SULPHUR EQUILIBRIUM BETWEEN SLAGS
AND IRON-CARBON ALLOYS.

THESIS

presented to the

University of Glasgow

for the degree of

Doctor of Philosophy

by

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March 1953.

I N D E X.

INTRODUCTION.

In many pyrometallurgical processes metal is refined by the action of a slag. The extent to which the change of metal composition can go in such an operation is limited by the equilibrium positions of the slag-metal reactions. These equilibrium positions can be determined in the laboratory and such determinations in controlled conditions are useful in contributing towards an understanding of the reactions. Slag-metal equilibrium studies have been used to investigate many aspects of steel making but until recently no work had been done using the types of metal and slag found in the blast furnace. This investigation was started with the object of examining sulphur partition at equilibrium between such metals and slags.

In recent years the raw materials charged to blast furnaces have shown a distinct tendency to increase in sulphur content. Attention has therefore been focussed on the blast furnace as a desulphurising unit; any way of increasing its efficiency in this matter would be of first importance. However, without information on the equilibrium slag-metal sulphur distribution there is no datum line from which to assess the desulphurising performance of a furnace.

Recent experimental results (1)(2) tend to confirm the view that, in a blast furnace, equilibrium is not reached with respect to sulphur. However conditions in these laboratory experiments may well have been different from those in the hearth of a blast furnace. It is only from experiments, in

which there can be sufficient variation of these conditions to cover the possible range of variation in a blast furnace, that a decision as to why existing laboratory data do not agree with blast furnace data, can be made. As part of this investigation it is proposed to vary the FeO content of slags and to study the effect of this on sulphur equilibrium. The reported FeO contents of blast furnace slags vary from about 0.1 per cent to 1 per cent and therefore, in this respect alone, conditions in experiments in carbon crucibles could be very different from those in the hearth of a furnace.

Apart from the direct bearing which the results of an investigation of this nature may have on the industrial process, there are fundamental issues which may be affected. As yet, very little is known of the thermodynamic activities of constituents in liquid slags, particularly those whose complexity approaches that of industrially used slags. Although more is known of the activities of substances in solution in iron, the problem here is by no means completely solved either. Slag metal equilibrium studies can be important sources of data from which activities can be calculated.

The experiments carried out during this investigation can conveniently be separated into two types:

(1) Those done in carbon crucibles and in which the slag composition was varied.

(2) Those done in alumina crucibles with varying slag FeO contents but with an otherwise constant slag composition.

In those sections in which technique is described and in which the results are discussed this division has been maintained for the sake of clarity.

REVIEW OF LITERATURE

There is, in the literature, a considerable amount of information which has some bearing on blast furnace desulphur-:isation. It is not proposed to give an exhaustive survey of this here but rather to indicate the salient features of the more important published work.

Examinations of samples withdrawn from the boshes and hearths of actual working blast furnaces have been made by Kinney[3] and by Mund, Stoecker and Eilender[4]. From the results of these investigations it was possible, to some extent, to follow the movements of sulphur between the phases present in the furnaces. Both sets of results indicated that as the metal descended the furnace its sulphur content reached a maximum at about the tuyere level. The sulphur content of the metal cast from the furnace was always below this value. Mund, Stoecker and Eilender attributed this high sulphur content to the extremely oxidising conditions obtaining in front of the tuyeres and to the reaction

$$FeO + CaS \longrightarrow FeS + CaO$$

They also found that the sulphur contents of metal samples withdrawn through tuyeres which were off blast were consistently lower than those taken through tuyeres on blast.

This work showed that desulphurisation of the iron takes place below the level of the tuyeres in a blast furnace. This can only be due to reaction between the liquid slag and metal.

Holbrook and Joseph[5] made a systematic attempt to find the desulphurising powers of blast furnace slags in a wide range of composition. They used small graphite crucibles in which the slag and metal were held at temperature for 30 minutes and then were quenched. All the experimental conditions were standardised so that a relative index of desulphurising power could be obtained for each slag. No attempt was made to see if equilibrium was reached between slag and metal.

Their measure of desulphurising power was the ratio $\frac{\% \text{ Sulphur in slag}}{\% \text{ Sulphur in metal}} = \frac{(S)}{[S]}$ (throughout, round brackets are used to denote constituents, concentrations or activities in slags and square brackets those in metals). They found that in magnesia free slags this ratio increased as lime replaced silica, to a lesser extent as lime replaced alumina and to a lesser extent again as alumina replaced silica. Magnesia was found to be less potent as a desulphurising agent than lime except in the very basic slags. In these its effect was thought to be to decrease viscosity and so allow the slags to exhibit their inherently strong desulphurising powers.

The effect of an increase of temperature in improving desulphurisation was found to be most marked in the slags of highest viscosity. The suggestion was also made that, in these experiments, desulphurisation was promoted by bubbles of CO formed in the reactions. These were envisaged as carriers of beads of metal up into the slag layer.

While an investigation of this kind is undoubtedly of great practical value it presents a complex picture since, in the results, the effects of differing rates of reaction and of differing equilibrium positions may be superimposed.

Lowry(6) pointed out that some desulphurisation ratios obtained in the blast furnace practice were considerably higher than those given by Holbrook and Joseph for slags of approximately the same composition. This indicated that the furnace quoted by Lowry was nearer to equilibrium with respect to sulphur than were the experiments.

Wentrup(7) made an examination of the factors involved in the desulphurisation of pig iron. While his main concern was the effect of manganese on desulphurisation in the ladle and the mixer, he did make some interesting calculations on desulphurisation inside the blast furnace. He considered that sulphur could enter the slag as FeS, CaS or MnS and obtained values for the equilibrium constants of the three transfer reactions from various sources. He was then able to calculate values of the equilibrium $\frac{(S)}{[S]}$ ratio for various hypothetical slag compositions. From these calculations Wentrup concluded that the governing effect of lime on desulphurisation could come into play only if the FeO and silica contents of the slag were kept low (e.g., $SiO_2 < 26\%$ and $FeO < 1\%$). With higher silica and FeO contents he contended that the main agent of desulphurisation was manganese. It has since been shown by Morris(8) that under normal

operating conditions in the blast furnace, desulphurisation
by separation of manganese sulphide from the metal is extremely
unlikely to occur.   This, however, does not detract from the
interest and value of those parts of Wentrup's calculations
which indicate that lime and FeO content are the controlling
factors in blast furnace desulphurisation.

McCaffery and Oesterle(9) did a series of experiments
to find the solubility of sulphur as CaS and as MnS in slags of
blast furnace composition.   They found, at 1500°C, that
solubilities were well in excess of anything normally found in
practice.   For example in a slag containing 40% CaO, 40% SiO$_2$
and 20% Al$_2$O$_3$ the solubility of sulphur as CaS was found to be
10.5% S, and as MnS 16%S.   Temperature was found to have a
much greater effect in increasing solubility than a change in
slag composition.   An increase in the alumina content of the
slag increased the CaS solubility limit and decreased the MnS
solubility limit slightly.

Martin Glockler and Wood(10) investigated the form of
occurrence of the sulphides FeS, CaS and MnS in a blast furnace
type slag (46% CaO, 41% SiO$_2$, 13% Al$_2$O$_3$).   They found evidence
of the presence of colloidal particles in the quenched glassy
slag when appreciable quantities of any of these sulphides were
present.   They also found that the solubility of FeS in this
slag at about 1400°C was 0.03% sulphur and of CaS 1.6% sulphur.

Hatch and Chipman[1] made what was probably the first study of the sulphur distribution between blast furnace type metals and slags at equilibrium.   They worked with synthetic slags ranging in composition from 28% to 43% SiO_2, from 31% to 52% CaO, from 5% to 26% Al_2O_3 and up to 19% MgO.   Their metals contained up to 7% silicon, the highest silicon contents being used with the most acid slags.   This was in order to minimise changes in slag composition due to reduction of silica during the course of an experiment.   The melts were done in graphite crucibles in an atmosphere of carbon monoxide and were stirred with a graphite stirrer.   Under these conditions all the slag-metal couples came to equilibrium with regard to sulphur within 7 hours.

With an increase in basicity the ratio $\frac{(S)}{[S]}$ increased; the best method of computing basicity was found to be obtained using the expression (CaO + $\frac{2}{3}$MgO) – (SiO_2 + Al_2O_3) in mols. per 100 gram of slag.   Increasing the temperature from 1425°C to 1500°C increased the distribution ratio for a given slag.   Some experiments with slags containing 2.5% and 5% sulphur, as compared to 1.5% in the majority, showed that the higher was the sulphur content of the slag, the higher was the $\frac{(S)}{[S]}$ ratio.   In other words at constant basicity and temperature the metal sulphur content was not proportioned to the slag sulphur content.

These results will be compared with those of the present work in a later chapter.

Grant, Kalling and Chipman(11) set out to study the effect of magnesia as compared to lime in desulphurisation, the effect of manganese additions and the rate controlling factors in the slow desulphurisation process. The slags they used were within the composition ranges studied by Hatch and Chipman. From their results they concluded that magnesia had no desulphurising power of itself but that it was equal, on a molar basis, to lime in the neutralisation of acid constituents. Additions of MnO to the slag during the course of the heats caused an immediate reversal of sulphur to the metal; this was returned to the slag as the MnO was reduced. Recovery from this reversal was found to be more rapid in the basic slags.

The rate of approach to sulphur equilibrium was found to be greater in the more basic slags. This can be strikingly shown in the following results taken from the paper.

Slag composition, Wt.%				Time to reach equilibrium, hours.
CaO	MgO	Al_2O_3	SiO_2	
40	2	15	43	10
50	10	15	25	1

This effect of basicity was also noticed, in a qualitative way, by Hatch and Chipman(1) and is, of course, quite in keeping with the findings of Holbrook and Joseph(5).

With this, and the sulphur reversion on adding MnO, in mind the authors suggested that the rate controlling step in desulphurisation was the reduction of silica. Accordingly an experiment was done with a slag containing 1% SiO_2, 50% CaO and 49% Al_2O_3. Sulphur equilibrium was reached in less than 40 minutes. This was taken to be confirmation of the view that slow reduction of silica and the consequent maintenance of an oxidising slag for long periods of time was the rate controlling step in the process.

Following upon this came the work of Grant, Troili and Chipman(12) who investigated more fully the effect of silica reduction on desulphurisation. They showed that the higher was the silicon content of the metal the faster equilibrium with regard to sulphur was obtained. They roughly established the silicon equilibrium position for the slags they used and found that the further the silicon content of the metal was below this, the slower was the attainment of sulphur equilibrium.

The theory advanced to explain this was the same as suggested by Grant, Kalling and Chipman. Slow silica reduction was envisaged as maintaining in the slag an oxygen potential sufficient to retard the sulphur transfer reaction.

An examination of the results on which this theory is based, and of those of Hatch and Chipman, shows that in some cases sulphur equilibrium was attained when the silicon content of the metal was well below the equilibrium silicon content. This suggests that the theory needs to be modified since a rigid application of it requires that the silicon reaction is at equilibrium before the sulphur reaction can be said to be at equilibrium.

Filer and Darken(2) took samples of slag and metal simultaneously as a blast furnace was casting. They remelted these in carbon crucibles at 1400°C, 1500°C and 1600°C and held them at temperature for up to 66 hours. Samples were taken, at various intervals of time, and analysed. From their results they deduced the temperatures at which the reactions concerning slag-metal transfer of sulphur, manganese and silicon would have been in equilibrium in the well of the furnace. The general conclusions were that while the silicon reaction might have reached equilibrium in the furnace the sulphur and manganese transfers probably had not. These were arrived at after comparison of the remelting results at the three temperatures with the analyses of the original samples. 1500°C was reckoned to be a reasonable temperature for the hearth of the furnace and the silicon distribution in the original samples was found to agree quite well with the results of the remelting experiments at this temperature. The sulphur and manganese distributions in the original samples were found

to correspond to equilibrium with hearth temperatures of about 1300°C and 1400°C respectively. It was therefore concluded that these reactions were out of equilibrium in the blast furnace. When, however, the sulphur and manganese reactions were considered together giving the reaction equation

$$[\underline{Mn}] + [\underline{S}] \rightleftharpoons (Mn^{++}) + (S^{=})$$
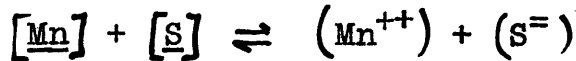
there were indications that this might have reached equilibrium in the furnace.

One interesting feature of this work was that in all the remelting experiments equilibrium was established with regard to sulphur within 2 hours.

The solubility of calcium sulphide in the slag was also investigated and the limit of solubility was found to lie between 3.5% and 4.5% sulphur at 1500°C. The presence of crystals of calcium sulphide, identified by X-rays, which had separated to the bottom of the slag, and could readily be seen in the glassy bulk of slag, was the evidence which led to this conclusion.

This does not agree with the figure of about 10% sulphur for 1500°C given by McCaffery and Oesterle(9). It is thought, however, that Filer and Darken's work shows more definite experimental proof of saturation than does that of McCaffery and Oesterle(9). On the basis of Filer and Darken's evidence the limit of solubility of calcium sulphide in a 45% CaO, 34% SiO$_2$, 14% Al$_2$O$_3$, 7% MgO slag at 1500°C is almost certainly below 4.5% sulphur. While Martin, Glockler and Wood(10) do

give a figure, for calcium sulphide solubility, of 1.6% sulphur it is for a more acid slag and a temperature of $1400^{\circ}C$. As the effects of these variables are not known valid comparisons cannot be made.

Richardson and Jeffes(13) have collected thermodynamic data on blast furnace reactions and have deduced equilibrium data from these. Unfortunately, owing to the non-ideality of the slag and metal solutions concerned and to the lack of values of activity coefficients for solutes in these solutions, translation of this information into immediately useful terms of concentration is not possible.

All the investigations of sulphur equilibrium described so far in this review have been made by experiments in carbon crucibles. Thus the effect of varying concentrations of FeO in the slag has not been investigated. While no such work has been reported for blast furnace type slags and metals Rocca Grant and Chipman(14) carried on an investigation of desulphurisation by slags of low FeO content. The slags they used were of the type found in the reducing stage of the basic electric steel furnace. Magnesia crucibles were used and the slags were saturated with magnesia.

They found that, at equilibrium, the sulphur distri-:bution was controlled by two factors. One was the basicity of the slag and the other the FeO content of the slag. The FeO content was the more important when it was below 2 molar% in the slag. With slags of FeO contents up to 10 molar%

their results indicated that desulphurisation was carried on
by the reaction

$$[FeS] + (CaO) \rightleftharpoons (FeO) + (CaS)$$
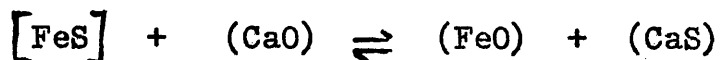
The effect of temperature, varying between $1550^{\circ}C$ and $1700^{\circ}C$,
was not noticeable.

Desulphurisation in the different fields of steelmaking
was then discussed. The way in which the equilibrium sulphur
distribution varied with FeO content and basicity was shown
for the blast furnace, using Hatch and Chipman's data, for
the basic open hearth furnace using Grant and Chipman's(15)
data and for the basic electric furnace from which slags have
an FeO content intermediate between the low value for blast
furnace slags and the high value for open hearth slags.

Partition of FeS between metal and slag was the
mechanism suggested by Grant and Chipman for desulphurisation
under open hearth conditions. In a critical review of this
type of desulphurisation, Carter(16) has shown that the
existing experimental results on equilibrium could be correlated
according to the equation

$$\frac{(S)}{[S]} = k.\frac{\Sigma(n_{MO})}{[O]}$$

where $\Sigma(n_{MO})$ is the sum of mol. fractions of the 'free' basic
oxides in the slag. This was calculated assuming that
particular compounds were formed in the slag.

Richardson(17) pointed out that this led to a reaction of the form

$$(O) + [S] \rightleftharpoons (S) + [O]$$
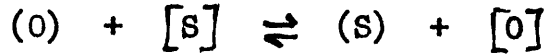
where (O) was the oxygen content of the basic oxides not neutralised by acid constituents, that is, where $\sum(n_{MO})$ was a measure of (O).

This indicated that desulphurisation by basic open hearth slags might not be caused by partition of FeS as was suggested by Grant and Chipman. Richardson deduced, on the basis that the above equation represented the mechanism, that FeO additions to slags would be expected to affect the sulphur equilibrium position in two ways. Such additions would increase the oxygen content of the metal in equilibrium with slag and would also increase the total 'free' basic oxides. In low FeO slags, associated with low oxygen metals the more important result of an FeO addition would be to increase the metal oxygen content. In high FeO slags, with which the corresponding metals would be relatively high in oxygen, the more important effect would be to increase the free basic oxide content of the slags.

This picture is qualitatively compatible with the results of the sulphur equilibrium studies, over the whole commercially used range of FeO contents, which were presented by Rocca, Grant and Chipman(14).

Several workers(18,19,20) have investigated the effects of other dissolved elements on the activity of sulphur in molten iron. These results have been collected and to some extent augmented by Sherman and Chipman(21) who have also devised an empirical method of obtaining the activity of sulphur in complex systems containing carbon, manganese, silicon, phosphorus, aluminium and copper as well as sulphur.

There have been no experimental measurements of the activities of lime and calcium sulphide in lime-alumina-silica-sulphur slag systems. Rosenqvist(22) made interesting calcu:lations of the calcium sulphide activity in some slags of this type but his results, as will be shown later, are of doubtful reliability.

Kitchener, Bockris and Spratt(23) investigated the carbon solubility limit of iron-carbon-sulphur alloys at temper:atures from $1200^{\circ}C$ to $1700^{\circ}C$ and with sulphur contents up to 1.4%. Subject to the condition that the alloy composition did not fall within the immiscibility gap of the iron-carbon-sulphur system, the results showed that the relationship between the sulphur content and the carbon content at saturation of alloys at one temperature was linear. Values of the activity coeffic:ient of carbon in the saturated alloys were deduced and the effect of sulphur on these was shown.

One feature of this work was that a long time was needed for the alloys to reach equilibrium with the carbon crucibles. In unstirred melts 3 hours was necessary at constant temperature, for a plain iron-carbon alloy to reach

equilibrium.   When 0.6% of sulphur was present 6 hours was the length of time needed to reach equilibrium.

Derge, Philbrook and Goldman(24) studied the mechanism of the transfer of sulphur across the interface from metal to slag.   The experiments were carried out in carbon crucibles and with lime-alumina-silica slags.   At the beginning of desulphurisation fairly large concentrations of iron were found in the slag and evidence was led to show that this was not present in the form of beads of metal.   As time went on the iron concentration passed through a maximum and fell. The magnitude of this maximum value was reported, in some cases, as high as 5% iron.   The maximum in iron content was reached within 2 hours in all the experiments.

The existence of this maximum in slag iron content was interpreted as proof that when sulphur crossed the inter-:face, iron was associated with it.   It was suggested that this was corroboration of the generally accepted mechanism of desulphurisation by blast furnace type slags.   This mechanism is outlined in the sequence of reactions:

$$[FeS] \rightleftharpoons (FeS)$$
$$(FeS) + (CaO) \rightleftharpoons (CaS) + (FeO)$$
$$(FeO) + C \rightleftharpoons [Fe] + CO$$
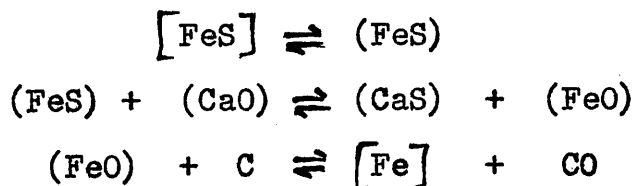
EXPERIMENTAL.
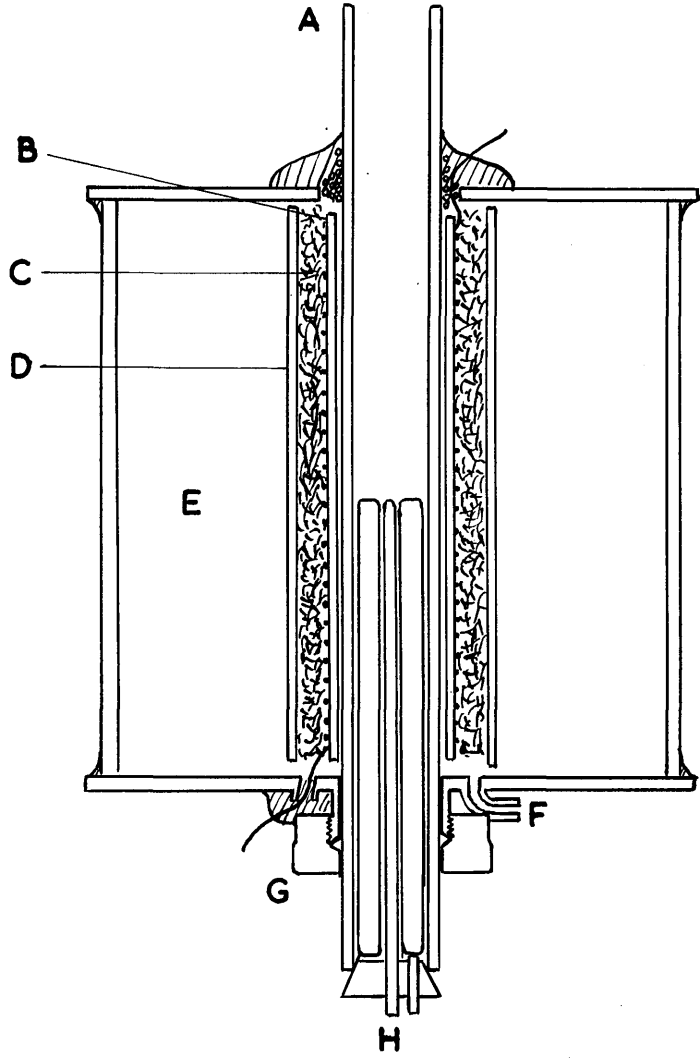
A	Mullite Working Tube.	E	Insulating Firebrick.
B	Alumina Winding Tube.	F	Gas Inlet.
C	Fused Alumina Particles.	G	Gland.
D	Outer Alumina Tube.	H	Thermocouple Sheath.

Figure 1.   Molybdenum Furnace.

FURNACE:

A molybdenum wire resistance furnace was used for
the experiments. The essential features of its construction
are shown in Fig.1. The gland, holding the 2" I.D. mullite
working tube at the bottom, was packed with asbestos rope.
The tube was not tightly held at the top but was encircled
with a coil of asbestos rope covered with an alumina cement-
asbestos mixture, as shown. This mixture adhered well to the
steel furnace case and was used to seal the hole for the
bottom terminal and the joints on the outside of the furnace
case.

The atmosphere used to protect the winding from
oxidation was a nitrogen-hydrogen mixture. This was obtained
by the catalytic cracking of anhydrous ammonia by iron
at $800^{\circ}C$. The gas was washed in water to remove any uncracked
ammonia, dried and introduced to the furnace through the gas
inlet on the bottom plate. While the furnace was on, this
gas was continuously passed into it.

The furnace gave satisfactory service if certain
precautions were taken. During the first heating of a newly
wound furnace about 4 days were taken to reach $1500^{\circ}C$. This
slow heating was to ensure that water vapour was not allowed
to oxidise the molybdenum. If, at any time, the working
mullite tube could be turned in the gland, this was removed
and repacked before the furnace was used again. If any repair
involved the use of alumina cement on the bottom of the

furnace this was allowed to dry for 12 hours before the furnace was used.   In normal operation $1500^{\circ}C$ was reached in 4 hours.

Temperature was measured with a platinum-platinum 13% rhodium thermocouple in a mullite sheath as shown.   This was standardised from time to time at the melting points of gold and palladium.   Temperature was controlled by the operation of a variable resistance in series with the winding. The temperature could be held within $\pm$ $5^{\circ}C$ of the desired value.

CARBON CRUCIBLES:

Graphite crucibles were made from 2" diameter rod supplied by the Morgan Crucible Company.   Their internal diameter was $1\frac{1}{2}$" and their height 4".

MATERIALS:

Armco iron was used for these experiments.   Its analysis was 0.019% C; 0.027% Mn; 0.002% Si; 0.031% S; and 0.008% P.   One preliminary experiment showed that this iron, heated in a carbon crucible in the molybdenum furnace, was saturated with carbon as soon as $1500^{\circ}C$ was reached. Therefore, saturation of the iron with carbon before charging to the crucible, was considered unnecessary.

FeS was prepared by mixing electrolytic iron powder and sulphur in the correct proportions and heating them in a silica crucible over a gas flame.

Slags were charged to the crucibles as intimate mixtures of the constituents in powder form. Freshly calcined calcium carbonate, pure silica sand and alumina and calcium sulphide powders were used.

METHOD:

100 gms. of Armco iron and 50 gms. of slag mixture were added to the crucible. When FeS was to be the source of sulphur 3 gms. of it was added and when CaS was the source 5% was mixed in with the slag. Experience in the early runs showed that about 30% of the sulphur added did not appear in the metal or the slag at the end of the run. These quantities of sulphur were intended to allow for this loss and to give a finishing slag sulphur content of about 1.5%. Analyses of the graphite of one crucible before and after it had been used showed that some sulphur had been picked up by the crucible material.

In the later experiments 25 gms. of slag was used instead of 50 gms. and in these 1.5 gms. of FeS was added to give the high sulphur starting metal.

The charged crucible was heated to the working temperature and held for a length of time which varied between 5 and 12 hours. This was the time necessary to reach equil- :ibrium and from the experience gained in the early experi- :ments it could be roughly predicted for any particular set of conditions. The working tube was closed at the bottom and the gas outlet from the top was taken through a water bubbler.

In some early runs an atmosphere of carbon monoxide was maintained in the working tube but later all the experiments were carried out in the atmosphere of nitrogen and carbon monoxide, obtained when air was allowed to come to equilibrium with the carbon of the crucible. It was evident that slag-gas reactions were extremely slow and could be neglected. The pressure of carbon monoxide with which the slag-metal reactions came to equilibrium was undoubtedly that in bubbles at the interfaces; this pressure was dependent on the total pressure of the system rather than on the partial pressure of carbon monoxide.

One hour before the end, and at the end of a run metal samples were withdrawn using suction through a fused silica tube. The samples obtained were immediately quenched in water. At the end of a run the slag was sampled with a brass rod.

Equilibrium, with respect to sulphur, was considered to be established when the sulphur analyses of the two metal samples from a run did not vary by more than 0.002%.

The sulphur contents of the metals dropped to equilibrium in all these experiments in carbon crucibles. This was found to be the case even when the sulphur was added as CaS and when the equilibrium sulphur content of the metal was greater than that of Armco iron. This must mean that at some

time during the heating up period or at the beginning of the run
the irons picked up sulphur from the slags. The consequence
of it is that, in these experiments, equilibrium was only
approached from one side, the sulphur transfer being from metal
to slag.

RATES OF REACTION:

In no experiment were sufficient samples taken to
ascertain exactly when equilibrium with respect to sulphur was
attained. Several observations can be made, however, regarding
factors which were found to have an effect on the rate of
approach to equilibrium.

When the sulphur was added as CaS, equilibrium was
reached more quickly than when it was added as FeS. This would
be expected if it was assumed that not all the sulphur trans-
:ferred from the slag to the metal in the early stages of a
run to which the sulphur was added as CaS. The starting
position of an FeS run would then be further from equilibrium
than that of an otherwise similar CaS run and the latter would
reach equilibrium more quickly.

High temperature and high slag basicity were found to
be factors which encouraged faster attainment of equilibrium.
In later runs (No.9 onwards) the weight of slag used over
100 gms. of metal was 25 gm. instead of 50 gm. as previously
used. This reduction of slag weight was found to give faster
approach to equilibrium. Silicon bearing irons were used in
two experiments and in these equilibrium was reached more

rapidly than in other, similar experiments to which no silicon was added.

These observations are necessarily qualitative since no study of reaction rates was made.

ALUMINA CRUCIBLES:

An attempt was made to manufacture satisfactory alumina crucibles by slip casting. This was unsuccessful. Even when alumina saturated slags were used they were 'soaked up' by the crucibles. This was undoubtedly due to the high porosity of the crucibles, but the high firing temperatures (well in excess of $1600^{o}C$), needed to reduce the porosity sufficiently, were not available. Therefore a modification of the crucible was devised which gave satisfactory service. This involved the insertion of a sleeve of sheet molybdenum and the moulding of an alumina cup inside this.

The slip cast alumina crucibles were made from alumina cement. This was first fired to $1000^{o}C$ to remove carbonaceous material and was then ground in a steel ball mill for 12 hours. It was washed by decantation in dilute hydrochloric acid until the supernatant liquid was colourless; the purpose of this was the removal of iron. The slightly acid slip was then cast into plaster of paris moulds of such a size that the resulting crucibles were 1.3/4" O.D., 1.3/8" I.D., and 2" high. The crucibles were air dried and fired to $900^{o}C$. The inside walls of the crucibles were smoothed and made parallel to each other and before the molybdenum was fitted they were
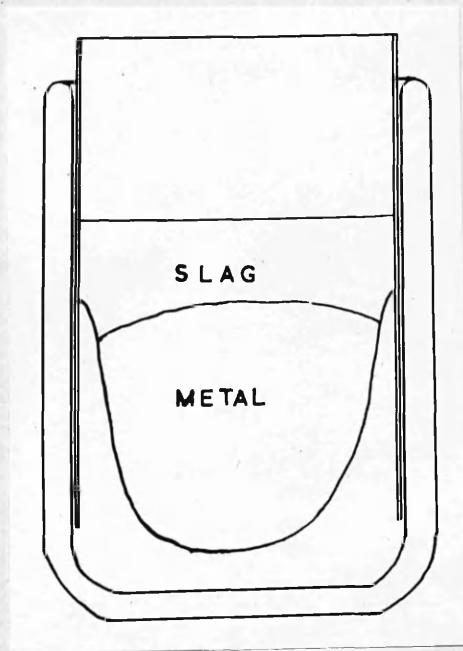
SLAG

METAL

FIGURE 2.

fired to 1200°C. 32 gauge molybdenum sheet was cut into pieces 5" x 2" and formed into a sleeve. This was put into the crucible giving an overlap of about 1". A cup of alumina cement was next moulded into the bottom of this to a height of about 1". This was allowed to dry and the whole was fired to 1600°C in an atmosphere of cracked ammonia. A photograph of a finished crucible is shown as Fig.2 along with a sketch of the set-up in a crucible when the metal and slag charges have been melted. The slag can be seen to come in contact with the metal, the alumina cup and the molybdenum but not with the walls of the crucible. The metal only comes in contact with the slag and the alumina cup.

In the experiments these crucibles were used inside a "sheath" which was simply a thin-walled graphite crucible 2" high. The purpose of this was to prevent the working tube being slagged in the event of a crucible failure. It also served to ensure that the gas phase was in equilibrium with carbon at the working temperature.

MATERIALS:

The metals used in these experiments had to have carbon, sometimes sulphur and sometimes silicon added to them. Silicon was added first, by melting Armco iron with ferrosilicon in a fireclay crucible. Sulphur and carbon were added by melting the iron in a graphite crucible with the requisite amount of FeS present. This was quenched in water after being held at 1500°C for about 10 minutes. The final stage in the

preparation of metal was to shape it so as to fit into the alumina cup of the composite crucible. This was done by melting 50 gms. of it in a small fireclay crucible of suitable shape.

The slags for the alumina crucible experiments were prefused. This was necessary to enable a reasonable amount of slag to be charged to the small crucible and also to minimise solution of the alumina of the crucible by the slag during melting down. The slag was made up from the oxide constituents to a composition 35% Al_2O_3, 34% CaO, 31% SiO_2. This was chosen since it was near to saturation with alumina at $1500^{\circ}C$; this was again to minimise attack on the alumina of the crucible. This slag was premelted in a graphite crucible. At this stage it did not contain sulphur. All these preliminary melting operations were carried out in a high frequency induction furnace.

In many of the experiments FeO was added to the slag. This was prepared by heating ferrous oxalate in vacuo to $1000^{\circ}C$ and quenching.

METHOD:

A metal bead weighing 50 gm. was put into the alumina cup of a composite crucible. 30 gm. of prefused slag in lump form was added and the crucible, in its carbon sheath, was heated to $1500^{\circ}C$ in the molybdenum furnace. A cracked ammonia atmosphere was used up to $1400^{\circ}C$ to prevent oxidation of the crucible molybdenum and thereafter the atmosphere was the same as was used in the carbon crucible runs.

A preliminary experiment was done to find out if reaction between slag and gas phases was of any consequence in this work.   A bead of Armco iron and some slag were taken to $1550^{\circ}C$ in a composite crucible in the nitrogen – carbon monoxide atmosphere.   Enough FeO was then added to give a 3% FeO slag and after holding for 3 hours at $1550^{\circ}C$ the slag was sampled. It was found to contain 3% FeO.   This was taken as proof that in these experiments slag-gas reactions are extremely slow and can be ignored.

In the experiments in which equilibrium was approached from high sulphur in the metal, 2% S iron was used. FeO was added to the molten slag in some experiments of this type.   This was done by dropping a small twist of thin paper, containing the FeO, down a 1" diameter steel tube.

When equilibrium was approached from high sulphur slags the sulphur was added.to the molten slag as CaS.   A corrective addition of silica was made along with this in order to maintain the lime/silica ratio at a constant value.   3 gms CaS and 2.1 gms SiO_2 were added in this type of experiment. FeO additions were also made to all the runs of this type; these additions were all made to the molten slags, in paper down the steel tube.   Zero time was taken as the time of the last addition .

Because of the smallness of the metal beads in these experiments it was found to be impracticable to sample by

suction through a silica tube. At the end of a run a slag sample was taken by means of a brass rod; the furnace current was then switched off. The slag remaining in the crucible was always solid within 10 minutes of this. The metal was sampled by breaking up the cold crucible and taking turnings from the bead. This procedure was deemed to give a satisfactory metal sample because of the quick freezing of the slag. The possibility of segregation during the cooling of the metal in the crucible was considered, but analyses from the top and bottom of a metal bead gave the same results. The majority of the metal beads showed a white cast iron type of structure and this fact indicates that segregation would not be expected.

Several metal and slag samples from these composite crucible experiments were analysed for molybdenum. None could be detected by chemical analysis. Some metals were also analysed for aluminium but again none could be detected.

PREPARATION FOR ANALYSIS:

The pencils of metal obtained as samples from the graphite crucible experiments were broken up and crushed in a percussion mortar. Turnings were taken from the alumina crucible metals except in three cases when they proved too hard even for a sintered carbide tool. In these cases the bead was broken and a sample was crushed in a percussion mortar.

The slag samples were crushed in a percussion mortar and ground in an agate mortar. Particular care was taken to avoid contamination by iron in these operations.

The small iron beads which were almost invariably to be seen in the slags were removed by magnetic treatment. The crushed slag was first gone over with a small hand magnet and then spread out on a piece of cardboard in a thin layer. This was then placed under the pole of an electromagnet and agitated so that the slag particles jumped from the cardboard. The slags were then dried and analysed.

This form of magnetic separation gave very consistent results. Two samples of the same slag, separately treated with the magnet and analysed for iron gave results which never varied by more than 0.01% FeO.

ANALYSIS:

The final metal samples were analysed for carbon, silicon and sulphur. The samples taken one hour before the end of the carbon crucible experiments were analysed for sulphur.

Carbon was estimated by combustion in oxygen at $1100^{o}C$ for 30 minutes. The CO_2 evolved was absorbed on soda asbestos and weighed. Special care was taken with the high sulphur metals to ensure that oxides of sulphur did not reach the soda asbestos. Two bubblers containing freshly prepared chrome-sulphuric acid were inserted in the train for this purpose.

The standard sulphuric acid analytical method was used for the estimation of silicon in the metal samples.

Sulphur was estimated by the combustion method. The metal samples were subjected to a stream of oxygen for 5 minutes in a small platinum furnace at 1300°C. The evolved gases were first passed through dry cotton wool to remove oxides of iron and were then bubbled through a column of one volume hydrogen peroxide. This solution had previously been neutralised with $\frac{N}{200}$ caustic soda solution. After 5 minutes bubbling the titration was done with this caustic soda solution and a mixed methylene blue - methyl red indicator. This indicator was made up by dissolving 0.08 g of methylene blue and 0.13 g of methyl red in 100 c.c. of ethyl alcohol. Since this method does not give complete evolution of the sulphur of the metal careful standardisation of technique was necessary in all the analyses. Standard cast irons of known sulphur content were put through, one after every four estimations.

The slags were analysed for silica, lime, alumina, sulphur and iron.

Silica was estimated gravimetrically by dehydration with sulphuric acid and subsequent treatment with hydrofluoric acid in a platinum basin. Any residue in this basin was dissolved by fusion with sodium carbonate and added to the main filtrate. This was then used for the estimation of lime, alumina and iron.

Lime was estimated by precipitation as calcium oxalate. After filtering, the precipitate was redissolved in sulphuric acid and titrated with standard potassium permanganate solution.

Alumina was precipitated as phosphate and weighed as $Al\ PO_4$.

A colorimetric method was used for the deter-:mination of iron. The pH of the solution was adjusted by the addition of sodium acetate solution and the iron was reduced with hydroxylamine hydrochloride-solution. The colour was produced with orthophenanthroline and its intensity was measured with a Spekker absorptiometer.

Sulphur was estimated gravimetrically by a nitric acid - bromine oxidation followed by precipitation as barium sulphate. Blank estimations were run with every batch of these analyses to allow for the small amounts of sulphur in the reagents and picked up from the atmosphere.

The estimated accuracies of these analysis methods can be summarised in a table.

Metal.		Slag.	
Carbon	$\pm$ 0.05% C	Silica)	
Silicon	$\pm$ 0.05% Si	Lime) Alumina)	$\pm$ 0.5% oxide.
Sulphur above 1% $\pm$ 0.01% S below 1% $\pm$ 0.002% S		Iron	$\pm$ 0.01% FeO.
		Sulphur	$\pm$ 0.03% S.

DISCUSSION OF RESULTS OF

EXPERIMENTS IN CARBON CRUCIBLES.

The results of the experiments done in carbon crucibles are given in Table I. The CaO figures represent the calcium present both as CaO and as CaS expressed as oxide, and the FeO figures represent the total iron left after magnetic separation, expressed as oxide. The 'excess base' values shown in the table have been evaluated by substituting the number of mols per 100 gm of slag of each slag constituent in the expression

$$CaO - (SiO_2 + Al_2O_3)$$

The few experiments brought to equilibrium at $1450^{\circ}C$ and $1550^{\circ}C$ give no evidence of an effect of temperature on desulphurisation. This can be seen from Figure 3 on which excess base of the slag is plotted against the ratio

$$\frac{Wt.\%\ S\ in\ slag}{Wt.\%\ S\ in\ metal} = \frac{(S)}{[S]}$$

The two points, representing experiments 26 and 59 in which silicon bearing iron was used, can be seen to be higher on the graph than the others.

On Figure 4 the results are shown compared with those of Hatch and Chipman(1) for 1.5% sulphur slags at $1500^{\circ}C$ and at $1425^{\circ}C$. The single result for $1500^{\circ}C$ of Filer and Darken(2) is also shown. In both of these other investigations magnesia bearing slags were used. The abscissa of Fig.4 is the expression

$$(CaO + \tfrac{2}{3}MgO) - (SiO_2 + Al_2O_3) \text{ in mols per 100 g. of slag;}$$

Expt. No.	Time (Hours)	Temp. °C.	Slag analysis wt. %						Metal Analysis wt. %				
			CaO	SiO2	Al2O3	FeO	S	Excess Base	Si	C	S	f_s	$\frac{(S)}{[G_s]}$
3	7	1550	46.1	35.1	19.1	–	1.13	+.055	0.88	–	0.022	6	8.56
5	7	1550	43.0	36.8	19.3	0.10	1.03	–.029	0.94	–	0.027	6	6.36
6	9	1500	42.4	38.2	18.8	–	1.67	–.061	0.22	–	0.042	6	6.63
7	12½	1450	45.1	38.2	16.1	0.11	1.64	+.011	0.10	4.92	0.077	5.2	4.07
8	9	1550	51.1	32.0	16.1	–	1.25	+.225	–	–	0.008	6	26.1
9	9	1500	40.0	39.9	20.9	0.09	1.72	–.156	0.38	4.85	0.117	5.5	2.66
11	7	1550	43.7	38.4	16.0	0.27	1.37	–.020	0.50	4.90	0.108	5.8	2.20
12	7	1500	45.4	36.6	16.0	0.30	1.29	+.031	0.13	5.08	0.075	5.7	3.04
23	6½	1500	29.9	24.5	44.7	–	1.17	–.323	0.78	3.94	0.200	3.9	1.52
26	7	1500	30.1	28.0	40.3	0.18	1.57	–.253	2.62	4.26	0.064	7.7	3.2
40	7	1500	30.6	25.2	44.0	0.12	1.13	–.310	0.46	4.94	0.110	5.9	1.75
42	9	1500	30.1	26.3	42.6	0.19	1.13	–.326	0.48	4.60	0.143	4.9	1.60
43	7	1500	48.0	32.4	18.5	0.18	1.68	+.136	0.56	5.09	0.017	6.5	15.3
44	7	1500	46.5	34.0	13.7	0.21	1.56	+.080	0.51	4.92	0.028	5.9	9.51
47	10	1450	46.9	34.1	18.2	0.29	1.30	+.090	0.67	5.00	0.016	6.4	12.7
53	7	1500	48.5	34.2	16.6	0.06	1.74	+.137	0.34	5.08	0.015	6.0	19.3
59	5	1500	49.1	34.4	14.6	0.12	1.75	+.162	3.82	4.03	0.008	9.7	22.6

TABLE I.

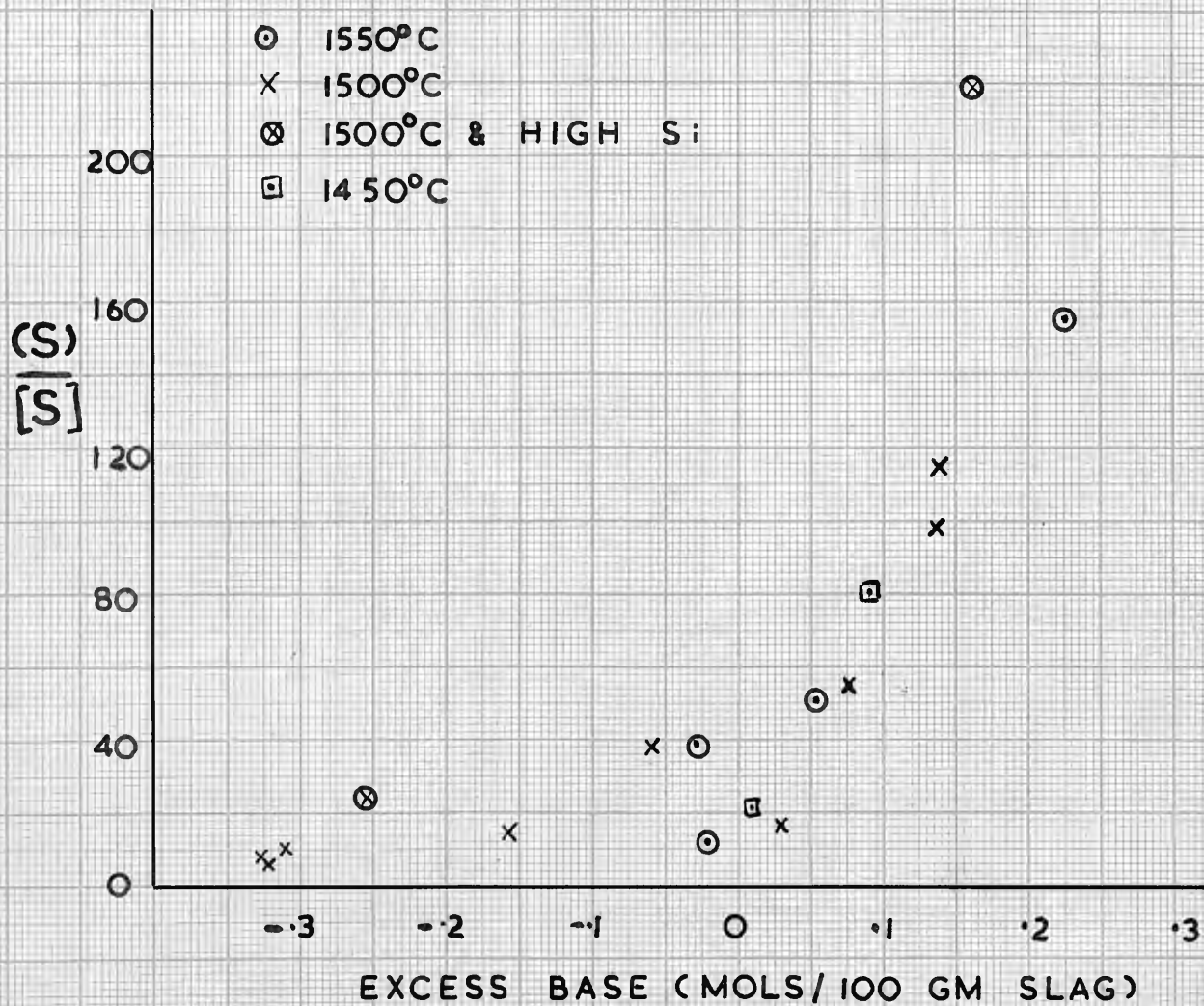Results of experiments in carbon crucibles.

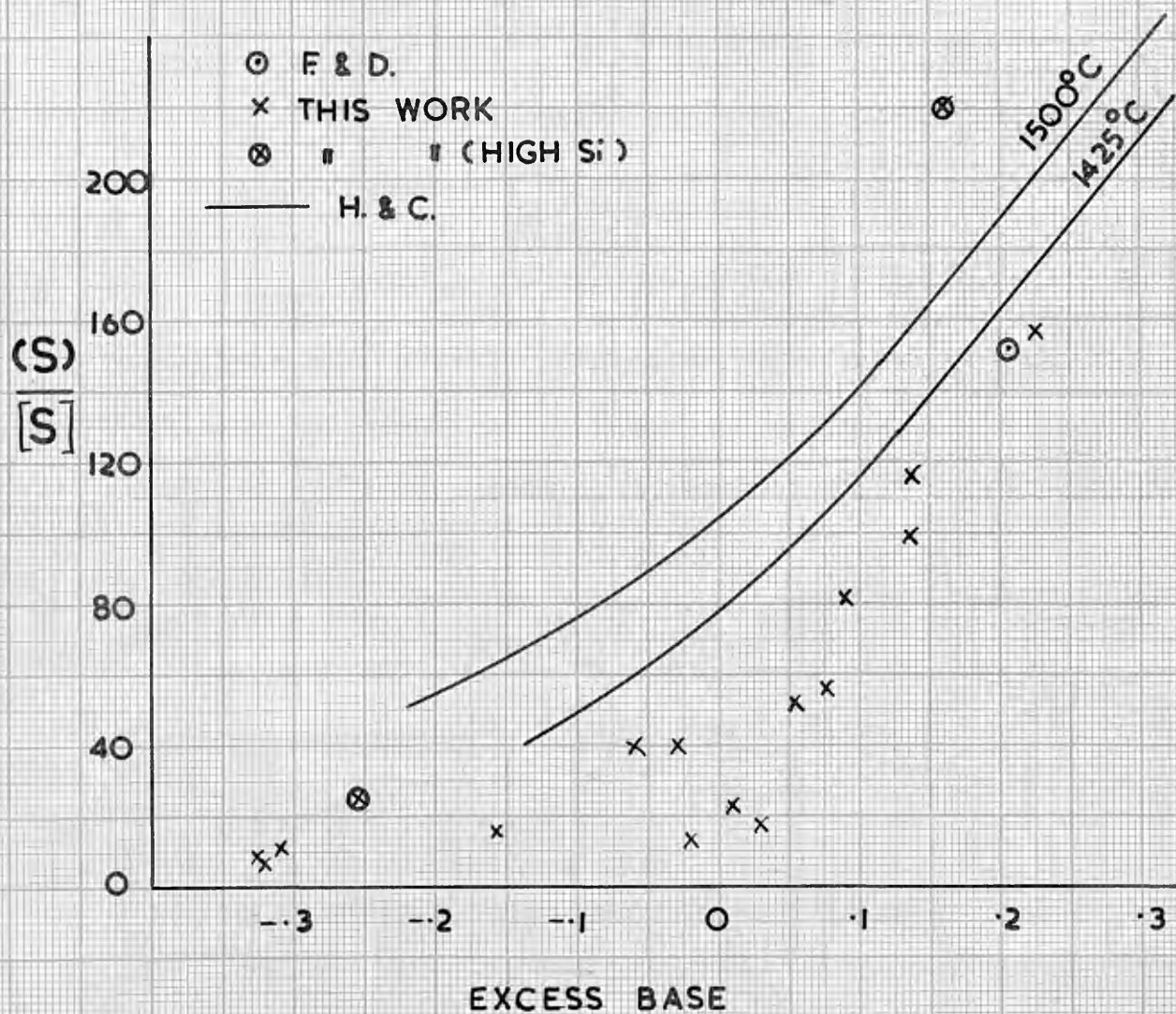Figure 3.   Results of experiments in
carbon crucibles.

Figure 4. Comparison with other investigations.

this was the expression which Hatch and Chipman found most use-
:ful as a measure of basicity in correlating their data.

Filer and Darken's result is in close agreement with
the results of this investigation while the best lines through
Hatch and Chipman's points are considerably higher. Indeed,
in the more acid slags the values given by Hatch and Chipman
for $\frac{(S)}{[S]}$ at 1500°C are about three times those found here.
This large discrepancy between the results of apparently similar
investigations requires explanation. A clue to the possible
reason for this difference is obtained from the results of
experiments 26 and 59. The metals of these experiments
contained 2.6% and 3.8% silicon respectively, while the silicon
contents of the metals of the other experiments were all less
than 1%. The equilibrium $\frac{(S)}{[S]}$ ratios for these experiments
are higher than the others on Figure 3; the results of Hatch
and Chipman, used in the construction of the line on Figure 4
represent experiments in which the metals contained silicon up
to 5%, the higher silicon contents being associated with the
more acid slags and the higher temperature. These facts are
consistent in indicating that the discrepancies on Figure 4
might be eliminated if the effect of silicon on the activity
coefficient of sulphur in the metal was known. Ideally, of
course Figure 4 should be drawn with an ordinate scale showing
the activity ratio $\frac{(a_s)}{[a_s]}$ rather than the weight percentage
ratio $\frac{(S)}{[S]}$.

Sherman and Chipman(21) have devised an empirical method of finding the activity coefficient of sulphur in multicomponent solutions in liquid iron.   This has been applied to the results represented on Figure 4.   The data which have been used are summarised in Figure 5.   The lines showing the effects of carbon and sulphur on the activity coefficient, f_S, have been drawn for 1500°C using the data on temperature effect given by Morris and Buehl(18) and by Sherman, Elvander and Chipman(20).   No such correction is possible in the silicon case since the effect of temperature has not been studied.

The method of using Figure 5 is best illustrated by an example.   Consider the metal composition of experiment 23, 3.94% C; 0.78% Si; and 0.200% S.   Firstly, the value of log f_S corresponding to the carbon content is found, from Figure 5, to be 0.51.   The silicon content of the binary iron-silicon alloy which would give this value of log f_S is next found and to this is added the actual silicon content of the alloy

$$6.45 + 0.78 = 7.23\% \text{ Si.}$$

The value of log f_S corresponding to this "equivalent" silicon content is read off and found to be 0.60.   From this the value corresponding to a sulphur content of 0.200% is subtracted and the value of the activity coefficient of sulphur in the alloy is given by:

$$f_S = \text{antilog } (0.600 - 0.005) = 3.9$$

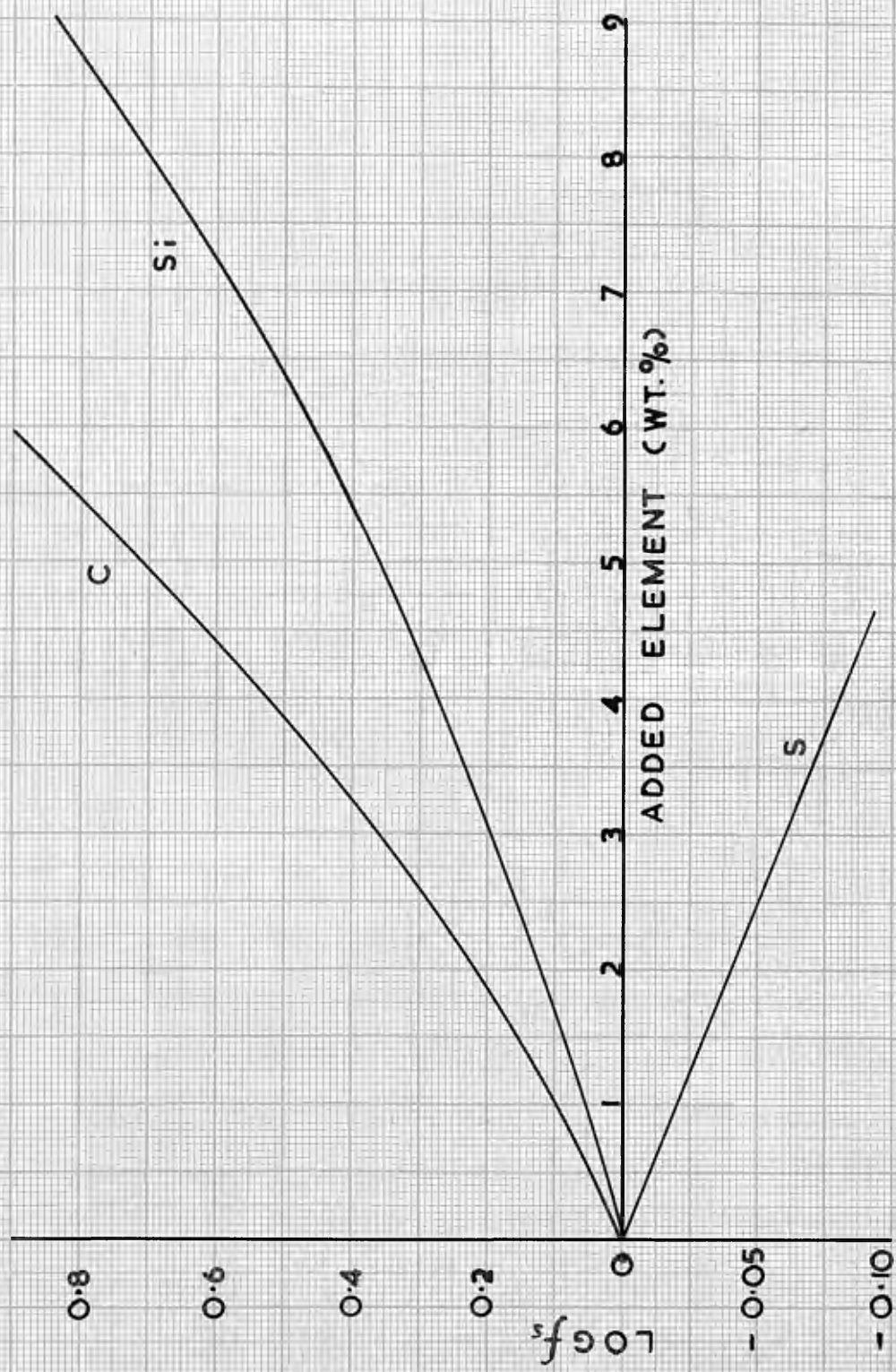When multiplied by 0.200 (the weight percentage sulphur content

Figure 5.   Graph for finding f_s in complex systems.

of the alloy) this gives the activity of sulphur in the alloy referred to an infinitely dilute solution of sulphur in iron as the standard state.

The last two columns in Table I give values of f_S, found in this way and of the ratio $\dfrac{(S)}{[a_S]}$

where $\dfrac{(S)}{[a_S]} = \dfrac{(S)}{f_S[S]} = \dfrac{\text{Wt. \% sulphur in slag}}{\text{Activity of sulphur in metal.}}$

Values of f_S and $\dfrac{(S)}{[a_S]}$ have also been obtained for the experiments which Hatch and Chipman(1) did with 1.5% sulphur slags. These are given in Table II. It should be noted that values of activity coefficient greater than 9 are the results of extra-:polation of the activity data.

The activity of sulphur in blast furnace type slags has not been experimentally determined. Rosenqvist(22) in his calculations of calcium sulphide activity in such slags used Hatch and Chipman's experimental results at three slag sulphur levels. He assumed an average activity coefficient of 5.8 for the sulphur in the metal; reference to Table II shows that this was not justified. As a result of Hatch and Chipman's technique of adding silicon to the melts under the more acid slags, there is a well defined increase in the activity coefficient as the slags become more acid.

An attempt was made to repeat Rosenqvist's calcu-:lations using values of f_S found by the method suggested by Sherman and Chipman. It was observed that the scatter of points representing 2.5% and 5% sulphur slags was considerable

Expt. No.	Temp. °C	Excess Base	Slag Analysis Wt.%			Metal Analysis Wt.%			f_s	$\dfrac{(S)}{[a_s]}$
			Al_2O_3	FeO	S	Si	C	S		
9	1425	+.175	13.72	---	2.07	0.53	4.67	0.013	5.4	29.5
14	1500	+.445	10.14	---	1.58	0.55	4.83	0.005	5.7	55.6
15	1425	-.136	14.7	---	1.48	2.41	4.18	0.058	8.3	3.08
16	1425	+.024	14.9	---	1.51	1.37	4.27	0.038	5.9	6.74
17	1500	+.332	14.92	---	1.56	0.65	4.76	0.006	5.6	46.8
18	1425	-.089	26.3	---	1.54	1.62	4.25	0.028	6.3	8.80
19	1500	+.316	10.48	0.027	1.59	1.40	4.54	0.006	6.2	42.9
	1425				1.58	1.05	4.41	0.007	5.6	40.4
21	1500	+.182	19.86	---	1.51	0.91	4.78	0.009	6.1	27.5
	1425				1.49	0.74	4.62	0.011	5.6	24.2
24	1500	+.149	16.82	0.033	1.47	1.41	4.53	0.009	6.2	26.4
25	1500	+.283	13.54	---	1.50	0.79	4.86	0.006	6.2	40.6
	1425				1.51	0.45	4.65	0.007	5.1	42.3
28	1500	+.109	19.98	---	1.45	1.76	4.48	0.013	6.8	16.5
31	1500	-.013	25.98	0.046	1.53	3.23	4.12	0.017	8.5	10.6
32	1500	+.112	17.28	---	1.62	2.53	4.28	0.012	7.4	18.2
	1425				1.61	1.83	4.29	0.013	7.1	17.4
33	1500	+.261	12.20	---	1.59	2.28	4.51	0.0075	7.9	27.0
	1425				1.56	0.91	4.56	0.008	6.0	32.5
35	1500	+.308	7.79	---	1.48	1.23	4.71	0.007	6.5	32.8
	1425				1.48	0.69	4.71	0.010	5.8	25.5
37	1500	+.062	14.30	0.026	1.57	4.80	3.70	0.011	11.1	12.9
	1425				1.56	3.79	3.76	0.015	11.0	9.5
38	1500	+.061	25.70	---	1.56	2.18	4.33	0.011	7.0	20.3
42	1425	-.012	26.0	---	1.61	2.46	4.24	0.019	8.9	9.5
49	1500	-.080	25.92	0.026	1.54	5.28	3.52	0.016	11.8	8.15
51	1500	+.246	10.32	0.039	1.61	1.93	4.45	0.007	6.9	33.2
57	1425	+.175	12.96	---	1.35	1.69	4.29	0.009	6.0	32.5

TABLE II.

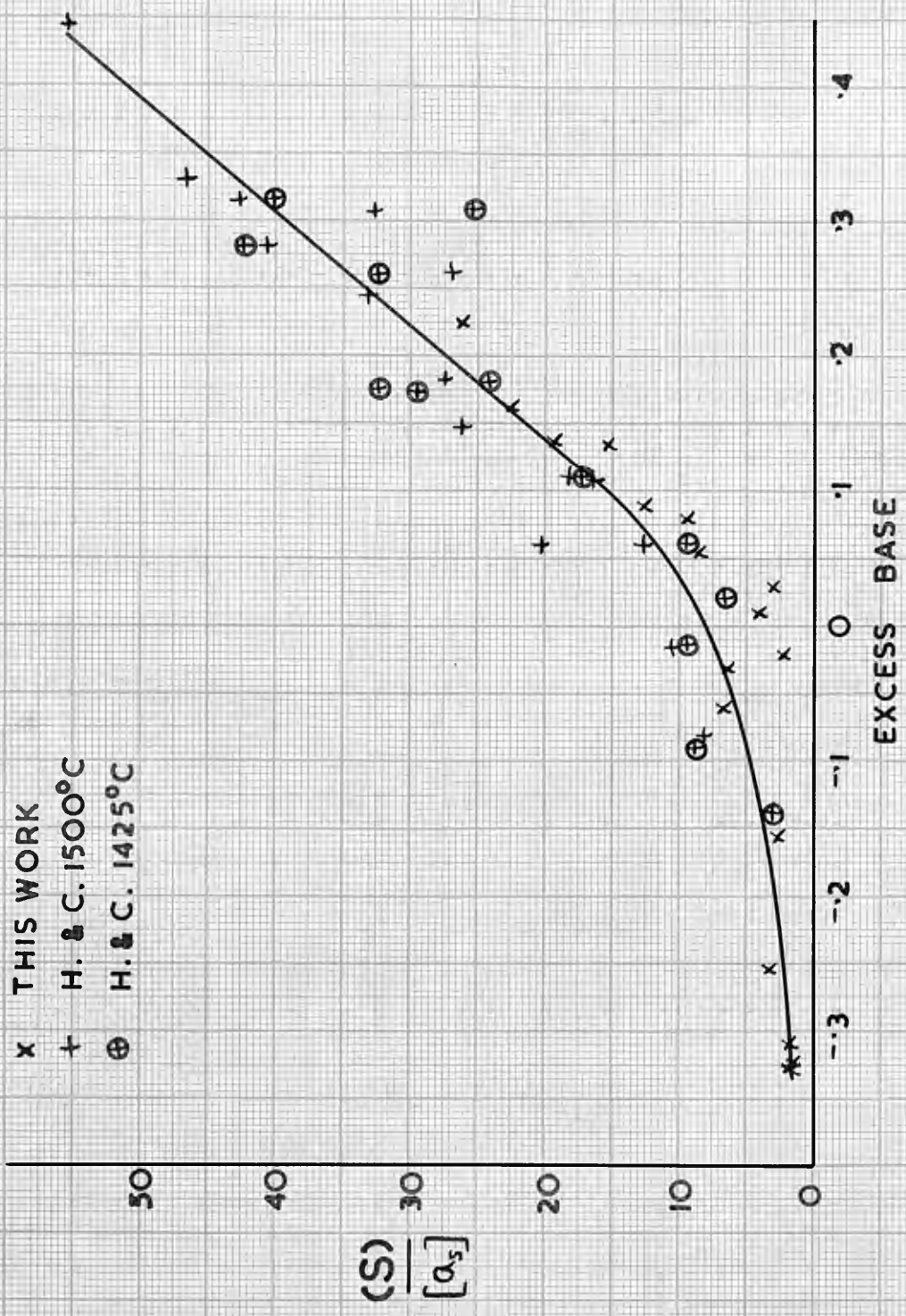Hatch & Chipman's results with 1.5% S slags.

Figure 6. Results of this work and of Hatch and Chipman plotted using $[a_s]$

and consequently the calculated values of (α_{CaS}) were extremely uncertain. Further uncertainty is introduced to these calcu-:lations by the use of a value for the activity of lime obtained from the lime-silica binary equilibrium diagram.

Calcium sulphide activity values obtained by calculations of this kind are therefore unreliable. Weight percentages of slag sulphur are used throughout this discussion and consequently the results, as presented here, do not take account of any variation which there may be in the activity coefficient of slag sulphur in the range from 1% to 1.8% sulphur.

On Figure 6 the ratio $\frac{(S)}{[\alpha_S]}$ is shown graphed against excess base and the results of this investigation (reported in Table I) are compared with the individual results of Hatch and Chipman (shown in Table II). An activity coefficient cannot be obtained for Filer and Darken's(2) result since the carbon content of the metal is not reported. The agreement, shown on Figure 6, between Hatch and Chipman's results and those of this investigation, is considered to be excellent for work of this nature. It is improved if a differentiation of the points on a basis of slag alumina content is made. This is shown on Figure 7.

This agreement provides confirmation of both sets of experimental results. It also comprises a valuable check on the method of finding metal sulphur activities and shows that the technique of combining data, found for binary and
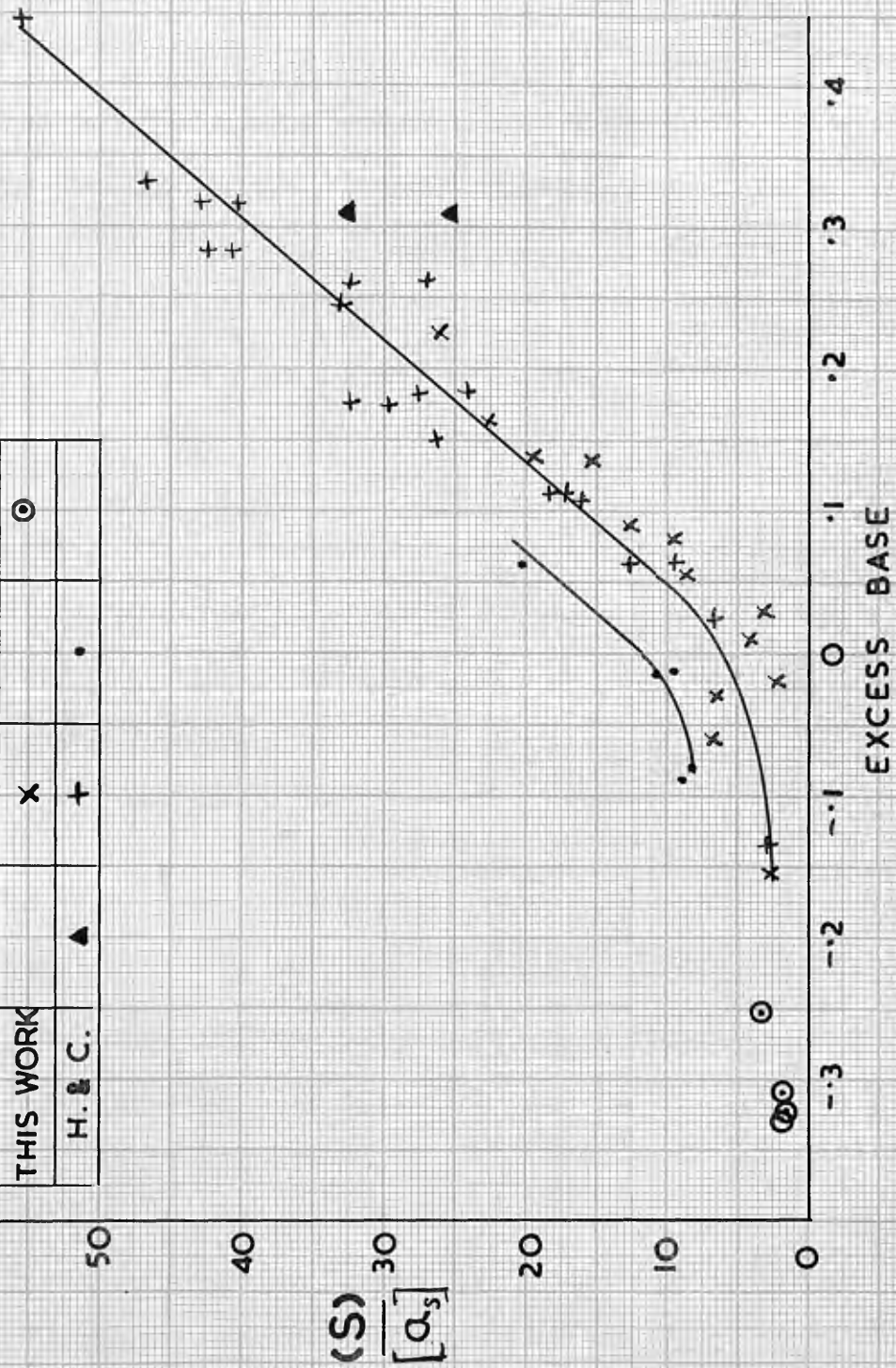
Figure 7. Experiments at temperatures from 1425°C to 1550°C.

ternary systems, for use in more complex systems is satis-
:factory.

When it is considered that the points on Figure 7
represent experiments done within the temperature range
1425°C to 1550°C, and that no temperature differentiation is
possible, it must be concluded that the effect of temperature
on the position of sulphur equilibrium is negligible.   This
is a rather different conclusion from that which Hatch and
Chipman reached.

The temperature effect which would be expected from
thermodynamic considerations can be shown.   Rosenqvist[22]
has given the free energy change for the desulphurisation
reaction:

$S_{(in\ Fe)}$ + (CaO) + C = (CaS) + CO; ΔG^{o} = 27,050 - 27.55 T.
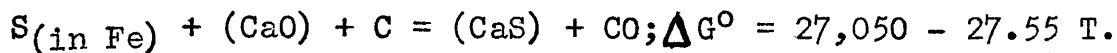
From this, where

$$K = \frac{(a_{CaS})\ p_{CO}}{[a_S](a_{CaO})[a_C]}$$

$K_{1450^{o}C}$ = 380, $K_{1500^{o}C}$ = 470, $K_{1550^{o}C}$ = 590.

Thus the experimental results are apparently at variance with
the thermodynamic data as far as temperature effect is concerned.
The changes in the activity coefficients of lime and calcium
sulphide with temperature are not known. If the discrepancy
was due to changes in these, the activity coefficient of calcium
sulphide would need to increase and the activity coefficient of
lime would need to decrease with increasing temperature;

neither of these seems likely. Therefore, if the thermo-
:dynamic data are reliable, and at present there are insuffic-
:ient grounds for doubting them, the discrepancy remains
unexplained.

The transition from the weight percentage ratio of
sulphur distribution used on Figure 4 to the ratio incorporating
the metal sulphur activity used on Figures 6 and 7, has brought
out clearly the important effect which silicon has on the
activity coefficient of sulphur in iron. The high metal
silicon contents which Hatch and Chipman used have therefore
been instrumental in bringing about a false interpretation of
the data on temperature effect. They have also tended to
distort comparisons of the sulphur ratios obtained in the lab-
:oratory and those encountered in blast furnace practice.

It is now possible to state the equilibrium results
on the basis of a 1% silicon iron saturated with carbon. Slags
containing 17.5% alumina and with $\frac{CaO}{SiO_2}$ (wt. per cent) ratios
of 1.2 and 1.5 have been chosen and are compared in the table.

$\frac{CaO}{SiO_2}$	Excess Base.	$\frac{(S)}{[a_S]}$	f_S (1% Si, C$_{sat}$)	$\frac{(S)}{[S]}$
1.2	+0.008	6	5.7	34
1.5	+0.163	21	5.7	120

Hatch and Chipman's results for these slags were 104 and 170. So it can be seen that striking differences are made by the adoption of this method of stating the results.

Since a well defined differentiation of the points on Figure 7, on a basis of slag alumina content, is possible it is clear that the excess base expression as a measure of lime activity does not take satisfactory account of alumina. Relative to the 10% to 21% alumina slags, the excess base of those containing less than 10% alumina has been overestimated and that of the 26% alumina slags has been underestimated. This indicates that as the alumina in slags increases there is a tendency for its behaviour to become less acidic; in other words it shows amphoteric properties. That this tendency does not continue with increasing alumina content up to 40% is shown by the low $\frac{(S)}{[a_s]}$ ratios obtained for the slags with more than 40% alumina. This is probably due partly to the simple dilution effect on lime of such large percentages of alumina, and partly to the solubility of sulphur in these slags being less than in lower alumina slags.

It can be seen that for the proper assessment of results of the kind discussed here, reliable figures for the activity of lime in slags are needed. A method for the determination of such values will be suggested later in the discussion.

In all the forms of desulphurisation reactions which have been suggested for blast furnace slags the oxygen potential of the system is included in one guise or another. In the equation

$$[FeS] + (CaO) = (CaS) + (FeO)$$
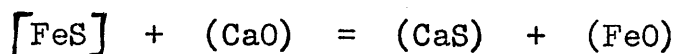
the Feo term is a means of the oxygen potential of the system. In the equation

$$[S] + (CaO) + C = (CaS) + CO$$
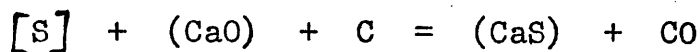
the ratio of activities of CO to Carbon is a measure of the oxygen potential. Having established equilibrium in the sulphur transfer reaction, it is important to know the oxygen potential with which it is established.

In these slag-metal systems it appears that there are two possible levels of oxygen potential with which the sulphur transfer might be in equilibrium. One is that defined by equilibrium with[1]atmosphere of CO and solid carbon and the other is that measured by the FeO content of the slag. These two oxygen potential levels may or may not coincide.

Attention is therefore focussed on the analysed values of slag FeO content both in this investigation and in other similar ones. The position can be summarised in a table :

Ref. No.		Range % FeO	Arithmetic Mean % FeO.
	Present Work.	0.06 - 0.30	0.18
1	Hatch & Chipman (a)	0.19 - 0.46	0.26
1	Hatch & Chipman (b)	0.020-0.100	0.039
2	Filer & Darken	0.06 - 0.23	0.14
11	Grant, Kalling & Chipman.	0.025-0.187	0.10

The figures in parenthesis indicate results obtained (a) with an ordinary magnetic cleaning method and (b) with an isodynamic separator.　It is rather surprising that such differences should be got from apparently similar investiga:tions in carbon crucibles.

　　　　The thermodynamic activity of FeO in equilibrium with solid carbon and 1 atmosphere pressure of CO can be calculated from the data given by Richardson and Jeffes(13). The standard free energy change of the reaction

$$CO + Fe = FeO + C$$
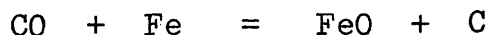
at $1500^{\circ}C$ is 27,475 cals. per gm. molecule, and using Chipman's (26) value 0.59 as the activity of iron when saturated with carbon, the activity of FeO can be found.

$$\frac{(a_{FeO}).\, a_c}{p_{co}.\,[a_{Fe}]} = \frac{(a_{FeO}).1}{1.\ 0.59} = \text{antilog} -\frac{27,475}{4.57.\ 1773}$$

$$= 0.000407$$

$$\therefore\ (a_{FeO}) = 0.00024$$

Therefore, if FeO is assumed to behave ideally at very low concentrations in the slags, Hatch and Chipman's lower FeO contents are closest to the equilibrium value. The analysed FeO contents of this investigation are very much higher than these and yet the agreement between the results of Table I and those of Hatch and Chipman, on Figure 7 is good. It was therefore decided to try to check the accuracy of the FeO analyses of this work.

To test the efficiency of the magnetic cleaning method normally used, several slags were resubjected to the field of an electric horse-shoe magnet of considerably greater power than the one used generally. There was found to be no change in the iron contents of these slags. The possibility that the high iron contents were due to FeS partitioned between the metal and the slag was investigated. No relation could be found between the metal sulphur activity and the analysed iron content of the slag; some relation of this kind would be expected if this were the cause of the high iron contents. The work of Martin, Glockler and Wood(10) indicates that this would not occur to any extent since they give the solubility of FeS in slags of this nature as 0.03%. No correlation could be seen between the basicity of the slags and their iron contents but a relationship was found with the sulphur contents of the slags. This is shown on Figure 8 where the sulphur content of the slags is plotted against the analysed iron content, expressed as FeO.
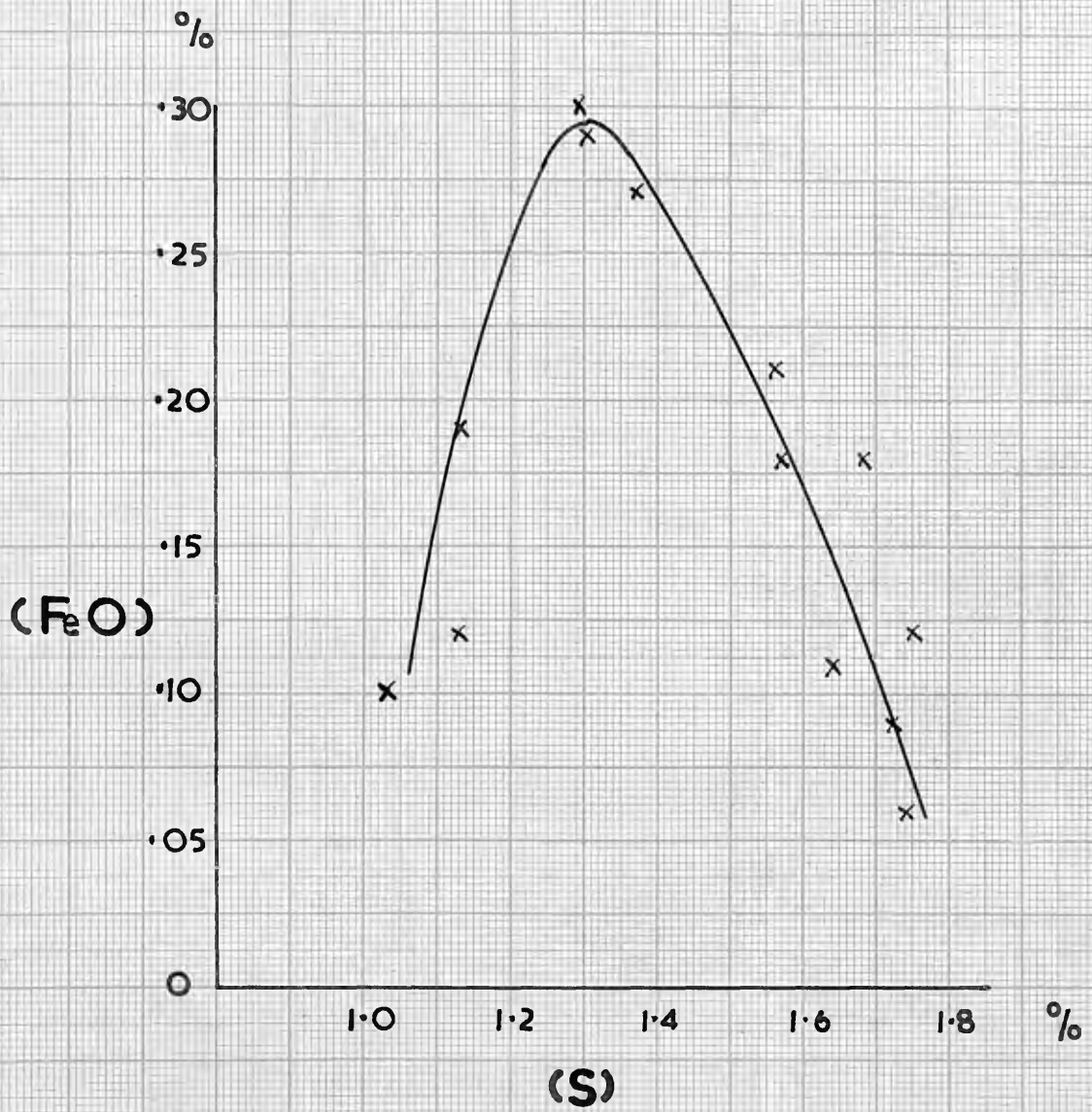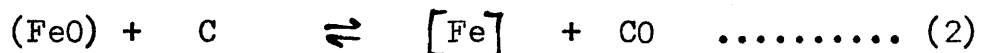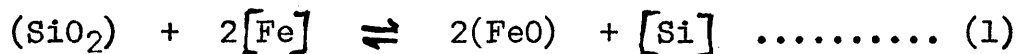
Figure 8.   Relationship between (FeO) and (S) for the slags of Table I.

A satisfactory explanation for the shape of Figure 8 cannot be advanced.   Since no reasonable mechanism can be suggested which would cause the iron content to vary with the sulphur content in this way, it must be taken to mean that in the range 1% to 1.8% sulphur the analysed slag iron content is affected by the presence of sulphur and is probably inaccurate.

By experiments in carbon crucibles with sulphur free lime-alumina-silica slags Arthur[27] has shown that the nearer silicon equilibrium between metal and slag is approached the lower is the FeO content of the slag.   The FeO contents he analysed varied from 0.11% in the slag over a low silicon iron to 0.02% in that over an iron in which the silicon was higher and near to equilibrium with the slag.   He explained these results by considering the two reactions proceeding in these slag-metal systems:

$$(SiO_2) + 2[Fe] \rightleftharpoons 2(FeO) + [Si] \quad \ldots\ldots\ldots\ldots (1)$$
$$(FeO) + C \rightleftharpoons [Fe] + CO \quad \ldots\ldots\ldots\ldots (2)$$

Both these reactions proceed in the directions of the top arrows.   The explanation proposed by Arthur is that at FeO contents below about 0.1% reaction (1) is more rapid than reaction (2) and, except in the case when reaction (1) is at equilibrium there is a state of dynamic equilibrium between the silica reduction reaction which is creating FeO and the slower reduction of FeO which is removing it.

Now, in this work by Arthur and in the present work the technique of preparation and analysis of slags was the same. This indicates that satisfactory FeO analysis can be made, using this technique, if sulphur is not present. Therefore it appeared that values near to the true FeO contents of the slags of Table I would be obtained from experiments to which no sulphur was added and in which silicon contents of the same order as those of Table I were used. Three such experiments were done with slags across the range of compos-:ition used in Table I and the results are given.

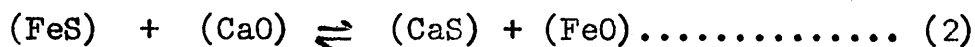| No.	CaO	SiO_2	Al_2O_3	FeO	Excess base	Si
56	29.2	26.8	43.6	0.11	−0.353	0.72
60(a)	44.9	39.8	15.9	0.12	−0.018	0.85
60(b)	51.5	33.2	15.5	0.09	+0.214	0.79

From this, the indication is that the slags of Table I, with the exceptions of 26 and 59 with higher silicons, have FeO contents of not less than 0.1%, not those shown in Table I.

It is of interest to note that the lowest sulphur slags shown on Figure 8 contain about 0.1% FeO, as analysed. This suggests that the disturbing effect of sulphur, as far as iron analysis is concerned, only becomes effective at sulphur contents above about 1%. This point is of importance in the next section where the majority of the slags discussed contain less than 1% sulphur.

The metal silicon contents obtained in this investi-:gation are generally much lower than are those of Hatch and Chipman(1).   In view of this and the silicon-FeO relationship already discussed,it would be expected that the FeO contents of Hatch and Chipman's slags would be lower than those of the present work.   The picture of the slags of Table I (except 26 and 59) having FeO contents of not less than 0.1% and of Hatch and Chipman's having FeO contents of about 0.03%, is quite compatible with this.

It is concluded that the FeO contents of the slags represented on Figure 7 vary, at least, between the limits 0.03% and 0.1%.   This means that equilibrium between the FeO of the slag and carbon has not been reached in all the experiments.   The good agreement among the sulphur distri-:bution results shows that the conditions controlling the sulphur equilibrium were the same in the separate investi-:gations.   The oxygen activities in the metals were the same in all the experiments since the metals were in equil-:ibrium with carbon.   Therefore, the conclusion must be that the sulphur distribution ratio has been determined by the oxygen potential C/CO (the oxygen activity in the metal), rather than by the oxygen potential Fe/FeO (the FeO activity in the slag).

This is at variance with the most commonly accepted mechanism of the sulphur transfer reaction, which is:

$$[\text{FeS}] \rightleftharpoons (\text{FeS}) \dots\dots\dots\dots\dots\dots (1)$$

$$(\text{FeS}) + (\text{CaO}) \rightleftharpoons (\text{CaS}) + (\text{FeO}) \dots\dots\dots\dots (2)$$

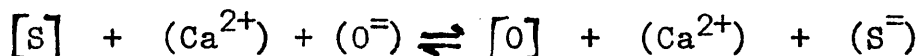$$(\text{FeO}) + \text{C} \rightleftharpoons [\text{Fe}] + \text{CO} \dots\dots\dots\dots (3)$$

Reaction (2) is homogeneous and would be relatively fast; it would, therefore, be impossible for this reaction to be out of equilibrium for long.

Alternatively the mechanism can be considered to be that of an interface reaction, written simply:

$$[\text{S}] + (\text{CaO}) \rightleftharpoons (\text{CaS}) + [\text{O}]$$
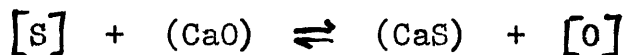
With the slag constituents written ionically this becomes

$$[\text{S}] + (\text{Ca}^{2+}) + (\text{O}^{=}) \rightleftharpoons [\text{O}] + (\text{Ca}^{2+}) + (\text{S}^{=})$$

In this reaction electrical neutrality is preserved on both sides of the interface.

Jost(25) has given an example of the mechanism of an interface reaction between solids which is precisely analagous to this. The case he quotes is the reaction between cuprous oxide and cobalt. The mechanism can best be illustrated thus:

Cuprous
Oxide   Cobalt

$2\text{Cu}^+ \quad \longrightarrow \quad 2\text{Cu}$

$\text{O}^=$

$\text{Co}^{2+} \quad \longleftarrow \quad \text{Co}$
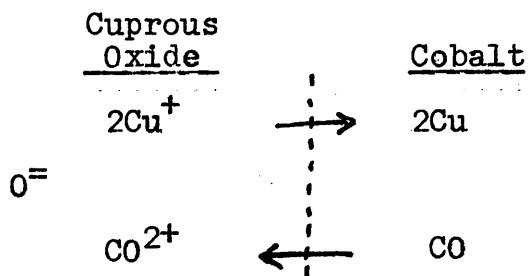
The simultaneous transfer of copper in one direction and cobalt in the other, preserves electrical neutrality on both sides of the interface.

Treatment of the slag constituents as ionic is probably as justified as the writing of molecular equations. The electrical conductivity of slags has been shown to be considerable(30) and this points to at least some measure of dissociation into ions in the liquid slag. The importance of the ionic treatment for this reaction is that it provides a mechanism whereby the oxygen activity in the metal is the controlling factor in desulphurisation. At equilibrium, of course, the FeO activity of the slag is equal to that of the metal. If it is postulated that, under certain conditions, this equilibrium is reached only very slowly then it would be possible for the oxygen activity of the metal to be different from the oxygen activity of the slag for fairly long periods of time.

Except in experiment 59, which contained more than the equilibrium concentration of silicon, silica reduction always took place. If a mechanism is to be proposed for this reaction on the same lines as for the sulphur reaction it would be

$$2(O^{2-}) + (Si^{4+}) + 2[Fe] \rightleftharpoons [Si] + 2(Fe^{2+}) + 2(O^{2-})$$
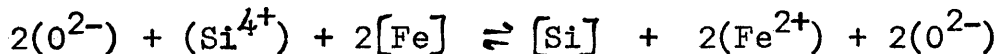
In this reaction FeO is formed in the slag in the same kind of way as CaS is formed by the sulphur transfer.

Rhe FeO formed in the slag by this reaction has to diffuse across an interface before it can react with carbon. It can either cross the slag-crucible or slag-metal interface. It is proposed that this reaction of FeO with

carbon is slow in these experiments, because it is thought that the diffusion of FeO in the slag and across the interfaces is slow at low FeO concentrations in the slag.   Such a picture of a diffusion controlled reaction is not uncommon in work with slags.   So far as is known there is no experi: :mental evidence as to the rate of diffusion of FeO in slags of this type.

The process of diffusion of FeO across the slag- metal interface can be considered as a reaction the equation of which might be written

$$\left(Fe^{++}\right) + \left(O^{=}\right) \rightleftarrows [Fe] + [O]$$
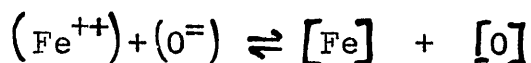
Again electrical neutrality is maintained.   It is important to notice that when oxygen crosses the interface in either direction by this diffusion or reaction, iron must also cross in the same direction.   A clear differentiation must be made between this process by which FeO is made to cross the inter- :face, and the transfer reactions

$$[S] + (O^{2-}) \rightleftarrows (S^{2-}) + [O]$$
$$\text{and } (Si^{4+}) + 2[Fe] \rightleftarrows [Si] + 2(Fe^{2+})$$
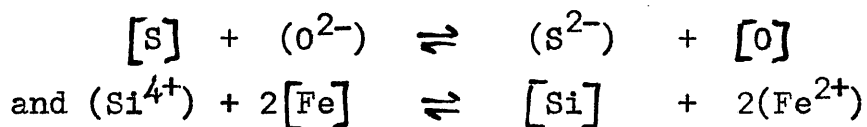
Oxygen can be made to cross the interface by the sulphur transfer, and FeO can be formed in the slag by the silicon transfer.   In these reaction cases various factors such as the activity of sulphur and silicon in the metal control the rates of the processes.   However, in the case of the simple transfer or diffusion of FeO across the interface the only variable factor controlling the rate of process is the activity gradient of FeO.

It should now be possible to describe in more detail the proposed mechanism of desulphurisation in these experiments.

Sulphur transfers from the metal to the slag according to an interface reaction which can be illustrated

$$
\begin{array}{ccc}
\text{Metal} & & \text{Slag} \\
S & \longrightarrow & S^{2-} \\
& & Ca^{2+} \\
O & \longleftarrow & O^{2-}
\end{array}
$$
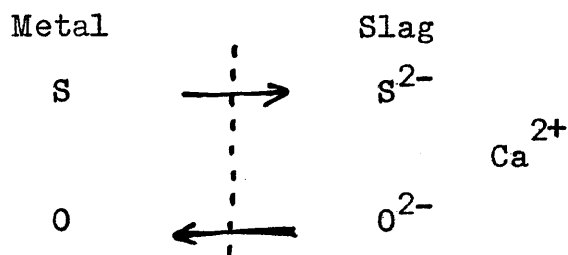
Oxygen is formed in the metal by this reaction. At the beginning of desulphurisation when the transfer reaction is most rapid fairly large concentrations of oxygen might be built up in the metal near the interface. This concentration of oxygen could be removed either by reaction with carbon in the metal

$$[O] + [C] \longrightarrow CO$$
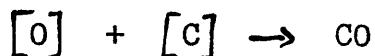
or by the transfer of FeO into the slag according to the reaction

$$[Fe] + [O] \rightleftharpoons (Fe^{2+}) + (O^{=})$$
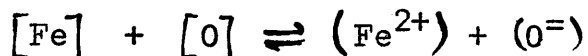
The reaction of oxygen with carbon will be controlled by the necessity for bubble formation while the reaction transferring FeO into the slag is only controlled by the difference of FeO activities between the metal and the slag. Therefore the extent of the transfer of FeO into the slag will be greatest in the initial stages of desulphurisation when oxygen is produced in the metal at the greatest speed.

This is probably the explanation of the maximum in slag iron content which was observed by Derge, Philbrook and Goldman(24) at the beginning of desulphurisation.

The other reaction taking place at the interface can be illustrated

$$\text{Metal} \qquad\qquad \text{Slag}$$

$$\text{Si} \quad \longleftarrow \quad Si^{4+}$$

$$20^{2-}$$

$$2Fe \quad \longrightarrow \quad 2Fe^{2+}$$
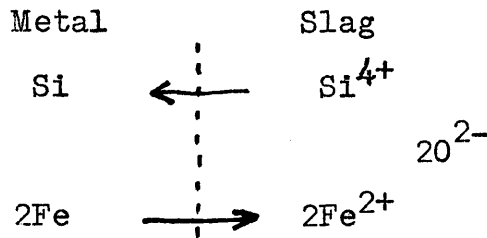
The FeO formed in the slag by this reaction has to diffuse across an interface before it can react with carbon.   If it diffuses across the metal-slag interface into the metal at a faster rate than can be coped with by the reaction

$$[O] + [C] \longrightarrow CO$$
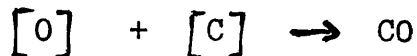
the oxygen activity of the metal will remain higher than that in equilibrium with carbon of unit activity.   This will tend to slow the sulphur transfer reaction in its approach to equilibrium.   The further the silicon content of the metal is below that in equilibrium with the slag the faster silica reduction.will be and the more effect it will have in slowing desulphurisation by this mechanism.

This phase in the desulphurisation process, when FeO produced in the slag by silica reduction transfers into the metal and hinders sulphur transfer, comes after the

initial phase of rapid sulphur transfer and consequent diffusion of FeO from metal to slag.

The effect of silicon on the rate of desulphur-:isation which was discovered by Grant, Troili and Chipman(12) is explained by this mechanism. In the present investigation also it was noticed that experiments 26 and 59 with silicon bearing irons, reached equilibrium more quickly than the others. Some idea of the importance of silica reduction as a producer of FeO can be got from figures calculated for experiment 23. In 7 hours the amount of FeO produced by reduction of silica was 4 gms whereas in that time the amount produced by the sulphur transfer reaction was 0.5 gm.

The final phase in the approach to sulphur equilibrium in the system is reached when the amount of FeO crossing the slag-metal interface into the metal per unit of time, can readily be dealt with by reaction with carbon. The sulphur transfer reaction can then approach equilibrium with the metal oxygen activity which is in equilibrium with solid carbon. From the results it appears that this state of affairs comes about when the average FeO content of the slag is at or below 0.1%.

In this description of the proposed mechanism of desulphurisation three phases, in time, have been mentioned. This division has been made purely to simplify the discussion of a somewhat complex subject. It is not proposed that the phases do not overlap.

This hypothesis seems to explain the observed facts satisfactorily. In particular it explains the agreement, shown on Fig.7, between Hatch and Chipman's(1) sulphur distribution ratios and those given here. This is because it attributes control of the sulphur equilibrium to the oxygen activity in the metal, which was the same in both investigations, being that defined by equilibrium with solid carbon and 1 atmosphere of CO. This agreement cannot be explained if Derge, Philbrook and Goldman's (24) mechanism is accepted. While other mechanisms may take some part in desulphurisation it is believed that the one outlined above is dominant in the conditions of the experiments.

DISCUSSION OF RESULTS OF

EXPERIMENTS IN ALUMINA CRUCIBLES.

Expt. No.	Time (Hours)	Sulphur added to	Slag analysis wt.%					Metal analysis wt.%				f_s	$\dfrac{(S)}{[a_s]}$
			CaO	SiO₂	Al₂O₃	FeO	S	Si	C	s		
14	3	Metal	31.3	23.3	43.6	0.50	0.38	0.11	2.42	1.03	1.9	.199
15	4	Metal	30.0	24.1	44.8	0.49	0.42	0.01	2.44	1.08	1.8	.212
16	6	Metal	29.6	25.4	44.9	0.48	0.41	0.12	1.98	1.13	1.6	.224
18	4	Metal	30.3	28.2	40.4	0.31	0.46	2.48	2.02	1.29	2.6	.135
22	6	Metal	28.6	26.1	44.2	0.21	1.02	1.91	1.64	0.700	2.1	.710
25	4	Slag	29.9	26.8	42.7	0.33	0.45	0.22	3.96	0.198	3.4	.661
27	5	Slag	28.3	25.7	44.5	0.33	0.82	0.26	3.68	0.241	3.1	1.11
30	4	Slag	29.6	31.0	37.7	1.29	1.21	0.10	2.76	0.622	2.1	.930
31	4	Slag	28.1	31.5	39.3	0.52	0.28	0.13	3.15	0.263	2.4	.443
32	4	Slag	31.4	24.9	42.1	0.88	0.64	0.17	3.61	0.301	2.9	.733
33	3½	Slag	32.0	25.1	41.5	0.61	0.48	0.10	3.56	0.324	2.8	.534
34	3	Slag	31.4	27.8	40.2	0.33	0.54	0.21	3.48	0.296	2.8	.641
35	3½	Metal	29.5	26.0	44.6	0.55	0.48	0.06	2.58	0.665	2.0	.371
36	3½	Slag	31.6	27.8	40.0	0.25	0.97	0.18	2.61	0.268	2.1	1.72
37	3	Metal	28.1	24.3	46.3	0.95	0.25	0.04	1.60	0.840	1.4	.207
38	3	Slag	29.3	29.1	41.6	0.24	0.62	0.28	3.28	0.161	2.7	1.43
45	3½	Metal	26.5	22.2	49.5	1.10	0.27	0.06	1.61	1.47	1.4	.132
46	3½	Metal	29.0	25.9	42.7	1.40	0.14	0.12	1.30	1.75	1.3	.063
48	3	Metal	28.7	22.9	47.5	0.61	0.69	0.23	2.20	1.32	1.75	.299
49	6	Slag	29.5	26.2	44.3	0.84	0.64	0.59	3.08	0.470	2.6	.516
51	6	Metal	28.2	25.4	45.3	1.50	0.16	0.02	0.30	4.18	0.88	.044
52	10	Slag	27.2	26.5	45.6	1.20	0.56	0.18	3.64	0.321	2.9	.606

TABLE III.

Results of experiments in alumina crucibles at 1500°C.

The results of experiments in the composite alumina-
molybdenum crucibles are given in Table III.   These were all
done at 1500°C.   Since alumina crucibles were used the slags
were alumina saturated.   In eleven of the experiments equilibrium
was approached from high sulphur in the metal and in the other
eleven from high sulphur in the slag.   An attempt was made to
keep the lime-silica ratio constant in order that the lime
activity should be the same in all the experiments.   The general
aim was to study the equilibrium partition of sulphur between
slag and metal at various levels of slag FeO concentration.

The results of experiments 14, 15 and 16, held at
temperature for 3, 4 and 6 hours respectively, indicate that
equilibrium was reached within 3 hours in a run to which the
sulphur was added to the metal.   Similar comparisons of the
results of experiments to which the sulphur was added to the
slag seem to show that equilibrium was not so quickly attained
in this type of experiment.   This will be dealt with more
fully later.

Silicon bearing metal was used in the two experiments
numbered 18 and 22.

Values of f_S, the activity coefficient of sulphur in
the metal were obtained, in the way described in the previous
chapter, from the information given by Sherman and Chipman(21)
and summarised in Fig.5.   A graph of the ratio $\frac{(S)}{[\alpha_S]}$ against
the FeO content of the slag shows a wide scatter of points from

which no reliable conclusions can be drawn. This does not necessarily mean that there is no relation between the activity of FeO in the slag and the ratio of sulphur activities in the slag and metal. The reason for it could be any or all of the following:

(1) The activity of FeO not being proportional to concentration over the range 0.2% to 1.5% FeO.

(2) The activity of sulphur in the slag not being proportional to concentration over the range 0.1% to 1.2% sulphur.

(3) Some of the experiments not having reached equilibrium.

Three experiments were done in an attempt to find values of the activity of FeO in these slag-metal systems. The experimental method was the same as that described for the experiments of Table III except that no sulphur was charged. FeO was added to the molten slag and the crucible was held at 1500°C for 5 hours to allow the carbon of the metal and the FeO of the slag to come to equilibrium. The essential results of these experiments can be summarised in a Table.

No.	% FeO.	% C.	% Si.
57	0.45	4.30	< 0.05
58	0.85	3.87	< 0.05
61	1.18	3.50	< 0.05

The reaction brought to equilibrium in these experiments is

$$FeO + C = Fe + CO \qquad \Delta G^o_{1500} = -27,475 \text{ cals/gm.mol.}$$
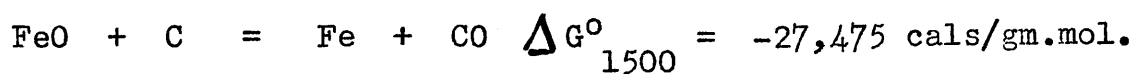
This free energy change is taken from the data given by Richardson and Jeffes(13). When the reaction is at equilibrium under 1 atmosphere pressure of CO the activity of FeO at 1500°C is given by

$$a_{FeO} = 0.000407 \text{ x } \frac{[a_{Fe}]}{[a_c]} \quad \ldots\ldots\ldots\ldots\ldots \text{ (1)}.$$

For these three experiments, in which for all practical purposes the metal is a simple iron-carbon binary alloy, values of the activity of carbon $[a_c]$ and iron $[a_{Fe}]$ can be obtained from Chipman's(26) data. So, in these cases, it is possible to evaluate the activity of FeO by measuring its effect on the carbon content of the metal.

If the effect of sulphur on the activity of carbon was known and if the value of the activity of iron in ternary systems could be found, values of the ratio $\frac{[a_{Fe}]}{[a_c]}$ could be obtained for all the experiments on Table III.

Kitchener, Bockris and Spratt(23) have recently published the results of an investigation into the effect of sulphur on the carbon content at saturation of iron-carbon-sulphur alloys. Chipman(26) has given data on carbon activities in binary iron-carbon systems. A method analogous to that of Sherman and Chipman(21) has been used to combine these data; the following is a description of the use of these data and the method to find the activities of carbon and iron in ternary iron-carbon-sulphur systems.

The data of Kitchener, Bockris and Spratt are only claimed to be accurate up to 0.84%S. For use in this work, however, they have been extrapolated to 1.75% sulphur and the results obtained do not show errors which can be attributed to this extrapolation. Experiment 51, which has a metal sulphur content of 4.18% has been omitted since this is considered to be well outwith the range of reasonable extrapolation.

The method used by Sherman and Chipman(21) to obtain sulphur activities involved the finding of an equivalent silicon content by summation of the effects on sulphur activity of all the solutes. Here it is proposed to find an equivalent carbon content and derive the activity coefficient of carbon in the alloy from this.

In all the alloy compositions reported by Kitchener, Bockris and Spratt(23) the activity of carbon is 1. The activity coefficient of carbon in these alloys is therefore the reciprocal of the carbon content and can be found for any sulphur content up to 1.75%. Fig.9(a) shows an extrapolated plot of log $f_c^{f_c}$ against carbon content obtained from Chipman's (26) work on binary iron-carbon alloys. $f_c^{f_c}$ is the activity coefficient of carbon in these alloys. From the extrapolated portion of this graph values of the carbon contents of binary iron-carbon alloys, which would have the same carbon activity coefficient as the carbon saturated iron-carbon-sulphur alloys, can be found. These iron-carbon alloys are, of course, purely imaginary since their carbon contents are greater than the
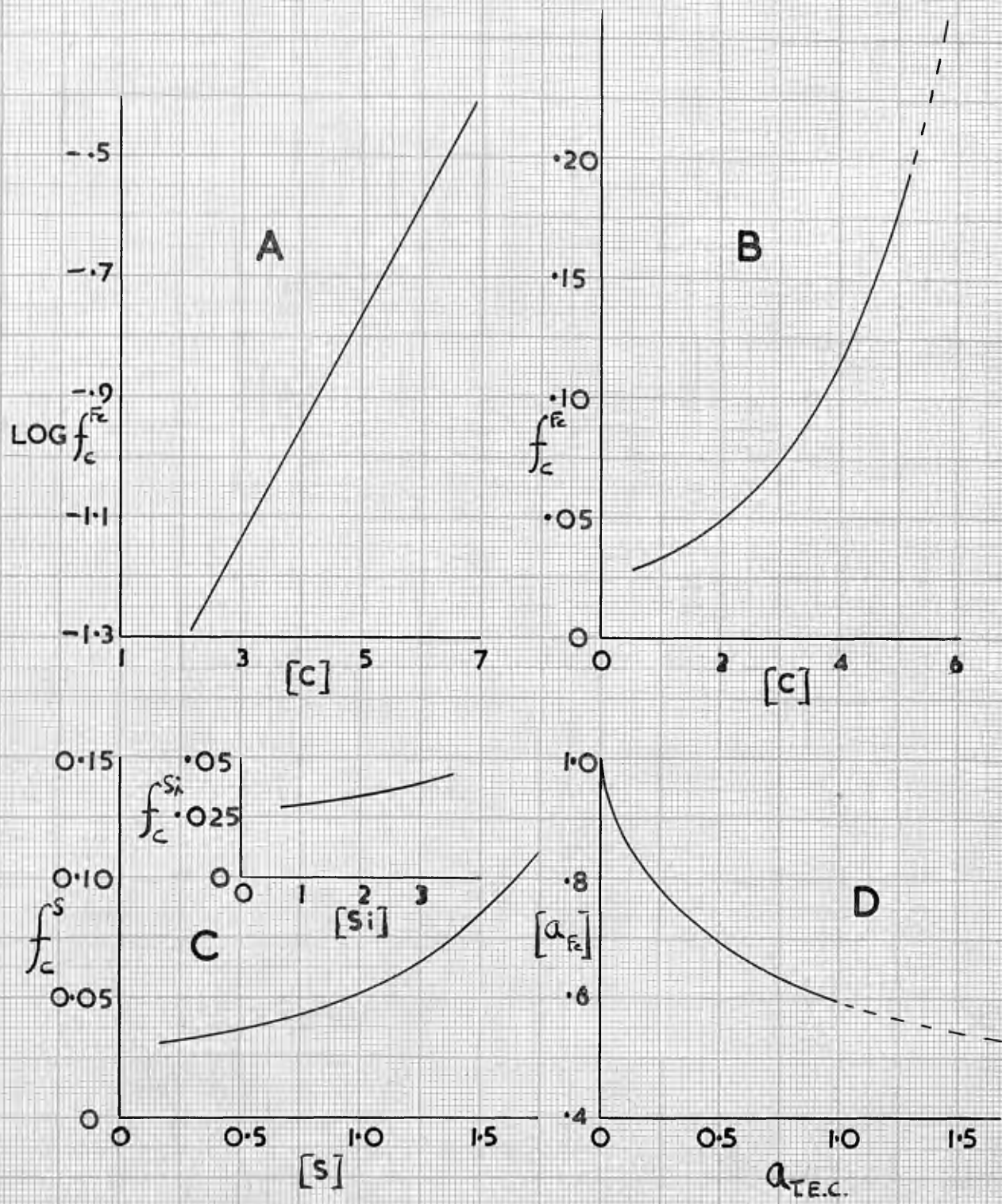
Figure 9.   Data used in finding $[a_c]$ and $[a_{Fe}]$

saturation value. The carbon contents of these "imaginary" alloys can be conveniently called total equivalent carbon contents. The symbol $C_{T.E.}$ has been chosen. This total equivalent carbon content of an alloy is the sum of two quantities; one is the actual carbon content of the alloy C, the other is the sulphur equivalent carbon content of the alloy $C_{S.E.}$

$$C_{T.E.} = C + C_{S.E.}$$

Now, for the ternary carbon saturated alloys C and $C_{T.E.}$ are known. Therefore $C_{S.E.}$ can be obtained for any sulphur content up to 1.75%. From the values of $C_{S.E.}$, so obtained, and reference to Figure 9(a) or 9(b) values of the activity coefficient of the sulphur equivalent carbon can be found. These are called f_c^s and are shown plotted against [S] on Fig.9(c).

On Figures 9'b) and 9(c) we now have data from which the activity of carbon in ternary alloys can be found. The process of obtaining an activity is virtually the reverse of that described above.

f_c^s is found from the sulphur content of the alloy and Fig.9(c). The carbon content of the iron-carbon binary which would have this activity coefficient is found from Fig.9(b). To this is added the actual carbon content of the alloy and so the total equivalent carbon content $C_{T.E.}$ is obtained. The activity coefficient which would correspond to this in an iron-carbon alloy is found from Fig.9(b) or if

necessary, from the extrapolated curve on Figure 9(c). This
is the activity coefficient of carbon in the alloy f_c and
activity is obtained using the equation

$$a_c = f_c \times C$$

This activity is referred to a graphite standard state.

In Table III experiments 18 and 22 are the only ones
in which the metal silicon contents are appreciable. To find
the a_c values for these metals the procedure was the same as
has been described except that an extra step was needed. This
step involved the finding of the sulphur equivalent, as far as
carbon activity is concerned, of the silicon content.

The graph used for this step was derived from
Chipman's(26) data on the carbon saturation of iron-carbon-
silicon alloys, the treatment being the same as was used for
the sulphur data. The graph is shown as an inset on Fig.9(c).
The silicon contents of the remainder of the metals were
ignored as far as the calculation of a_c was concerned.

Values of the activity of iron in the alloys were also
required. The effects of carbon, sulphur and in two cases
silicon on the activity of iron had to be taken into account.
It was considered that the best way to do this would be to make
use of the total equivalent carbon figures. This quantity is
the sum, as far as carbon activity is concerned, of all the
solute atoms in the iron expressed as carbon. Also, the total
equivalent carbon activity coefficient, f_c is known. To

obtain the activity of carbon a_c, f_c was multiplied by only that portion of the solutes which was present as carbon. The activity of the total equivalent carbon $a_{T.E.C.}$ is given by

$$a_{T.E.C.} = f_c \times C_{T.E.}$$

The activity of iron was obtained from a Gibbs-Duhem integration(26) on the iron-carbon system using $a_{T.E.C.}$. The result of the Gibbs-Duhem integration is shown as Fig.9(d); in two cases values of $a_{T.E.C.}$ were greater than 1 and the dotted extrapolation was used for them.

This is believed to be the most satisfactory method of using the available data to find values of the activity of iron in these complex systems.

On Figure 10 values of the ratio $\frac{[a_{Fe}]}{[a_c]}$ for the experiments of Table III are shown plotted against the FeO content of the slag. Three points representing the experiments to which no sulphur was added (57, 58 and 61) are also shown. In the construction of the line shown on Figure 10 more weight was given to these three points than to the others since they represent systems in which the metals were iron-carbon binary alloys and consequently in which there is less liklihood of error in the calculation of $[a_c]$ and $[a_{Fe}]$. Experiments 22, 36, 37 and 38, which are not represented on Figure 10, give values of $\frac{[a_{Fe}]}{[a_c]}$ very considerably higher than the others. This is thought to be due to the irons not being properly carbon saturated before they were charged to the crucibles. Recent
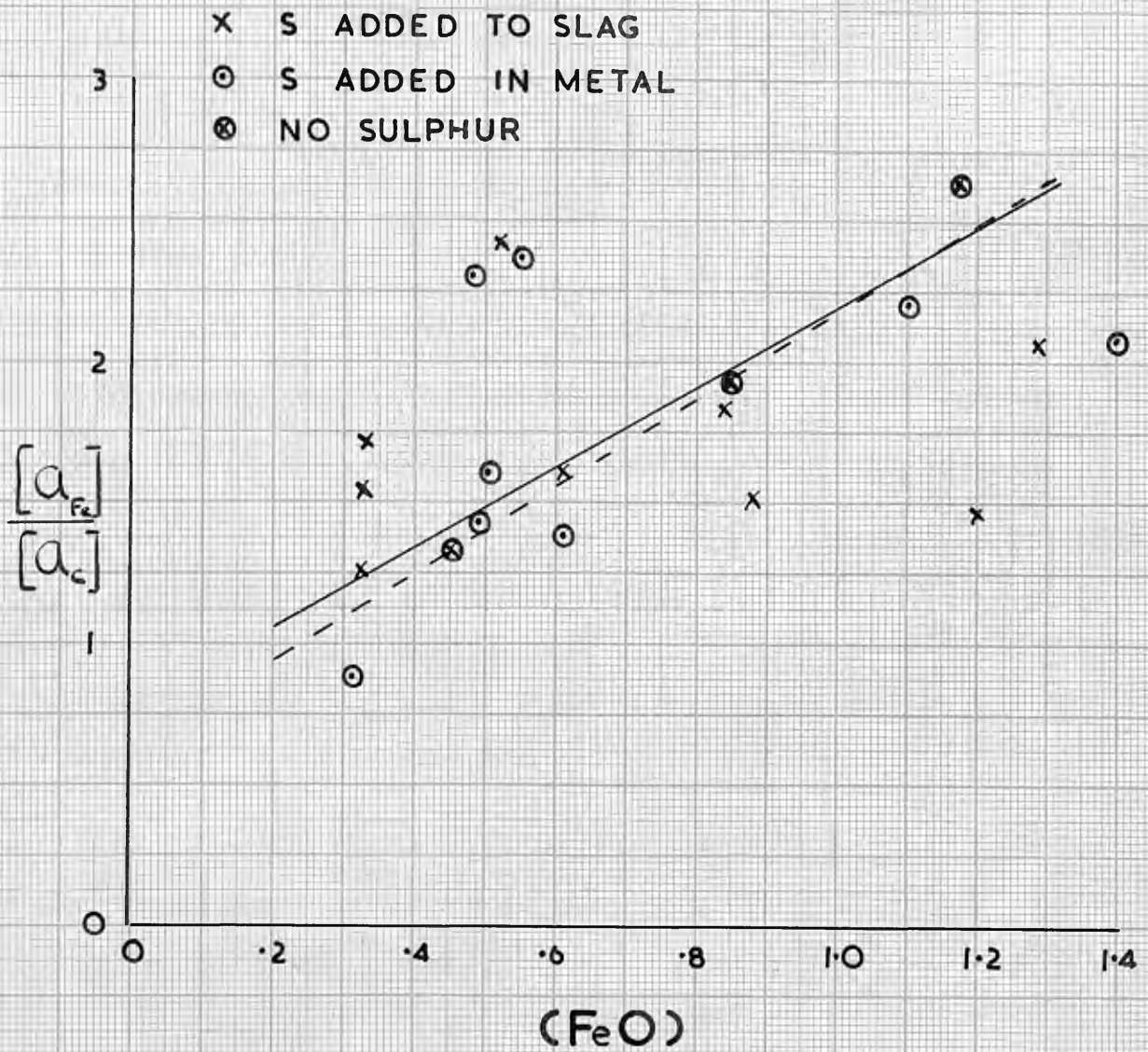
Figure 10.

work(23) has shown that iron approaches equilibrium with a carbon crucible very slowly.   In view of this it may be that insufficient time was allowed for carbon saturation of the metals of these experiments.   It is significant that three of them (22, 36 and 38) have the lowest FeO contents reported in Table III;   these would be the ones most likely to be affected by insufficient carbon pick-up.

The dotted line on Figure 10 is the best line through Arthur's (27) results, obtained from experiments on the effect of FeO on the silicon content of iron.   The agreement is good.
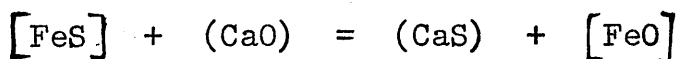
From the line on Figure 10 and the equation

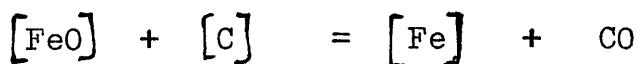$$a_{FeO} = 0.000407 \cdot \frac{[a_{Fe}]}{[a_c]}$$

values of the activity of FeO can be found for slag FeO contents up to 1.5% in this slag.   Activities found in this way are referred to the pure FeO standard state and can be given in a Table.

% FeO	0.2	0.6	1.0	1.4
$a_{FeO} \times 10^3$	0.44	0.62	0.89	1.11

The desulphurisation reaction can be written

$$[FeS] + (CaO) = (CaS) + [FeO]$$

Proceeding at the same time is the reaction

$$[FeO] + [C] = [Fe] + CO$$

These reaction equations can be added together to give the composite equation:

$$[FeS] + (CaO) + [C] = (CaS) + [Fe] + CO$$
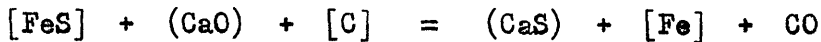
When this reaction is at equilibrium the expression

$$\frac{(a_S)[a_{Fe}] \, p_{co}}{[a_S][a_{c-o}][a_c]}$$

is constant.   In these experiments (a_{CaO}) and p_{CO} are constant and the expression simplifies to

$$\frac{(a_s)[a_{Fe}]}{[a_S][a_c]} = K_s^1$$

Values are known for all the terms in this expression except (a_s), the activity of sulphur in the slag.

Now

$$(a_s) = f_{(s)}.(S).$$

where $f_{(s)}$ is the activity coefficient of sulphur in the slag.

Therefore

$$\frac{f_{(s)}.(S)[a_{Fe}]}{[a_S].[a_c]} = K_s^1$$

This expression should be constant at all values of (S), therefore by graphing values of

$$\frac{(S)[a_{Fe}]}{[a_S][a_c]}$$

against corresponding values of (S) the way in which $f_{(s)}$ changes with (S) can be found.   This graph has been constructed and is shown as Figure 11.   The points representing experiments 22, 36, 37 and 38, have all been omitted since they are shown in the discussion on Fig.10 to have apparently erroneous values of the $\frac{[a_{Fe}]}{[a_c]}$ ratio.   On Fig. 11 a differentiation has been made between the points representative of the two directions of approach to equilibrium.   These can be seen to lie in two fairly well separated groups.   In addition there are on, Figure 11, four
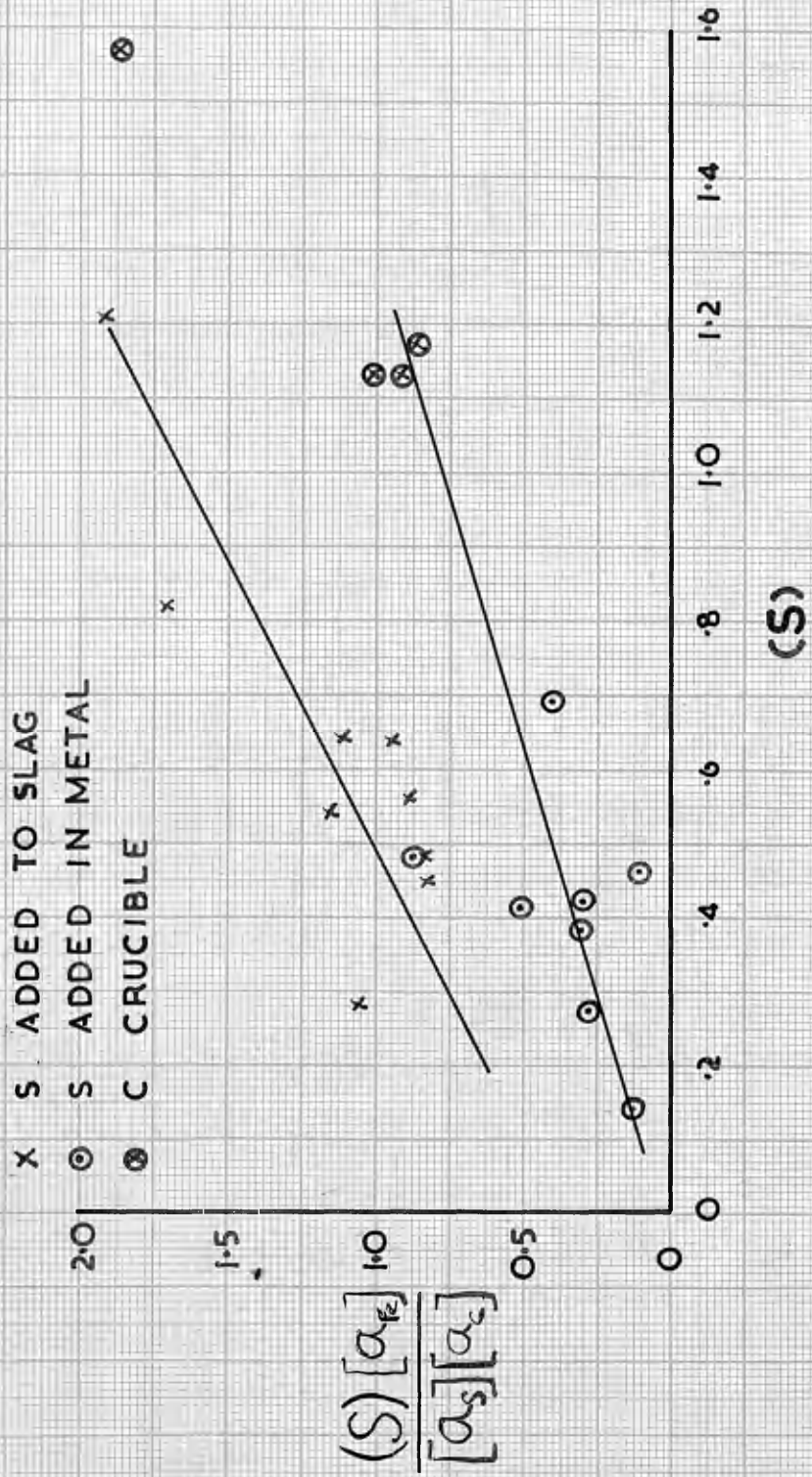
Figure 11.

points representing experiments reported in Table I. These
are numbered 23, 26, 40 and 42 and were done in carbon crucibles
with the alumina saturated type of slag used in all the experi-
:ments of Table III.

On Figure 10 the scatter of points about the line is
considerable. The effect of this scatter on a graph of the
type shown as Figure 11, can be eliminated if, for each
experiment, a value of the activity of FeO, obtained as were
those in the table on page 59 is used in place of the ratio
$\dfrac{[a_{Fe}]}{[a_c]}$. The graph of the expression

$$\frac{(S)}{[a_s]} \cdot a_{FeO}$$

against (S) is shown on Fig.12. Points representing all the
experiments reported in Table III are plotted on this graph
as also are the four points representing carbon crucible exper-
:iments. Fig.12 shows as definite a separation into two
groups, of the points representing the two types of approach
to equilibrium, as Fig.11. At slag sulphur contents of up
to 1.2% the points from the carbon crucible experiments agree
well with the line drawn through the lower set of points.
The experiments in which high sulphur slags were the source of
sulphur give values of $\dfrac{(S)}{[a_s]} \cdot a_{FeO}$ which are rather more than twice
those given by experiments in which equilibrium was approached
from the other side.

A discrepancy of this kind could mean that equilibrium
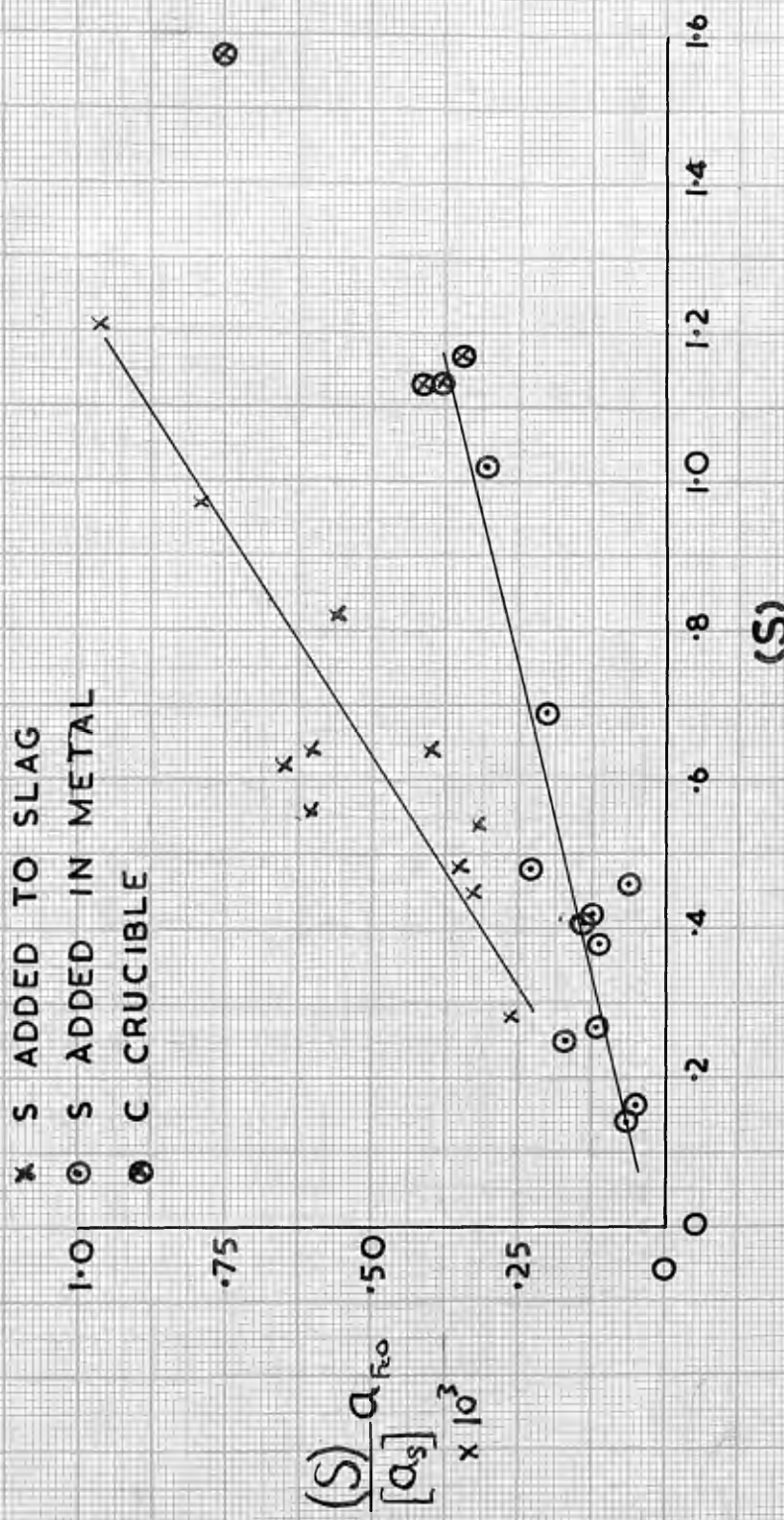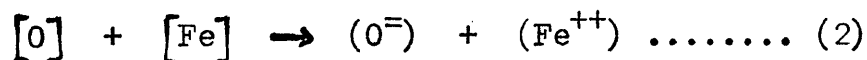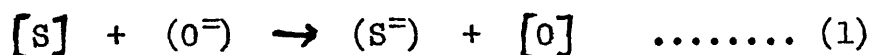has not been reached by either mode of approach. On the other

Figure 12.

hand it might mean that equilibrium has been reached by one approach but not by the other. In the present case, the fact that the carbon crucible experimental results are in good agreement with the high sulphur metal approach results provides evidence that these are in equilibrium. Therefore the experiments in which high sulphur slags were the source of sulphur cannot have reached equilibrium. That approach to equilibrium in this direction is very slow is indicated by the fact that in one case 10 hours, and in another case 6 hours were allowed for experiments of this type. The points representing these experiments are not lower on Figure 12 than other similar experiments given shorter times.
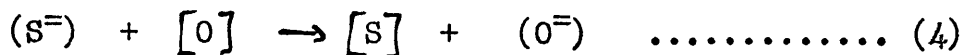
An explanation can be suggested for this marked difference in the rates of approach to equilibrium of the two types of experiment. It is based on a consideration of the reactions which proceed during the approach to equilibrium. Considering first the type of experiment in which the sulphur is charged as high sulphur metal. The reactions are

$$[S] + (O^=) \rightarrow (S^=) + [O] \quad \ldots\ldots\ldots (1)$$
$$[O] + [Fe] \rightarrow (O^=) + (Fe^{++}) \quad \ldots\ldots\ldots (2)$$
$$[O] + [C] \rightarrow CO \quad \ldots\ldots\ldots (3)$$

They all proceed in the directions of the arrows.

If the reaction rates are comparable the effect of reactions (2) and (3) will be to increase the speed of desulphurisation by reaction (1) since both (2) and (3) reduce $[O]$.

If the other approach to equilibrium is now considered the directionsof reactions (1) and (2) are changed but (3) still proceeds in the same direction. The reactions for this type of approach can be written:

$$(S^=) + [O] \longrightarrow [S] + (O^=) \quad \dots\dots\dots\dots (4)$$
$$(Fe^{++}) + (O^=) \longrightarrow [O] + [Fe] \quad \dots\dots\dots\dots (5)$$
$$[O] + [C] \longrightarrow CO \quad \dots\dots\dots\dots (6)$$

In experiments of this type, reported in Table III, FeO was always added to the molten slag; this accounts for the inclusion of reaction (5). It must be stressed that these do not represent a sequence of reactions but rather a set of reactions which proceed together. Of reactions (5) and (6) one, (5), helps the sulphur transfer reaction by creating oxygen in the metal and the other, (6), hinders it by removing oxygen from the metal.

Thus the reaction of carbon with oxygen in the metal can be seen to have a helpful effect on metal to slag transfer of sulphur but to hinder slag to metal transfer. This is believed to be a reasonable explanation of the experimentally observed difference in reaction rates of the two directions of transfer.

Since it has been shown that only the experiments to which the sulphur was added in the metal have reached equilibrium, the further discussion of results will only be concerned with these.

The positive gradient of the lower line on Fig.12 must be attributed to a decrease in the activity coefficient of the sulphur in the slag as the sulphur content increases. From Figure 12 values of the activity of sulphur in the slag can be found for slag sulphur contents up to 1.2%. By extrapolating the lower line the value of $\dfrac{(S)}{[a_s]} a_{FeO}$, for an infinitely dilute solution of sulphur in the slag, is obtained. When activity is measured on the dilute solution scale the standard state is an infinitely dilute solution and activity is defined as being equal to percentage composition in this dilute solution. Therefore the activity coefficient, $f_{(S)}$, is 1 in this dilute solution. Since, at equilibrium, the expression

$$\frac{f_{(S)} \cdot (S)}{[a_S]} a_{FeO}$$

should be constant for all values of (S), values of $f_{(S)}$ can be obtained from Figure 12. Then since

$$(a_S) = f_{(S)} \cdot (S)$$

the activity of sulphur can be found and this is shown on the left hand side ordinate scale of Fig.13, plotted against (S).

These activity values show negative deviation from Henry's Law and at about 1% sulphur they approach a steady value. This indicates that at this concentration of sulphur the slag is saturated with a phase of constant sulphur activity.
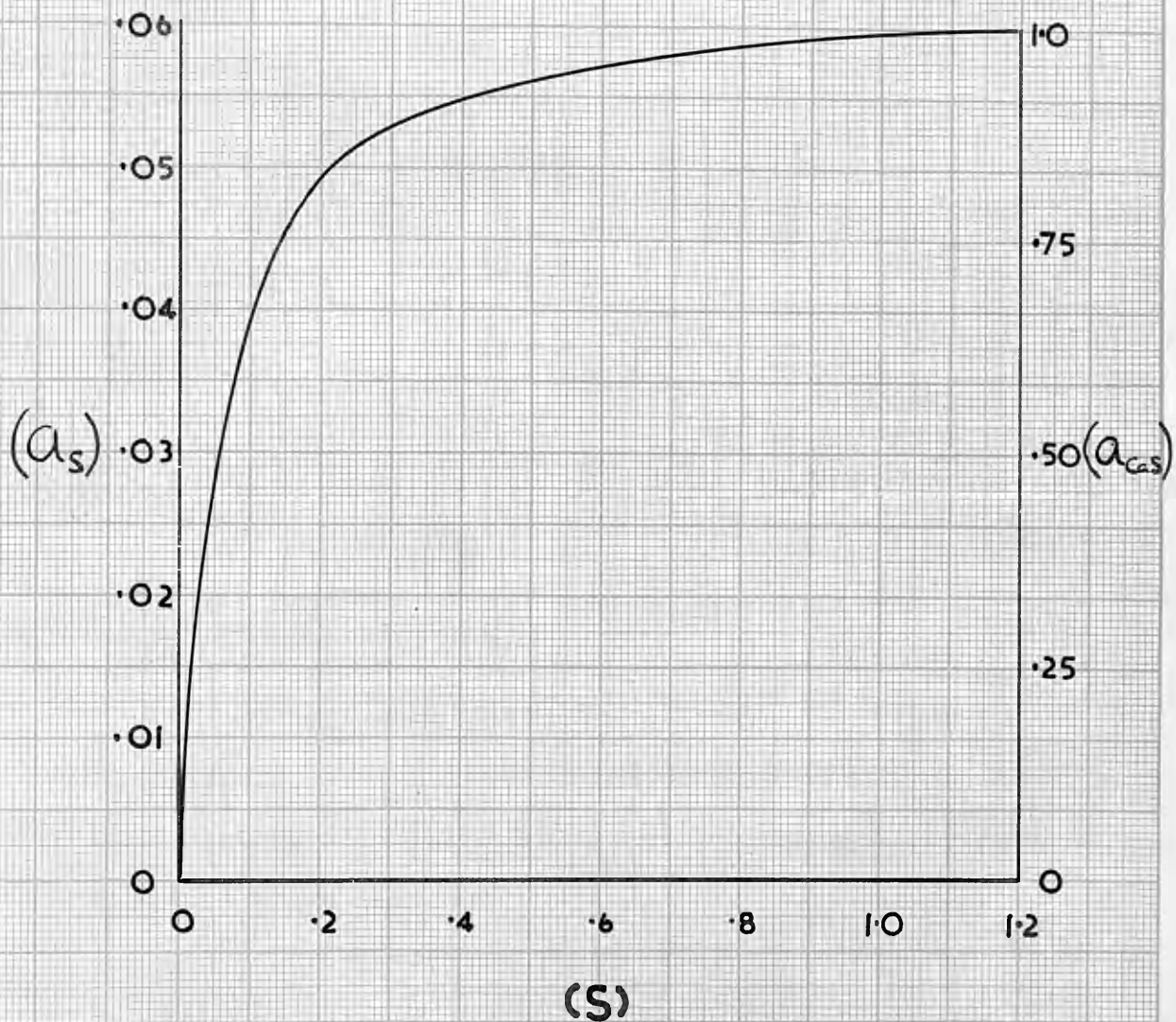
Figure 13.

Filer and Darken have reported, working with a more basic slag, saturation with calcium sulphide at about 4.5% sulphur.

Three further experiments were done in an attempt to check that the activity of sulphur in the slag reaches a constant value as indicated by Figure 13.   Metal and slag were brought to equilibrium at 1500°C in the way described for the experiments of Table I.   The sulphur input, as CaS, was varied in order to give higher slag sulphur contents than usual.   The results are given in the following Table.

Expt. No.	CaO	SiO$_2$	Al$_2$O$_3$	(S)	[Si]	[C]	[S]	f_s	[a_s]
63	30.2	26.5	41.7	1.03	0.52	4.84	0.122	5.7	0.695
64	29.2	26.7	42.7	1.56	0.61	4.80	0.127	5.7	0.723
65	28.5	27.3	41.8	2.14	0.65	4.73	0.128	5.6	0.716

This shows that the activity of sulphur in the metals in equilibrium with these three slags is constant, proving that the activity of sulphur in the slag is constant at sulphur contents above 1%.

The slags from these experiments were examined for crystals of calcium sulphide, such as were found by Filer and Darken(2), but none could be seen in them.   Despite this it is believed that the results given here, in conjunction with Filer and Darken's proof of calcium sulphide saturation in a more basic slag at 4.5% sulphur, together provide sufficient

evidence that the slag used here becomes saturated with calcium

sulphide at about 1% sulphur at 1500°C.

So the ordinate scale of Figure 13 could be changed

to measure the activity of calcium sulphide (aCaS) where the

standard state is pure calcium sulphide.

Then 0.06 on the (a_S) scale becomes 1 and 0.03 becomes

0.5.   This scale has been constructed on the right hand side

of Fig.13.

This activity curve of calcium sulphide shows strong

positive deviation from ideality.   Such deviation is generally

associated with a tendency towards immiscibility.   That there

is such a tendency in calcium sulphide-calcium silicate melts

has been shown by Schenck(28) in a review of the literature on

the subject.

Using values of (a_{CaS}) obtained from Fig.13 a

graph has been constructed showing the ratio $\dfrac{(a_{CaS})}{[a_S]}$ plotted

against the FeO content of the slags for the experiments of

Table III which reached equilibrium.   The carbon crucible

experiments with the same slag composition are also represented

on this graph which is shown as Figure 14.   The line shows

that FeO has an important effect on the sulphur distribution

at concentrations below about 0.5%.

If it is assumed that the shape of the calcium

sulphide activity curve of Figure 13 persists for more basic

slag compositions than the one for which it has been determined,

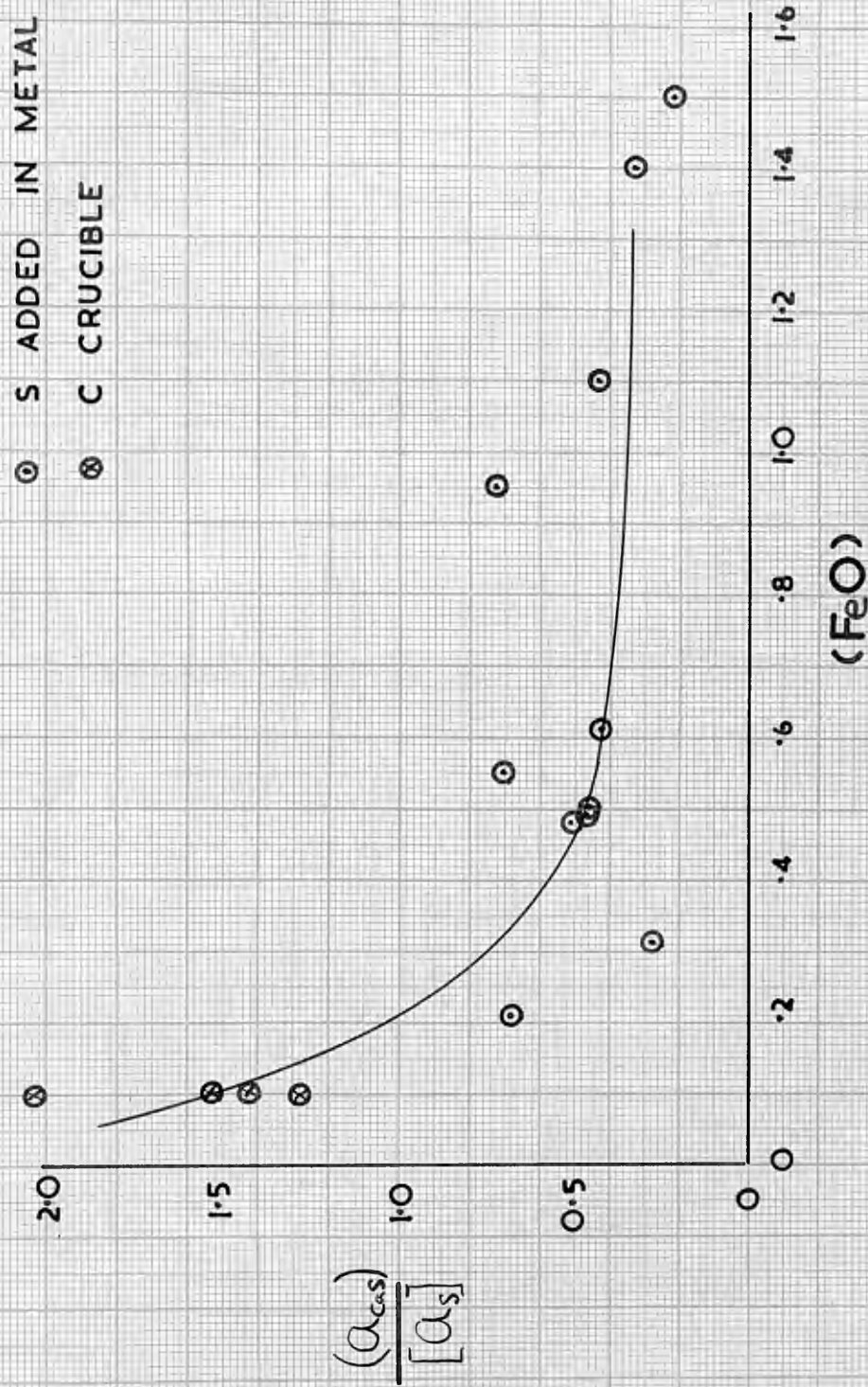comparisons of lime activity can be made for slags of

Figure 14. The effect of (FeO) on the sulphur distribution ratio $\dfrac{(a_{CaS})}{[a_S]}$

different compositions.   While the shape of activity curve
is taken to be the same, the solubility of calcium sulphide
in the slag probably increases with increasing basicity.
The slags chosen for comparison here are those of experiments
40 and 53 reported in Table I.   Their approximate compositions
are

Expt. No.	CaO	SiO$_2$	Al$_2$O$_3$
40	30%	25%	45%
53	48%	35%	17%

Since slag 53 is of approximately the same composition as
Filer and Darken's(2) slag the calcium sulphide solubility
has been taken as 4.5% sulphur.   The activity of calcium
sulphide in this slag is found, from Fig.13 with the
abscissa scale going up to 4.5% instead of 1%, to be 0.93.
The calcium sulphide activity in slag 40 is 1.   From Table I
the activities of sulphur in the metals in equilibrium with
these slags are found to be 0.090 for 53 and 0.645 for 40.
Both of the experiments were carried out in carbon crucibles
consequently the activity of FeO need not enter into the
comparison

$$\frac{(a_{CaO}^{53})[a_S^{53}]}{(a_{CaS}^{53})} = \frac{(a_{CaO}^{40})[a_S^{40}]}{(a_{CaS}^{40})}$$

$$\therefore \frac{(a_{CaO}^{53})}{(a_{CaO}^{40})} = \frac{(a_{CaS}^{53})}{(a_{CaS}^{40})} \frac{[a_S^{40}]}{[a_S^{53}]}$$

$$= \frac{0.93}{1.0} \cdot \frac{0.645}{0.090} = 6.7$$

An approximate assessment of the activity of lime in these types of slags can be obtained from another source. If the assumption is made that alumina and silica are equivalent, on a molar basis, in the neutralisation of lime, data on lime activity in binary lime-silica slags can be used. This has been done for the two slags compared above using the activity data given by Bell, Murad and Carter(29). The values obtained in this way were for slag 53, 0.015 and for slag 40, 0.002.

This agreement is surprisingly good, considering the assumptions which have been made. It does serve as a check on the assumption that Figure 13 is applicable to more basic slag compositions if the solubility limit of calcium sulphide is known and if the abscissa scale is adjusted accordingly.

Hatch and Chipman(1) did experiments with slags containing 1.5%, 2.5% and 5% sulphur and found a distinct line for each of these sulphur levels when they plotted $\frac{(S)}{[S]}$ against excess base. Using Fig.13, and taking 4.5% sulphur as the calcium sulphide solubility limit for all their slags, values of (a_{CaS}) have been found for these results. Figure 15 is a graph of the ratio $\frac{(a_{CaS})}{[a_S]}$ against excess base for all Hatch and Chipman's results at 1500°C. The dotted lines have been drawn to include all the points representing slags containing between 7.5% and 22% alumina. This is thought to be a very good correlation for slag-metal work. It does show that, even with the rough simplification involved by taking 4.5% sulphur as the calcium sulphide solubility limit in the
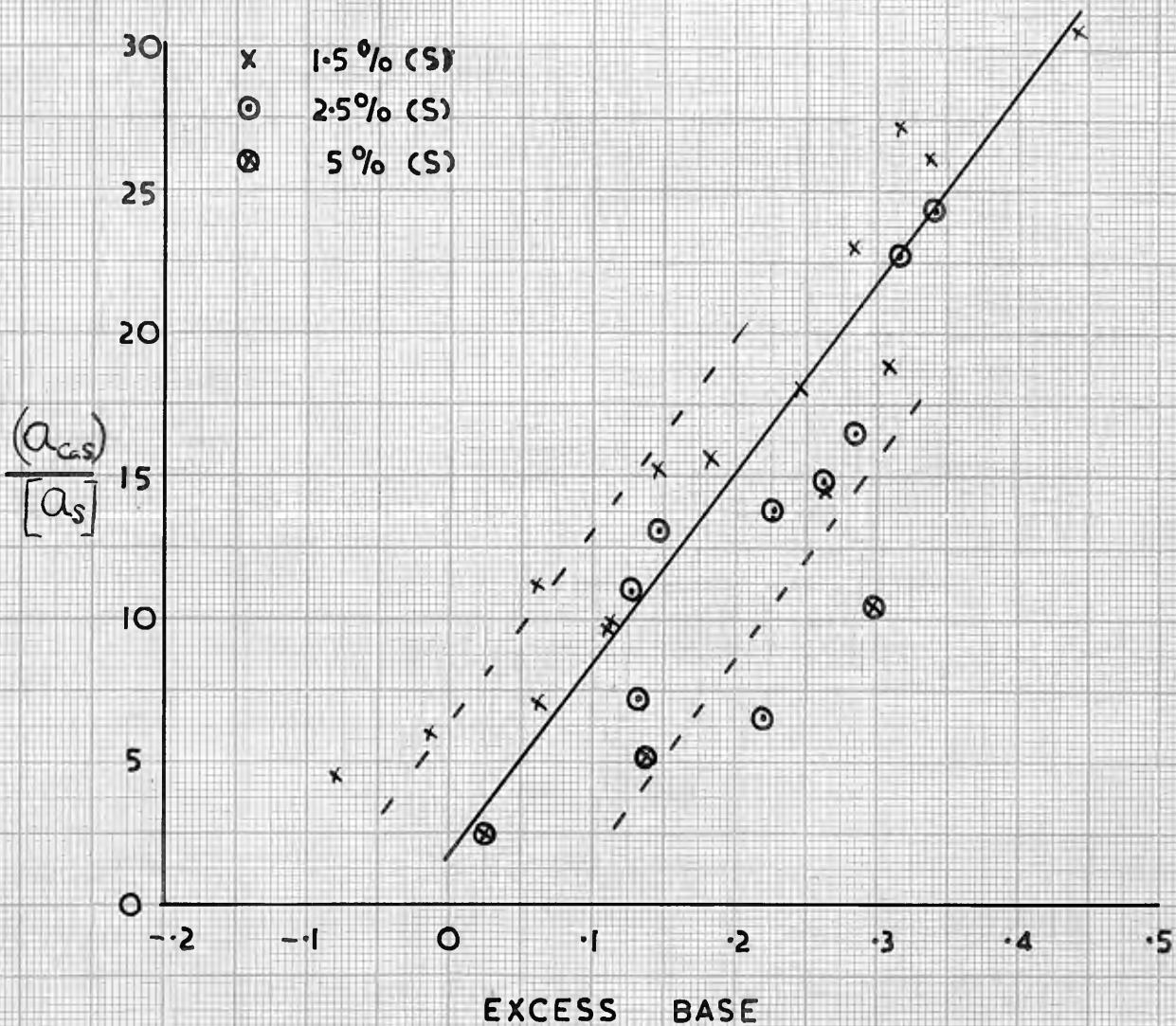
Figure 15.   Hatch and Chipman's 1500°C results.

slags of this fairly wide basicity range, the use of Figure 13 in this way is justified.

It has been shown that comparisons of lime activity can be made using the slag-metal equilibrium results. Absolute values of lime activity can be found if reliable therodynamic data are available. Using Rosenqvist's(22) data on the desulphurisation reaction we have, at $1500^{\circ}C$,

$$K = \frac{(a_{CaS}) \cdot p_{CO}}{(a_{CaO})[a_s][a_c]} = 470$$

Experiment 40 was carried out in a graphite crucible and therefore for this case the expression simplifies to

$$\frac{(a_{CaS})}{[a_s](a_{CaO})} = 470$$

The activity of calcium sulphide in slag 40 was 1 and the activity of sulphur in the metal in equilibrium with it was 0.675 (on the 1% sulphur solution reference state scale). Therefore

$$(a_{CaO}) = \frac{1}{470 \times 0.675} = 0.003$$

This is the activity of lime referred to pure lime as the standard state. The value is in good agreement with 0.002 which was that obtained using Bell, Murad and Carter's(29) data.

This points the way to an interesting and experiment-:ally fairly simple way of finding the activity of lime in slags. If a slag is saturated with calcium sulphide and brought to equilibrium with metal, by measuring the activity

of sulphur in the metal and doing the calculation outlined above, a value of the activity of lime in the slag can be found.   The accuracy of the value obtained depends very much on the accuracy of the thermodynamic data.

CONCLUSION.

The experiments in carbon crucibles have shown the effect of varying slag composition on the position of sulphur equilibrium. It has also been established that in experiments of this type the equilibrium is with the C/CO oxygen potential and not with the Fe/FeO potential as measured by the FeO content of the slag. The most surprising result of the work is that the effect of temperature on this equilibrium is negligible.

It has been shown that Hatch and Chipman's results, as originally presented, gave a false impression of the effect of temperature on equilibrium. The effect of metal composition on the activity coefficient of sulphur has now been satisfactorily worked out and it can be seen that what Hatch and Chipman took to be an effect of temperature on the equilibrium position of the sulphur transfer reaction, was in reality merely a secondary effect of temperature on metal composition. This effect of temperature on metal composition is probably operative to some extent in blast furnaces, but the experimental evidence, shown in Figure 7, that the primary effect of temperature on sulphur equilibrium is negligible, is regarded as very conclusive.

This is not in agreement with Rosenqvist's thermo:dynamic data for the desulphurisation reaction, which indicate that a 60% increase in the reaction constant would be expected for a rise in temperature from 1450°C to 1550°C. If both sets of data are reliable the only way in which this discrepancy can be explained is by postulating large changes in the activity coefficients of lime and calcium sulphide with temperature.

The changes required would be an increase in the activity
coefficient of calcium sulphide and/or a decrease in that of
lime with increasing temperature. Now the solubility of
calcium sulphide in slags would be expected to increase with
increasing temperature and therefore its activity coefficient
would decrease. In the case of lime, increasing temperature
would be expected to promote dissociation of groupings in the
slag and so increase the activity coefficient. An explanation
on the basis of changing activity coefficients, therefore,
runs contrary to accepted ideas on slag constitution. Before
the extent of the discrepancy is accurately known, values of
the activity of lime and calcium sulphide in slags of different
composition and temperature must be found.

Concerning the mechanism of desulphurisation it has
been found that it is best expressed by a reaction of the form

$$[S] \; + \; (O^=) \; \rightleftharpoons \; (S^=) \; + \; [O]$$
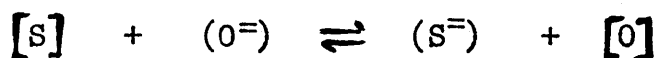
It follows that the lower is the metal oxygen activity the more
complete is desulphurisation. It can therefore be suggested
that an effective method of desulphurisation might be to add
a deoxidant, such as aluminium, to pig iron under a slag layer.
This could be done in the ladle or the mixer. Theoretically,
by this means, the oxygen activity in the metal could be
brought well below that in equilibrium with carbon of unit
activity and the resultant lowering of the metal sulphur
concentration could be considerable.

CaO	MgO	SiO$_2$	Al$_2$O$_3$	S	Excess Base.	Equilibrium (S)/[a$_s$]	[si]	[s]	[P]	[Mn]	[C]	f_s	Actual (S)/[a$_s$]
48.5	2.6	33.4	13.3	1.48	+.221	30	.69	.027	.40	1.39	4.25	4.5	12.2
44.5	3.2	35.1	14.3	1.59	+.123	18	.71	.036	–	2.36	4.3*	4.1	10.8
38.2	6.1	34.0	18.2	1.34	+.039	8	.75	.078	1.03	1.10	3.9	4.4	3.9
39.6	3.4	34.7	18.7	1.57	0	6	.63	.083	1.61	1.06	3.8*	4.6	4.1
35.7	4.7	33.7	26.0	1.80	-.099	8	.60	.13	2.0	1.4	3.8*	4.7	2.9

TABLE IV.

Comparison of equilibrium and blast furnace data.

*Carbon content assumed.

To attempt to ascertain whether equilibrium with the C/CO oxygen potential is reached in blast furnace practice, typical slag and metal analyses from various sources(31,32,33,34) have been compared with the equilibrium data shown on Figure 7. Examples of such comparisons are given in Table IV.

These are data from various basic iron practices. Unfortunately some of the available data do not include metal carbon contents and for those marked with an asterisk in the table, [c] has been assumed.   It can be seen that the equilib-:rium ratios are from 1.5 to 3 times the actual ratios.   While this is a considerable difference it is not as large as Hatch and Chipman's(1) results at first suggested.

It is pertinent to consider why equilibrium with the C/CO oxygen potential is not established in a blast furnace. It might be because the iron is not carbon saturated and consequently the oxygen activity is higher than it would be if the iron was carbon saturated.   However, the fact that kish appears with iron while it is casting in many practices does suggest·that carbon saturation is reached.

The more probable explanation of failure to reach equilibrium with the C/CO oxygen potential in a blast furnace is that there exists a state of affairs similar to that suggested as the second phase in the approach to equilibrium in carbon crucibles.   That is, the rate of transfer of oxygen from the slag to the metal is sufficiently high to

retard desulphurisation. While analysed FeO contents of blast furnace slags are erratic and unreliable they are invariably greater than 0.1% which figure as has been shown here, is the FeO content below which the rate of transfer of oxygen into the metal is not sufficiently great to retard desulphur-:isation. If this is the reason then the desulphurisation reaction in a blast furnace should be at equilibrium with an oxygen potential between the value corresponding to the metal oxygen activity and the higher value corresponding to the slag FeO activity.

It would be of considerable interest to find out if this is the case in blast furnaces. The oxygen activity in the metal could be measured by the ratio $\dfrac{[a_{Fe}]}{[a_c]}$ if the effects of manganese and phosphorus on the activity of carbon were known. Use of the activity data for FeO found in this work would yield values for slag FeO activity.

The results of the alumina crucible experiments have been used to derive values of the activity of FeO in the slag and consequently to show the effect of varying slag FeO content on desulphurisation in the absence of solid carbon. The activity of calcium sulphide in the slag has been shown to have very pronounced positive deviation from ideality. Evidence has been produced to show that this shape of activity curve also holds for more basic slags than the one for which it was derived. The indication from this is that, in normal blast furnace practice, an increase in sulphur load, with its

consequent increase in slag sulphur content, should make for increased efficienty of desulphurisation.   In other words the higher the slag sulphur content, the higher should be the ratio $\dfrac{(S)}{[a_S]}$

A method of finding the limit of solubility of calcium sulphide in slags has been suggested and it has been shown that this leads to a method of finding lime activity values.   This is interesting and also possibly important since there are no reliable figures for lime activity in ternary slags.

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APPENDIX A.

The conclusion is made on page 36 that the effect of temperature on the position of sulphur equilibrium between slags and metals is negligible. This is based solely on the experimental results represented on Figures 6 and 7. On these graphs data from two independent investigations, at temperatures from 1425°C to 1550°C, are brought on to a common basis for comparison. No temperature differentiation can be made and this is the proof advanced for the conclusion regarding the effect of temperature.

APPENDIX B.

It should be made clear that values for the activity of FeO derived from the data in Figure 10 were based on the results of experiments for which no sulphur was present, i.e., from experiments 57, 58 and 61 and data taken from Arthur(27).

Extrapolation of the line on Figure 9(c) beyond 0·84%[S] was used in the calculation of $[\alpha_c]$ and $[\alpha_{Fe}]$ for seven of the sulphur bearing experiments represented on Figure 10. The points representing these seven experiments do not show, on Figure 10, a worse scatter than the others whose metal sulphur contents are within the range of the data. This has been taken as an indication that the extrapolation is justified.

The results of the sulphur bearing experiments have been incorporated on Figure 10 in an attempt to show that equilibrium has been reached between the FeO of the slag and the carbon of the metal. They play a very small part in determining the location of the line on Figure 10; therefore the accuracy of the extrapolation can have virtually no effect on the accuracy of the FeO activity values obtained from Figure 10.