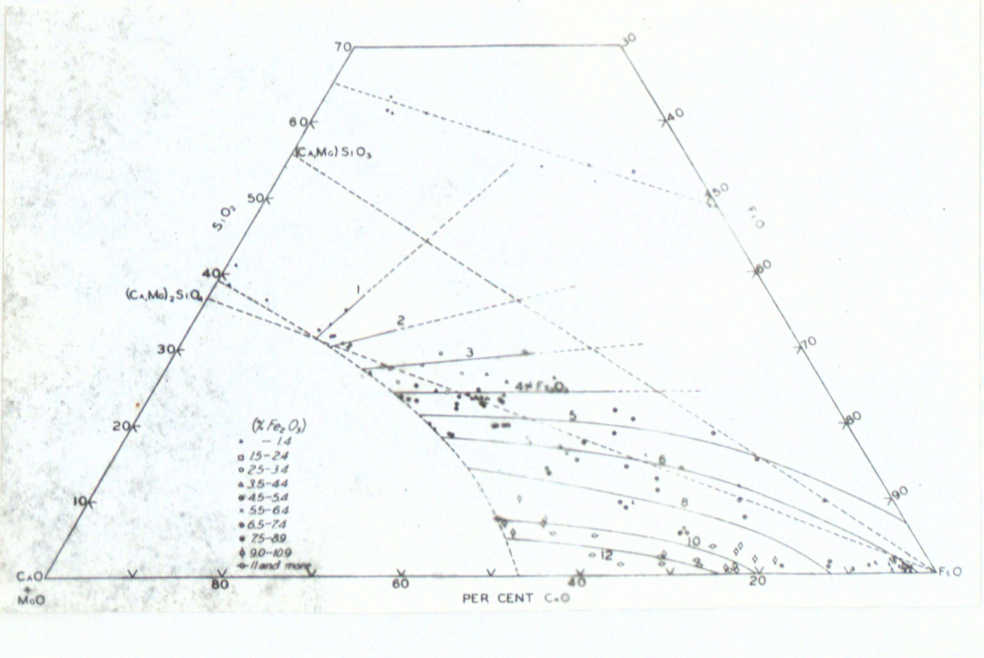


Fig. 18. Percentage Fe_2O_3 in slags in equilibrium with liquid iron at 1600° C (72)

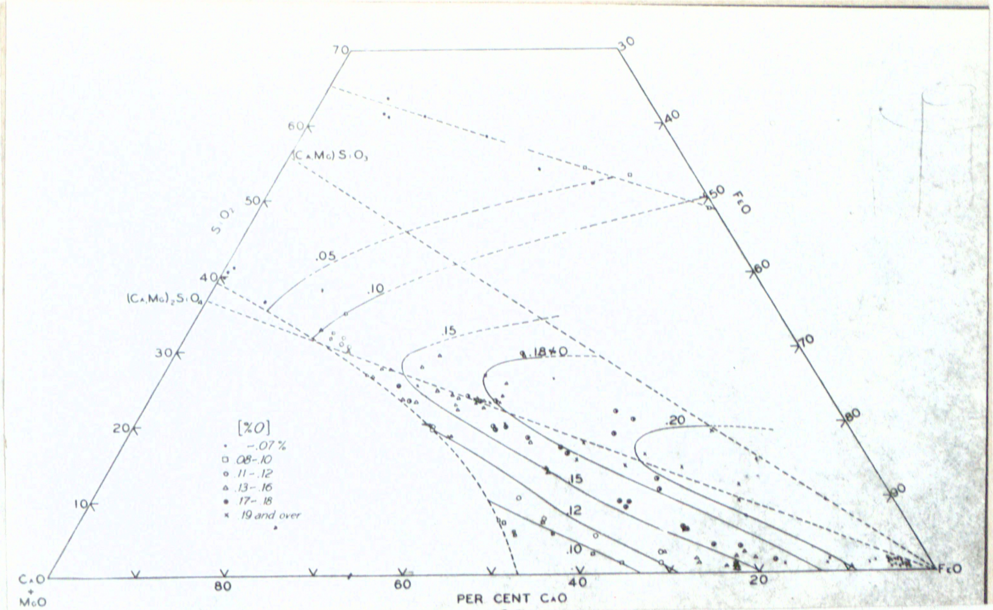


Fig. 15. Oxygen content of metal at 1600° C in equilibrium with slags of the system (CaO + MgO) - FeO - SiO_2 (72)

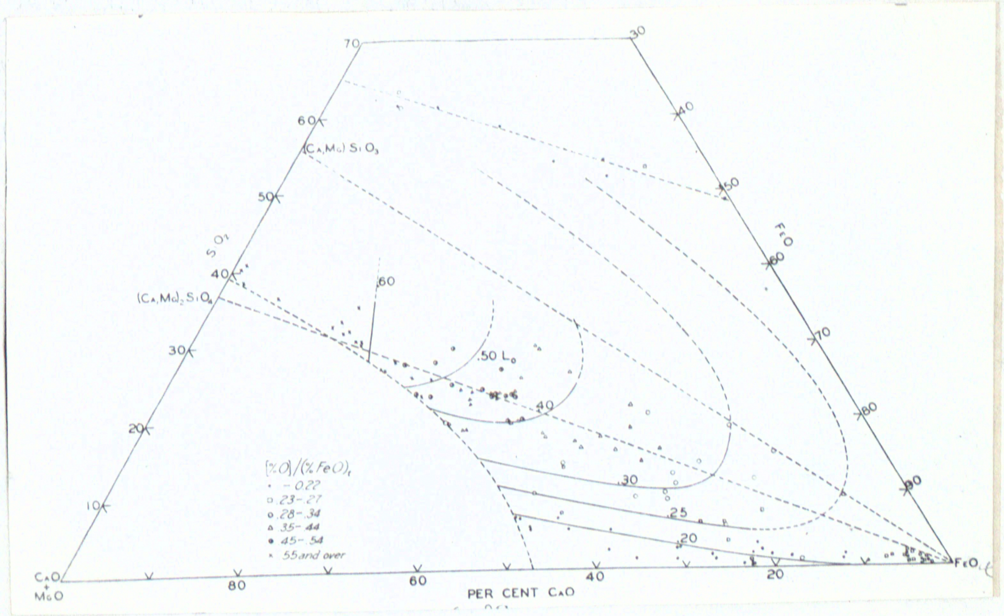


Fig. 16. Distribution ratio at 1600° C of oxygen between slag and metal L = (% O) / (% FeO) total (72)

$$K_{Mn} = \frac{(FeO)}{(MnO)} \frac{Mn}{Fe} = .0032 \pm .0005 \text{ at } 1550 - 1560°C.$$

$$\log K_{Mn} = - 7280\ T^{-1} + 1.503$$

Fetters and Chipman (72) have studied the equilibria of liquid iron and slags of the system $CaO - MgO - FeO - SiO_2$ in some detail. Their furnace was heated by induction and was the same as the one used in the Series B experiments of the last reference (71).

They allowed thirty minutes for the attainment of equilibria.

The analyses covered are shown in Fig. 14.

Fig. 15 shows the oxygen content of the metal corrected to 1600°C. in equilibrium with the various slag analyses.

Fig. 16 shows the distribution at 1600°C. of oxygen between slag and metal.

$$L_o = \%\ O\ /\ \%\ (FeO)_T$$

Fig. 17 shows the calculated values of the activity if the FeO in the slag is plotted on a mol fraction basis.

Fig. 18 shows the per cent Fe_2O_3 in slag in equilibria with liquid iron at 1600°C.

Fig. 19 shows the apparent solubility of MgO in the slags at 1600°C.

Fig. 20 shows the deviation from Raoult's law of slags in the system $2\ CaO \cdot SiO_2 - FeO$.

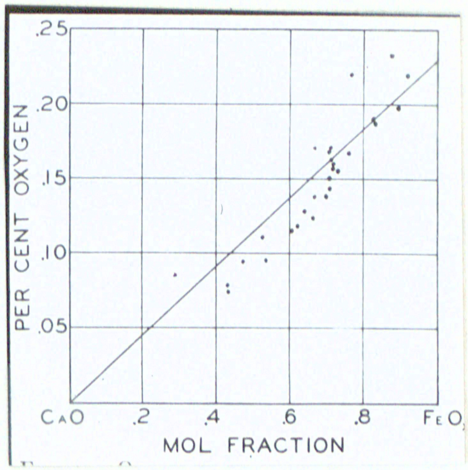


Fig. 21. Oxygen in metal vs. mol fraction FeO_t in slag system FeO-CaO (72)

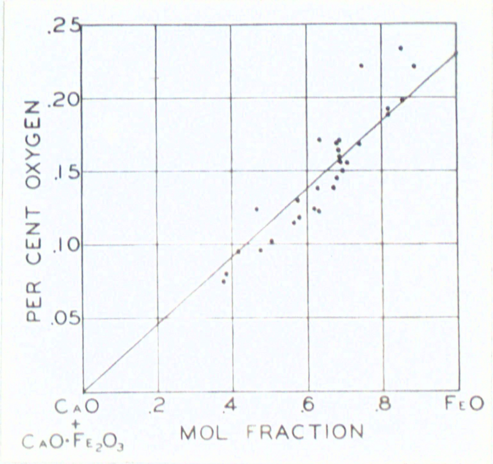


Fig. 22. Oxygen in metal vs. mol fraction FeO in slag system $FeO-CaO-CaO{:}Fe_2O_3$ (72)

Fig. 21 shows an apparent deviation in ideality in the system CaO - FeO_x.

Fig. 22 gives the oxygen in the metal versus mol fraction FeO in the slag system FeO - CaO - CaO • Fe_2O_3.

A thermodynamic study of the data is not attempted, but the authors point out that the existance of 2 CaO SiO_2 and CaO • Fe_2O_3 is indicated.

C. Open Hearth Studies on Slag-metal Equilibria

There has been a great deal of work on the study of the course of the reactions in open hearth furnaces, both basic and acid. Numerous attempts have been made to establish relationships between the components of the slags, and to apply the law of mass action to these components. These attempts have been, in general, surprisingly successful in consideration of the fact that the open hearth furnace is a method of utilizing rates of reaction rather than equilibria conditions. It would seem that towards the end of a heat, the slag and metal have approached a state which, while probably not at equilibrium, at least admits of treatment by the law of mass action to give what might be called working equilibrium constants.

The partition of FeO between the slag and metal only approaches equilibrium when the carbon is less than one tenth of one per cent, and the manganese content is less than .05. If the carbon content is above this value, it completely controls the oxygen content of the bath by the reaction.

$$[FeO] + [C] \longrightarrow [Fe] + CO\uparrow$$

The round brackets refer to slag composition, the square to metal composition.

Since a part of the heats that have been studied contain carbon and manganese above these values, no conclusion can be drawn concerning the distribution of FeO between the slag and the metal, for the pure $CaO - SiO_2 - FeO$ system.

Wilson (48) advanced the theory of "automatic viscosity". He claimed that when a slag departs from its optimum viscosity reactions take place which will bring this viscosity back to its original value. He said that MnO behaved the same as FeO in the slags, that Al_2O_3 was neutral and that FeO was acidic in nature.

Colclough (49) said that slags were formed essentially of a tetra-calcic phosphate of lime with $CaO \cdot SiO_2$, MgO and MnO along with it. The addition of acid oxides to the slag caused a reversion of phosphorus to the metal, but basic oxides did not alter the existance of this compound. He claimed that a stable compound of lime and ferric oxide exist in the slag. He later made an effort to apply the law of mass action to open hearth slags (50) while carefully stating that equilibrium is not attained. He reported a constant for Manganese as .0010 and studied the rate curves for several heats.

Schleicher (51) carefully analyzed twenty-five basic open hearth slags. He claims the CaO + MgO + MnO is a constant, and that MnO is a linear function of CaO + MgO. The formula $(CaO + MgO) = - 13/14\ MnO + 60$ fits his data. The iron content of acid slags is a linear function of $(SiO_2 + P_2O_5)$.

$$FeO\% = -.732\ (SiO_2 + P_2O_5) + 26.4$$

Tammann and Oelsen (52) investigated the slag-metal relationship in an open hearth furnace. When the mol ratio

$CaO : SiO_2$ exceeds two, the lime and silica are combined and the other oxides are merely in solution. For ratios less than two, part of the iron and manganese oxides combine with the silica. The ortho silicate ($2\ CaO \cdot SiO_2$) is stable or slightly dissociated in steel making practice. The ratio $FeO : Fe_2O_3$ decreases with increasing basicity and decreasing temperature. This ratio varies in the open hearth with the depth of the slag layer from 2.4 on the surface to 3.2 just over the metal. They reported that $K_{Mn} = \frac{(MnO)}{(FeO)} \frac{100}{Mn}$ has a slight dependence on temperature.

Bach (53) followed the variation of the iron and manganese content of the slag with basicity $CaO : SiO_2$. He reports that the iron content increases with basicity, and he shows the course of several heats with varying basicity. He defines CaO/SiO_2

1.24 - 1.53 - acid
1.55 - 1.81 - medium
1.82 - 2.42 - basic
2.91 - 3.43 - highly basic

He correlated the appearance of a small cake of slag with basicity.

Richarme (54) during a study of dephosphorization defined acidity as:

$$A = \frac{\frac{SiO_2}{1} + \frac{P_2O_5}{1.77} + \frac{Al_2O_3}{1.69} + \frac{Fe_2O_3}{4}}{\frac{SiO_2}{1} + \frac{P_2O_5}{1.77} + \frac{Al_2O_3}{1.69} + \frac{Fe_2O_3}{4} + \frac{CaO}{1} + \frac{MgO}{.71} + \frac{MnO}{1.27} + \frac{FeO}{1.28}}$$

This formula relates the acidities and basicities to silica and lime respectively. He found that A had the following effect on dephosphorization:

$A > .32$ - no dephosphorization.

$.32 > A > .26$ - dephosphorized in oxidizing atmosphere.

$.26 > A > .21$ - dephosphorization in neutral atmosphere.

$.21 > A$ - dephosphorization in a reducing atmosphere.

Salmang and Kaltenbach (55) investigated $FeO - SiO_2$ and $CaO - FeO - SiO_2$ slags in relation to the state of oxidation of the iron at 1230°C., 1320°C., 1410°C. They observed that CaO favors the formation of Fe_2O_3 and that increasing temperature favors the formation of FeO. Al_2O_3 favors the formation of FeO in the presence of silica. An increase in the lime silica ratio decreases the $FeO : Fe_2O_3$ ratio, and an increase in silica increases the ratio.

Herty, Cristopher, Freeman and Sanderson (13) made a series of investigations on open hearth slags. They found that the available FeO decreases with basicity, on the basis that the available FeO in the metal is proportional to the FeO in the slag. They also found that $FeO : Fe_2O_3$ ratio decreases with basicity and concluded that the CaO was present as $2\,CaO \cdot Fe_2O_3$. At zero basicity they found that the Fe_2O_3/FeO ratio was 0.2, and any Fe_2O_3 above this was combined with CaO.

Bardenheuer and Thanheiser (56) followed the course of eight open hearth heats. They claim that the controlling reaction is the carbon-oxygen reaction, and the FeO in the slag begins to exert some control at .2% C. They found that high lime tended to fix the Fe_2O_3 content.

Schenck and Riess (57) investigated the slag-metal relationships in a 20 ton basic open hearth furnace. They claimed that MnO was present as free MnO and as a silicate, along with free SiO_2; that the compounds $FeO \cdot SiO_2$ and $CaO \cdot SiO_2$ existed in the slag. From their data they calculated "equilibrium" constants.

$$2\ FeO \cdot SiO_2 \qquad \log D_1 = \frac{-11230}{T} + 7.76$$

$$2\ MnO \cdot SiO_2 \qquad \log D_2 = \frac{-18880}{T} + 10.77$$

$$CaO \cdot SiO_2 \qquad \log D_3 = \frac{-3186}{T} + 2.61$$

$$3\ CaO \cdot Fe_2O_3 \qquad \log D_4 = \frac{-39684}{T} + 27.20$$

They claimed that the FeO existed as free FeO, a silicate and combined with lime, and that the CaO existed as free CaO, a phosphate, silicate and combined with FeO.

Schenck and Bruggenmann (58) studied ten acid open hearth heats. They determined the equilibria existing between manganese and silicon in the metal.

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

$$\log K_{Si} = \frac{-11106}{T} + 4.495$$

The distribution ratio of FeO in the slag to FeO in the metal was given as .0134 at 1577°C. Optical temperatures were taken on a spoon sample taken from the furnace and a 25°C. correction added for cooling.

Husson (59) used the Richarme acidity measure to study the open hearth process. He assumed that the FeO existed as $FeO \cdot SiO_2$. Then with x mols of FeO, the excess FeO would be (x - 1) mols and $w = \frac{x - 1}{x}$ would be the fraction of free FeO. Substituting this into the acidity of Richarme, he got

$$A = \frac{60}{60 + 56x}$$

and eliminating x, he got

$$w = \frac{1 - 1.936\,A}{1 - A}$$

$$\text{Free FeO} = f = FeO_w = FeO \cdot \frac{1 - 1.936\,A}{1 - A}$$

Using the ternary diagram he calculated iso-free FeO lines.

Korber (60) studied the effect of additions on the reactions between liquid iron, iron and manganese etc. He studied the effect of carbon on the manganese silicon equilibrium. Also the effect of temperature, phosphorous, and sulfur. Carbon, phosphorous and temperature all have the same effect as to direction in that increasing any one of these shifts the equilibrium. This is shown in Fig. 23.

Ivanov and Romodin (61) studied the oxidizing power of basic open hearth slags. They used the rate of carbon drop and (MnO)/[Mn] as criteria for oxidizing power. The oxidizing power increased up to a certain basicity, 3.1, along with the FeO and Fe_2O_3. Over 3.2 to 3.3 basicity the oxidizing power decreased with basicity. He explained this by the increase in viscosity. His maximum rate was .30%C/hr. on a 70 ton open hearth. His slag analyses varied widely with MgO and Al_2O_3.

Chipman and Fetters (62) have made a statistical analysis open hearth data from a number of plants and for a number of carbon contents. They define a "corrected" lime-silica ratio as

$$R = \frac{(CaO)}{(SiO_2) + .634\ (P_2O_5)}$$

They segregated their data into groups of carbon content and studied the manganese constant and various distribution ratios. They established the following relationships:

Increase with carbon

$[C]\ [FeO]$, $[Mn]$, $(FeO)/[FeO]$, $(S)/[S]$ at higher carbons only.

Decrease with carbon

$[FeO]$, (FeO), (Fe_2O_3)

Independent of carbon

$(Fe_2O_3)/(FeO)$, $(MnO)/[Mn]$

At constant carbon an increase in R was accompanied by an increase in (FeO), (Fe_2O_3), $(Fe_2O_3)/(FeO)$, $(FeO)/[FeO]$ $(S)/[S]$.

D. Thermodynamic Studies - No Experimental Results

Several efforts have been made to apply physico-chemical laws to the various conditions and reactions prevailing in an open hearth furnace. These attempts have been seriously handicapped by a lack of precise data, a lack which is not surprising when the experimental difficulties are considered. In spite of these handicaps, a number of attempts have been made by means of assumptions to extend our knowledge of slag-metal reactions.

Styri (63) made a number of calculations based on the fragmentary data then (1923) available on the theoretical equilibrium in reversible reactions in steel making.

McCance (64) summarized the data which had been collected up to the time he published his article.

Hadfield (65), as chairman of a symposium on physical chemistry of steel making, summarized the essential problems of the steel industry and suggested several methods of attack.

Sauerwald (66) developed the possibility of the use of mass action equations in steel making reactions quite elaborately. He suggested that a rotating liquid crucible could be used to study slag-metal reactions.

Sauerwald and Hummitsch (67) compiled the available data on molten steel and iron into an excellent table. He covered Fe - O, Fe - FeO - CaO, Fe - O - C, Fe - Si - O, Fe - Mn - O, Phosphorous and Sulfur.

Chipman and Murphy (68) reviewed the available data and by means of a number of assumptions and approximations calculated new equations.

Ulich, Schwartz and Cruse (69) tabulated the heats of reaction for a number of metallurgical reactions.

The most complete compilation of data has been made by K. K. Kelly (70) in the Bureau of Mines.

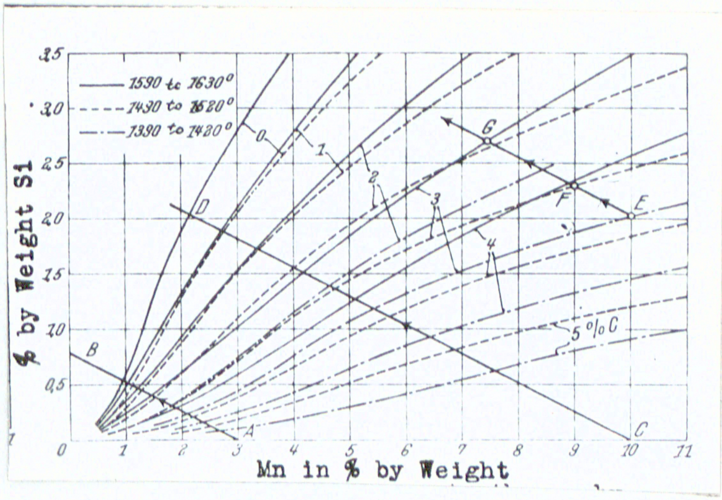


Fig. 23. Shifting of silicon isotherms by carbon for three temperatures.

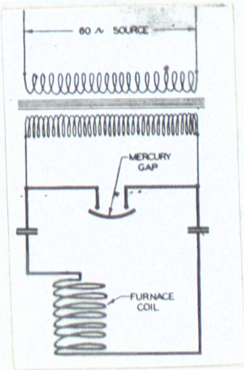


Fig. 24. Simplified diagram of converter circuit.

E. Temperature Measurement

There are two methods available for measuring the temperatures of liquid iron and slag. One of these is the optical method, and is limited by our knowledge of the emissivities of the surface of the slag or metal. The other method is a thermoelectric method and is limited by the resistance of the refractory protection tubes to the extremely corrosive action of the slag.

The optical pyrometer is suitable only under ideal conditions, i.e. known emissivities, no smoke or other light absorbing medium, etc. These conditions are rarely obtained in practice. Tables of emissivities are available for various materials in the open (44) but these emissivities may vary with the depth to which the furnace crucible is filled (79).

A color pyrometer called "Bioptix" has recently appeared in use in Germany. It was originated and developed by G. Naeser (80, 81, 82). It is designed to measure the ratio of the intensities of two selected colors. This ratio is a function of temperature and is independent of emissivities.

Only a few of the elements are suitable for making a thermocouple which can be used in the range 1500 - 1750°C. The first to be used generally for high temperature measurement was the Le Chatlier couple of platinum and platinum-rhodium. This couple is satisfactory but is quite expensive. Since the rhodium has an appreciable vapor pressure at these temperatures, and the thermoelements are quite susceptible to contamination, it must be recalibrated frequently.

Fitterer (83) has used carbon and silicon carbide as thermoelements and claims that these are usable up to at least 1800°C. with one per cent error. His claims have been questioned by other workers.

Osan and Schroeder (44) have used tungsten and molybdenum for the thermoelements. They calibrated the couple by comparison with platinum-platinum-rhodium thermocouple and an optical pyrometer. Each lot of wire was uniform in itself, but different lots varied. They exposed the couple to various gases without effect. They estimated the limits of accuracy to plus or minus 5°C.

Lieber (84) measured open hearth temperatures using a tungsten-molybdenum thermocouple with the cold end water cooled.

Schofield and Grace (85) describe the use of a platinum-platinum-rhodium thermocouple sheathed in a thin walled fused silica tube. The temperature was read within a few seconds of the time of immersion and the couple withdrawn intact.

The optical method was unsuitable for this work; Fitterer's thermocouple could not be used because of contamination with carbon; therefore tungsten-molybdenum thermocouples and platinum-platinum-rhodium thermocouples were used. The latter was used only occasionally as a check.

A. General Considerations

In the selection of a furnace for the study of slag-metal equilibria, several points must be considered:

(a) The atmosphere must be controllable.

(b) The slag and metal must be at the same temperature.

(c) The temperature must be maintained at a constant setting over a period of time.

(d) The metal must be stirred in order that equilibrium may be obtained rapidly.

These conditions are best satisfied by the induction furnace. The power supply is essentially a spark-fed oscillator, Fig. 24, one part of the inductance of which comprises the coil of the furnace, the charge being heated by the induced eddy currents. The unit used in these experiments as a power supply is the Ajax-Northup 30 KVA converter which is amply described elsewhere (77).

This type of furnace provides a solution to all the above conditions but (b). The slag is not affected by the high frequency field, and so must be heated by other means. There are several possible solutions to this problem, and they will be discussed in greater detail later.

B. Furnace

Three types of furnaces were tried in this study. Of the first two, brief mention will be made only, the third

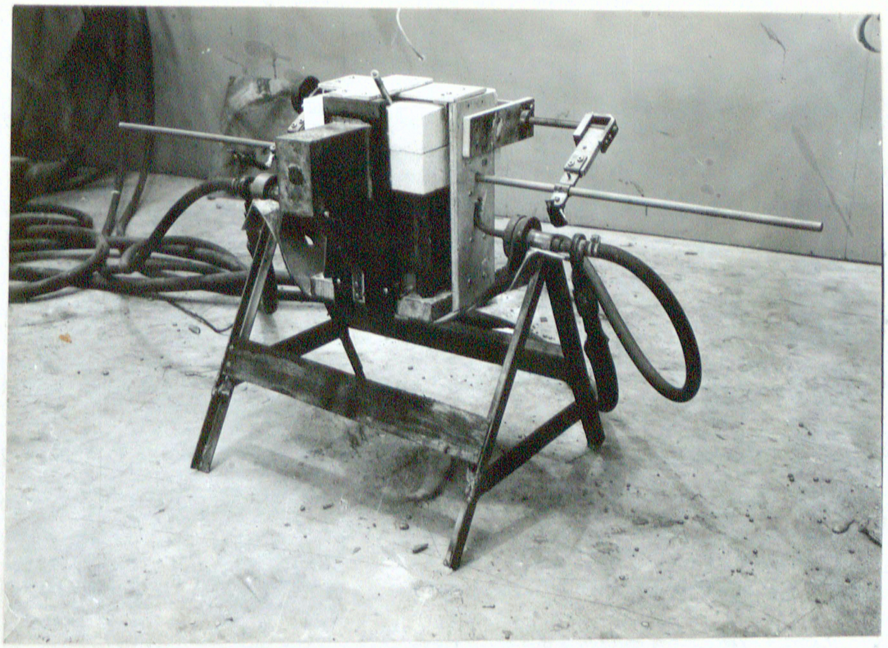


Fig. 25. Arc-induction furnace

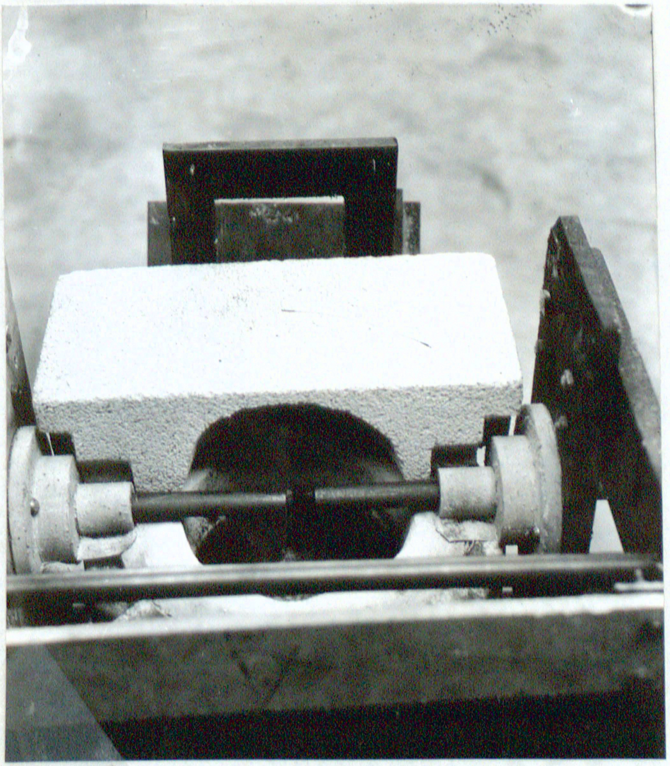


Fig. 26. Furnace chamber of arc-induction furnace with electrodes in position.

being the one which was finally found suitable and adopted.

The first furnace was constructed by Drs. Jette and Chipman (71) in their work on the slag-metal equilibrium problem, and was used in their "Series A" experiments recently reported. It was subsequently discarded because of its limitations as to sampling, since it was necessary to use the whole heat as the sample. Also, with the carbon slag heater used, there was about a 200-300° differential between temperature of the metal and that of the upper surface of the slag.

The second furnace was constructed using the same coil as the first and the same pouring arrangement. (See Fig. 25 and 26) In this furnace the metal charge was heated by induction, and the slag was kept hot by means of an alternating current arc which was struck above the bath. The arc and bath were covered by a dome roof made of Babcock & Wilcox K-30 insulating fire brick, cemented on the outside surface to make the rather porous K-30 reasonably gas-tight. Pure, dry nitrogen was fed into the furnace chamber through a silica tube in a hole in the roof. After the metal was molten, considerable quantity of slag was added through another hole in the roof, and the arc was started. Slag had to be added from time to time to keep the bath covered,

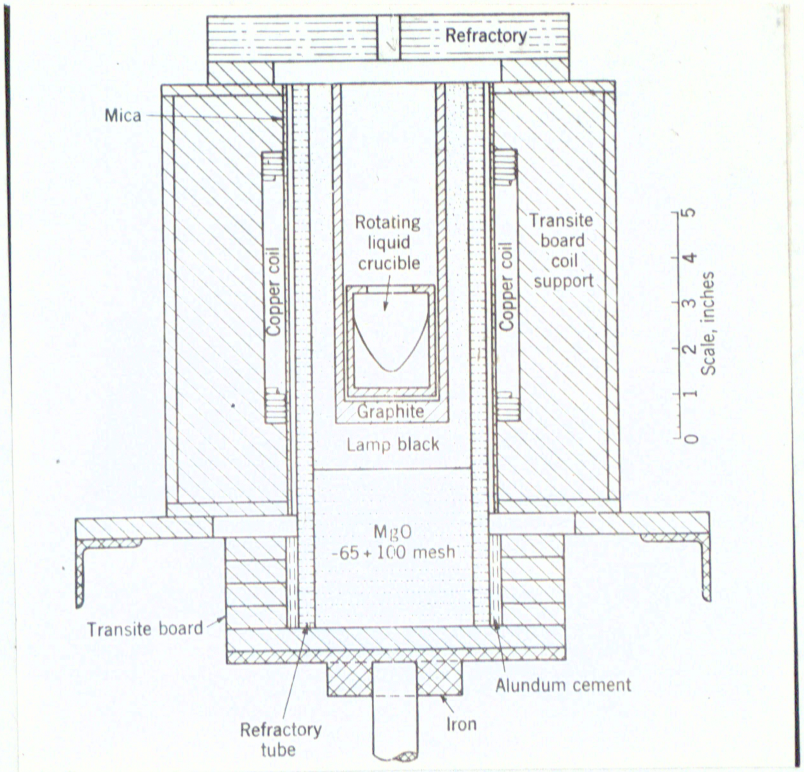


Fig. 27. Section of high frequency induction laboratory furnace using rotating liquid crucibles (72)

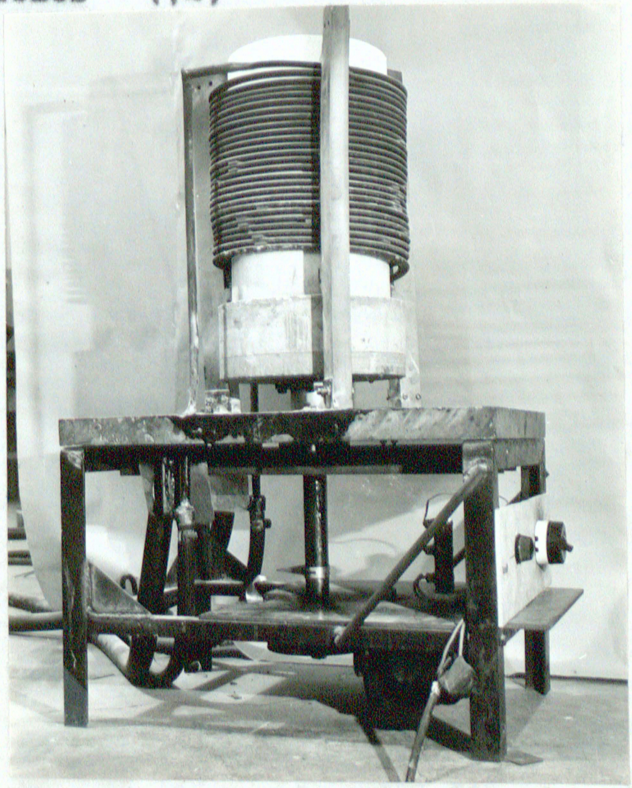


Fig. 29. Furnace with the fireclay flue line removed.

since the magnesia crucible soaked up large quantities of it. After the heat had been molten for about one hour, the temperature was taken by means of a tungsten-molybdenum thermocouple (to be described later), and the heat was poured immediately into the copper mold. The use of the arc kept the slag hot enough, but since the whole heat made up the sample, it seemed that progress would be slow. Also, considerable difficulty was experienced in making a gas-tight seal between the K-30 lid and the edge of the crucible. For these two reasons, the furnace was discarded.

The third furnace and that which was finally used, was an adaptation of a furnace described by Barrett, Holbrook and Wood (76). In their work, they used a rotating furnace with the liquid metal forming a cup in which the slag was collected, so that it did not come in contact with the crucible walls. They constructed three types of furnaces. The first was essentially a rotating refractory cylinder containing the magnesia crucible which was itself heated by a graphite crucible (Fig. 27). In the sedond, only the magnesia crucible rotated, the cylindrical graphite heater being stationary. In the third, the coil and crucible revolved, and the metal was heated directly by induction.

The design finally used is shown in Fig. 28, and will be described in some detail. The outer case (A) is a fire clay flue liner, and is for control of the atmosphere. The top (B) and base (C) are alberene stone. The coil supports (D) are of "Formica" a phenolin resin, pressed paper material. The driving mechanism (E) rotates the steel shaft (F), the alberene base to the furnace (G), the transite ring (H), the silica tube (I), and the K-30 lid (K). All other parts of the unit are stationary, including the coil (L), and the Al_2O_3 entry tube (M).

It was found desirable to keep the amount of transite used to a minimum. Transite, which is largely cement, gives off large volumes of water vapor when the temperature is raised. This water vapor acts as a powerful oxidizing agent on molten iron, and equilibrium could not have been attained until all the iron had been converted into iron oxide.

The fireclay flue liner (A), was cemented to the alberene base (C), by means of Cenco "Plicene," an asphalt base cement which can be applied with a torch. All water and power leads were brought in through the alberene base (C) and cemented in with Plicene so that they were gas-tight. The oil seal cup was also cemented on to the alberene in this manner. The alberene top (B) was made gas-tight with the fireclay flue liner by means of ordinary impervious medical adhesive tape. This made a surprisingly

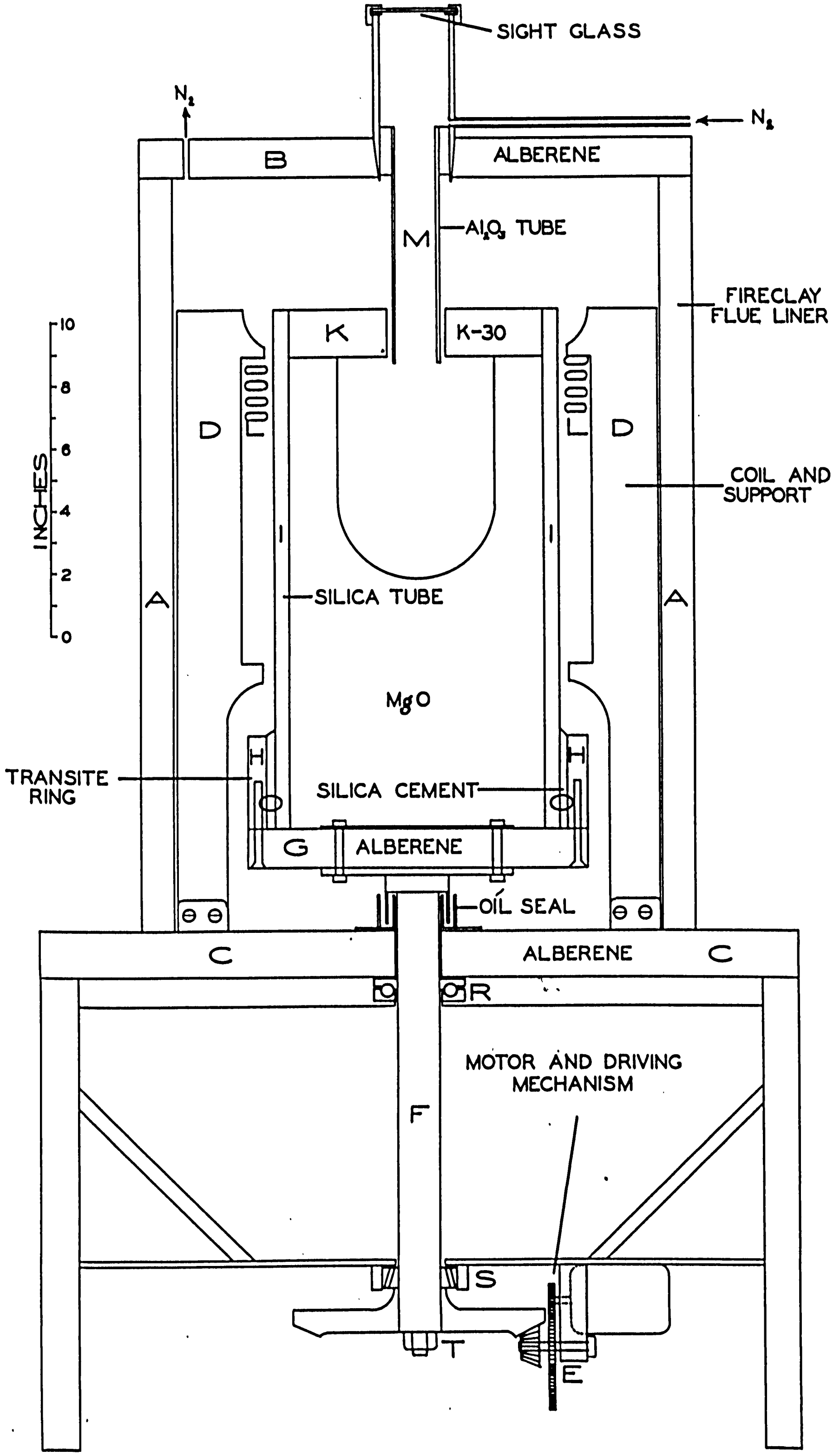

SIGHT GLASS
N$_2$
N$_2$
B
ALBERENE
M
Al$_2$O$_3$ TUBE
FIRECLAY FLUE LINER
K
K-30
10
8
6
4
2
0
INCHES
D
D
L
L
COIL AND SUPPORT
I
I
SILICA TUBE
A
A
MgO
H
H
TRANSITE RING
SILICA CEMENT
G
ALBERENE
OIL SEAL
C
ALBERENE
C
R
MOTOR AND DRIVING MECHANISM
F
S
T
E

FIG 28

Fig. 30. Furnace viewed from the top with the alberene lid off.

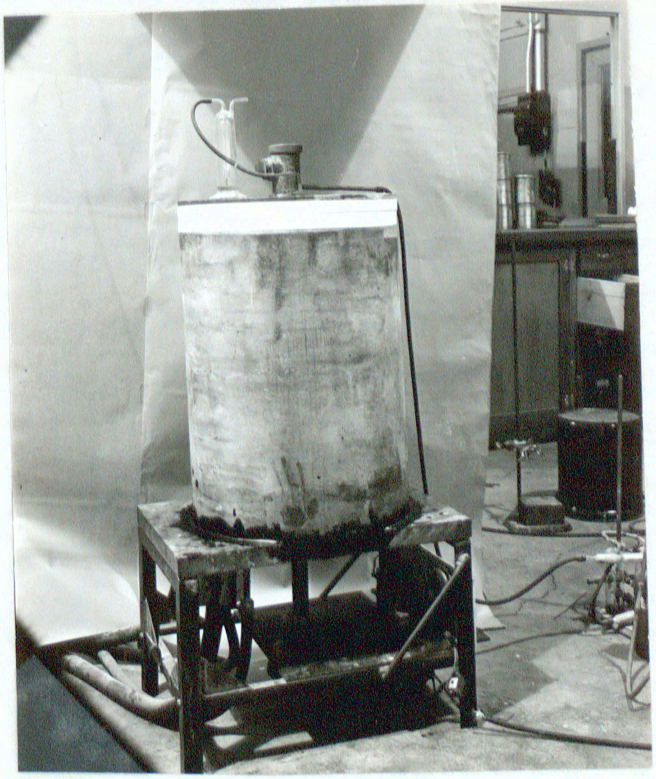


Fig. 31. Furnace assembled ready to operate.

good seal, even when the top of the furnace became quite hot.

The brass sight tube was threaded directly into the alberene, and no precautions were necessary here to make it nearly gas tight, since the resistance of the path was sufficient to support the slight gas pressure under which the whole unit was run. The cap on the sight tube was fixed in such a way that a half turn would completely release it, through the use of a "breech thread." The gasket material used under the pyrex window was high pressure steam gasketing made by "Garlock," and stood the rather high temperature (for gasket materials), without failure. After several types of cement (C) had been tried with varying success between the transite ring (A) and the silica tube (I), the one finally used was a silica cement supplied by the Harbison-Walker Company. This is an air setting cement composed of silica sand of about 80 mesh and finer mixed with sufficient sodium silicate to bond it. Care was taken to completely fill the narrow slot with this cement. Fig. 29 shows the furnace with the flue line case removed. Fig. 30 shows the furnace viewed from the top with the alberene lid off. The iron shell is in place. Fig. 31 shows the furnace completely assembled and ready to operate.

The alignment of the silica tube is of great importance, and should be done carefully. Since these tubes are never round, they must be aligned as nearly as possible about an axis of rotation, more or less by trial and error.

The crucible cover which had been cut from two standard size Babcock & Wilcox K-30 insulating brick, was then centered as carefully as possible. A strip of sheet mica was inserted between the K-30 cover and the silica tube to provide an expansion joint. MgO sand was poured around the mica to form a seal. This sand was not tamped, since it was found that the K-30 brick would expand enough to break the silica tube if the sand were tamped. The life of these covers was materially lengthened by coating the under surface of the lid with Al_2O_3 cement. The most satisfactory cement for this purpose was found to be one part of Norton's high temperature "Alundum" cement and one part of 40 mesh and finer Al_2O_3.

C. Crucible

After the rotating mechanism was complete, a graphite crucible was made with a magnesia crucible inside of it, the whole being covered with a graphite lid, in a way

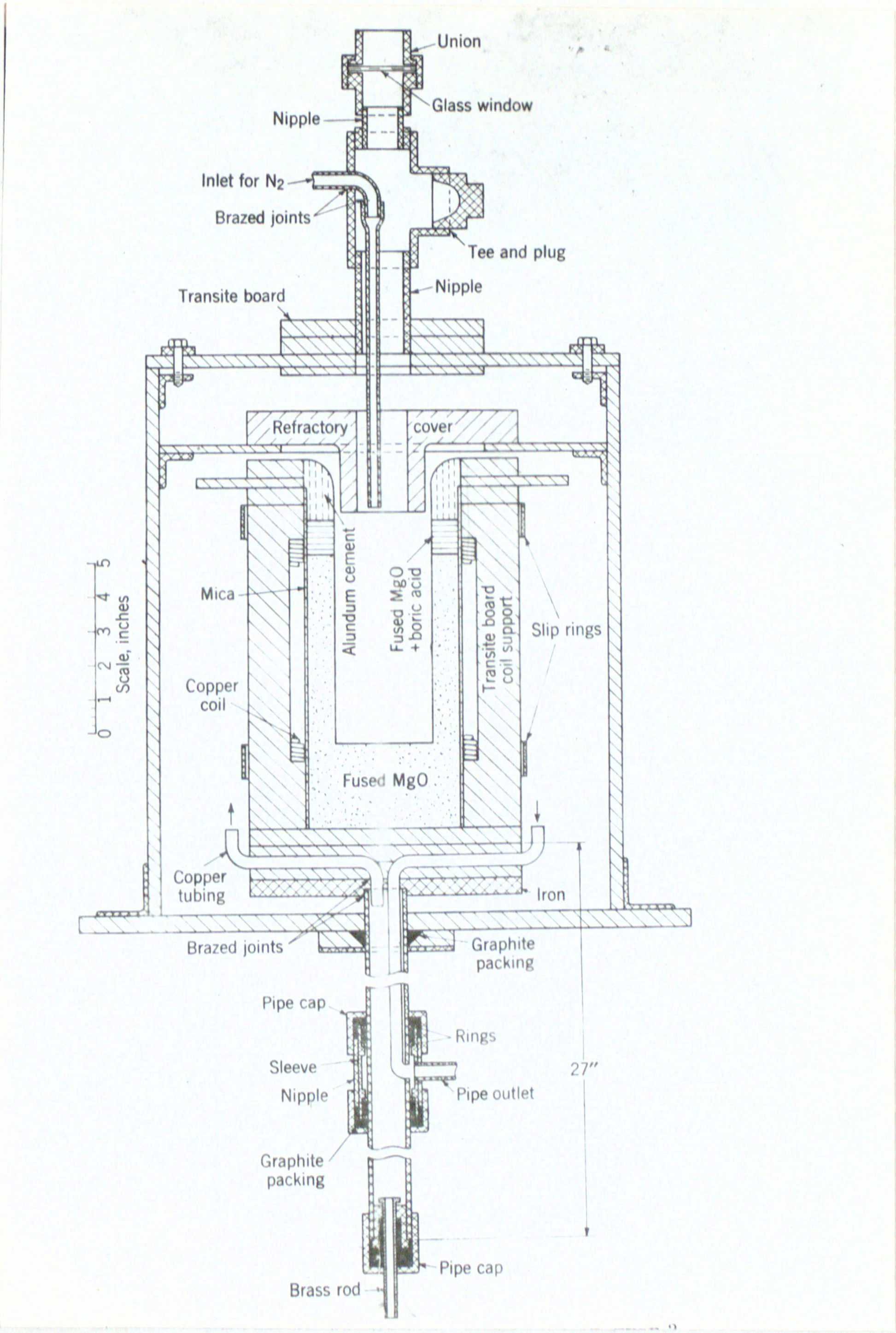


Fig. 32. Type three of Barrett Holbrook & Wood

similar to Type I in Barrett, Holbrook, and Wood's paper. It was found that the carbon content of the metal could not be kept low enough for the experiments, and the crucible arrangement illustrated in Fig. 32 was tried. In this setup, sheet metal was formed into a cylinder, and a flat bottom welded on. This was centered and magnesia poured around it. An Ingot Iron charge was added and the whole melted down. The melting of the sheet metal cylinder sintered the magnesia next to it, forming a refractory crucible. These cans could not be made sufficiently round. Also, the refractory crucibles formed around the sheet metal liner had cracked all around the angle at the bottom, allowing metal to penetrate into the magnesia. To rectify these troubles, Ingot Iron sheet metal cans were ordered from a metal-working company. These cans were spun on a lathe and so were perfectly cylindrical. The bottom was left round to eliminate the stresses set up in the corners of the old can. These have performed perfectly satisfactorily. They were placed in position on the 60 mesh and finer magnesia and centered by rotating to within ± .005". Then the 60 mesh and finer magnesia sand was carefully poured around the shell and settled by tamping with a 1/4" wire so as not to disturb the alignment. When the magnesia sand had been tamped with the rod until no further settling was observed, the alignment was checked, and if it were out, was corrected. Further tamping was accomplished by means of a flat wooden piece so that the top of the sand would be hard. The alignment was then checked for the last time and the charge placed in the furnace.

For several of the heats made to determine the solubility of FeO in liquid iron, the outside of the liner was coated heavily with a slip made of ball milled magnesia in absolute alcohol, as recommended by J. G. Thompson and M. A. Mallett (75). This did cut down the penetration of FeO into the crucible, but since it did not affect the solubility values in any way, the practice was not used generally. The penetration was rarely more than 1/16" on a solubility run, even without the protective wash.

D. Atmosphere

The nitrogen used was ordinary commercial tank nitrogen. This was passed through a furnace containing copper wire at about 450° C. to remove the .5 per cent oxygen. Then it was passed through askarite to remove any CO_2, through H_2SO_4 bubbling towers, and finally over P_2O_5 to remove the water.

On a preliminary design, a transite pipe and lid were used instead of the flue liner and alberene. The dew point on the exit gases was +20° C. It was thought that the transite was causing this trouble, and it was replaced with the flue liner and the alberene. The exit gas then checked +18° C. To overcome this, the Al_2O_3 entry tube (M) was used to conduct the nitrogen directly into the furnace chamber. The dew point on the entry gas was then checked at -38° C., and on a sample taken directly from the furnace chamber at -29° C. A continuous stream of nitrogen of about 3 cubic feet per hour was kept going through the furnace to cause a current of gas to flow between the Al_2O_3 entry tube and the K-30 brick crucible cover.

E. Rotation

The rotating mechanism caused more difficulty than any other problem. In the first furnace, the shaft was made too light, and the bearings were somewhat loosely fitted steel sleeve bearings, in which there was considerable play. The final design utilized a tapered roller bearing (S) (Fig. 28) at the base, and a ball bearing (R) at the point where the shaft goes through the alberene base (C). The top race of the bearing (R) was welded to the shaft and the lower race welded to two angle iron supports which were bolted to the frame. These supports were insulated electrically from the rest of the frame to avoid making a completed circuit in the neighborhood of the coil. The bolt (T) was then tightened to take all play out of the assembly.

In earlier attempts the cement zone (O) was made much too short, and it was found necessary to use the transite ring (H) to provide at least three inches of backing for the cement. Care was taken to completely fill the space with cement.

The motor used at first was a D-C series wound motor, so that the speed could be varied by means of a rheostat over wide limits. This was later changed to a constant speed A-C motor which operated at 220 R.P.M. It was necessary to operate the furnace slowly during the tamping and aligning period, and at 220 during the run. This is somewhat faster than a theoretical analysis calls for, and may be accounted for on the basis of the strong counter currents caused by the high frequency field tending to push the metal up in the center. Considerable turbulence was present in the

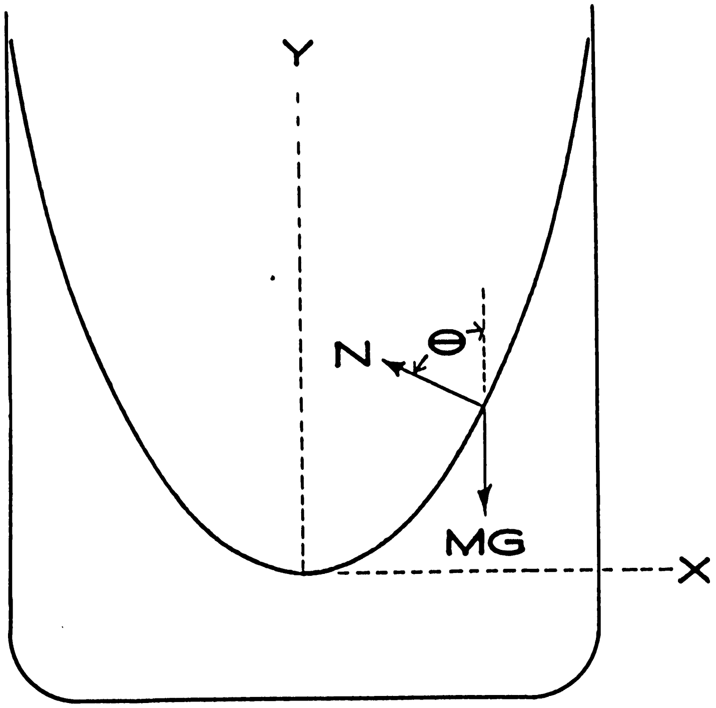


FIG. 33

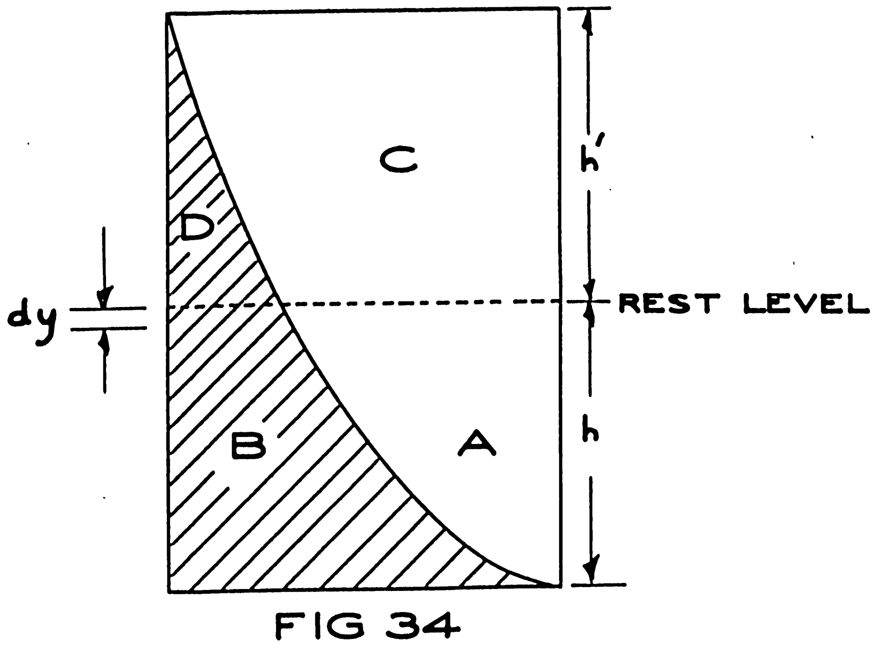


FIG 34

rotating metal, while the field was on, but it completely disappeared when the power was cut off.

The shape of the surface of the metal during rotation is a parabloid. The derivation of the shape of this surface as a function of speed is as follows (Osgood "Mechanics" - page 105):

Picture a particle floating on the surface of the liquid. The condition that this particle will not move along this surface is that there is no vertical component. For this to be so,

(1) $N \cos \theta = mg$ (Fig. 33)

the resultant of N and mg must equal the centripital force.

(2) $N \sin \theta = mw^2x$ (2)/(1)

$$\frac{N \sin \theta}{N \cos \theta} = \tan \theta = \frac{mw^2x}{mg} = \frac{w^2x}{g} \quad \text{or}$$

$$\frac{dy}{dx} = \frac{w^2x}{g}$$

Integrating $y = \frac{w^2x^2}{2g}$, the equation of a parabola.

In Fig. 34, the letters in the areas correspond to volumes: i.e., that volume which would be swept out by the area during one complete revolution. The volume of the metal when at rest, A + B, must equal the volume of the metal during rotation B + D, so A + B = B + D, since no metal is lost, and cancelling B, we have A = D.

The volume of the element xdy is $\pi x^2\,dy$, so the total volume of C + A is $\pi\int_0^y x^2dy$; but $y = x^2$ (eq. of a parabola). Volume parabloid $= \pi\int_0^y y\,dy = \frac{\pi y^2}{2}$

The volume of the cylinder is $\pi x^2 y$ but $y = x^2$, so

Vol. cylinder $= \pi y^2$, which is twice the volume of the parabloid. From this

$C + A = D + B$ Substitute (1)

(3) $C = B$

Subtract (3) from (2)

$$\begin{array}{l} A = D \\ \underline{C = B} \end{array}$$

$A - C = D - B$ or

$A + B = C + D$ Since they have a common base $h = h^1$.

Substitute into (1) and let $x = r$ the radius

$$2\,h = \frac{w^2}{2g}\,r^2$$

$$h = \frac{w^2}{4g}\,r^2$$

r^2 = 2-1/2" $= (6.35)^2$ cm. At 200 r.p.m. or $\frac{20\cancel{0}}{6\cancel{0}}$ 10 r.p.s.

$w^2 = \frac{2\pi\ 10}{3}^{\,2}$ radius/sec.

g = 980 dynes

$$h = \frac{4\pi^2\,100}{9} \cdot \frac{1}{4.980} \cdot (6.35)^2$$

$$= 4.5 \text{ cm.}$$

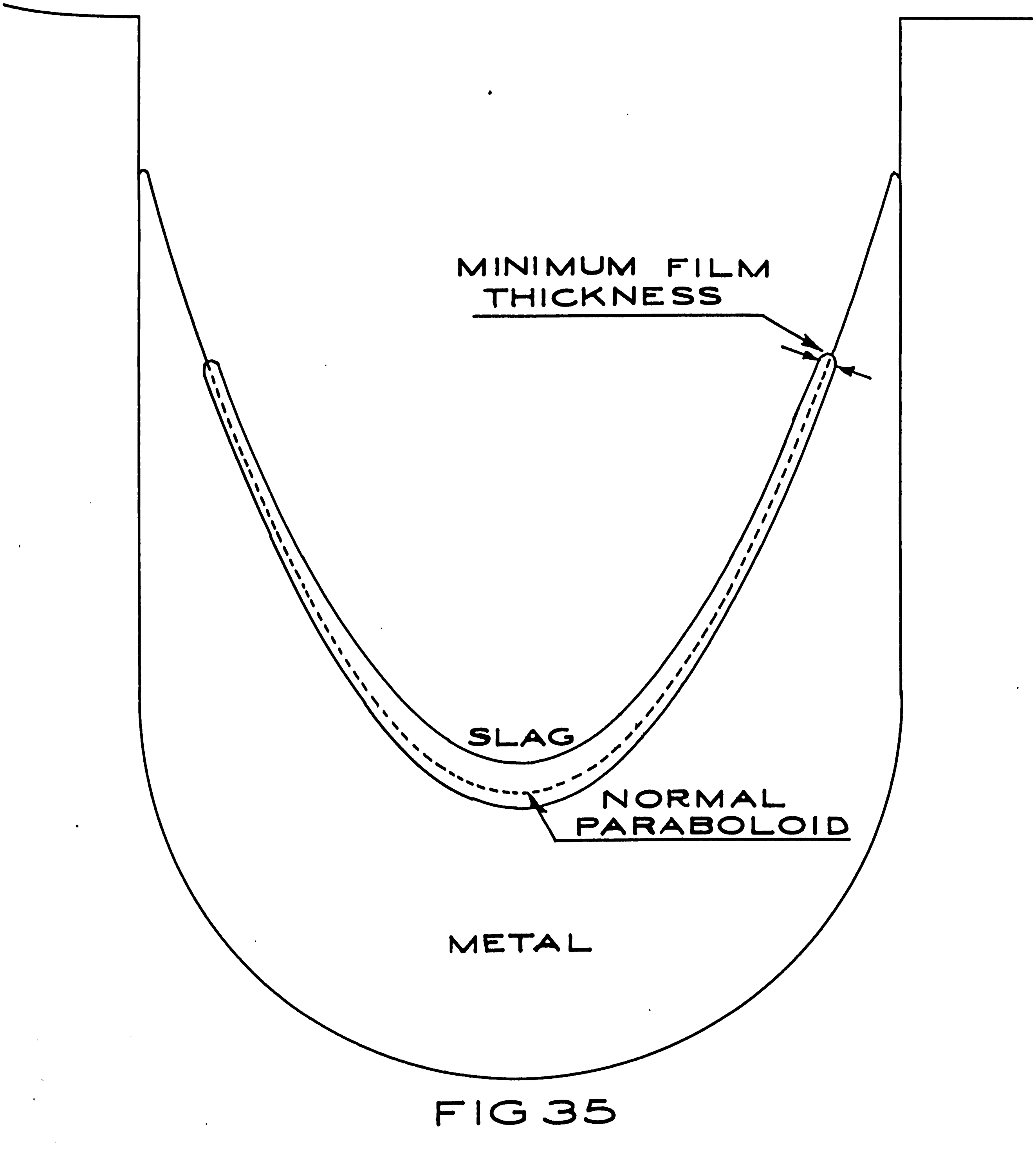


FIG 35

Fig. 36. Liquid crucible solified during rotation.

As can be seen from the derivation, the density of the liquid cancels out, so the slag and metal surfaces should form two paraboloids of revolution which are merely displaced along the axis of rotation of the crucible. If an infinitely thin film of slag could form, a slag layer could not be kept on the metal, since it would gradually creep up the metal walls and be absorbed by the crucible. The interfacial tension existing between the slag and the metal prevents this by establishing a minimum film thickness. This effect is shown in Fig. 35. The slag also displaces its weight of iron with the displacement taking place normal to the paraboloid (B). Fig. 35 is drawn assuming that the slag has 1/4 the density of the metal. The assumed speed of rotation is 220 RPM. This curve checks exactly the actual shape of the metal which was allowed to solidify with the power off, as is shown in Fig. 36. When the power is on, however, the induced convection currents in the metal tend to make the parabola shallower.

Charge

The charge consisted of the sheet metal liner, which weighed one pound, plus eighteen pounds of ARMCO ingot iron of the following typical analysis:

C - .015
Mn - .005
P - .008

S -	.018
Si -	.004 (probably all SiO_2)
Cu -	.032
Ni -	.017
Co -	.004
Pb -	.005
As -	.011
Cr -	.008
Total	.137%

After a number of runs had been made, the old heats were used directly as a charge, after pickling, along with sufficient of the bars to make up the weight to 18 pounds. The carbon was checked several times and was always .006% and Mn .003% on the heats after the Fe_2O_3 had been added.

The Fe_2O_3 used in the slag was Baker's C.P. analyzed reagent and was considered pure enough for the study. The CaO was obtained by calcining Baker's C.P. analyzed $CaCO_3$ at 1000°C. The CaO was kept sealed in bottles until it was needed. The SiO_2 used was 40 mesh and fine crushed vitreosil tubing which assayed 99.5% SiO_2. The vitreosil was used in preference to the quartz sand because it went into solution more easily. From a number of minimum values obtained from the slags by analyses, it appeared that about .4% Al_2O_3 was present and about .08 MgO.

Sampling

Slags

The slags were sampled from the furnace by means of small 16 gauge ingot iron spoons. Blanks 1-3/8" in diameter

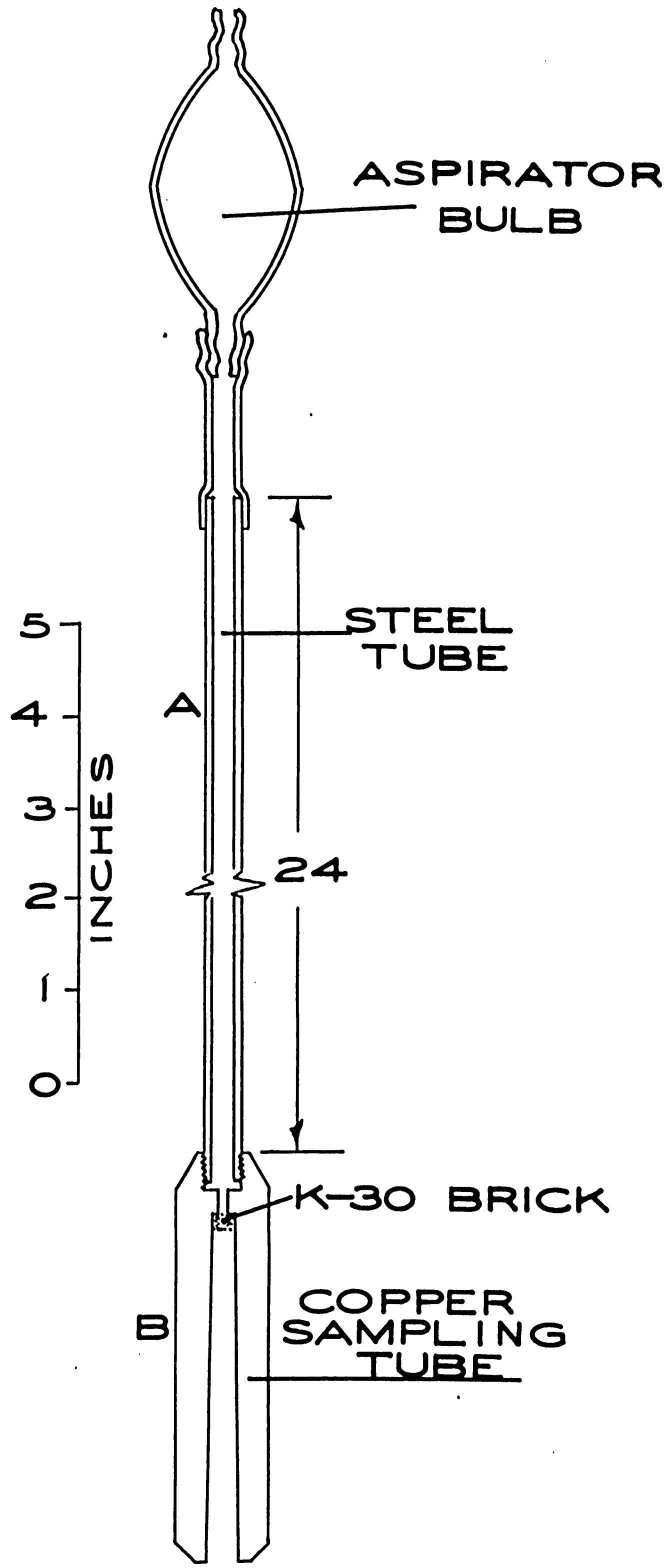

ASPIRATOR BULB
5
4
3
2
1
0
INCHES
A
STEEL TUBE
24
K-30 BRICK
B
COPPER SAMPLING TUBE

FIG 37

were forced through a 1" die on the physical testing machine to make a cup 1" in diameter and 1/2" deep. These were welded to a rod and pickled before use. Some care must be taken in sampling the slag, since the layer is usually very thin. The slag and spoon were then quenched in distilled water. With care and practice, sufficient slag could be obtained with one spoon for complete analysis. These slags were analyzed for SiO_2, CaO, MgO, Al_2O_3, FeO, Fe_2O_3, other constituents such as P_2O_5, sulphur being very low, were not considered in this study. Consecutive samples showed that duplicate results could be obtained by this sampling method, and that the slags were homogeneous.

Metal

A drawing of the metal sampler is shown in Fig. 36. A 1" piece of copper rod was drilled axially and then reamed with a standard #6 tapered pin reamer. The dimensions of this reamer are .345" diameter at the large end and .279" at the small end. The whole length of the reamer, about 3 1/2", was used to get as long a sampler as possible. The pipe (A) served as a handle and as a tube through which the sampler could be sucked up. The K-30 plug prevented the metal from getting up into the pipe. This plug was cut almost to size and forced into the sampler, the dust and fragments being carefully blown out. The outside of the copper was wiped with a cloth which had a small amount of vasoline on it. This put a film of oil on the sampler, not enough to increase the carbon content of the bath any, but enough to blow the slag away by gas evolution, and inhibit the solidification of the metal on the outside of the sampler. The bevel at the bottom of the copper tube (B) excludes some of the slag which would have been carried down into the metal on a flat bottom, and then drawn up into the sample with the rush of metal. The bevel at the top of the copper tube is so that the samplercan be withdrawn quickly from the furnace chamber without catching on the bottom of the Al_2O_3 tube.

In taking a sample, the bulb is depressed, the sampler lowered rapidly into the melt until it is felt to strike the bottom of the crucible, the bulb released, and the sample immediately withdrawn and quenched into water. After it is cool, the sample can usually be easily withdrawn from the sampler. The metal that adheres to the outside does not interfere. If the sample sticks, it can always be driven out by inserting a piece of drill rod (preferably heat treated) through the hole (C) in the upper end of the copper tube, and hitting it a few blows with a hammer. The cold heats are much more difficult to sample, using this device, than the hot heats. With a cold heat, a ball of metal freezes immediately on the outside of the sampler, and often melts the sampler before it can be withdrawn and quenched.

To facilitate removing this balled up sampler from the furnace, the outside diameter of the copper was reduced to 3/4" for cold heats. No difficulty was experienced in sampling heats above 1590°C. The hottest heat sampled was at 1690°C.

Several samplers were tried, using different diameter holes. The #7 tapered pin reamer gave a sample that had holes in it, since the metal tended to run out before it solidified. If the sampler was left in the furnace long enough to solidify, the copper usually melted in some place. The #6 T.P.R. was the most successful. A #4 T.P.R. was also tried, but the sample obtained from this proved to be inhomogeneous from end to end, so the #6 was used exclusively.

Table 4 shows some homogeneity results on a sample. The numbers refer to consecutive sections of the sample. In each case all the sample numbering from the top or small end was analyzed.

Table 4

		1	2	3	4	5	6
#6 T.P.R.	Ox	.152	.152	.153	.152	.154	.153
	N_2	.054	.028	.027	.029	.029	.033
#4 T.P.R.	Ox	.297		.274			.265
	N_2	.032		.037			.040
#4 T.P.R.	Ox	.192		.187			.184
	N_2	.015		.013			.031

The erratic nitrogen values can be partly explained on the basis of the small samples taken, usually 2.5 to 3 grams. It was also found that the metal on the outside of the sampler checked that on the inside.

	Ox	N2
Inside	.171	.023
Outside	.173	.020

Table 5 gives a comparison of three different sampling methods. The dipped samples were taken in the rotating furnace, and so were solidified in nitrogen. The poured samples were poured over the lip of a 12-pound magnesia lined induction furnace into a cylindrical copper mold one centimeter in diameter and about nine centimeters long.

The dipped samples show that they are all right if they do not solidify in the presence of an appreciable amount of slag. If this occurs, then the sample is invariably lower than the true value.

All the poured samples were taken from iron saturated with FeO. They give results which are apparently a function of temperature. The postulation of two effects will explain these results. First, the liquid iron, even though saturated with FeO, will form a film of iron oxide on the surface which will be trapped by the metal as it solidifies. This will result in an apparent increase in oxygen content. On the other hand, the metal must flow over the cold lip of the

TABLE 5

Comparison of Sampling Methods

Copper Sample	Dip Sample	Poured Sample	Remarks
.164	.149	-	2/3 metal, 1/3 slag in spoon.
.168	.130	-	1/4 metal, 3/4 slag in spoon.
.137	.139	-	very sma ll amount of slag.
.143	.125	-	small amount of slag.
.150	.142	-	1/10 slag, 9/10 metal.
.182	-	.184	1532°C.
.192	-	.212	1548°C.
.188	-	.215	1554°C.
.234	-	.237	1604°C.
.300	-	.290	1673°C.
.327	-	.299	1686°C.
.216	-	.235	no temperature.

the crucible, and in doing so FeO may be precipitated out on cooling. A balance of these two factors at any temperature might give a true result. At any rate, pouring the sample leads to erratic results, as does dipping, unless the metal solidifies out of contact with slag. The lower oxygen results on metal solidified in contact with slag indicate that equilibrium is attained very rapidly.

Two consecutive samples were taken about two minutes apart, so it was felt that the sample represented the heat.

Heat R-26	Sample 1	.242	Two minute interval
	2	.240	
Heat R-24	Sample 1	.170	Three minute interval
	2	.169	

The sampler has since been used on larger induction furnace heats to study the oxygen content, and has proved more convenient and more accurate than other methods of sampling.

Temperatures

Of the several methods that have been used in measuring temperatures of molten steel, the thermoelectric method stands out as much superior to various optical methods. The use of a thermocouple at these high temperatures and in the presence of metal and slag involves numerous difficulties. In the first place the resistivity of the refractories normally used drops to a low value, and that of the thermoelements goes up. There is considerable danger that unless the refractories used are chosen with some care, they will exert an appreciable shunting effect on the thermocouple. In the measurement of temperatures in the presence of both slag and metal, several effects must be guarded against. Of primary importance is the possibility of contamination of the couple by iron vapor or carbon monoxide and dioxide in the furnace gases. Also a choice must be made as to protection tubes. This may be governed by two basic factors: the rate at which the slag and metal erode the tube, and the rate at which thermal equilibrium is established.

If the temperature equilibrium is rapidly reached, the rate of erosion by slag need not become important. The problem has been attacked from both directions, but in the case of this experiment the resistance to slag and metal erosion was sacrificed to the end of obtaining rapid readings. Silica protection tubes were used throughout and Norton "alundum" insulators were selected for the electrical insulators.

Two types of thermoelements were used, tungsten-molybdenum and platinum - 10% rhodium platinum. Since the technique of handling each of these is somewhat different, they will be discussed separately.

The platinum couple was first annealed by passing sufficient current through it to heat it to a cherry red for about ten minutes. It was sometimes possible to locate points of contamination by the difference in color while hot.

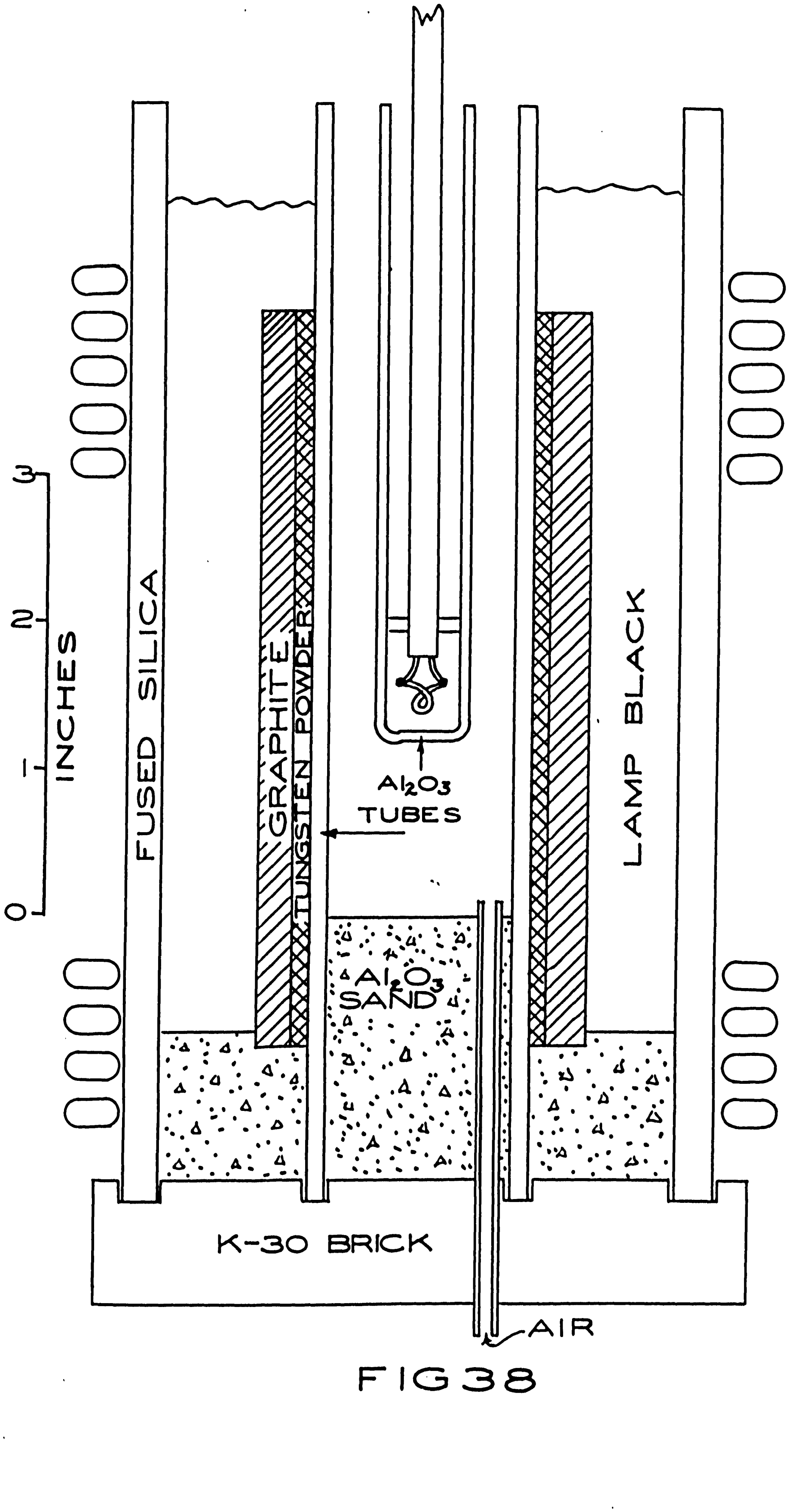

INCHES
0
1
2
3
FUSED SILICA
GRAPHITE
TUNGSTEN POWDER
Al_2O_3 TUBES
LAMP BLACK
Al_2O_3 SAND
K-30 BRICK
AIR

FIG 38

The wires were then threaded through the insulators and it was calibrated at the melting point of palladium (1550°C.) by the following method.

The welded hot junction was clipped off and a piece of palladium wire 1/2" long of .018" diameter was welded into the couple where the head had been. A loop was then formed in the palladium so that in case there was some strain in the thermocouple, the palladium would not be broken just before its melting point was reached. The couple was then placed in a gas tight protection tube which had previously been carefully burned out with oxygen, and put into the furnace shown in Fig. 38.

This furnace was simply a carbon tube, heated by induction, insulated with lamp black, the carbon being kept out of direct contact with the gas-tight Al_2O_3 tube by means of tungsten powder. The whole system was built to exclude reducing gases which are so harmful to platinum couples. The furnace was heated slowly and the E.M.F. of the thermocouple followed closely on a Leeds & Northrup "Portable Semi-precision Potentiometer", until the palladium wire melted. The point at which this happened was unmistakable, the breaking of the contact being accompanied by a wild swinging of the galvanometer. The point could be duplicated to within .01 m.v. which was sufficiently accurate for this study. The displacement of this point from the standard curve for this type of couple was then used to draw the calibrating curve for the actual couple, the calibrating curve being drawn "parallel" to the standard curve through the zero point and the experimental point.

The wires were clipped off about 1/2" above the palladium beads on the ends, rewelded, and used. The procedure was carried out periodically.

The tungsten molybdenum thermocouple has been used somewhat before (44, 84) but is not generally well known as a method of measuring high temperatures.

The most suitable source of wires was Fan Steel Corporation. These wires had an excellent homogeneity. They differed very little from one end of a coil to another, but each coil was sufficiently different to make it necessary to provide a separate calibration. The chief offender in this respect was the tungsten. Four thermocouples were made up from two lots of wire. The results are shown in Table 6. The numbers are millivolts at the "apex" of the calibration curve.

Table 6

Combinations of Wires				M.V.
Tungsten	A	Molybdenum	B	1.41
"	"	"	C	1.41
"	D	"	B	1.19
"	"	"	C	1.23

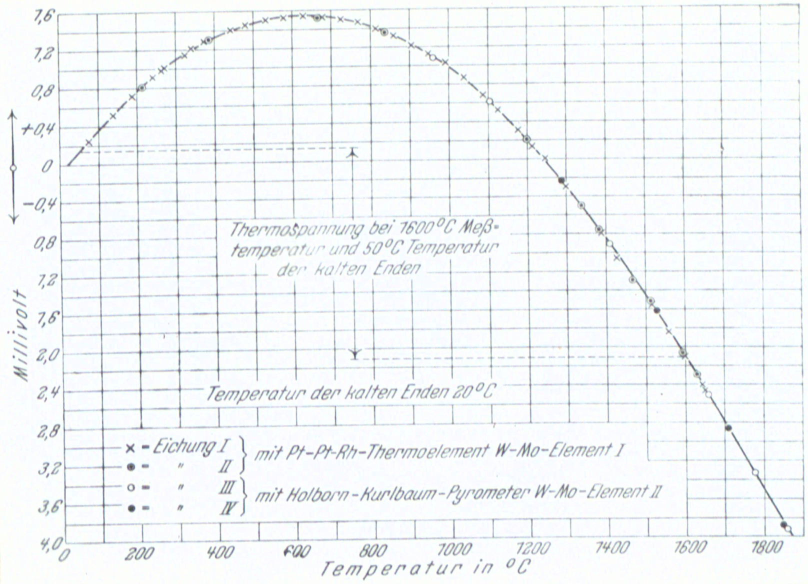


Fig. 39. A typical calibration curve for tungsten-molybdenum thermocouples. (74)

Typical calibration curve is shown in Fig. 39, taken from the paper by Osan and Schroeder (74). The thermoelectric curve of the couple goes through a maximum at about 600°C., through zero at about 1200°C. The useful portion is in the relatively flat range (A). The change in millivolts with temperature in this region is about .007 mv/deg.C as compared to .012 mv/deg.C for platinum.

The usual method of calibration was to determine the melting point of copper, nickel, and iron, using these three points, to determine constants in the equation of the parabola $mv = aT^2 + bT + C$. This calculated curve was then taken as the calibration.

Several efforts made to calibrate the thermocouple against a platinum thermocouple were unsuccessful, due to the difficulty in establishing a black body. The probable error at 1600°C. on this basis was about ± 10°C.

The molybdenum wire (both wires were .020" diam.) was much the more ductile of the two, so in making up a thermocouple, all the bending was confined to the molybdenum. The two wires of suitable length (9") were placed parallel in a vice about 1/8" apart, and protruding about 5/8". The molybdenum wire was then wrapped three or four times around the tungsten wire, leaving a short piece of tungsten, 1/8" protruding from the coil of molybdenum wire. The wires were then welded together with an arc welder, by momentarily

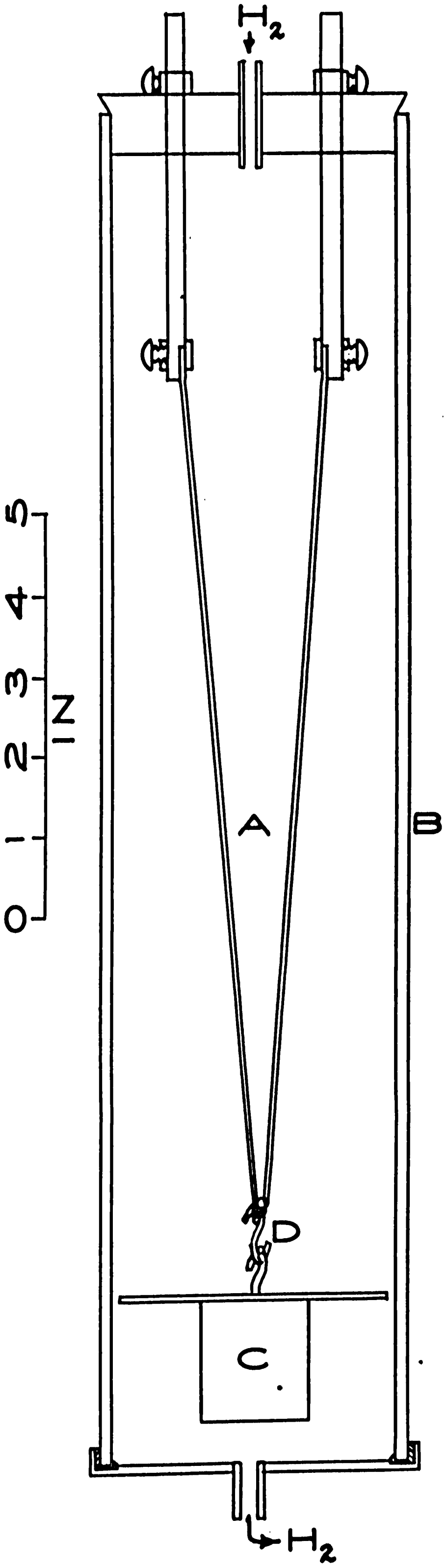


FIG 40

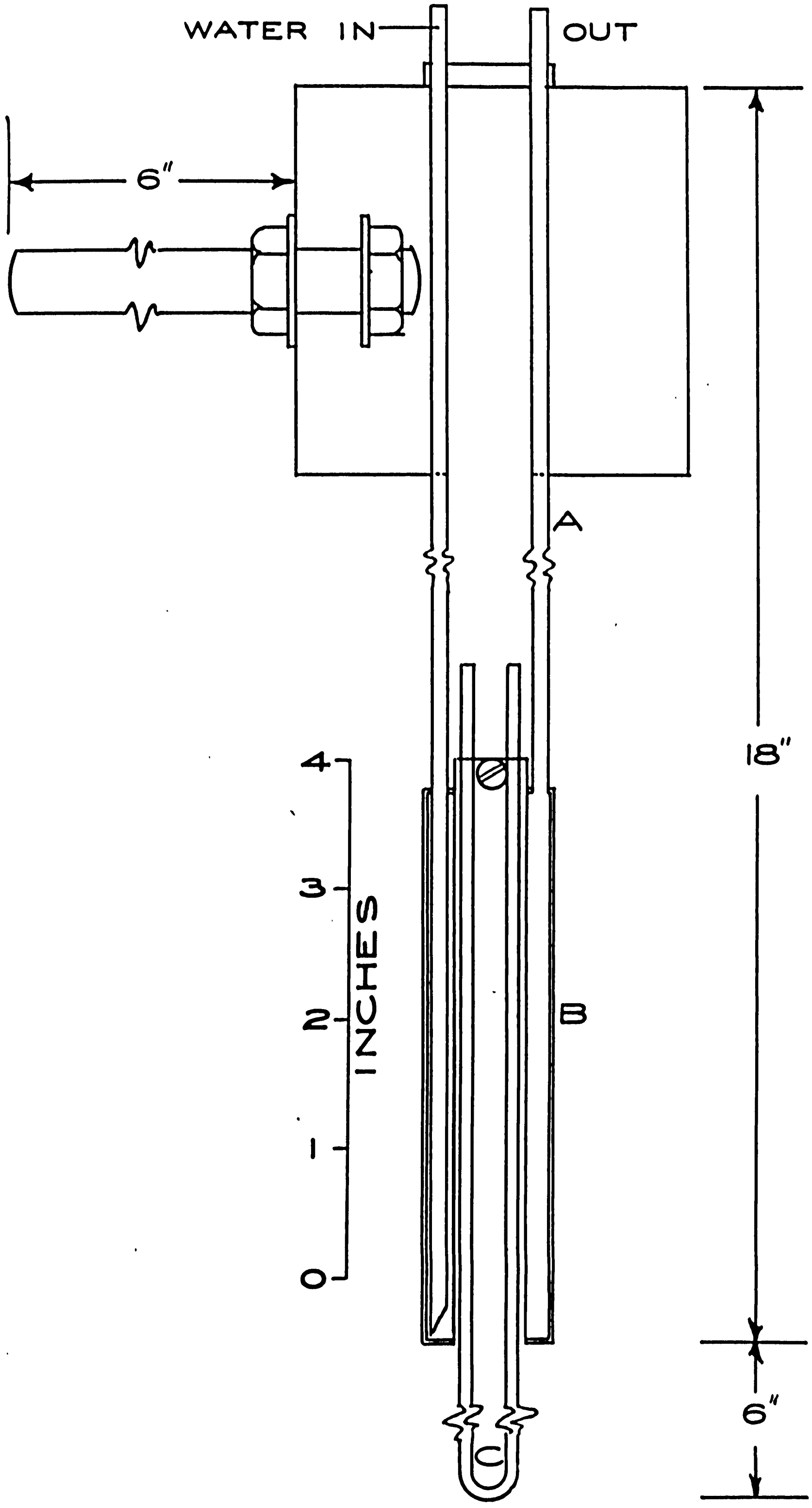


FIG 41

striking an arc from the wires to a carbon electrode. This melted the protruding tungsten wire down over part of the molybdenum, making a good solid bead.

At first these wires were used in the same condition as received from the suppliers, but it was found that they apparently recrystallized during the measurement of the high temperatures, changing the calibration by producing an inhomogeneity in the wire at some point. This was completely remedied by annealing the wires in hydrogen for about five minutes at a temperature close to the melting point of molybdenum (2625°C.). The annealing was accomplished as shown in Fig. 40 by suspending the couple (A) in a silica tube (B). The weight (C) held the couple in position, and was attached to the thermocouple by the tungsten wire hook (D). The current was gradually raised until the molybdenum wire melted. A setting somewhat below this was used for subsequent thermocouples. This treatment made the tungsten wire very fragile, so that it had to be handled with care. It was found that this annealing treatment did not affect the e.m.f. characteristics in the zone of 0-100°C., so the green wire could be used as compensating lead wire.

Both types of thermocouples were used in a water cooled tube shown in Fig. 41. The tube was constructed of copper tubing water leads (A) leading to the central cooling chamber (B). As the silica protection tube (C) eroded away or failed, the end was cut off and resealed by means of an oxy-acetylene torch. The silica tube was moved down as the end had to be repaired until it became too short to clamp at the point (D) when another tube was fused on.

In this way all the silica tube could be utilized. A small coupling block was used to make the connection between the couple and the lead wire. It was made of a Formica cylinder about 3/4" long, small enough to fit into the silica tube, with the electrical contact being made by a "jam" fit into two small brass tubes imbeded in the Formica. The electrical contact so obtained was sufficiently good.

OUTLINE AND PLAN OF THE WORK

The present work was undertaken as a preliminary to a study of the mechanism of reactions in the open hearth furnace and development of methods for the control of these reactions. A study of reaction rates would be greatly aided by a knowledge of the end point, or equilibrium conditions to be expected. Since FeO is the most important single chemical species involved in the refining action of open hearth slags, a knowledge of the equilibrium distribution of FeO between the slag and the metal was considered essential. To gain this knowledge, several furnaces were constructed, and one finally selected which seemedto offer the widest experimental possibilities. Due to the unusual features involved in this furnace, considerable time had to be spent in developing an adequate experimental technique. Because of this, the first few heats were of no value as far as producing reliable data, but were useful in standardizing the methods to be used in operating the furnace. There were numerous mechanical breakdowns during the first part of the work, and the causes of these were gradually eliminated.

After the furnace had been put into such a condition that no further experimental difficulties were anticipated, a study of the distribution of FeO between liquid iron and iron oxide slags was initiated. This was necessitated by the apparent unreliability of the data previously reported by Korber, Oelsen, and Herty. Having established the saturation values for FeO in iron, the effect of varying the lime and silica content of the slags was studied. The variations of these two componenets which were used were kept, for the most part, in the region of the ternary diagram which had not previously been covered by Fetters and Chipman.

It was then possible, from the fractional saturation of the metal, and the known fact that the solution of FeO in liquid iron is ideal (89), to calculate the activity of FeO in the slag.

Using the calculated activities, an effort was made to correlate this with the mol fraction on the assumption of various reasonably simple compounds in the slag. The only justification for these assumptions was that they offered the attractive possibility that the solution of FeO in these slags could be treated by Raoult's Law. It is realized that this cannot be taken as proof for the existence of these compounds. The use of such assumptions has been amply justified by Dolezalek (86,87). Such assumptions have also met with considerable opposition, especially by Hildebrand (88), and it is certain that in a good many cases they cannot be justified. It is well known that the approach to ideality is increased by increasing temperatures. Since these experiments were carried out at 1550-1650°C., the assumption of ideality is not unreasonable. If it is possible by means of any reasonable assumptions to account for the experimental results, this will greatly simplify the problem of extrapolation to slag compositions other than those actually studied.

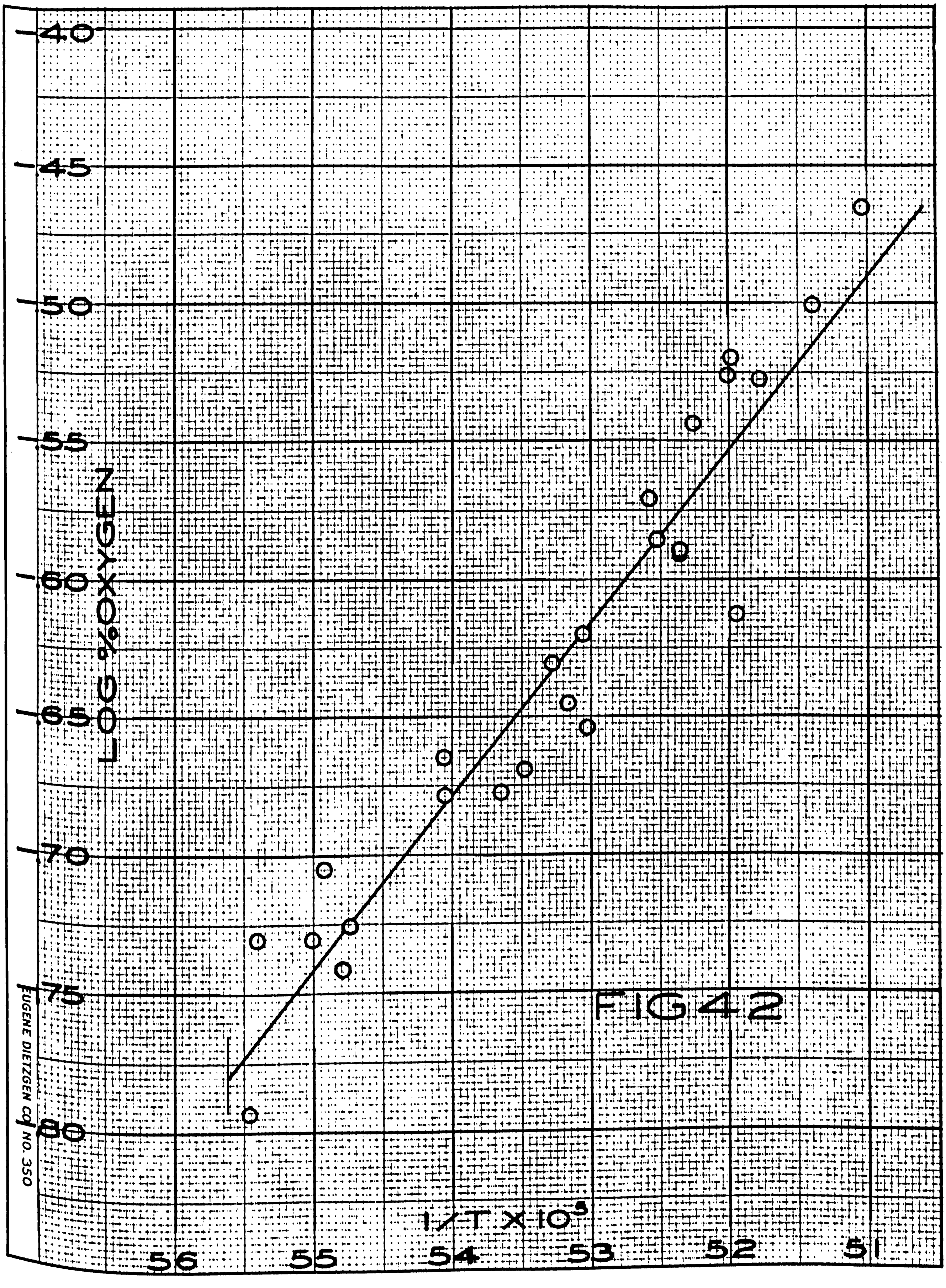


FIG 42

THE SOLUBILITY OF IRON OXIDE IN LIQUID IRON

The previously reported work on the solubility of FeO in liquid iron has been carried out on the assumption that Nernst's distribution law is valid, i.e. that $(FeO)/[FeO] = K$, where the square brackets represent concentrations in the metal and the round brackets, concentrations in the slag. This involves the assumption that the ideal solution laws are obeyed, and consequently that the activity coefficients are unity.

The principle work reported along this line is summarized in Table 4. The most complete work was done by Herty, and by Korber and Oelsen, whose results agree fairly closely, and by Chipman and Fetters, whose solubility values are significantly lower. The results obtained in this investigation are shown in Fig. 42, and are only slightly different from those obtained by Fetters and Chipman. Chipman (90) has since reported that, as a result of the data shown in Table 5, the solubilities reported by him at the higher temperatures may be in error, as some slag was trapped in his sampler. This would tend to change the slope of his line, and make it move nearly in agreement with that reported in this thesis. The solubility of FeO in liquid iron may be expressed by the equation:

$$\log \% \text{ Oxygen} = \frac{-6320}{T} + 2.734$$

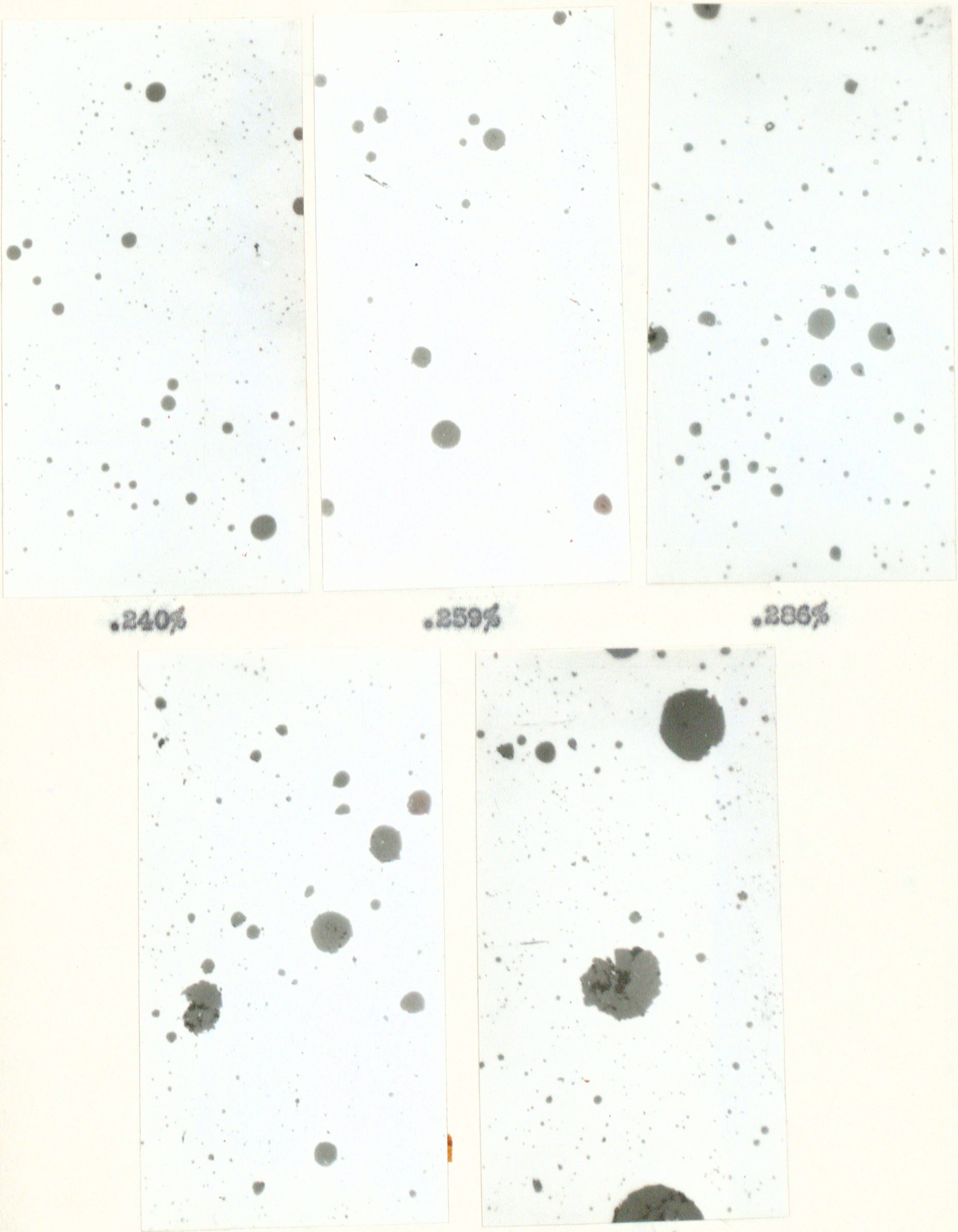
as calculated by the method of least squares.

An effort was made to determine the reason for the discrepancy between this work and that reported by Herty, Korber and Oelsen. To check on the effect of the different sampling methods, a small ten-pound heat was melted in air in an open magnesia crucible. The metal was saturated with FeO, and samples were taken by the copper sampler and also by pouring a small amount of the metal into a similar sampler. Temperatures were taken with the tungsten-molybdenum thermocouple. The results are shown in Table 5. When these results were corrected for dissolved MgO, those taken with the sampler fell on the calculated line within the apparent experimental error, while those which were poured through the air are quite erratic. The tendency of the poured samples seemed to be for those which were poured at low temperatures to run high in oxygen, and those poured at the high temperatures to run low. It has been shown previously that a dipped sample will check the copper sampler, provided the amount of slag which is trapped in the sampler is kept very low. Herty used dipped and poured samples, as did Korber and Oelsen, the latter stating thatpoured samples were used for high temperatures only. On the basis of this experiment, neither of the two techniques of sampling used by Herty and Korber, if properly handled, could lead to the excessively high oxygen contents reported.

The effect of atmosphere was considered next. Both Herty and Korber and Oelsen melted their heats in air. The small heat described above was also melted in air, and no significant difference from those samples taken in nitrogen could be determined. Several samples were taken from the rotating crucible furnace, while a stream of air flowed over the melt, without altering the results. Chipman (90) has actually run a gas mixture of 10% H_2 and 90% N_2 over the surface of the slag without any appreciable effect on the solubility.

The most important variable remaining is the temperature. Six of the points on the graph in Fig. 40 were taken with a platinum thermocouple. The rest of the temperatures were measured with the tungsten - molybdenum thermocouples. There is no significant difference between these two types of temperature measurement as shown by solubility values. Herty says that he occasionally checked the temperature of his melts with a platinum couple. The balance of the readings, as were all of those of Korber and Oelsen, were taken with an optical pyrometer, which, as has been shown elsewhere, is not reliable.

Up to the present time, this difference in the oxygen solubility in liquid iron has not been reconciled. Every attempt to reproduce the curve of Herty, Korber and Oelsen has only strengthened the evidence in favor of the solubility line reported in this thesis. It seems necessary, therefore, to conclude that for some reason their results are in error, with the most probable error being in their measurement of temperatures. The relationship between oxygen solubility and temperature given in Fig. 42 will be used as a basis for the calculation of fractional saturation values.



.240%

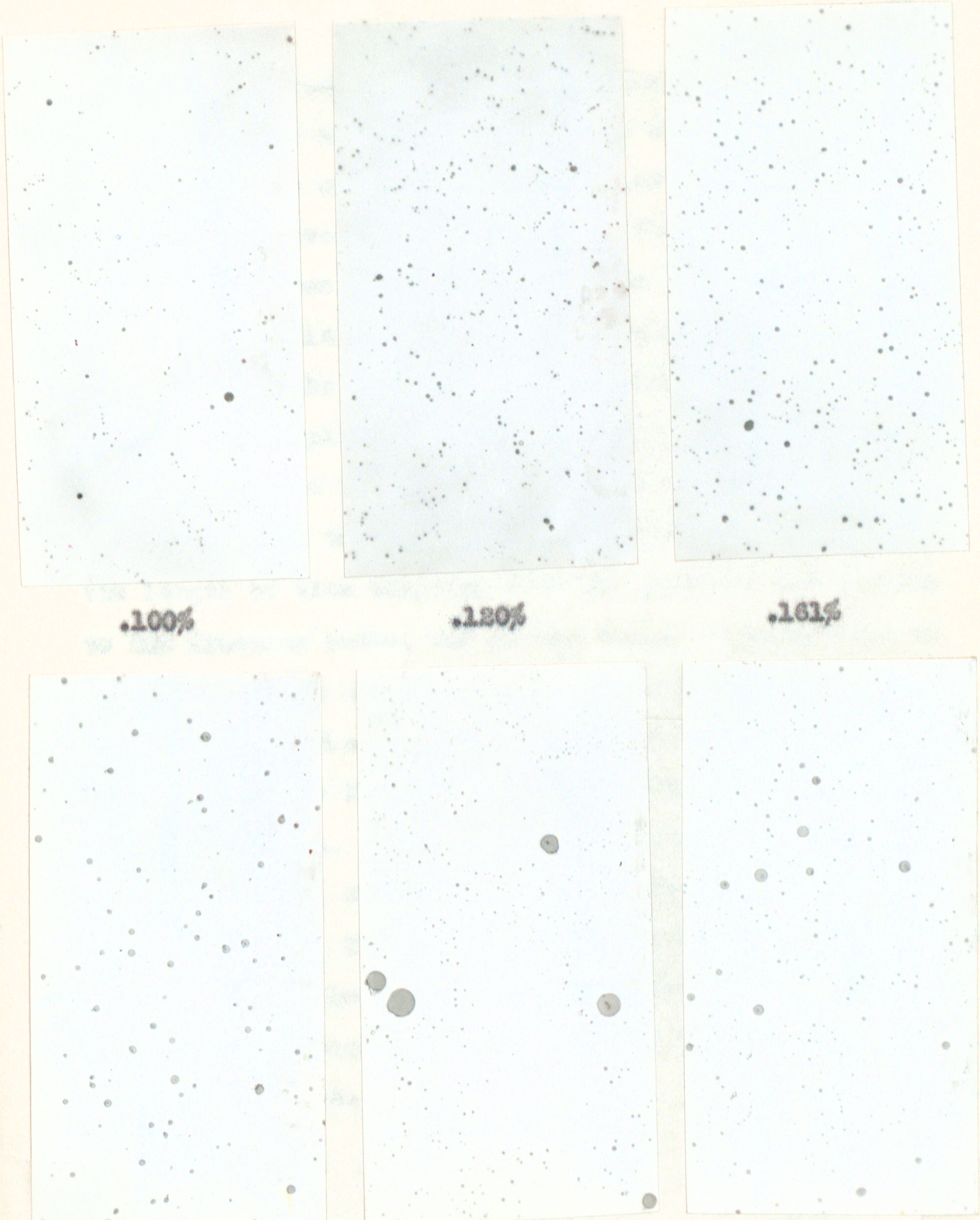
.259%

.286%

.300%

.327%

Fig. 49 (Cont'd)



.100% .120% .161%

.181% .210% (Some slag in sampler) .222%

Fig. 49

As an addition to the study of the solubility of iron oxide in liquid iron photomicrographs of a number of samples ranging in oxygen content from .10 to .33 were prepared. These are shown in Fig. 49. The most interesting thing about these pictures is that the inclusionsfall into two types. It is probable that the larger inclusions were formed during the cooling of the liquid metal from the temperature of sampling to the freezing point. This type of separation, of a liquid from a liquid, would give the particles a chance to grow. The size would be a function of the length of time elapsing from the start of the cooling to the freezing point, and of the degree of saturation of the metal. This mechanism is substantiated by the fact that the boundaries of the larger inclusions are very irregular due to the encroachment of the crystals of the solidifying iron. Some of them have small iron globules in the interior, showing that some iron is dissolved in the iron oxide. The very fine inclusions lie in the crystal boundaries for the most part and undoubtedly are precipitated at the freezing point during the actual solidification of the metal.

THE DISTRIBUTION OF IRON OXIDE BETWEEN SLAGS OF THE SYSTEM $(CaO + MgO) - SiO_2 - FeO$ AND PURE LIQUID IRON

The primary aim of this thesis was to determine the distribution of iron oxide or oxygen, between the slags of the system $(CaO + MgO) - SiO_2 - FeO$ and liquid iron. The portion of the diagram investigated is shown in Fig. 47. The lines A and B represent the approximate location of the solid boundaries indicated by Bowen and Schairer in Fig. 8. The location of the lines is undoubtedly altered by the presence of MgO in the slags and any placement of points in the fields which should be solid may be attributed to this.

A. Effect of Temperature

In order to plot the results on a comparable basis, it was necessary to correct for the temperature effect. Chipman and Fetters (72) have shown that the temperature dependence of the oxygen distribution for these slags is the same as for the pure iron oxide slags. The temperature correction was made graphically, since this was sufficiently accurate, and since the actual calculation was somewhat tedious. An example follows:

Sample R-36-5 Oxygen - .136 Temperature 1575°C.

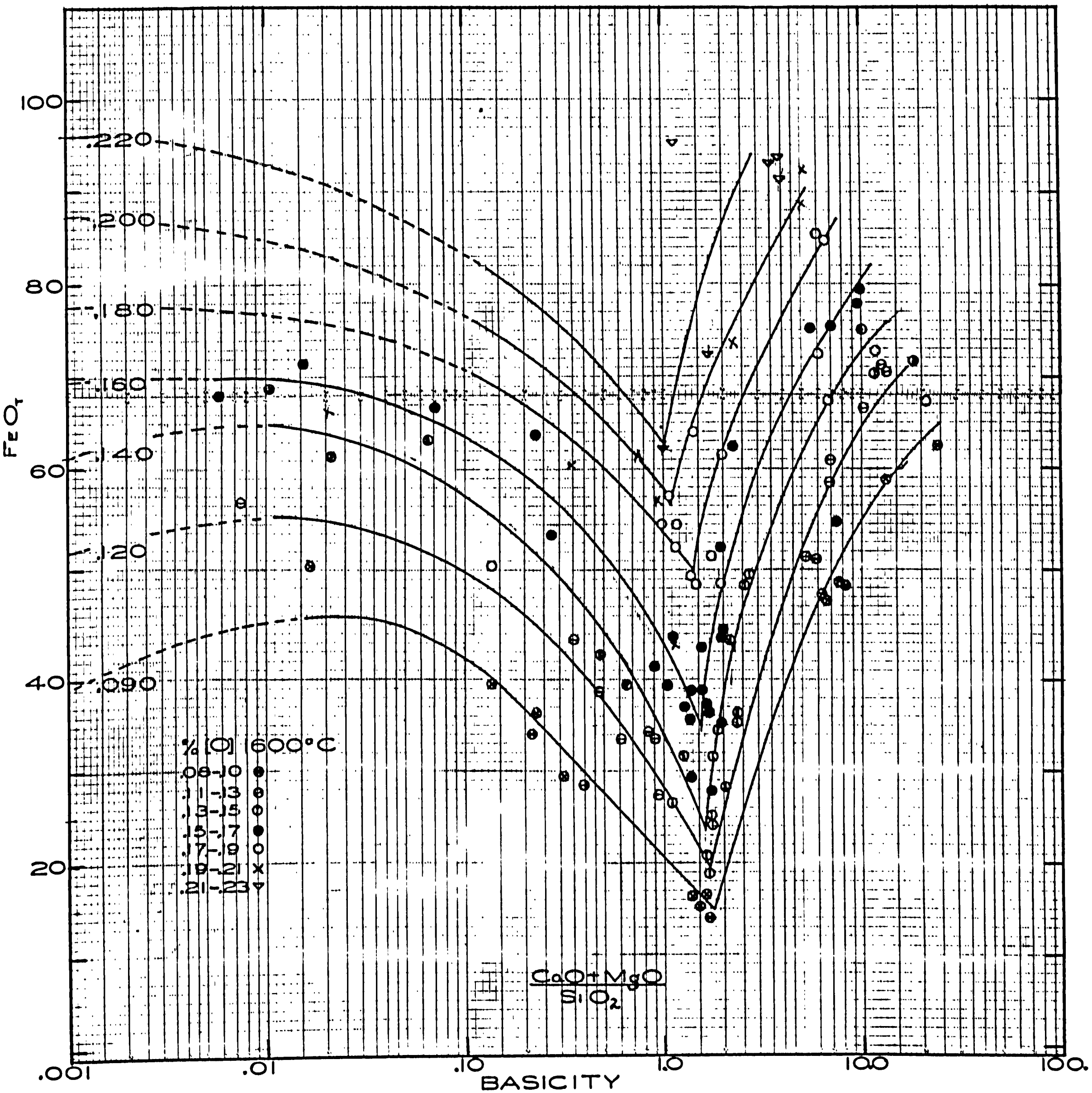

FeOT
100
80
60
40
20
.220
.200
.180
.160
.140
.120
.090
% [O] 1600°C
.08-.10 ⊗
.11-.13 ⊖
.13-.15 ⊘
.15-.17 ●
.17-.19 ○
.19-.21 x
.21-.23 ▽
CaO+MgO / SiO2
.001
.01
.10
1.0
10.0
100.
BASICITY

FIG 44

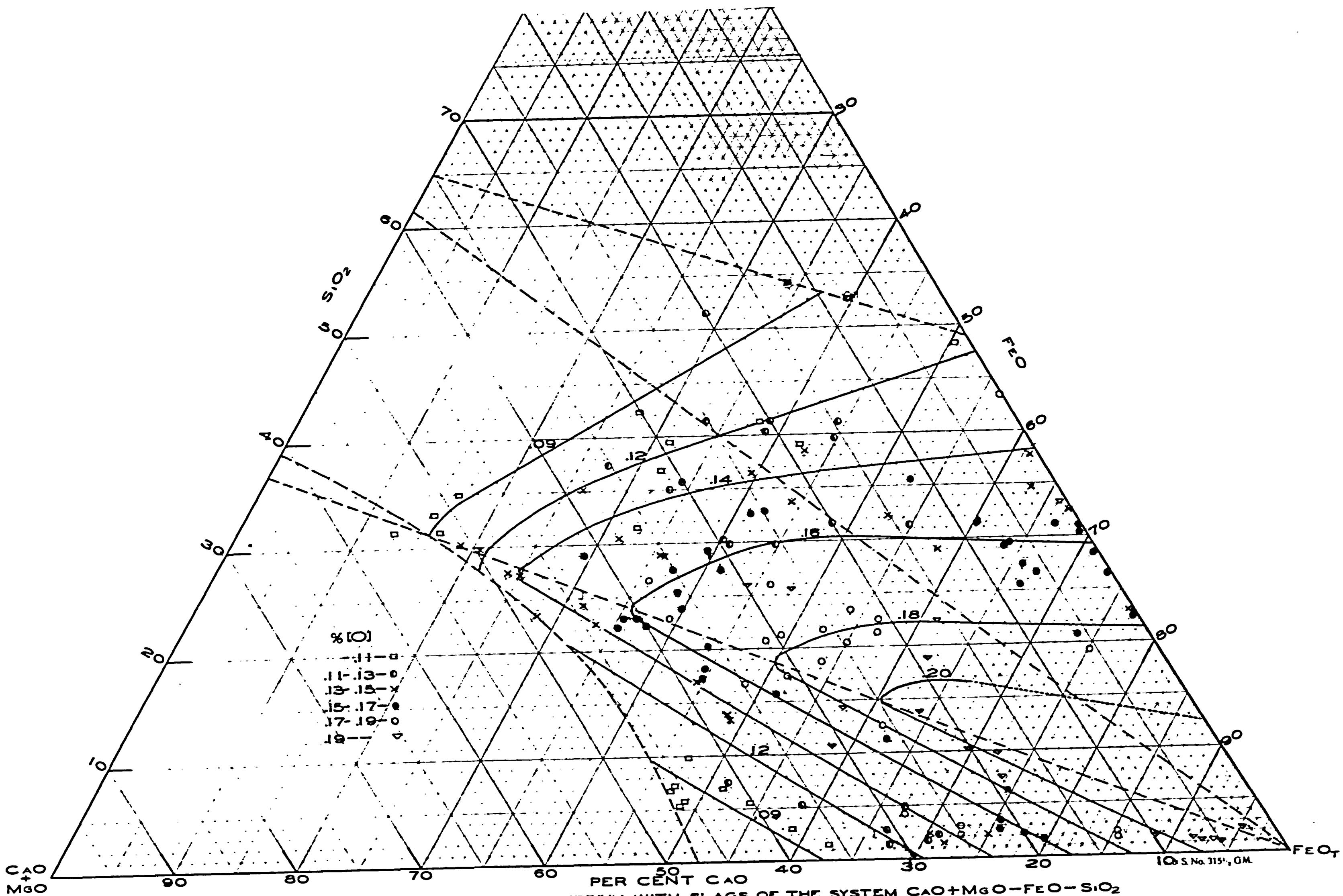


FIG 43 OXYGEN CONTENT OF METAL AT 1600°C IN EQUILIBRIUM WITH SLAGS OF THE SYSTEM CaO+MgO–FeO–SiO$_2$

The saturation value was taken from a graph as .206% oxygen. .136/.206 = .660, the fractional saturation. The saturation value at 1600°C. is .229% oxygen, so at 1600°C., the corrected oxygen content is .660 x .229% = .151% oxygen. The distribution coefficient, L_o, can be corrected very simply by merely using the corrected oxygen content in its calculation. All the data, including that obtained by Fetters and Chipman was calculated in this manner.

B. Effect of Composition

The results of correcting the oxygen values to 1600°C. are plotted in Fig. 43. Since a ternary diagram is somewhat awkward for an operating man to use, the results are replotted in a somewhat different manner in Fig. 44. Here all data is kept on a per cent basis, and basicity, defined as % CaO + % MgO/% SiO_2 is used to combine two of the variables, (CaO + MgO) and SiO_2. The utility of this diagram is that it enables an open hearth operator to immediately define an oxygen potential between the slag and metal. If a furnace is being operated at a basicity of 2.7, and an FeO_t of 30%, the saturation value to be expected would be about .095% oxygen. However the actual oxygen content of the metal as calculated from its carbon content may be only .015%. An oxygen potential may be said to exist between the slag and the metal of .080%.

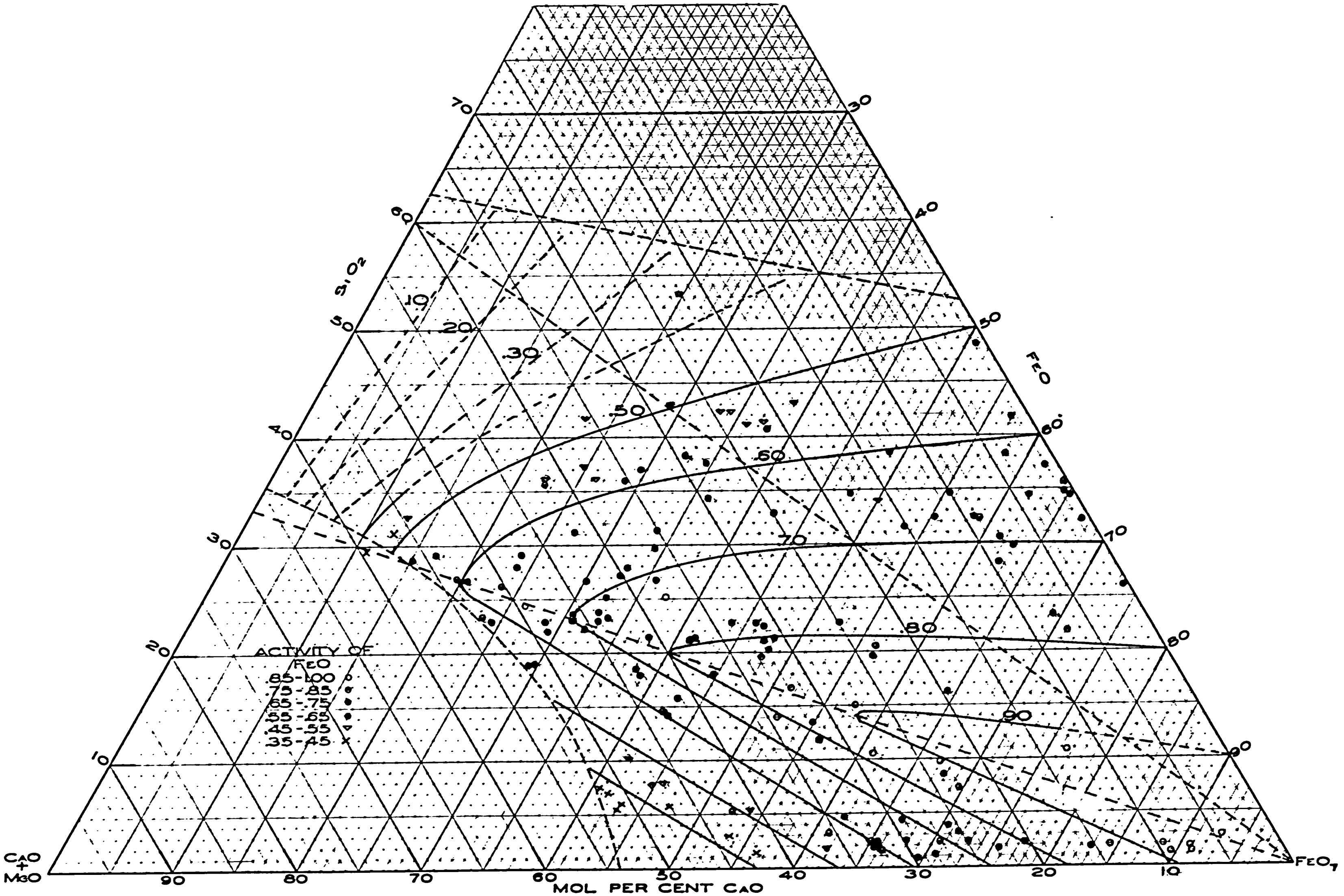


FIG 45 ACTIVITY OF IRON OXIDE IN SLAGS PLOTTED ON A MOL FRACTION BASIS

The magnitude of this potential will materially alter the rate of the various refining reactions in the furnace.

In Fig. 45, the data is plotted on a mol fraction basis. Since it has been shown (89) that the solution of FeO in liquid iron is ideal, we shall define the standard state of FeO in liquid iron as its saturation value. This saturation value for any temperature will have an activity of one. Activity is directly measured then by fractional saturation, and may be determined for any oxygen content merely by dividing the per cent oxygen in the metal by the concentration it would have at saturation at that temperature.

We may define the system under consideration as composed of liquid iron as one solvent, and a solution composed of lime and silica as the other. These two liquids will be considered as being completely immiscible in each other. While this assumption is probably not completely true, the mutual solubilities can be supposed to be very slight. When a condition of this kind exists, it indicates that there is an enormous deviation from Raoult's law, i.e. that the liquids are sufficiently unlike so that their molecules will not interchange with each other. Since this deviation from Raoult's law is selfevident, and since the FeO, the solute which is distributed between these two solvents, forms an ideal solution with one of the liquids, the

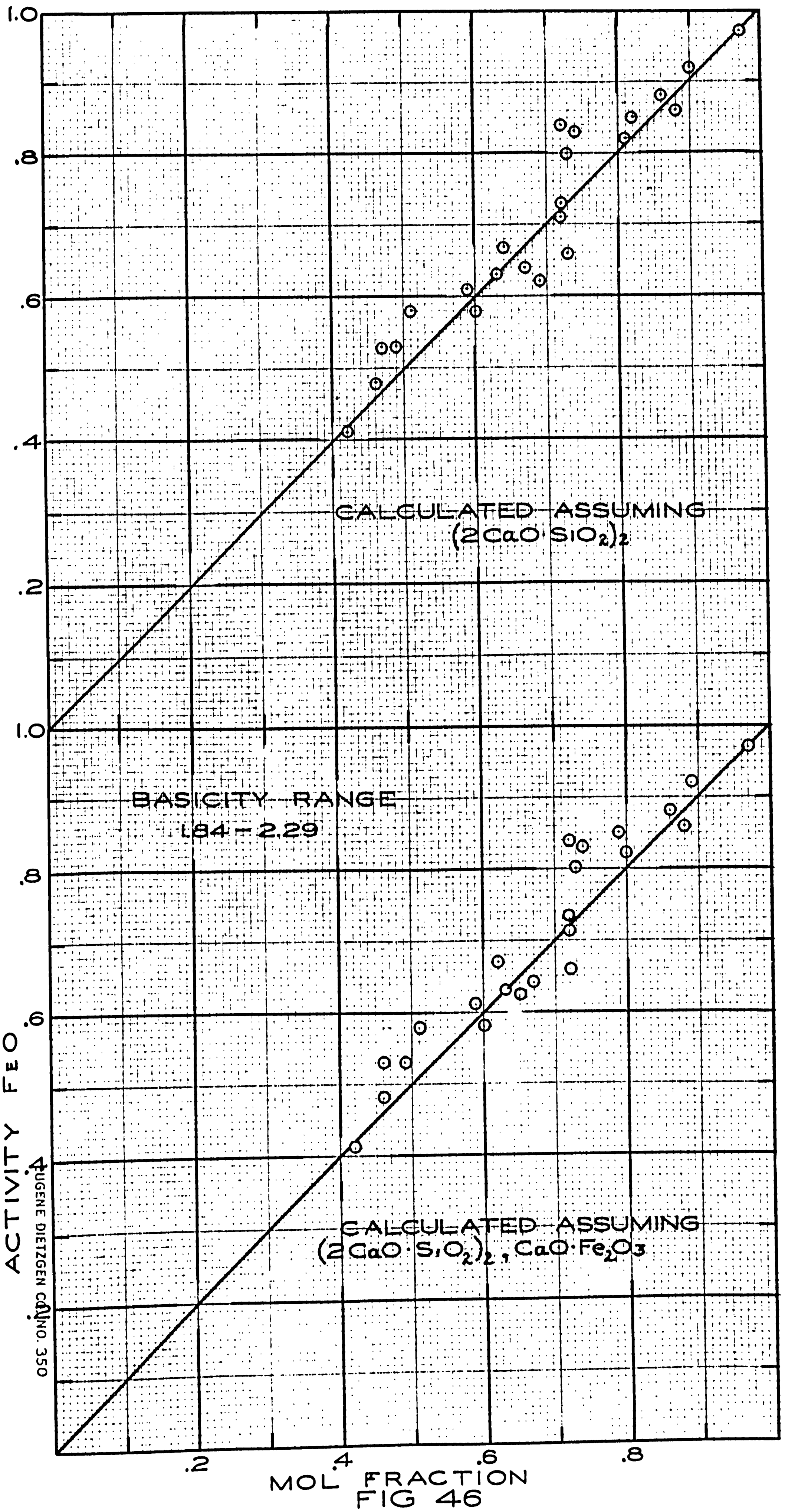

1.0
.8
.6
.4
.2
1.0
.8
.6
.4
.2
CALCULATED ASSUMING
$(2CaO \cdot SiO_2)_2$
BASICITY RANGE
1.84 – 2.29
CALCULATED ASSUMING
$(2CaO \cdot SiO_2)_2$, $CaO \cdot Fe_2O_3$
ACTIVITY FeO
.2
.4
.6
.8
MOL FRACTION
EUGENE DIETZGEN CO. NO. 350

FIG 46

iron, we can expect that its solution in the slag will be far from ideal. However we are dealing with a substance, FeO, which itself forms two liquid layers with iron. It is probable, therefore, that, were the iron oxide more soluble in liquid iron a great deviation from Raoult's law would be found. It is also true that in general, like substances tend to form ideal solutions. The fact that the slag is made up, at least analytically, of oxides, would indicate that the deviation from Raoult's law might be smaller in the slag than in the metal. Also the fact that this system is at such a high temperature would tend to bring it closer to ideality. Since the mol per cent of FeO in the two solvents differ so widely, no direct comparison of ideality can be made.

It is generally accepted that at these temperatures the silica takes on the characteristics of an acid, and lime that of a base. It is significant, therefore, that at a mol ratio of 2 to 1, there is a sharp break in the iso activity lines in Fig. 45. Chipman and Fetters have investigated the possibility of the compound 2 $CaO \cdot SiO_2$ and their results are shown in Fig. 20. It is apparent that either they have chosen their compound wrong or that the solution is non-ideal. If the compound is chosen as the double molecule $(2\ CaO \cdot SiO_2)_2$, the deviation from ideality is almost completely eliminated. Fig. 46 is drawn on the

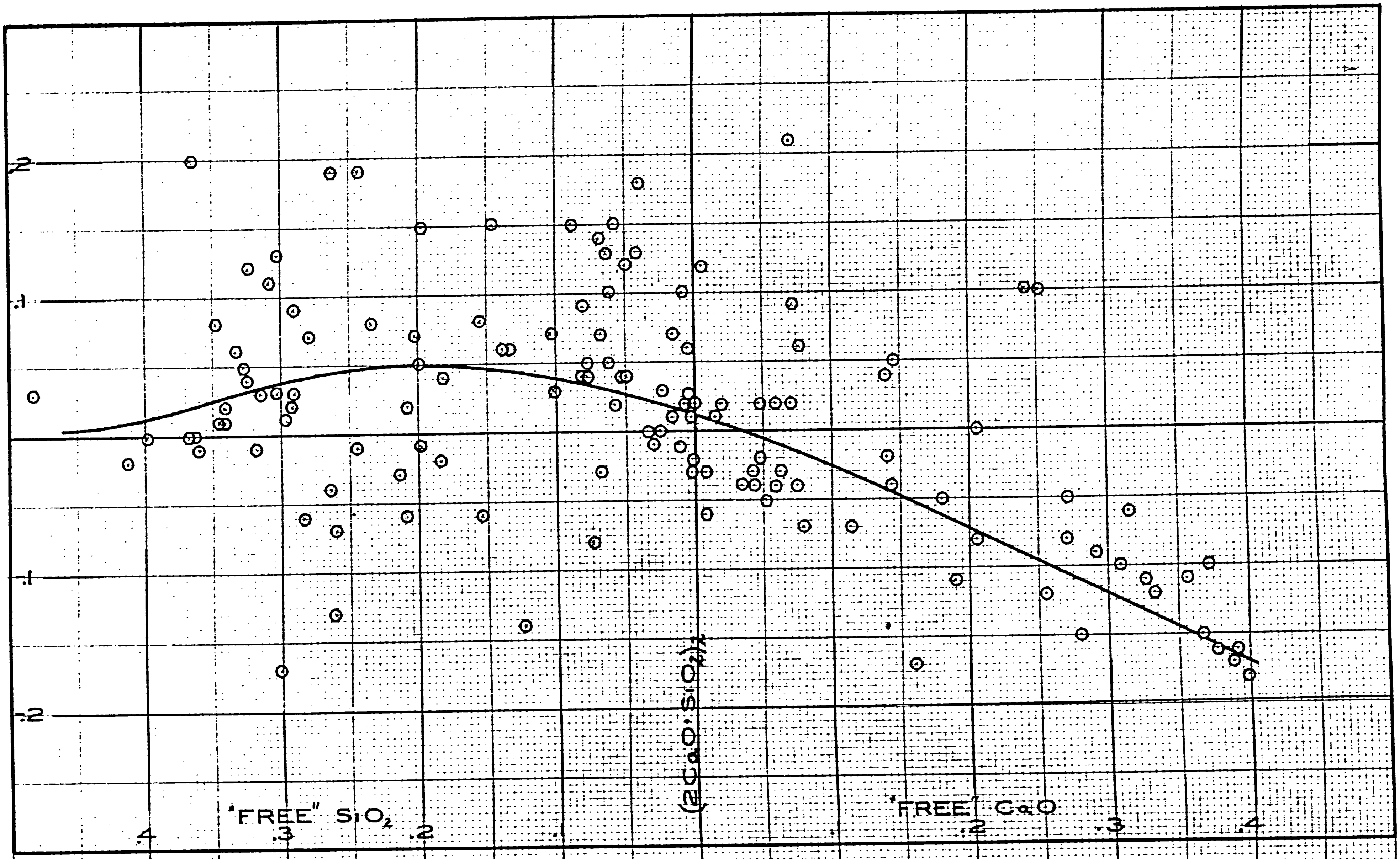


FIG 48 DEVIATION FROM RAOULTS LAW AS A FUNCTION OF BASICITY

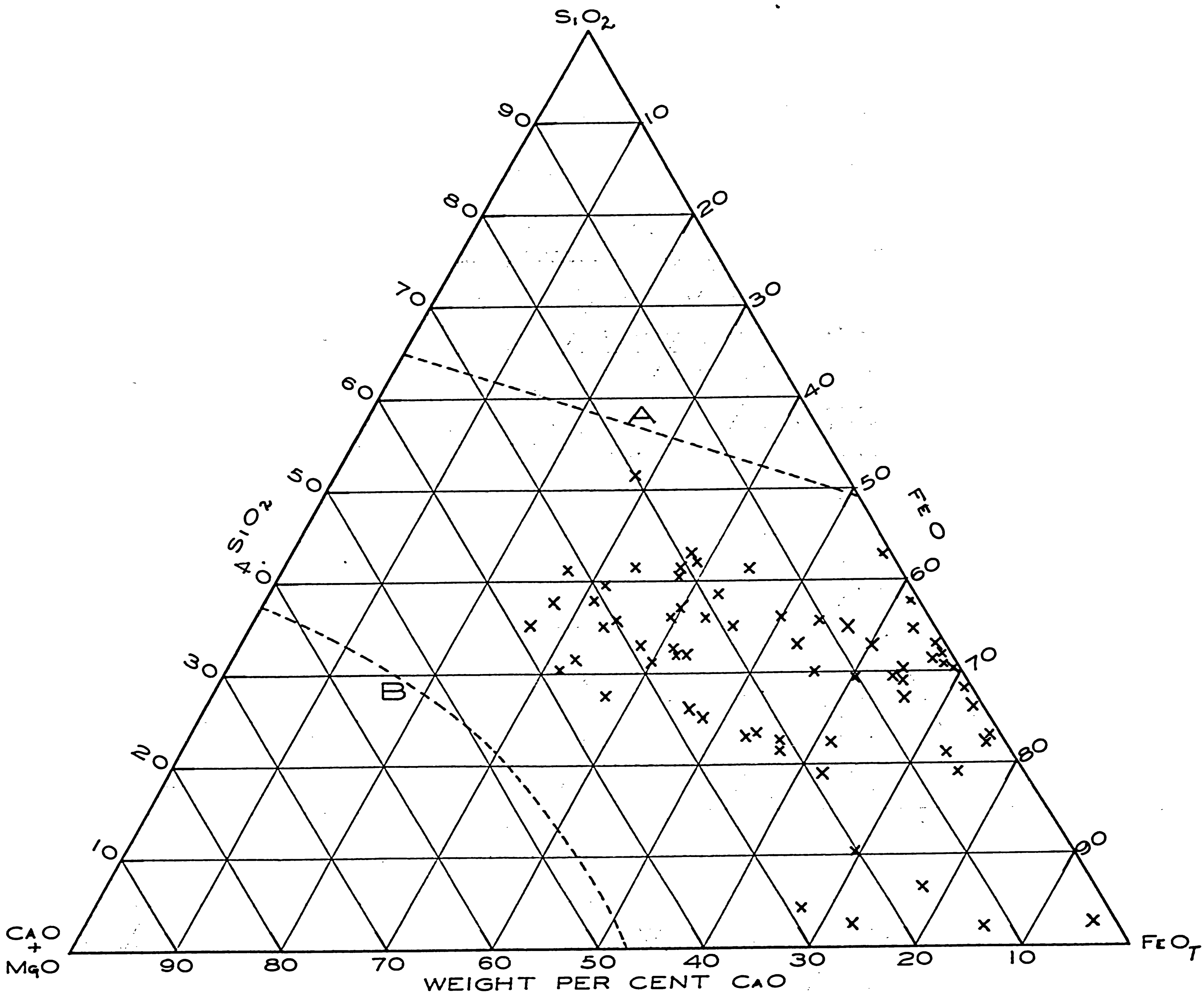

SiO2
90
80
70
60
50
SiO2
40
30
20
10
10
20
30
40
50
FeO
60
70
80
90
A
B
CaO
+
MgO
FeOT
90
80
70
60
50
40
30
20
10
WEIGHT PER CENT CaO

FIG 47

TABLE VII

SUMMARY OF EXPERIMENTAL DATA

Heat No.	Metal Test	Total Fe	FeO	Fe_2O_3	CaO	SiO_2	MgO	Al_2O_3	Total %	% O	% N_2	Temp.	L_o	% O Corr. to 1600°C	L_o Corr. to 1600°C	R_1 $\frac{CaO+MgO}{SiO_2}$
R-20	1	52.18	66.30	.92		30.20	.32	.28	98.02	.144	.044	1588	.209	.151	.220	.0107
	4	45.75	58.25	.69		36.12	.76	1.96	97.83	.144	*	1623	.234	.119	.213	.0212
R-21	1-B	42.70	53.29	1.84		42.20	.31	.31	99.00	.148	.037	1640	.263	.126	.223	.0074
	2	52.50	66.51	1.15		29.96	.18	1.21	99.31	.181	.043	1642	.262	.153	.221	.0059
	3	52.02	65.27	1.84		26.72	.41	4.67	98.91	.182	.039	1641	.259	.154	.215	.0155
	4	49.93	62.79	1.61		29.88	2.11	1.46	97.85	.185	.047	1632	.277	.162	.243	.0705
	5	47.68	60.72	.69		33.70	2.21	.71	98.03	.156	.040	1627	.247	.140	.222	.0655
R-24	1		61.61	10.42	24.06	2.08	.24	.26	98.67	.170	.026	1581	.233	.184	.252	11.66
	2		64.37	9.40	18.15	6.26	.54	.36	99.08	.192	.020	1581	.258	.208	.279	2.986
	3		53.70	11.85	27.65	4.12	.10	.87	98.29	.170	.020	1584	.273	.182	.270	6.732
	4		77.24	6.54	.09	2.02	12.23	1.80	99.92	.169	.022	1584	.198	.181	.212	6.106
	6		51.13	2.04	9.62	34.96	.77	.95	99.47	.149	.022	1584	.277	.159	.295	.275
	7		56.09	3.27	8.70	28.98	1.21	1.17	99.42	.175	.028	1581	.290	.190	.315	.341
	8		60.69	2.04	3.73	28.98	2.82	.66	98.92	.148	.028	1573	.232	.156	.245	.226
	9		36.78	1.43	14.30	40.58	5.42	.66	99.76	.100	.029	1567	.258	.114	.295	.486
	10		29.06	2.25	7.71	39.11	21.17	.46	99.76	.085	.031	1559	.271	.101	.322	.739
R-25	6		87.91	7.15		2.25	2.59	.23	100.13	.192	.021	1556	.202	.230	.242	1.150
R-26	3		64.00	2.25		33.14	.67	.29	100.35	.221	.021	1635	.334	.192	.290	.0202
	4		60.69	.41		22.20	16.33	.41	100.04	.236	.021	1650	.385	.193	.315	.735
	5		50.94	4.91		22.16	20.72	.49	99.22	.247	.022	1662	.438	.192	.342	.935
	6		47.82	5.22		23.00	22.54	1.43	100.31	.242	.023	1665	.449	.186	.345	.980
	8		50.21	5.93		20.74	21.12	1.51	99.51	.242	.020	1660	.424	.189	.331	1.018
	10		62.71	5.11	7.50	9.28	12.10	.93	98.13	.244	.021	1634	.351	.211	.303	2.005
R-28	1		55.73	5.52	16.10	18.42	2.41	.82	99.00	.223	.023	1608	.359	.214	.344	1.005
	2		37.70	1.43	19.25	36.10	4.29	.40	99.17	.146	.025	1612	.369	.139	.351	.649
	3		42.85	1.02	10.51	40.62	3.84	.39	99.23	.136	.028	1629	.307	.120	.271	.353
	4		30.52	2.66	29.81	34.46	1.24	.40	99.10	.134	.025	1615	.401	.126	.377	.901
R-29	6		31.26	1.02	19.48	31.12	15.84	.79	99.51	.128	.027	1668	.392	.0975	.298	1.135
	7		33.47	3.07	34.00	26.52	.08	.53	97.67	.159	.028	1604	.425	.156	.417	1.286
	8		23.91	1.84	37.22	34.00	.17	.38	97.52	.146	.026	1608	.554	.141	.534	1.100
	9		25.38	1.64	20.82	36.80	13.41	.42	98.47	.129	.032	1608	.470	.124	.452	.930
R-30	5		40.56	1.42	18.16	37.60	.08	.48	98.30	.145	.023	1595	.339	.148	.346	.485
	6		38.19	2.02	25.15	31.76	.13	.61	97.86	.157	.025	1590	.381	.164	.498	.796
	7		27.46	.81	19.72	50.66	.08	.50	99.23	.115	.023	1597	.402	.117	.409	.391
	8		31.83	1.21	24.64	40.80	.08	.50	99.23	.127	.028	1606	.380	.123	.368	.606
	9		27.10	3.75	36.70	29.30	.08	.48	99.41	.164	.031	1641	.520	.139	.440	1.255
	10		31.64	1.62	29.10	34.60	.08	.90	97.94	.168	.029	1657	.492	.126	.369	.843
R-36	1	55.9	62.3	10.8	5.62	20.30	.20	.17	99.39	.171	.026	1615	.233	.161	.219	.287
	2	44.0	46.3	11.7	7.72	34.30	.12	.14	100.28	.158	.026	1612	.276	.150	.262	.229
	3	49.6	54.9	9.9	5.50	28.84	.14	.20	99.48	.160	.034	1604	.247	.157	.242	.200
	4	49.0	54.1	9.9	6.20	29.16	.14	.17	99.67	.140	.033	1574	.219	.156	.244	.217
	5	46.3	53.6	6.4	6.51	32.81	.08	.15	99.55	.136	.039	1575	.225	.151	.250	.204
	6	50.2	57.1	8.4	5.09	26.45	2.48	.12	99.64	.140	.039	1576	.214	.155	.237	.286
	7	56.4	62.6	11.1	4.45	18.6	.99	2.40	100.14	.168	.036	1584	.224	.179	.238	.292
	8	40.93	42.0	11.85	4.8	22.62	18.40	.17	99.84	.187	.030	1590	.350	.195	.365	1.025
	9	37.2	40.8	7.8	5.70	25.40	20.75	.24	100.69	.182	.039	1582	.379	.196	.409	1.042
	10	36.1	40.0	7.1	6.00	26.14	21.92	.24	101.40	.180	.035	1588	.390	.186	.403	1.068
	11	36.2	40.3	7.0	12.22	34.96	5.91	.14	101.53	.155	.037	1572	.335	.174	.376	.547
	12	30.8	20.2	21.6	10.06	35.88	12.58	.24	100.56	.109	.046	1586	.270	.116	.287	.631
	13	29.8	27.9	11.7	17.49	43.64	1.07	.14	101.94	.114	.038	1585	.299	.122	.320	.425
	14	40.7	43.1	10.3	12.99	32.84	.08	.19	99.50	.120	.040	1592	.225	.124	.233	.398
	15	38.6	40.8	9.9	12.66	35.22	.65	.31	100.23	.136	.039	1607	.272	.132	.264	.406
	16	43.2	46.7	9.9	11.50	30.49	.61	.22	99.42	.143	.041	1614	.253	.135	.238	.397
	17	29.4	34.8	3.3	20.25	41.07	.08	.22	99.72	.124	.038	1618	.325	.115	.301	.495
R-37	1	59.0	69.1	7.5		22.48	.08	.5	99.66	.151	.032	1597	.196	.152	.197	.0036
	2	56.8	67.7	5.9		26.46	.08	.2	100.36	.114	.036	1586	.155	.121	.165	.0030
	3	59.1	69.9	6.7		22.68	.04	.3	99.62	.137	.039	1595	.178	.139	.181	.0018
	4	51.9	63.3	3.8		32.30	.08	.3	99.78	.143	.037	1601	.212	.142	.211	.0025
	5	33.1	39.5	3.8		32.46	21.43	.51	97.70	.150	.041	1615	.340	.141	.319	.660
	6-R	37.5	39.3	2.8		32.36	24.22	.41	99.09	.162	.040	1617	.381	.151	.355	.135
	7-R	21.0	26.2	.8	20.37	41.56	9.02	.44	98.39	.098	.044	1579	.355	.107	.388	.707
	8	23.9	26.1	5.2	19.01	38.38	10.76	.55	100.00	.093	.044	1572	.299	.104	.334	.776
	9	28.0	29.8	6.9	19.45	43.16	.08	.48	99.87	.096	.041	1589	.263	.100	.274	.453
	10	30.9	32.8	7.7	17.85	42.18	.04	.41	101.08	.105	.042	1595	.264	.107	.269	.424
	11	29.9	22.1	7.1	18.20	32.56	10.07	.31	100.34	.125	.038	1614	.323	.117	.302	.868
	12	30.8	35.7	4.4	17.03	31.15	11.24	.48	100.00	.158	.040	1609	.396	.152	.381	.897
R-22	1									.297		1655				
	2									.286		1640				
R-23	5									.222		1613				
	6									.210		1577				
	7									.216		1577				
	8									.256		1637				
	9									.257		1637				
R-25	1									.214		1597				
	2									.210		1591				
	4									.226		1608				
R-26	1									.268		1629				
	2									.259		1631				
	9									.244		1652				
	11									.161		1530				
R-29	1									.181		1552				
	2									.186		1545				
R-30	1									.240		1612				
	2									.302		1651				
	3									.298		1650				
R-38	1									.188		1554				
	2									.234		1604				
	3									.313		1673				
	4									.342		1687				
	6									.197		1548				
	7									.186		1532				

*Data missing or questionable.

assumption that this molecule exists. The lower half was drawn assuming that $CaO \cdot Fe_2O_3$ was also present, but the resulting data is not quite as good as the upper figure. It is realized that the fact that such an assumption works does not by any means prove the existance of the compound. It does, however, offer itself as an easy method of extrapolation, and the dotted lines in Fig. 45 are calculated on the assumption of this compound.

To investigate the rest of the ternary diagram, the graph in Fig. 48 was constructed. The large experimental error is evident, and is not surprising considering the experimental difficulties. The "free" silica and free lime are calculated assuming that the $(2\ CaO \cdot SiO_2)_2$ is undissociated.

The acid side of the diagram indicate that at each end of the range plotted, i.e., the pure $(2\ CaO \cdot SiO_2)_2$ and the pure SiO_2, the approach to ideality is quite close. It would seem probable, therefore, that intermediate concentrations would also be ideal. However this is not always the case, especially for polar liquids, as there may be an induced dipole. The data in this intermediate region is rather inconclusive and lack of time prevented further study.

The basic side of Fig. 48, the "free" CaO side, exhibits a pronounced negative deviation with increasing basicity. An explanation of this effect can be made in a number

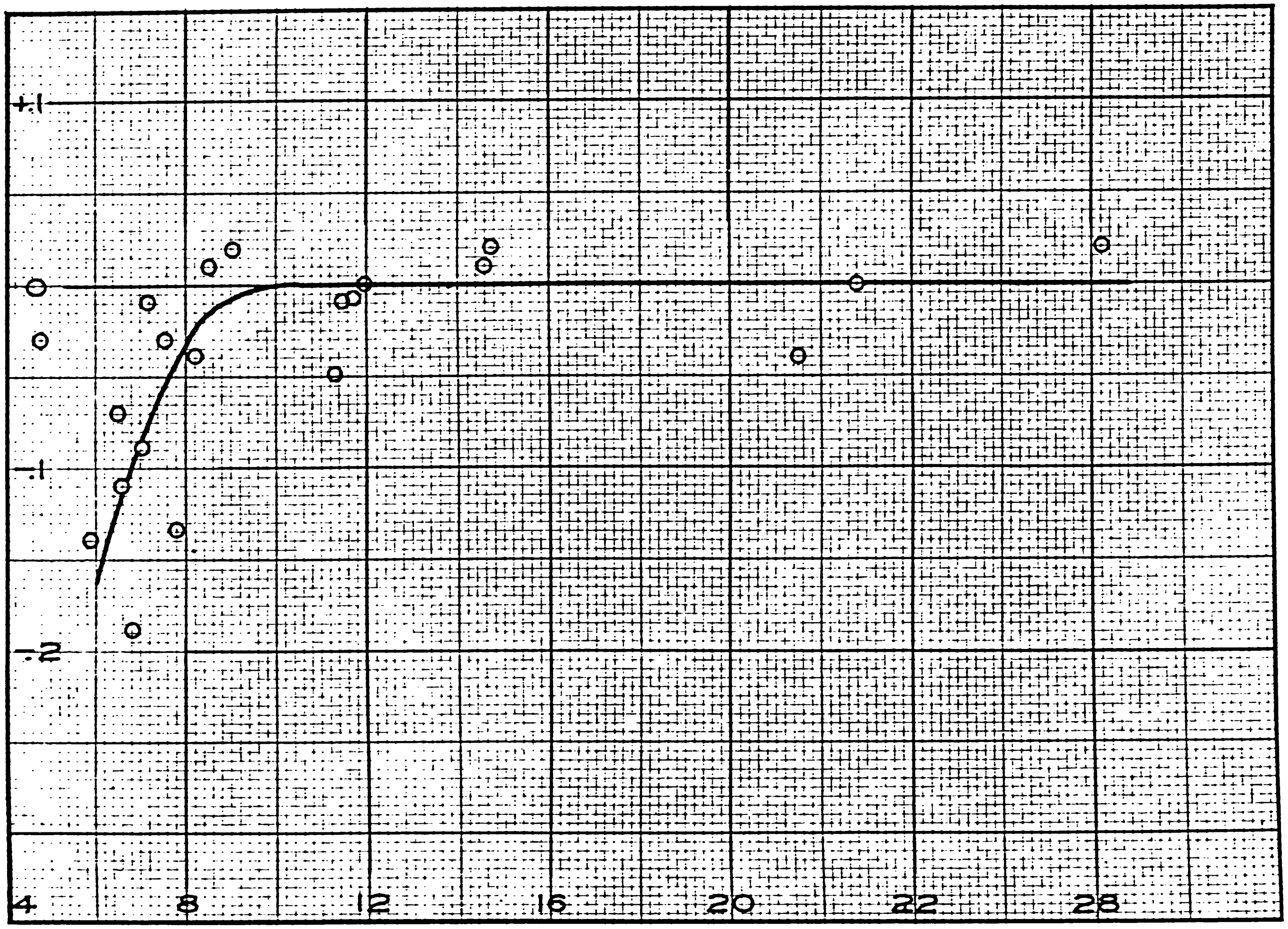


FIG 50 Deviation of mol per cent from ideality vs. basicity.

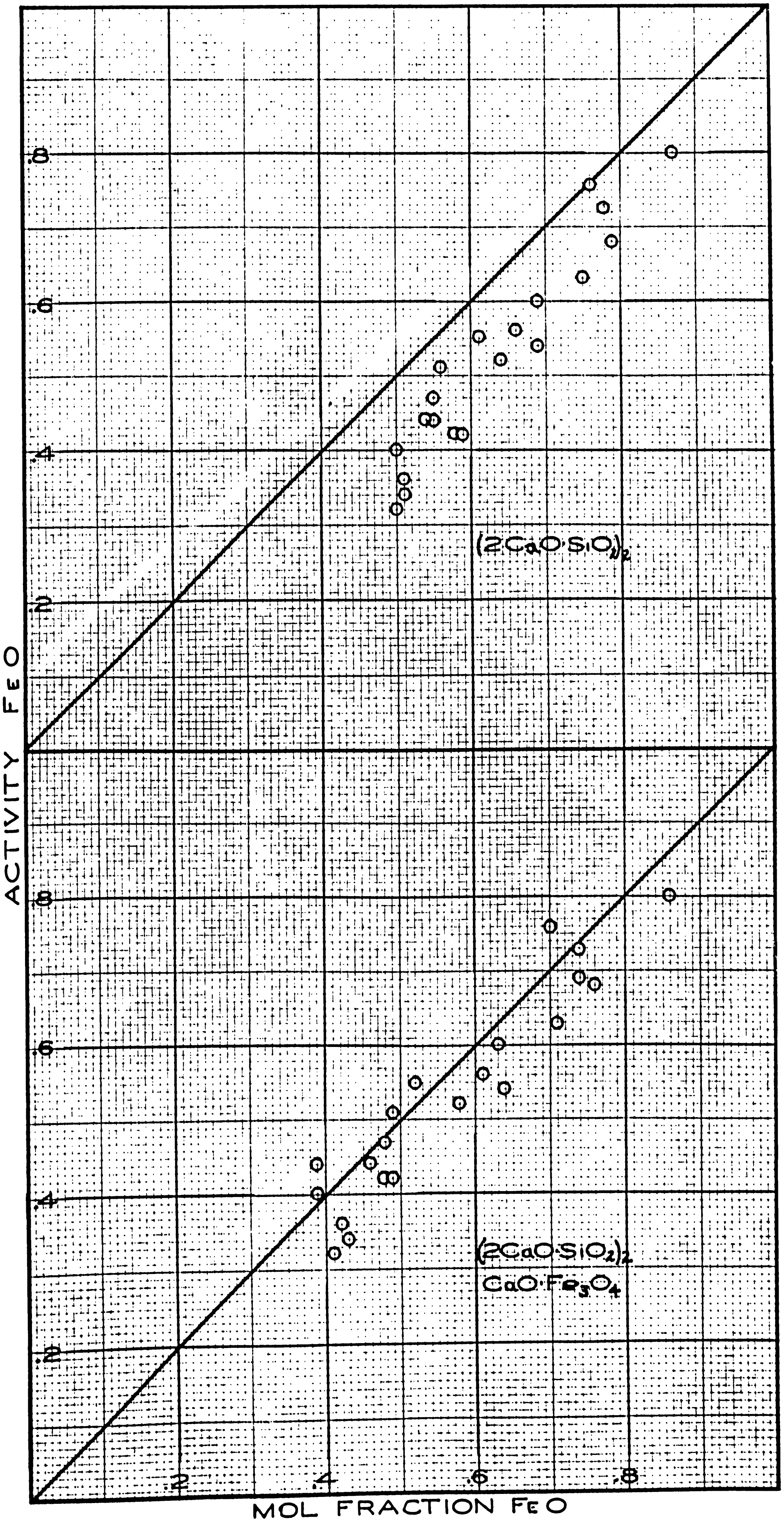

ACTIVITY FeO
.8
.6
.4
.2
(2CaO·SiO2)2
.8
.6
.4
.2
(2CaO·SiO2)2
CaO·Fe3O4
.2
.4
.6
.8
MOL FRACTION FeO

FIG 51

of ways, none of them very simple. Fig. 18 shows that the Fe_2O_3 content increases with the basicity. This strongly suggests that a compound is formed. This compound might be one of several which have been observed petrographically in solid slags. The most important of these are $CaO \cdot Fe_2O_3$, $2\ CaO \cdot Fe_2O_3$ and $CaO \cdot Fe_3O_4$. However if we plot mol per cent FeO as analyzed and separate from Fe_2O_3 against the deviation from ideality, Fig. 50, with no compounds of any kind postulated, it is apparent that at very high basicities, above 10, the dicalcium silicate is probably dissociated. However the Fe_2O_3 must be combined in some manner with the CaO since it increases with increasing CaO content. The compound which at least partly explains this deviation at intermediate basicities is $CaO \cdot Fe_3O_4$. Fig. 51 shows a comparison between the plots obtained in the basicity range above 5 by assuming that the only compound is $(2\ CaO \cdot SiO_2)_2$, and by assuming that two compounds, $(2\ CaO \cdot SiO_2)_2$ and $CaO \cdot Fe_3O_4$ exist.

A part of the investigation was to determine the effect of magnesia on the activity diagram Fig. 45. This can only be answered qualitatively since there was insufficient time for an investigation into the $MgO-SiO_2-FeO$ system. In general, high magnesia slags tend to be very crystalline, the surface presenting the appearance of a mesh of interlacing crystals. Excessive MgO contents seem to make the results erratic, but at the MgO contents encountered in normal open hearth practice, up to 10%, no serious error is introduced by substituting magnesia for lime in the various calculations.

Incidental to the slag studies it was found that the rim ofbare metal allowed for a slow absorption of nitrogen. The end point toward which all these heats tended was .040% nitrogen. This is in agreement with the work reported by Chipman and Vaughn (91).

SUMMARY

This thesis presents the results of an experimental study of the equilibrium between slags of the system (CaO + MgO) - SiO_2 - FeO at the temperatures encountered in steel making practice.

The solubility of iron oxide in liquid iron under pure iron oxide slags was redetermined and modified slightly from that of previous investigations.

The equilibrium oxygen content of the metal at 1600°C. is a function of composition of the slag as is also the activity of iron oxide in the slag.

The variation of the activity of iron oxide in slag has been almost completely explained by the assumption of a certain molecular species in the slag. The assumption of these species allows the slag to be treated as an ideal solution. The indications are that no compound is formed between silica and ferrous oxide at 1600°C.; that the dicalcium silicate exists as a double molecule $(2\,CaO \cdot SiO_2)_2$ and is undissociated at 1600°C. except at very high basicities, where its concentration is low; that at mol basicities greater than 2, the excess lime combines with the iron oxide to form $CaO \cdot Fe_2O_4$ in amounts depending on the free CaO available after the formation of the $(2\,CaO \cdot SiO_2)_2$.

The effect of magnesia has been qualitatively found

to be almost the same as lime in concentrations at least up to ten percent. The solubility of nitrogen in pure iron has been checked at .040%.

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