A STUDY OF THE THERMODYNAMICS OF LIME/ALUMINA/SILICA

SLAGS CONTAINING CALCIUM SULPHIDE.

by

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A Study of the Thermodynamics of Lime/Alumina/Silica slags containing Calcium Sulphide.

The primary object of this investigation was to study the solubility and thermodynamic properties of calcium sulphide in lime/alumina/silica slags and so obtain data relevant to the desulphurisati[on] reaction in the blast furnace. In addition it was hoped that these da[ta] could be used to give valuable information on the activity of lime in the system.

Experimentally, the problem was studied from the gas/slag reaction:

$$CaO + \tfrac{1}{2}S_2 = CaS + \tfrac{1}{2}O_2 \quad \ldots\ldots\ldots\ldots\ldots (1)$$

A gas mixture of CO, CO_2 and SO_2 was used to supply a sulphurising potential to lime/alumina and lime/alumina/silica slags at $1,550^\circ C$. These slags were contained in platinum crucibles and could be quenched out of the hot zone of the furnace to prevent sulphur loss on cooling. Sulphur analysis of the slags after they had come to equilibrium with the gas mixture enabled a correlation between slag sulphur content and gas sulphurising potential to be obtained. By plotting the results on a graph of slag sulphur percentage against sulphurising potential, the point at which the slag became saturated with calcium sulphide could be recognised. At this point, the sulphur content of the slag increa[sed] considerably for only a slight increase in gas sulphurising potential.

In/

In this way, the slag sulphur content, corresponding to calcium sulphide saturation was obtained for a range of slags and these result have been discussed. Furthermore, from equation (1):-

$$a_{CaO} = \frac{a_{CaS}}{K.A.} \quad \text{where } A = \left(\frac{pS_2}{pO_2}\right)^{\frac{1}{2}} = \text{sulphurising potential.}$$

However at calcium sulphide saturation $a_{CaS} = 1$ and since the value of the equilibrium constant is known, lime activity values at calcium sulphide saturation can be calculated. These results are also discus It has been shown, that for the calcium sulphide contents being consid the lime activity of the slag is likely to remain substantially consta but indications are that for highly basic slags, γ_{CaS} is not constant. Lime activity results of other workers have been recalculated using γ_C values obtained in this investigation for lime/alumina slags and good agreement with the present results is noted.

The scope of the investigation has been rather restricted becaus the lime activity data on the basis of which the work was planned has been shown to be unreliable. It was observed that as the lime conten of the slags moved away from lime saturation, the lime activity decrea more rapidly than available data indicated. As a result, the sulphur ising potential available from the gas mixture used here was insuffici to saturate, with calcium sulphide, the wide range of slags planned in the first instance.

CONTENTS.

CHAPTER I.

INTRODUCTION.

I. INTRODUCTION.

During the past twenty years there has been a steadily growing interest in the thermodynamics of high temperature reactions. This interest has developed from the realisation that the fundamental laws of physical chemistry can be applied, with some success, to the complex reactions of ironmaking and as the industry becomes more securely based scientifically, the full potential of the process may be used more effectively and will depend less on the decisions of long service craftsmen.

The obvious way of obtaining information on the thermodynamics of these reactions was through a study of the molten slags used in the modern blast furnace; and since the sulphur and silicon reactions were of greatest interest to the practical ironmaker, it followed that the removal of sulphur by lime alumina silica slags should receive close attention. From the point of view of sulphur removal, the blast furnace is more efficient than the open hearth furnace because the high carbon content of blast furnace iron increases the sulphur activity coefficient and this in turn means that the task of removing the sulphur as calcium sulphide dissolved in the blast furnace slag, is more readily accomplished. Thus, the industrialist would like maximum sulphur removal in the blast furnace to reduce, as far as possible/

2.

possible the metallurgical load on the steelmaking furnace. To this
end, therefore, it is useful to know the extent to which equilibrium
is achieved in the blast furnace as only this will indicate whether
or not, thermodynamically, the full potential of the reaction is being
utilised.

Slag/metal investigations of the desulphurisation by lime-
alumina-silica slags have yielded valuable information on the relative
desulphurising ability of various slag compositions. The most
commonly accepted mechanism of the desulphurisation reaction is:-

$$[FeS] = (FeS) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$
$$(FeS) + (CaO) = (CaS) + (FeO) \quad \ldots\ldots \quad (2)$$
$$C + FeO = Fe + Co \quad \ldots\ldots\ldots\ldots \quad (3)$$
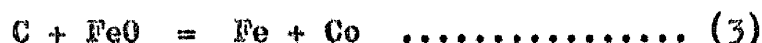
From the point of view of the subsequent discussion, however,
it will be more convenient to consider the simpler, though equally
valid equation:-

$$CaO + \underline{S} = CaS + \underline{O} \quad \ldots\ldots\ldots\ldots \quad (4)$$

This reaction was studied from the point of view of desulphurisation
in the steel furnace, notably by Grant and Chipman (1), but little
progress was made because of the complexity of the reaction constituents.
A major difficulty in this type of reaction was slag attack on the
crucible/

crucible (usually alumina or magnesia) which immediately led to complications in interpretation of the results because of the resultant alteration in slag composition. For a satisfactory interpretation of the results obtained from this type of reaction a knowledge of the thermodynamic properties of all four constituents of reaction (4) above was necessary and since little or no data were available any conclusions which could be drawn were, of necessity, somewhat restricted.

Iron making reactions could, however, be studied a good deal more readily because a graphite crucible could be used along with high carbon iron, thereby eliminating the problem of crucible reaction and also fixing the oxygen potential of the system and simplifying interpretation of the results. Additionally, the lime-alumina-silica slag used in the blast furnace is considerably less complex than the typical steelmaking slag. For these reasons, therefore, the study of the desulphurising reaction by an iron-making reaction has certain attractions. One of the major experimental difficulties here, however, is the very slow approach to equilibrium. Hatch and Chipman (2) studied the sulphur distribution ratios between metal and slag of blast furnace composition and in an effort to overcome this difficulty they used a stirring device. They concluded, however, that stirring had little effect on the rate of attainment of equilibrium.

At the time of this investigation no data were available on the effect of carbon on the activity coefficient of sulphur and although the oxygen potential of the system had been fixed, thermodynamic data for sulphur dissolved in the metal and for lime and calcium sulphide were still not available. These authors, therefore, restricted interpretation of their results to the relative desulphurising capabilities of various slag compositions.

Subsequently, the effect of carbon, silicon and phosphorus on the activity coefficient of sulphur dissolved in high carbon iron was investigated by several workers and the results were summarised by Sherman and Chipman (3). Taylor and Stobo (4) used this information in their investigation of sulphur partition between blast furnace metal and slag. This investigation was similar to that of Hatch and Chipman. As a result of the increased thermodynamic data available at this time, these authors were able to calculate sulphur activities in the metal corresponding to sulphur percentages in the slag. Again, however, full interpretation of the results was restricted by lack of thermodynamic data on lime and calcium sulphide. . Also, it was estimated from this work that the percentage sulphur corresponding to calcium sulphide saturation was about 4.0%, for a slag of blast furnace composition. This value was in good agreement with that reported by Filer and Darken (5) and was less than half the value suggested by

McCaffery/

McCaffery and Oesterle (6) who obtained calcium sulphide solubility levels of the order of 10 - 12% S for blast furnace slags at 1,550°C. These latter authors did, however, conclude that the calcium sulphide solubility level tends to increase as the mole fraction of alumina increases and it will be shown that, in the present investigation a similar effect was noted.   Although Hatch and Chipman did not report calcium sulphide saturation levels for the slags investigated, their data were later used by Rosenqvist (7) who estimated that unit calcium sulphide activity corresponded to 10% Sulphur in the slag.   This calculation was based on lime activity values derived from the equilibrium diagram of the system $CaO - SiO_2$ given by Darken (8).   When more recent data on lime activities, now available, are used the value of 10% obtained originally is reduced to about 5% and is more in line with the results of Filer and Darken and Taylor and Stobo.

It is clear from the work summarised above that as thermodynamic data have become available they have been used to aid interpretation of the experimental results and to make deductions which are less empirical and of more absolute value.   Much of the information, however, concerns the metal and the constituents dissolved therein whereas the data available on the thermodynamic properties of the components of the slag is somewhat limited, particularly with reference to lime and calcium sulphide.

More recently, however, several workers have published the results of investigations designed to obtain information on lime activities in blast furnace slags containing sulphur and some of this work will now be considered.

Certain authors, notably Carter and Macfarlane (9) and Bell and Kalyanram (10) have studied the desulphurising properties of slags from the gas/slag reaction:

$$CaO + \tfrac{1}{2}S_2 = CaS + \tfrac{1}{2}O_2 \quad \ldots\ldots\ldots\ldots (5)$$
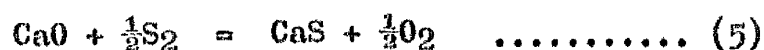
by subjecting lime-alumina-silica slags to a sulphurising gas atmosphere. This method has certain important advantages when compared with the slag-metal studies mentioned earlier. Firstly, elimination of a metal phase permits the use of metal containers and there is no possibility of alteration in slag composition as a result of crucible attack. Also, assuming that the thermodynamic properties of the gas phase are known, the relevant partial pressures which can be calculated may be equated to activities since it can be reasonably assumed that the gases will behave ideally at the high temperature and low pressure of the experiment. Since this technique was first suggested, it has proved to be a very prolific source of data on the thermodynamic properties of the constituents of molten slags.

Before considering some of the results obtained from slag/gas equilibria it should be mentioned that the transfer of sulphur from a suitable/

suitable gas phase to a lime containing slag may be represented apart from equation (5) by the equation:

$$CaO + \tfrac{1}{2}S_2 + 3/2O_2 = CaSO_4 \quad \ldots\ldots (6)$$

It is clear that, whether or not the reaction will proceed according to equation (5) or (6) depends on the oxygen potential of the system and Fincham and Richardson (11) have shown that when $pO_2 < 10^{-5}$ atm, sulphur transfer takes place entirely by sulphide formation. The oxygen pressures used in all the work discussed here were always considerably less than 10^{-5} atm and consequently only reaction (5) need be considered.

The free energy change for reaction (5) can be determined from the data of Rosenqvist (7) for the reaction:

$$CaO(S) + H_2S = CaS(S) + H_2O \quad \ldots\ldots (7)$$
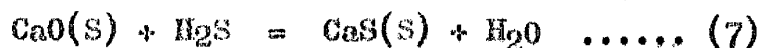
along with the free energies of formation of H_2O and H_2S to give the value of:

$$G = 23,020 - 1.25T$$

as the free energy change for reaction (5). The data obtained by Rosenqvist for reaction (7) have recently been confirmed by Filipouska (12) and can be considered to be very reliable.

It will be noted, from reaction (5) that a study of this reaction should yield, directly, valuable information on the activity of lime.

This, however, presupposes a knowledge of the thermodynamics of calcium sulphide in slag solution. To date, adequate information on the activity coefficient of calcium sulphide has not been available, and although certain workers have managed to circumvent this problem their calculations have of necessity involved certain assumptions concerning the behaviour of the activity coefficient of calcium sulphide. Thus the lime activity values obtained, while of considerable significance, have not been entirely satisfactory. It is clear therefore, that a knowledge of the activity coefficient of calcium sulphide is important, not simply from the point of view of calculation of calcium sulphide activities but also for accurate estimation of lime activities.

Carter and Macfarlane and Bell and Kalyanram investigated sulphur pick-up by lime-alumina-silica slags at sulphur levels considerably below the calcium sulphide saturation value, and these authors used these data to calculate lime activities in the melt, making certain assumptions with regard to the activity coefficient of calcium sulphide. They compared the results obtained for the individual slags, with the sulphur pick-up of a standard slag of unit lime activity, assuming that γ_{CaS} did not vary significantly throughout the slag range investigated, and lime activities were calculated on this basis.

This assumption, while only approximate was the best that could be made in the absence of any more reliable information. The work of these authors will be discussed in more detail in a later chapter.

Fincham and Richardson (11) have carried out a similar type of investigation using a wide range of slag compositions and have compared the desulphurising power of the slags through the function referred to as the sulphide capacity, C_S where:

$$C_S = \%S \left(\frac{pO2}{pS_2}\right)^{\frac{1}{2}}$$

Again, these authors have made valuable comparisons without being able to calculate true activity values and on this basis have been able to come to some relevant conclusions regarding the most suitable conditions for efficient desulphurisation.

More recently, Chipman (13) and Kay and Taylor (14) have carried out a fairly complete survey of silica activities in the lime-alumina-silica system. From these silica activity measurements by a Gibbs-Duham type calculation these authors have been able to obtain lime activity values. The actual values allotted to the iso-activity limes of Kay and Taylor, depending as they do on the lime activity values obtained by Carter and Macfarlane in the lime-alumina binary, are open to doubt but the actual shape of the contours is much more reliable.

Although various data have lately become available on the thermodynamic properties of lime in lime-alumina-silica slags, it is clear that none of it is absolutely reliable and further clarification will be necessary. With regard to the thermodynamics of calcium sulphide, the data are almost non existent; almost all the work reported on the desulphurising ability of slags has been of a comparative nature, and in the absence of complete data on the thermodynamic properties of calcium sulphide it will remain so.

CHAPTER II.

EXPERIMENTAL TECHNIQUES AND PROCEDURE.

INTRODUCTION.

The experimental methods available for the determination of calcium sulphide solubility levels, may be considered under two headings:

(1) Techniques involving physical measurements.

(2) Techniques involving a study of the thermodynamics of lime-alumina-silica slags containing sulphur.

Although many of the investigations carried out to date have involved a thermodynamic study of slag systems containing sulphur, some workers have successfully used a physical technique and the results of some recent Russian publications will be mentioned.

Panov and Rudneva (15) undertook a petrographic examination of slag samples in the lime-silica system to which progressively increasing amounts of sulphur had been added up to 25% calcium sulphide. Lime to silica ratios of 0.8 to 1.5 were studied and the slags quenched in water from various temperatures. They reported that at 1,450°C, free calcium sulphide appeared in slags of lime-silica ratios between 0.8 and 1.0 when more than 6% calcium sulphide was present. (This corresponds to a sulphur content of approximately 3%). When the lime-silica ratio was between 1.25 and 1.50 free calcium sulphide did not appear until the slag/

slag contained more than 7.0% calcium sulphide, i.e. the saturation level of the slags increased as the slag basicity increased. (This is contrary to the findings of Sharma and Richardson (16)).

The uncertainty in this type of investigation lies in the ability to distinguish the calcium sulphide crystals when they emerge from the matrix as a free phase, because, optically calcium sulphide is little different from the background slag. Furthermore, supersaturation readily occurs in calcium silicate systems and this may delay precipitation. It is, however, an interesting technique and if carefully interpreted, valuable results may be rapidly obtained.

The work described above, is to some extent complementary to the work of Panov, Kulikov and Tsylev (17) who studied the viscosity of lime-silica-calcium sulphide slags in an endeavour to gain some information relevant to the effect of calcium sulphide on the viscosity of blast furnace slags.

Slags of different lime-silica ratio were studied and the variation of viscosity with increasing calcium sulphide contents was noted. It was observed that initial additions of calcium sulphide lowered the viscosity until a minimum value was reached and thereafter the slag viscosity increased. This increase in viscosity was attributed to the formation/

13.

formation of calcium sulphide as a free phase and therefore the
minimum point in the viscosity/calcium sulphide content, curve,
represents the calcium sulphide saturation level for the slag under
consideration.

In some cases this minimum value was very indefinite.   Indeed,
a pronounced minimum was only obtained at the lowest temperature of
the experiment $(1,400^{o}C)$ and in these cases, supplementary experiments
showed the presence of pseudowollastonite on both sides of the curve.
This makes concise interpretation of the results rather difficult.
More reliable information can therefore be obtained from the curves
drawn from the data for higher temperatures but here, the minimum point
is much less distinct.

Again, as in the previous paper, it was noted that the calcium
sulphide saturation level increased with increasing slag basicity.
The calcium sulphide saturation values also seem to agree fairly well
with the saturation values observed from the petrographic examination.

Both these physical methods are extremely useful techniques and
will yield results much more rapidly than will a thermodynamic investigation,
however, apart from the limitations already mentioned they suffer from
the disadvantage that they indicate only the calcium sulphide saturation
level for the slags under investigation, and give no data on the

Thermodynamic/

14.

thermodynamic properties of calcium sulphide when sulphur is
absorbed below the saturation level.   Since it was the purpose
of this investigation to determine calcium sulphide solubility
limits for a range of slags and also to obtain information on the
behaviour of the activity coefficient of calcium sulphide below
saturation none of the physical techniques just described was
considered suitable.   Information of this nature can only be
obtained from a careful thermodynamic study of the slag in question
by a suitable reaction, and this was adopted as the most satisfactory
experimental approach.

This type of investigation involves observing when the activity
of calcium sulphide, dissolved in the slag, becomes constant and
equal to unity.   Before this point is reached, the slag has absorbed
varying amounts of sulphur and the complete series of results supplies
information on the thermodynamic properties of calcium sulphide below
saturation as well as a fairly clear indication of the/sulphur content
corresponding to calcium sulphide saturation.   There remained the task
of deciding whether a slag/metal or a slag/gas reaction would be more
suitable.

It has been mentioned that previous workers were able to obtain
calcium sulphide saturation limits from a study of slag/metal reactions
although the achievement of equilibrium was doubtful; also, slag/gas
reactions/

reactions, previously studied, had in the main, concerned sulphur contents considerably below calcium sulphide saturation. Furthermore, for the slag/gas reactions it was realised that, with fairly acid slags of high silica activity the possibility of silica reduction by carbon monoxide and the subsequent attack of the platinum crucibles could not be excluded.

There was, therefore, some uncertainty about the wisdom of proceeding with a gas-slag investigation and when the work was initiated it was suggested that a series of slag/metal reactions should be carried out. For reasons which will be made clear later, the slag/metal study failed to yield results which could be considered reliable and when, ultimately, a slag/gas investigation was initiated the results obtained therefrom were much more useful. Both series of experiments will now be described but because of the relative lack of success in the slag/metal investigation this method will be described only briefly.

2. SLAG-METAL INVESTIGATIONS.

These reactions were carried out by melting carbon saturated
iron, containing sulphur, and a lime-alumina-silica slag of approximately
blast furnace composition (i.e. 40% lime, 20% alumina and 40% Silica)
in a graphite crucible of $1\frac{1}{2}"$ internal diameter.   This crucible was
contained in a mullite tube which could be heated evenly to $1,500^{\circ}C$
over a distance of three inches in a platinum wound resistance furnace.
The crucible was supported in the hot zone of this vertical furnace by
refractory stools, the furnace tube being sealed at the top and bottom
by rubber bungs with an internal atmosphere at high temperature, of
CO and nitrogen resulting from the air, initially trapped within the
tube.   The topmost rubber bung contained an observation window through
which the progress of the reaction could be noted.   A mullite thermo-
couple sheath passed through the lower bung and the sheath passed up
through the refractory stools to touch the bottom of the crucible.   In
this way an accurate temperature measurement could be obtained from the
Platinum-Platinum/13% Rhodium thermocouple inserted in the sheath.
Also, an outlet tube from the lower bung through a mercury seal, prevented
any pressure build-up within the furnace.   No stirring device was
incorporated in the experimental set up.

The/

The crucible was charged with 50 gms of metal, containing up to 10%S and 100 gms of slag, and inserted into the reaction tube which was then sealed and brought up to temperature.   For about five hours the melt was allowed to remain undisturbed and sulphur was transferred from the metal to the slag according to the mechanism of reactions (1), (2) and (3) below:

$$[FeS] = (FeS) \quad \dots\dots\dots\dots\dots \quad (1)$$
$$(FeS) + (CaO) = (CaS) + (FeO) \quad \dots\dots\dots \quad (2)$$
$$C + (FeO) = Fe + CO \quad \dots\dots\dots\dots \quad (3)$$
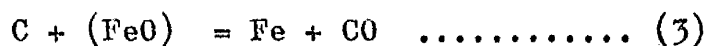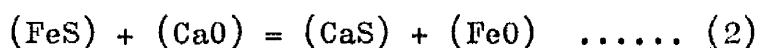
Thereafter, metal samples were drawn off every two hours and analysed for sulphur by the usual method of combustion by oxygen.   These metal samples were obtained by drawing a small quantity of metal into a narrow bore silica tube using a rubber aspirator.   The samples so obtained were then quickly quenched in a large volume of water.

When two consecutive samples indicated a constant sulphur content, it was considered that equilibrium had been achieved and a slag sample was removed by dipping a $\frac{1}{8}$" diameter brass rod into the slag layer and then quenching the rod into a large volume of water.   This slag sample was also analysed for sulphur.

By repeating this procedure with an increased percentage sulphur in the metal it was possible to obtain equilibrium values of sulphur content of the metal with a corresponding value for sulphur in the slag.

When the slag was saturated with calcium sulphide, the sulphur content of the metal at equilibrium remained constant but the sulphur content of the slag increased considerably and in this way, the saturation level could be recognised.

A series of experiments of this nature was carried out but it could never be definitely considered that equilibrium had been achieved. Initially, the sulphur content of the metal decreased rapidly and it appeared as though equilibrium would be readily obtained. However, consecutive samples, drawn off after 10 or 12 hours still showed a very slight decrease in the sulphur content of the metal and it was concluded that silica reduction was taking place. On several occasions, the crucible was maintained at temperature for twenty four hours but it was noted that sulphur transfer from the metal to the slag was still taking place. Further, it was observed that, as the sulphur content of the slag increased, so the viscosity increased and this alone would tend to slow down the rate of sulphur transfer across the slag-metal interface.

Experiments in which both slag and metal initially contained sulphur were no more successful although, theoretically, equilibrium ought to have been attained more rapidly. Some consideration was given at this stage to the idea of incorporating a stirring device in the system. This was rejected, however, because it had been noted by

other/

other workers (Hatch and Chipman) that the silica reduction reaction, which was preventing the attainment of equilibrium, was largely unaffected by stirring. In addition a device of this nature would remove the main advantage of the slag/metal technique which was experimental simplicity.

In view of these considerations, therefore, a series of slag/gas investigations was initiated using a slag of fairly high lime activity to minimise the possibility of crucible attack due to silica reduction. As will be seen, these experiments proved to be much more successful and a detailed description of the method follows.

3. SLAG-GAS EXPERIMENTS.

Basically the experimental procedure here, involved subjecting a number of slags to a gas mixture of a known sulphurising potential at $1,550^{\circ}C$, and allowing these slags to come to equilibrium with the gas atmosphere. It will be most convenient to describe the apparatus involved, the method of slag preparation and the experimental technique in separate sections. The apparatus used to control and analyse the gas mixture is shown in figs. 1 and 2.

Choice of gas mixture.

A gas mixture of sulphur dioxide, carbon dioxide and carbon monoxide was used throughout for the gas/slag experiments. This gas mixture was chosen because considerable experience had been gained by other workers in the department investigating similar reactions and the technique had been fairly well established over a period of several years. In addition, the lime activity data available when the work was begun (Kay and Taylor (14), Carter and Macfarlane (9) and Chipman (13)) indicated that this type of gas mixture would give sufficient sulphurising potential to enable a fairly wide range of lime-alumina-silica slags to be investigated. When these factors were considered it seemed that this was the most reasonable technique to adopt. It was realised that, with increasing silica activity, as more acid slags were investigated the highly reducing conditions necessary to obtain a high sulphurising potential/

Key to Figs. 1 & 2.

1. Bleeder Columns
2. Drying Agent — $Mg(ClO_4)_2$
3. Manometer Tubes
4. Glass Wool
5. Sulphuric Acid
6. Sample Tube
7. Crucible Container
8. Refractory Stools
9. Thermocouple
10. Midvale Bulb — Soda Asbesto
11. Water.
12. Dilute HCl Soln.

Fig. 1

CHANNEL III

CHANNEL II

CHANNEL I

NITROGEN

TO ATMOSPHERE
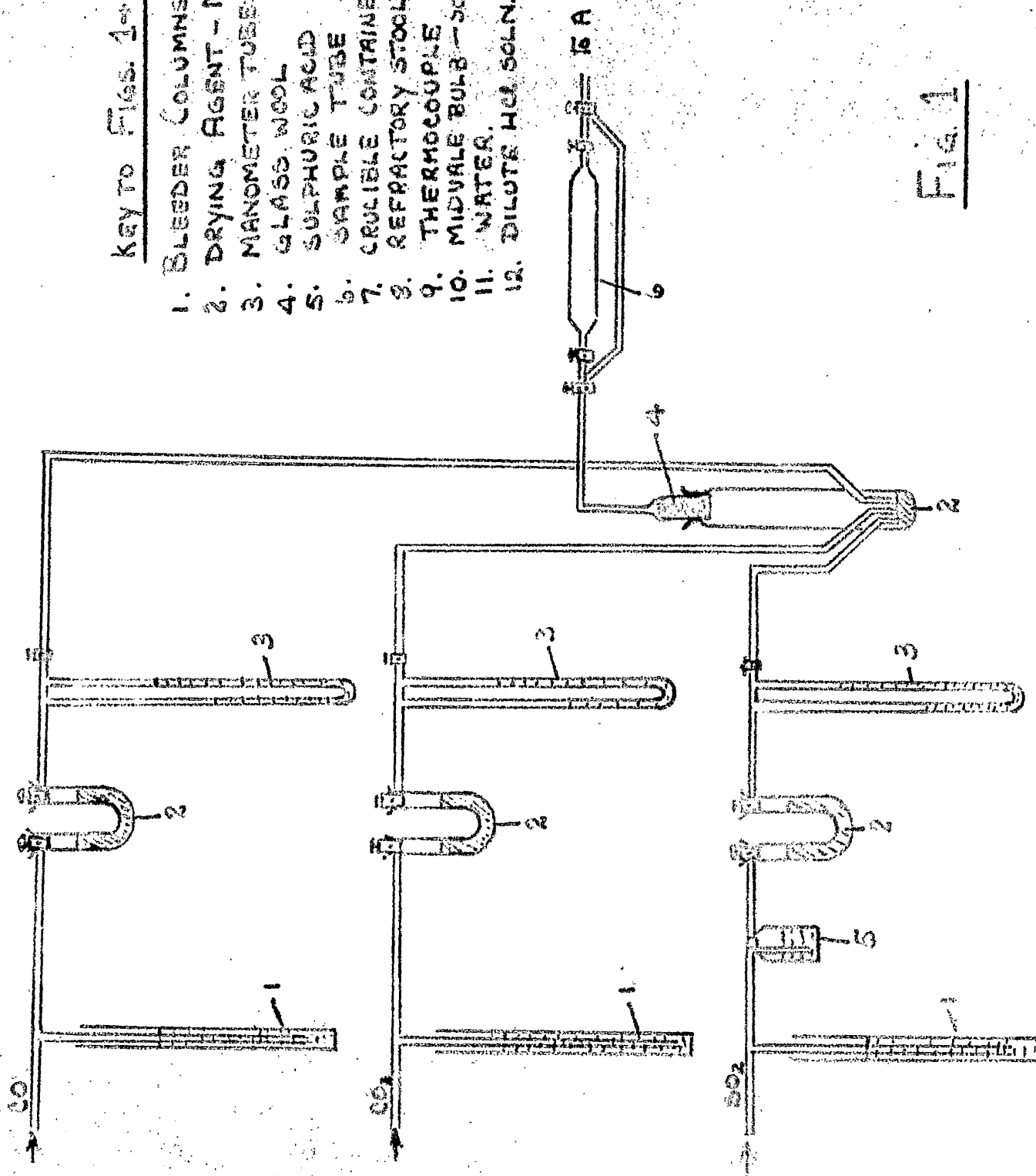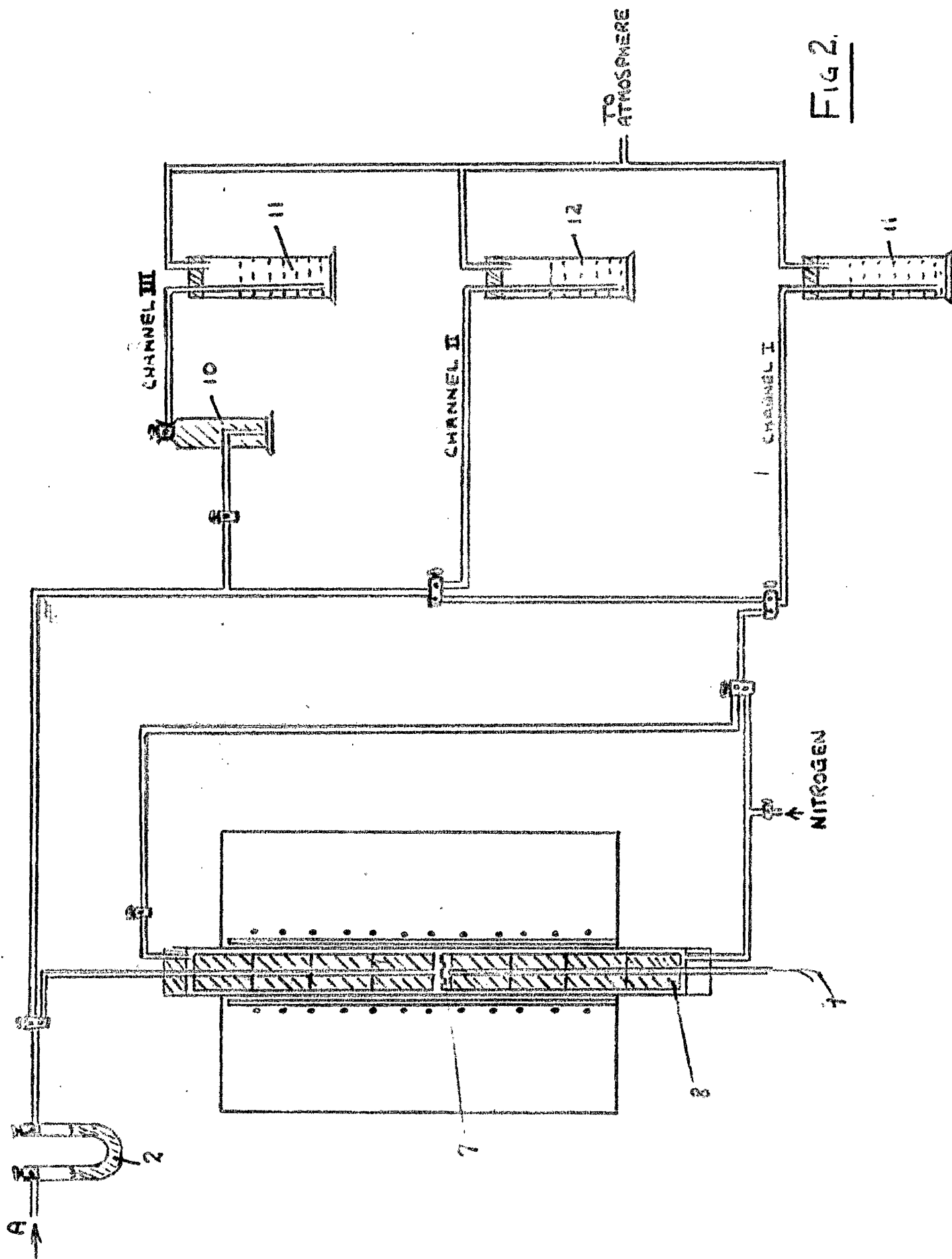
Fig 2.

potential would result in silica reduction and the consequent attack

on the platinum crucibles.   This was considered to be the limiting

factor from the experimental point of view but available lime and

silica activity data indicated a wide field for investigation before

crucible attack became significant.

As will be seen, however, it was found that the lime activity,

as the slag composition moved away from lime saturation, decreased

much more rapidly than available data indicated.   This meant that the

sulphurising potential available from the gas mixture of SO_2, CO_2 and

CO (see appendix) was insufficient to saturate, with calcium sulphide,

the range of slags which it had been hoped to investigate.   The only

alternative was to use a gas mixture with a higher sulphurising

potential, the obvious choice being one of hydrogen sulphide, hydrogen

and carbon dioxide.   Plans were made accordingly to change over to

use this new gas mixture and complete the study of the ternary slags.

For reasons which will be made clear later, it became necessary to

restudy the lime-alumina binary system and the plans for using the

new gas mixture had to be postponed.

Gas/

Gas Preparation.

All three gases $(SO_2, CO_2$ and $CO)$ were obtained from cylinders. The gas flow was metered by capillary flow meters containing low vapour pressure manometer oil. Control of the gas flow was achieved by capillary venturis and bleeder columns. These latter devices simply allowed the flow rate to be controlled by allowing a quantity of the gas to bubble out of the system through a head of water, the depth of which could be varied, and thus varying the amount of gas which could be passed into the system.

The gases were dried before metering. For the CO and CO_2 this was achieved by simply passing through tubes filled with magnesium perchlorate (anhydrone). The SO_2 was first dried through concentrated H_2SO_4 and then passed through magnesium perchlorate. After drying and metering the gases were mixed before passing into the analysis section of the apparatus. Again, this mixing tube contained magnesium perchlorate thus ensuring that the gases, at this stage, prior to analysis contained a negligible quantity of water vapour. The various drying agents were renewed regularly to ensure efficient removal of moisture.

Gas Analysis.

After mixing, the gases could, by a system of two-way stop cocks, be diverted into any one of three channels. One channel allowed the gases to exhaust to atmosphere by means of an outlet to a ventilation shaft, thus preventing contamination of the laboratory. Before an analysis was attempted, it was always considered advisable to allow the gas mixture to pass through the system, undisturbed for about an hour, so ensuring complete mixing. Also, since the SO_2 flow rate was inevitably considerably slower than that of either CO or CO_2, the SO_2 supply was always turned on first, followed by the CO_2 and then the CO.

Having allowed the gases to bubble through the system for about one hour, the gas mixture was diverted into channel two where the SO_2 was absorbed by the solution of 95cc water + 5cc 1/4 HCl contained in this flask. Normally the gas mixture was passed into this solution for one or two minutes, (accurately timed) thereafter the flask was removed and the suphurous acid solution was titrated against a standard KI/KIO_3 solution, using a starch indicator. This gave the rate of flow of SO_2 in the system as x cc.s/min.
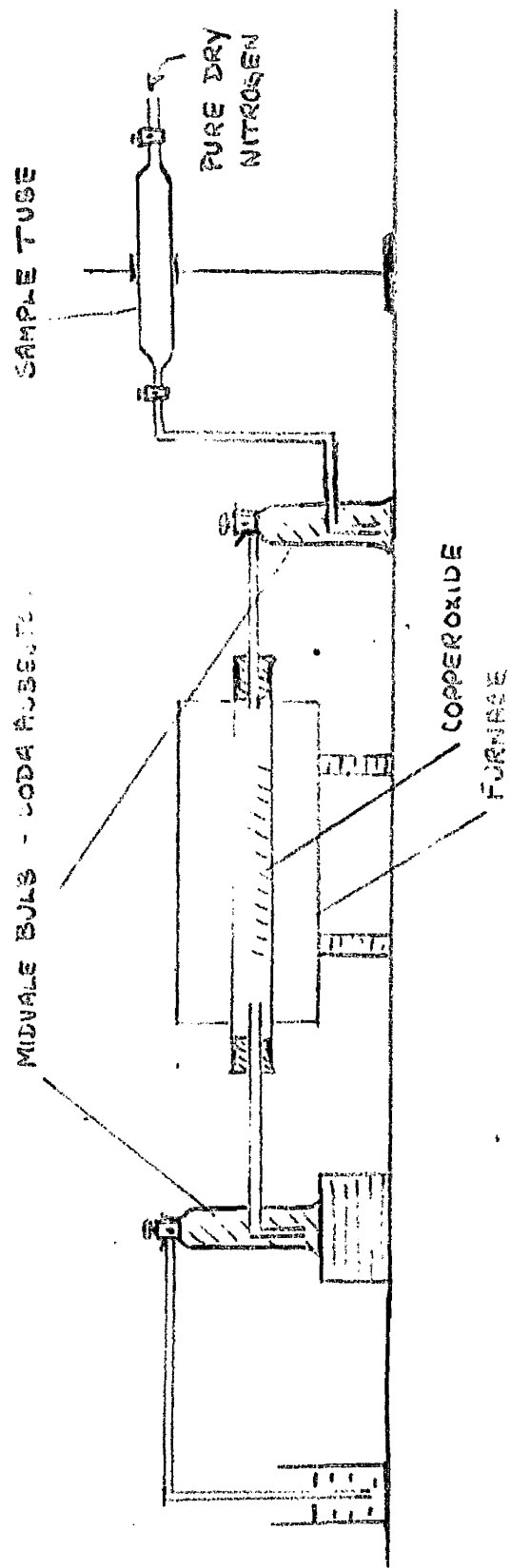
This/

SAMPLE TUBE

PURE DRY
NITROGEN

MIDVALE BULB - SODA ABSORB

COPPER OXIDE

FURNACE

Fig. 3 - APPARATUS TO DETERMINE

$$\frac{CO}{CO_2 + CO_2} \quad RATIO$$

This procedure was repeated till a consistent value for the rate of flow of SO_2 was obtained. The gas could now be diverted into channel three there both the SO_2 and the CO_2 were absorbed in a midvale bulb containing soda asbestos. This absorption was normally allowed to take place for five minutes. By subtracting the weight of SO_2 passing per minute (obtained from the titration data), the weight of CO_2 passing per minute could be calculated and thus the volume rate of flow of CO_2 in cc.s/min.

The final stage in the analysis involved removing a sample of the gas from the system and connecting it to the apparatus shown in fig. 3. The gas sample was then blown through the system by nitrogen gas and the CO_2 and SO_2 were absorbed in a midvale bulb containing soda asbestos. The remaining gas (CO) was oxidised by passing through a silica tube containing copper oxide at a temperature of $500^{o}C$ wherein the CO was oxidised to CO_2, thereafter being absorbed in another midvale bulb containing soda asbestos. The nitrogen which was used to push the gas sample through the system and which also acted as a dilutent, was passed for 10 minutes at a rate of 50 cc/min., and finally for about 25 - 30 minutes at 100 cc/min. This ensured complete absorption and the oxidation of the CO by the copper oxide was very efficient provided the tube was recharged with freshly oxidised copper oxide whenever more than half the quantity had been reduced.

From analysis of this gas sample the ratio of $\dfrac{CO}{CO_2 + SO_2}$ was obtained and this, coupled with the information gained previously, gave the flow rate of CO and hence complete analysis of the gas mixture.

Normally a gas analysis took about one hour to complete and care had to be taken that diversion of the gas from one channel to another did not alter the flow rate. This could be readily avoided by careful adjustment of water levels in channels 1 and 3. It should be mentioned that the level in channel 2 was of course dictated by the fact that this flask had to contain 100 cc. of dilute acid solution. After a little experience with the apparatus minor adjustments to water level to maintain constant flow rates could be made very readily and negligible fluctuation resulted. Occasionally irregular flow rates and inconsistent analyses would occur and this trouble was usually caused by a breakdown of the stop-cock lubricating grease, a result of sulphur dioxide attack. This caused leakages in the system and it proved to be well worthwhile to regrease the stop-cocks in the system after every two or three runs. The apparatus was of very similar design to that used by Kalyanram (18) etc., with the noteworthy modification that P.V.C. tubing largely replaced the rubber tubing used by the earlier workers. Previously it had been necessary to replace the rubber tubing after every run (18), however the P.V.C. tubing was replaced after perhaps 10 or 12 runs.

The rubber tubing became hard and brittle – the result of sulphur attack – but the P.V.C. tubing, normally transparent, became blackened by the SO_2 and although there was no evidence to indicate that any deterioration had occurred, it was considered advisable to replace tubing affected in this way.

Quite the most troublesome malfunction was the deposition of sulphuric acid vapour in the venturi of the SO_2 flowmeter. This resulted, eventually in the blockage of the venturi and although the flowmeter indicated a positive pressure of SO_2 none of this gas was passing through the system. Removal of the venturi and careful washing, first with hot water and then with acetone, followed by drying in an oven at approx. $100^{o}C$ was the only satisfactory way in which the trouble could be remedied.

Slag Preparation.

Initially several lime/alumina/silica slags were prepared by melting the appropriate quantities of 'analar' calcium carbonate, aluminium oxide, and acid washed silica, contained in a carbon crucible, in a high frequency induction furnace. Some preliminary work had indicated that complete conversion of calcium carbonate to lime by calcination at $1,000^{o}C$ was most unlikely. Consequently no attempt was made at preliminary calcination of the calcium carbonate used in preparation of the slags.

Normally, the materials were mixed and compressed prior to melting and the molten slag was cast into a button mould After solidification the slag was finely crushed in a percussion mortar, charged again into the carbon crucible and remelted, cast, allowed to solidify and crushed in the percussion mortar to pass a 30 B.S.S. sieve. This material was then ground in a mechanical agate mortar to complete the preparation.

After several preliminary experiments using these straightforward ternary slags it was concluded that satisfactory results would only be obtained if the slags charged into the experimental furnace contained a known quantity of sulphur initially. The reason for this was that as the slags picked up sulphur from the gas atmosphere, lime was converted to calcium sulphide, and thereby altering the composition of the slags. If the slags contained some sulphur initially less sulphur would be required from the gas phase, to bring the system to equilibrium and therefore, there would be very little change in composition.

Sulphur containing slags were therefore prepared by simply adding CaS to the original slags and remelting, crushing and grinding as before. This method, however, proved to be far from satisfactory. No analar CaS was available and the material used appeared to be non stoichiometric; with the result that the final slag, when analysed for sulphur, rarely contained more than half of the amount added originally.

The problem was overcome by adding sulphur to the slags in the pure form of flowers of sulphur and complete details of the technique will be described. The slags were prepared in pairs viz., one straightforward lime-alumina-silica slag, prepared as previously described and a second sulphur containing ternary with the same CaS free lime content. These two slags could then be mixed in suitable proportions to give various sulphur content slags with identical CaS free lime contents.

In most cases the sulphur containing slags were made up with 4%S and it was necessary to calculate the amount of lime which would combine with this 4% of sulphur to give CaS. This quantity of lime was then added (as calcium carbonate) to the basic lime-alumina-silica slag composition. The slag was then melted twice being crushed and ground as before. Normally 20 gms of slag were prepared in this way and before sulphur addition this quantity was divided into two 10gm portions. It had been previously ascertained that addition of the calculated amount of sulphur was insufficient to give the final analysis of 4%S because of evaporation loss during melting. Hence it was necessary to add to one 10gm portion a large excess of sulphur (perhaps four or five times the calculated quantity) which was carefully mixed with the previously melted and finely ground slag. This mixture was then compacted and melted in a carbon crucible in a high frequency induction furnace.

After crushing and grinding the slag was analysed for sulphur and was usually found to contain rather more than the required 4%S. It was then a simple matter to calculate the amount of the second 10 gm portion (i.e. material with the same percentage lime but containing no sulphur) which had to be added to 'dilute' the sulphur content to exactly 4%S. When this addition had been made the slag was remelted, crushed, ground and analysed again. In all cases the sulphur content was found to be within the acceptable range of 3.9 - 4.1%S.

It should be mentioned that although sulphur loss was considerable when melting the slag with flowers of sulphur, once the sulphur had combined with the 'excess' lime to give calcium sulphide little or no sulphur loss was noticed. The loss of sulphur from slags to which stock calcium sulphide had been added can be explained by the probability of some free sulphur existing in this material which volatilised on heating.

As a result of this method of slag preparation two series of slags were obtained. One series of lime-alumina-silica slags with a corresponding series of slags containing 4%S which had the same composition when considered on a CaS free basis. Thus by mixing the corresponding slags from each series it was possible to obtain any slag sulphur content from 0 to 4%

In exactly the same way two series of lime-alumina slags were prepared and could be mixed to give a similar range of sulphur contents.

Slag Analysis.

Lime Estimation.

All the slags prepared in the manner just described were analysed for lime by the normal calcium oxalate method.

Sulphur Estimation.

Several methods of sulphur estimation were available.

(1)   gravimetric - sulphur estimated as barium sulphate.

(2)   evolution   - sulphur estimated as hydrogen sulphide.

(3)   combustion
        by oxygen   - sulphur estimated as SO_2.

(4)   combustion   - sulphur estimated as SO_2.
        by CO_2

By far the most convenient method is combustion by CO_2.   This technique is extremely accurate because no sulphur trioxide is formed, thus eliminating the necessity for calibration of the apparatus (c.f. combustion with oxygen) and since an interval of 30 - 60 minutes is normally required to complete the analysis it is a fairly rapid method (c.f. gravimetric technique).   This particular method was developed and described by Fincham and Richardson (19).

After removing the slags from the furnace, the platinum crucible was peeled off and the slag pellet was then prepared for analysis.

The pellet was crushed in a percussion mortar and a 0.1gm sample was weighed and transferred to a preignited boat. This boat was then placed in a 1" aluminous porcelain combustion tube in a resistance furnace with a platinum/13%Rh winding which readily gave the required temperature of $1,480^{\circ}C$. CO_2 was passed through the system at 250cc/min. and the SO_2 formed was absorbed in two flasks each containing 5% 1/4HCl and 5% 1%KI in water solution. The SO_2 so absorbed was continuously titrated using a starch indicator till a standard blue colour was obtained. As previously indicated the time required to complete an analysis varied to some extent but on average 30 minutes was quite sufficient.

No rubber tubing was used in the system to eliminate any possibility of sulphur loss due to reaction with the rubber. Some determinations were carried out after the crushed slag had been sized to −30 +120 with the appropriate B.S.S. sieves but no significant difference in the sulphur analysis was observed. Also, according to Earnshaw (20) the slag should be crushed in the percussion mortar with a single hammer blow, since any more than one blow appeared to lower the sulphur content of the slag. Although, in the present work, no evidence was gained to support this it was decided to persevere with the single blow technique since this permitted satisfactory crushing of the slag anyway.

Crucible Manufacture.

The only material which, it was considered would endure under the experimental conditions was platinum. Small crucibles were made from platinum foil (0.002" thick) by cutting discs $\frac{3}{4}$" diameter and annealing them in a gas flame. Thereafter the discs were carefully pressed into a hemispherical depression in a lead block by a suitably shaped steel plunger. The complete pressing operation was not carried out in a single action as this tended to cause tearing of the foil and an unsatisfactory crucible. When the foil was half formed it was once again annealed before the final pressing was carried out. The result was a cup shaped crucible $\frac{1}{2}$" diameter, which could readily contain 0.4gm. slag and which was an adequate quantity for the purposes of the reaction.

It was realised, after some preliminary work that although platinum was an excellent and reliable material at low CO/CO_2 ratios, and with basic slags, it was attacked under the severely reducing conditions required for acid slags. For these an increased CO/CO_2 ratio was necessary to give adequate sulphurising potential and this, together with the increased silica activity resulted in silica reduction. The product of this reduction, silicon, alloyed with the platinum crucible material and the crucibles were completely destroyed. To overcome this problem /

problem some iridium foil was obtained and an effort made to produce similarly shaped crucibles of this, extremely brittle material. The iridium foil was rather thicker (0.005") than the platinum foil and it was quickly realised that the technique used to make the platinum crucibles was not satisfactory for the iridium. It was concluded that to form even a small depression in the surface of the foil, the pressing would have to be carried out while the material was hot. It was learned (21) that the maximum deutility of iridium occurred at a temperature of $1,500^{\circ}C$ but it was decided to carry out preliminary attempts at $800^{\circ}C$.

A disc ($\frac{3}{4}$" diam.) of iridium foil was placed in a graphite mould into which a small depression had been cut and a second piece of graphite with a complimentary impression was pressed down on top of the disc when the arrangement had reached a good red heat. On removal it was observed that the iridium had decrepitated and although this technique was tried several times and with numerous modifications, a satisfactory crucible was rarely produced.

Finally a steel mould, with a slight depression cut therein, was used along with a suitably shaped former and after heating to $800^{\circ}C$ a satisfactory dished shape crucible was obtained. It should be emphasised that this crucible was not hemispherical like the platinum crucible and indeed to produce a crucible of this shape from the iridium foil used here would be an extremely difficult task.

To explain the lack of success with the graphite mould it was
suggested that the carbon was having a further embrittling effect
on the iridium.

Furnace Arrangement.

The experiments were carried out in a resistance furnace, wound
with 18 s.w.g. $Pt.$ 13%Rh wire, which carried a 2" i.d. mullite tube
35" long (See figure 2.).   Carefully packed insulation, along with
the rather heavy gauge wire enabled the furnace to reach a temperature
of $1,550^{\circ}C$ within $2\frac{1}{2}$ hours and the hot zone at this temperature was
constant to within $\pm 5^{\circ}$ over a length of about 3 inches.   Power was
supplied to the furnace by a 20 amp Veriac auto transformer and the
temperature was controlled automatically by a Kelvin & Hughes type
controller connected to a $Pt./13\%Rh$ thermocouple.   This combination
allowed a temperature of $1,550^{\circ}C \pm 2^{\circ}C$ to be readily maintained.
Temperature within the reaction tube was measured by a second $Pt./13\%Rh$
thermocouple, and a Cambridge potentiometer.   This thermocouple had
been calibrated against the melting point of palladium $(1,559^{\circ}C)$ and
the estimated error was not more than $\pm 4C^{\circ}$.

The reaction tube was sealed at each end with a rubber bung which
carried the inlet and outlet tubes for the gas mixture; the dead space
within the tube was filled with refractory stools which prevented thermal
diffusion and also acted as radiation shields, preventing excess heating
of the rubber bungs.

The platinum crucibles were contained in an alundum tray which rested on top of the lower set of refractory stools. This alundum tray was shaped to accommodate 4, 5 or 6 crucibles and the distance between the top of the tray and the bottom of the upper set of refractory stools was $\frac{1}{2}$ - 1". Thus the gas mixture emerged from the inlet tube and impinged on the molten slags in the platinum crucibles below, at the reaction temperature $(1,550^{\circ}C)$. The distance between the gas inlet tube and the slag surface was maintained not greater than 1" to prevent any possibility of thermal diffusion. After a run had been completed, the slags had to be quenched to prevent any loss of sulphur due to air oxidation on cooling. To accomplish this the lower rubber bung was removed from the mullite tube and the reaction tray was immediately lowered a distance of four inches. This ensured that the slags had moved out of the hot zone and would solidify almost instantaneously. On rare occasions, the tray would stick in the hot zone and fail to drop down with the stools, giving suspect results.

Experimental Procedure.

Normally four slag-filled crucibles were charged into the
furnace at room temperature. The furnace was then switched on and
allowed to heat up to the operating temperature. At the same time
the furnace tube was flushed out with oxygen-free nitrogen which was
allowed to bubble through the tube until the operating temperature was
reached and the system was ready to receive the sulphursing gas mixture.

The gases were now turned on in the order previously described;
SO_2 first, then CO_2 and finally CO. After about one hour, the gas
mixture was analysed and by this time the temperature in the furnace
was approximately $1,000^{o}C$. A satisfactory gas analysis was rarely
achieved in less than 2 hours and by this time the furnace had reached
the operating temperature. The gas mixture was then introduced at the
bottom of the reaction tube and allowed to pass out through the top
for about 20 minutes. In this way all the nitrogen was flushed out of
the system and the reaction tube was filled with the sulphurising gas
mixture. The gas flow was then reversed and the gas passed in through
the top of the furnace where it passed down into the reaction zone and
impinged on the molten slags; thereafter it was led out of the furnace
and to the atmosphere. That the gases, on passing down through the
furnace to the reaction zone, became sufficiently preheated, was indicated
by the fact that the reaction zone temperature did not decrease when the
gases were admitted.

Usually the gas was allowed to pass into the reaction zone for about
2 hours, then the slags were quenched in the manner previously
described and the furnace and gases switched off. During a run,
a gas sample was removed for analysis to ensure that the gas composition
as analysed was identical to that passing into the furnace.

After some operating experience had been gained some slight
variations on the above general procedure were developed. It was of
considerable benefit to maintain the reaction furnace at a temperature
of 900 - 1,000°C instead of allowing it to cool each time to room
temperature. In this way, less time was required for the furnace to
reach operating temperature and the only disadvantage was a rather
alarming rate of failure of the refractory stools due to spalling.
It was considered, however, that the saving in time considerably offset
the refractory failure and since no reaction tubes spalled the
modification proved very useful.

Also, to make use of the full furnace capability, alundum trays
capable of holding five and six crucibles (instead of four) were developed
and used successfully.

In the original series of runs, ternary slags with no initial
sulphur content were used and all the sulphur finally contained in the
slags had been absorbed from the gas mixture.

This meant that the oxygen of the lime was replaced by sulphur
from the gas according to the equation:

$$CaO + \tfrac{1}{2}S_2 = CaS + \tfrac{1}{2}O_2$$

Thus the final composition of a slag containing perhaps 2.5%S was
considerably different from the original composition in that some of
the lime had been converted to CaS.   The nett effect of this was that
as sulphur was absorbed by the slag, the slag became more acidic due
to replacement of lime and instead of an obvious break in the curve
of %S against A value when sulphur saturation was reached, a smooth
curve was obtained and it was impossible to quote an exact or indeed
an approximate sulphurising potential to correspond to calcium sulphide
saturation of the slag.   When this had been realised, it was suggested
that the most convenient way of overcoming this difficulty was to have
an initial sulphur content in the slags so that for a given sulphurising
gas potential, a slag sulphur content could be chosen so that the amount
of sulphur gained (or lost) by the slag would be a minimum and hence
the composition change of the slag would be as little as possible.
Consequently, slags were made up, as previously described, with up to
4%S so that the initial sulphur composition could be anything between
0 and 4%S.   An added advantage of this technique was that the time of
a run was considerably reduced since the system was much nearer equilibrium.
Also, since the equilibrium could be approached from both sides, i.e.
gain or loss of sulphur/

sulphur by the slag, it was not of paramount importance to bring the system of absolute equilibrium.

This approach proved to be much more satisfactory and the sulphurising potential of the gas which corresponded to sulphur saturation of the slag could be readily recognised.   Slag preparation was a much more exacting and time consuming process but this was more than offset by the knowledge that the results obtained could be considered much more reliable than those gained in the first series of experiments.

Limitations of the Apparatus.

When the work was first suggested it was the intention to investigate the solubility and activity of Calcium sulphide in a slag of blast furnace composition (i.e. 40%lime, 40%silica, 20%alumina) however it soon became obvious that with the gas mixture used, it would be impossible to supply enough sulphur to the slag to exceed CaS solubility. To encourage maximum sulphur pick-up it was essential to lower the oxygen potential of the system as far as possible and the high CO/CO_2 ratios which this necessitated, along with high slag silica activity caused severe attack of the platinum crucibles and even with iridium crucibles, which were not attacked, the required sulphurising potential was simply not available from this gas mixture. Consequently, the investigation had to be restricted to basic (i.e. high CaO activity) lime-alumina-silica ternary slags and to lime-alumina binaries for which the sulphurising potential for saturation was available and the danger of crucible attack was reduced by the low (zero in the case of the binaries) slag silica activity.

For work requiring higher sulphurising potentials a mixture of H_2/H_2S and CO_2 is probably more useful, the main advantage in this case being that the gas used to supply sulphur to the system viz., H_2S does not also supply oxygen (c.f. SO_2) because as previously mentioned, to supply /

supply a high sulphurising potential the oxygen potential of the system must be very low.

This is obvious from the relationship:

$$\text{Sulphurising Potential} \quad A = \left(\frac{P_{S_2}}{P_{O_2}} \right)^{\frac{1}{2}}$$

CHAPTER III.

RESULTS.

RESULTS.

The results obtained during the course of this investigation
are shown in tabular form in tables II and III.   In table I the
compositions of the slags used in the experiments are given, the
method of preparation of these slags has already been described.

For slags CA2 and M, the useful maximum limit of the sulphurising
potential of the gas had been reached without calcium sulphide
saturation being obtained.   If, as expected, this work is continued
with an $H_2/H_2S/CO_2$ gas mixture only a few more results should be
required to complete the investigation of these slags.

Since it was the purpose of this work to study the equilibrium:

$$CaO + \tfrac{1}{2}S_2 = CaS + \tfrac{1}{2}O_2$$
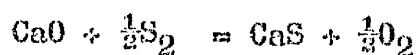
as the reaction proceeded in either direction i.e. it was possible
to charge slags with higher or lower sulphur potentials than the gas
mixtures with which they were in contact, the actual time of individual
experiments could be fairly short.   This was because:

(1)   The absolute attainment of equilibrium was not essential since
      the equilibrium was being approached from both directions.

(2)   Since the total final sulphur content of the slag did not have
      to be supplied entirely by the gas atmosphere, a long period of
      gas/slag contact was unnecessary.

TABLE I.

Slag Compositions at Calcium Sulphide Saturation.
(Calculated on a CaS free basis.)

Slag sulphur content at CaS saturation.

Slag No.	%CaO	%Al₂O₃	%SiO₂	NCaO	NAl₂O₃	NSiO₂	%S	NCaS
CA1	50.5	49.5	–	0.650	0.350	–	1.8	0.040
*CA2	45.0	57.0	–	0.564	0.436	–	–	–
CA3	53.5	46.5	–	0.67	0.324	–	1.8	0.040
CA4	58.35	41.65	–	0.723	0.277	–	1.8	0.039
CA5	45.0	55.0	–	0.600	0.400	–	4.0	0.100
C	54.0	34.9	11.50	0.645	0.229	0.126	3.1	0.065
D	50.3	47.6	2.08	0.645	0.534	0.024	1.8	0.042
E	56.5	32.0	11.40	0.670	0.208	0.125	4.0	0.083
F	54.5	42.5	3.03	0.675	0.289	0.035	1.9	0.032
G	56.85	38.1	5.08	0.690	0.255	0.058	2.0	0.043
H	54.4	38.1	7.60	0.660	0.254	0.086	2.0	0.043
K	54.0	32.4	13.90	0.638	0.210	0.153	4.5	0.094
L	46.5	48.4	5.10	0.598	0.342	0.060	3.7	0.083
*M	44.0	51.0	5.12	0.571	0.364	0.062	–	–
N	46.4	43.7	10.20	0.580	0.302	0.119	3.5	0.077

* For slags CA2 and M, saturation was not achieved and the compositions of these slags have been calculated on a calcium sulphide free basis at 4.0% sulphur.

TABLE II. — Results for Lime-Alumina Slags.

Slag No.	Run No.	Time of Run(hrs)	Gas Analysis		A value	Slag sulphur analysis (%)	
			CO/CO_2	%SO_2		Initial	Final
CA1	99	5	4.8	1.5	950	1.0	1.40
	113	2	10.0	1.2	1,700	2.0	Sat.
	119	2	7.0	1.5	1,400	2.0	1.5
	121	2	6.0	1.6	1,200	2.0	1.4
	122	2	5.0	1.35	1,000	2.0	1.3
	141	2	6.0	1.3	1,100	1.0	1.2
	142	2	3.5	1.3	700	1.0	1.05
CA2	81	2	7.5	1.35	1,400	2.0	0.96
	82	2	13.0	1.60	2,500	2.0	1.32
	83	2	16.5	1.7	3,100	1.0	1.40
	84	2	22.0	1.5	3,500	3.0	2.35
	89	2	47.0	0.9	5,600	4.0	3.20
	115	2	13.0	0.9	2,100	1.0	1.40
	127	2	73.0	1.3	6,500	4.0	3.70
CA3	107	2	1.8	1.6	400	0.0	0.85
	108	2	3.5	1.5	800	1.0	1.60
	109	2	2.6	1.3	500	2.0	1.55
	117	2	4.6	1.3	900	2.0	1.60
	122	2	5.3	1.35	1,000	2.0	Sat.
CA4	109	2	2.6	1.3	500	2.0	Sat.
	161	2	2.3	1.6	400	2.0	1.80
	161R	2	0.45	1.6	100	0.0	0.43
	164	2	2.0	0.9	300	2.0	1.60
CA6	125	1½	49	1.3	5,500	2.0	2.90
	126	2	63	1.3	6,100	2.0	3.80
	127	2	73	1.3	6,500	4.0	Sat.
	135	2	33	1.2	4,600	2.0	2.7
	139	1½	12	1.1	2,100	0.0	1.05
	140	2	7.5	1.3	1,400	0.0	0.90
	141	2	6.0	1.3	1,100	1.0	0.90
	146	2	47.0	1.6	5,300	4.0	3.50
	150	2	22.0	0.9	3,300	3.0	2.6

TABLE III. — Results for Lime-Alumina-Silica Slags.

Slag No.	Run No.	Time of Run(hrs.)	Gas Analysis.		A value	Slag sulphur analysis (%)	
			CO/CO_2	%SO_2		Initial	Final.
C	76	$2\frac{1}{2}$	6.0	1.3	1,100	1.0	1.35
	79	2	4.5	1.3	850	2.0	1.70
	80	$2\frac{1}{2}$	3.0	1.6	700	1.0	1.07
	81	2	7.5	1.35	1,400	1.5	1.99
	114R	2	12.0	1.3	2,100	2.0	2.5
	156	2	14.0	1.7	2,650	4.0	2.7
	160	2	17.0	1.8	3,300	4.0	Sat.
D	80	$2\frac{1}{2}$	3.0	1.6	700	1.0	1.2
	111	2	7.0	1.3	1,300	2.0	1.66
	119	2	7.0	1.5	1,400	1.0	1.46
	121	2	6.0	1.6	1,200	2.0	1.52
	122	2	5.3	1.35	1,000	2.0	1.40
	143	2	2.0	1.2	400	1.0	0.50
	163	2	2.7	1.2	500	2.0	0.80
	170	2	8.4	1.0	1,500	2.0	Sat.
E	107	2	1.8	1.6	400	1.00	1.09
	108	2	3.5	1.5	800	1.0	2.0
	110	2	5.2	.17	1,100	2.0	2.16
	111	2	6.7	1.3	1,300	3.0	2.40
	112	2	8.3	1.4	1,500	3.0	3.30
	113	2	10.0	1.2	1,700	4.0	3.50
	114	2	12.0	0.9	2,000	4.0	3.89
	115	2	13.0	0.9	2,100	4.0	Sat.
F	107	$1\frac{1}{2}$	1.8	1.64	400	1.0	0.95
	108	$1\frac{1}{2}$	3.5	1.60	800	1.0	1.23
	117	2	4.6	1.3	900	2.0	1.88
	122	2	5.3	1.35	1,000	2.0	Sat.
	142	2	3.5	1.30	700	1.0	1.20
	143	2	2.0	1.3	400	0.0	0.70
	163	2	2.7	1.16	500	2.0	1.45
G	142	2	3.5	1.3	700	2.0	2.06
	143	2	2.0	1.3	400	1.0	1.42
	162	2	4.0	1.6	800	2.0	Sat.
	163	2	2.7	1.16	500	2.0	1.85
H	140	2	7.5	1.3	1,400	2.0	Sat.
	141	2	6.0	1.3	1,100	2.0	1.63
	142	2	3.5	1.3	700	1.0	1.60
	143	2	2.1	1.3	400	2.0	0.80
	144	2	6.5	1.5	1,300	1.0	1.98

TABLE III Ctd.

Slag No.	Run No.	Time of Run(hrs)	Gas Analysis. CO/CO_2	$\%SO_2$	A value	Slag sulphur analysis (%) Initial	Final.
K	137	2	13.5	1.7	2,700	2.0	2.60
	141	2	6.0	1.3	1,100	2.0	1.70
	143	2	2.1	1.3	400	2.0	0.58
	144	2	6.5	1.5	1,300	1.0	1.40
	156	2	14.0	1.7	2,650	5.57	4.35
	160	2	17.0	1.8	3,300	5.57	Sat.
L	126	2	63.0	1.3	6,100	2.0	3.1
	135	2	33.0	1.2	4,600	1.0	2.75
	137	2	13.5	1.7	2,700	0.0	1.40
	139	$1\frac{1}{3}$	12.0	1.1	2,100	2.0	1.30
	141	2	6.0	1.3	1,100	0.0	0.80
	144	2	6.5	1.5	1,300	1.0	0.88
	145	2	20.0	1.6	3,400	2.0	2.02
	147	2	67.0	1.4	6,200	4.0	Sat.
	150	2	22.0	0.9	3,300	4.0	2.22
	152	2	56.0	1.5	5,700	4.0	3.60
M	127	2	73.0	1.3	6,500	2.0	2.80
	135	2	33.0	1.2	4,600	3.0	2.05
	138	2	31.0	1.6	4,400	4.0	1.90
	145	2	20.0	1.6	3,400	1.0	1.30
N	127	2	73.0	1.3	6,500	2.0	3.1
	128	2	90.0	1.6	6,800	4.0	Sat.
	137	2	13.5	1.7	2,700	1.0	1.22
	138	2	31.0	1.6	4,400	3.0	2.40
	144	2	6.5	1.5	1,300	0.0	0.70
	145	2	20.0	1.6	3,400	2.0	1.50
	146	2	47.0	1.6	5,300	4.0	2.85
	152	2	56.0	1.5	5,700	4.0	2.91

Thus, as will be noted, the average duration of individual experiments was two hours. All these experiments were carried out at a temperature of $1,550^{\circ}C$ and no attempt has been made to investigate the effect of temperature. The flow rate, throughout was maintained at not less than 150cc/min. and in many cases, particularly at high CO/CO_2 ratios the flow rate was considerably greater than this. Carter and Macfarlane (9) examined the problem of thermal diffusion in this type of investigation and concluded that the effect was negligible. This is perhaps to be expected when it is realised that the ratios of the densities of the three gases is not great and that the inlet gas is adequately preheated as it passes down the furnace to the reaction chamber which is contained entirely in the hot zone.

It will be noted that the results do not include any record of the appearance of the slags when they were removed from the experimental furnace, however, it will be useful to make some comments on this here. Slags of very low sulphur content (less than 0.5%) appeared completely glassy, but as the sulphur content increased an opaque region developed, originating around the edge of the slag in contact with the platinum crucible. From these observations it appeared that the sulphur content of the slag affected the rate of crystalisation and tended to prevent undercooling or glass formation.

Also, it would not be correct to assume that since a crystaline phase was present when the slags were removed from the furnace, this phase was also present at the operating temperature. In this connection, to attach too much significance to slag appearance could be very misleading.

It is true that the appearance of a slag definitely saturated with calcium sulphide was always the same. The surface of such a slag on removal from the furnace was always covered by a thick uneven crust. However, it was considered quite impossible to determine, by slag appearance alone, the sulphur content at which calcium sulphide began to appear as a separate phase.

CHAPTER IV.

DISCUSSION.

DISCUSSION.

Originally it was the object of this investigation to study the solubility and thermodynamic properties of calcium sulphide in lime-alumina-silica slags only. As has already been made clear, the lime activity data at the time of commencement of the work indicated that the gas mixture used here would supply sufficient sulphurising potential to enable much of that region of the lime-alumina-silica system, liquid at 1,550°C as shown in fig. 16, to be investigated. Initially the results of Sharma and Richardson (22) for the lime-alumina system appeared to be perfectly reasonable and there seemed no justification for repetition.

From an initial series of results, however two points emerged:

(1)   The gas mixture would not supply sufficient sulphursing potential to saturate with calcium sulphide, the wide range of slags planned originally.

This resulted from the fact that the lime activity decreased much more rapidly than available data indicated, as the slag composition moved away from lime saturation.

(2)   There appeared to be some discrepancy between the results being obtained here and the results reported by Sharma and Richardson for the lime-alumina binary system.
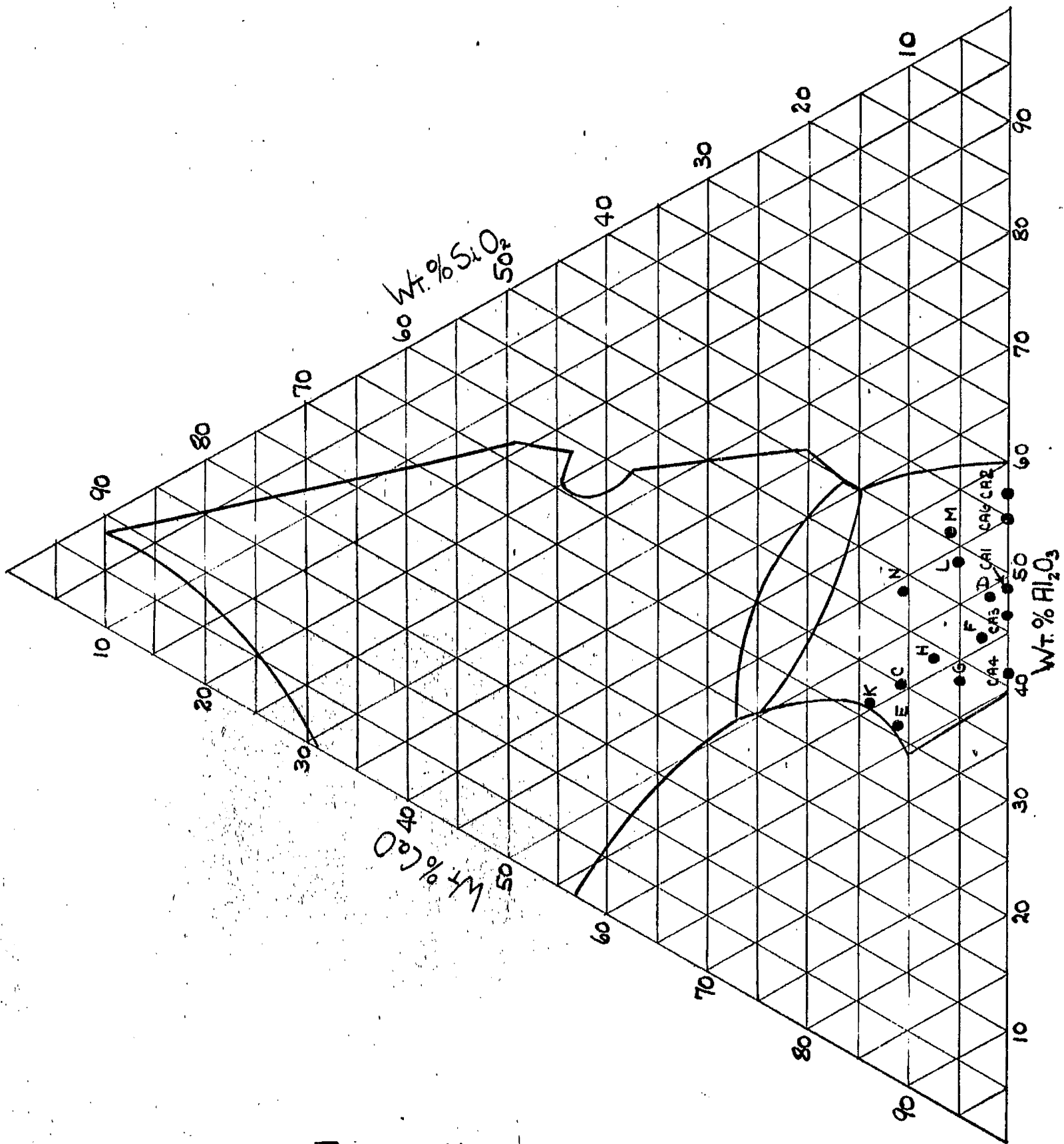
FIGURE-16

This latter deduction was made largely from the observation that in the ternary system, fairly close to the binary, the percentage sulphur corresponding to calcium sulphide saturation for the slag appeared to increase as the mole fraction of alumina increased, whereas the reverse was the case for the binary slags of Sharma and Richardson. On this basis therefore, it seemed not only justified but of considerable importance to investigate some binary composition (lime-alumina) slags.

With regard to the first point mentioned above, the only solution to the problem was to use, H_2, H_2S, and CO_2 as the sulphurising gas mixture. According to Sharma and Richardson, however, the complete range of lime-alumina slags could be investigated within the sulphurising potential range of 450 – 1,850 a range which was well within the scope of the CO, CO_2, SO_2 gas mixture.

At this stage therefore, two lines of progress were available:

(1) Change to a gas mixture of H_2, H_2S and CO_2 and complete the ternary system.

(2) Maintain the original gas mixture and investigate the lime-alumina binary.

The second alternative was chosen because it was accepted that a change over in the gas mixture being used and the necessity of several changes in the experimental set-up which would result, would involve a certain amount of delay.

Furthermore it was essential that every effort should be made to isolate the source of the apparent discrepancy in the binary system if the ternary results were to be considered reliable.

It was only after the binary slag investigation was well under way that it was concluded that the results of Sharma and Richardson had been misleading and that the sulphurising potential required to saturate the high alumina slags was very considerably greater than that indicated by these authors. Indeed for the high alumina slags the sulphurising potential was not available from the CO, CO_2, SO_2 mixture and a change of gas mixture would again be essential to complete the study.

Had it been realised at the outset that the sulphurising potential to saturate the complete range of lime-alumina binary slags was not available from the gas mixture of CO, CO_2, SO_2 then a change over to H_2, H_2S, CO_2 although involving several weeks delay would undoubtedly have been profitable; however, in the circumstances, this sequence of events could not have been foreseen or deduced from the data available.

Although, as has been explained, the main object of the research was a study of the lime-alumina-silica system, the results obtained for the lime-alumina system will be discussed first. This is because a knowledge of the lime-alumina results is necessary to complete the saturation level contours and the iso-lime activity lines discussed for the ternary system.

The Lime-Alumina System.

The results obtained for the lime-alumina system at $1,550^{\circ}C$, detailed in table II, have been plotted as shown in figs. 4, 5 and 6. Although it was intended that the calcium sulphide free lime content of the slags should remain constant it was essential that some sulphur should be gained or lost by the slag used in each experiment and this of course resulted in an alteration in the calcium sulphide free lime percentage. Some measure of the effect of this on the position of the final points can however, be obtained by making a slight correction, derived from a plot of the variation of sulphurising potential (A value/ with percentage lime at suitable percentage sulphur levels. The data for this graph was obtained from the uncorrected plots for the individual slags. This correction is only approximate but it will be noted that the adjustment required to individual points is, with one exception, very small and within the limits of experimental error.

From figures 4 and 5 it can be seen that for each slag a point is reached at which the sulphur content of the slag increases markedly for only a slight increase in the sulphurising capacity of the gas mixture with which it is in equilibrium. This point represents calcium sulphide saturation for the slag and since calcium sulphide is present as a free phase, $a_{CaS} = 1$.

FIGURE-4

FIGURE-5

SLAG – CA2

(%S)

A VALUE

FIGURE – 6

49.
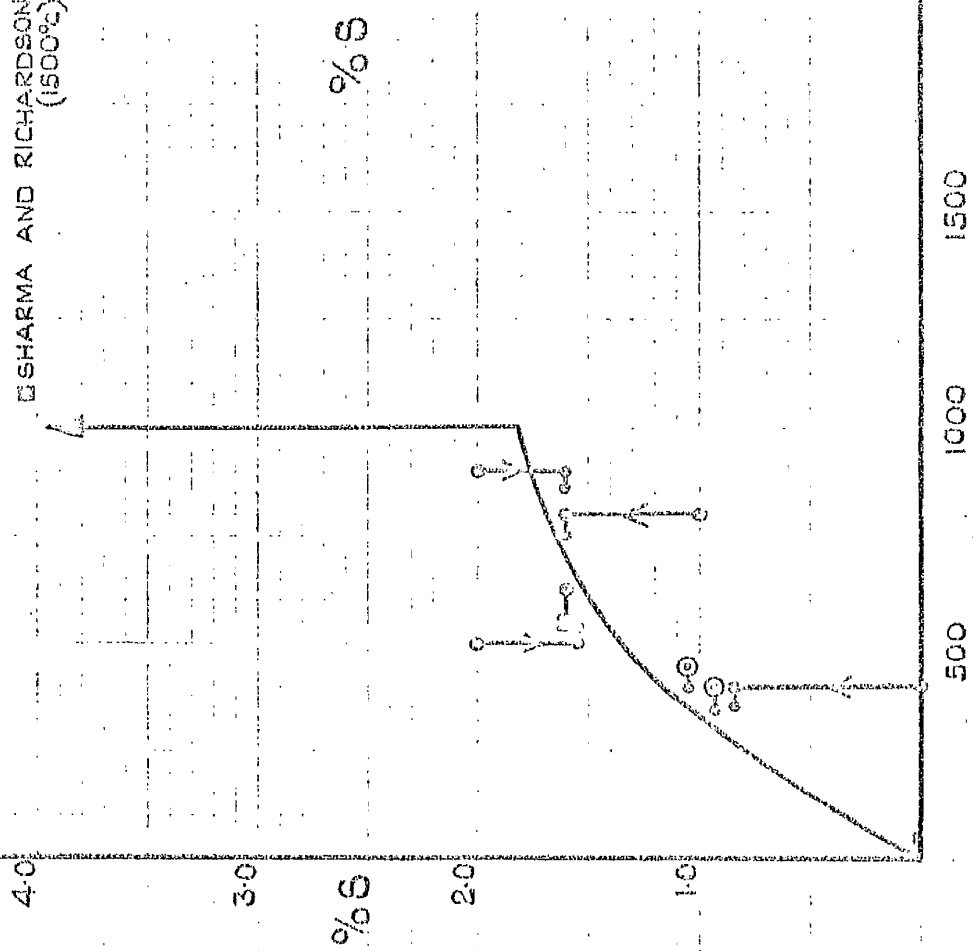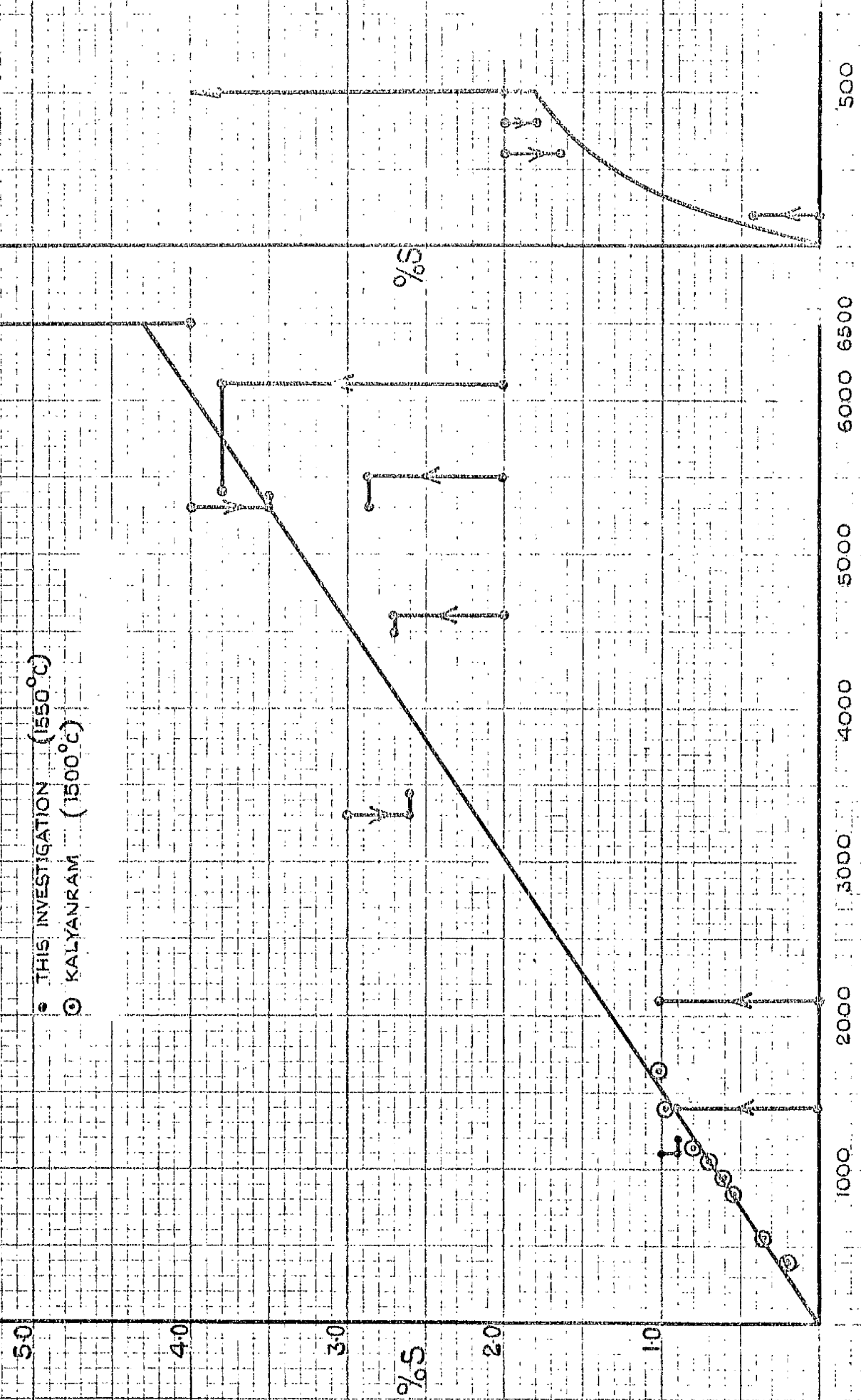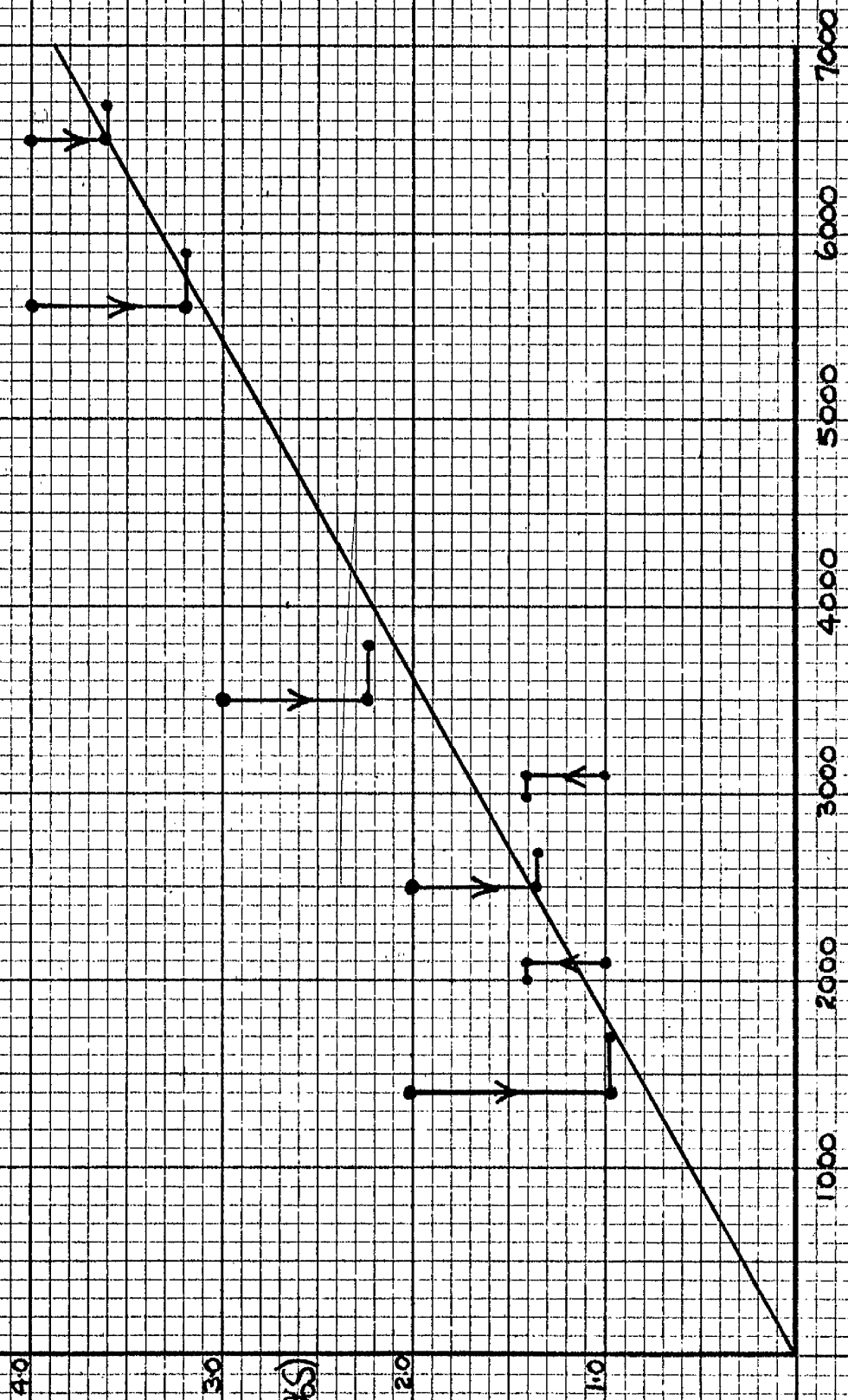
The sulphur contents corresponding to CaS saturation for each slag are plotted in figs. 17 and 19 and will be discussed later.

The equation for the reaction:

$$CaO + \tfrac{1}{2}S_2 = CaS + \tfrac{1}{2}O_2 \quad \cdots\cdots\cdots\cdots (5)$$
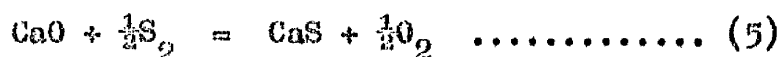
$$\text{gives} \quad K = \frac{a_{CaS}}{a_{CaO}} \left(\frac{P_{O_2}}{P_{S_2}} \right)^{\frac{1}{2}}$$

At calcium sulphide saturation, $a_{CaO} = \dfrac{1}{K.A}$, and thus a value of the lime activity corresponding to the slag composition at saturation can be obtained. These lime activities are plotted in figure 7.

Kalyanram and Bell (10), Carter and Macfarlane (9) and Sharma and Richardson (22) have also studied the behaviour of lime-alumina slags in contact with a sulphurising gas mixture but these workers studied the reaction at a temperature of $1,500^{o}C$. Reaction (5) does have a large temperature coefficient as indicated by the alteration in the value of the equilibrium constant for a 50°increase in temperature viz:-

$$K_{1500} = 2.75 \times 10^{-3}$$
$$K_{1550} = 3.32 \times 10^{-3}$$

It would therefore be expected that the experiments at higher temperature would show an increased slag sulphur content but this presupposes little change in the sulphurising capability of the gas mixture with increased temperature.

LIME ACTIVITIES IN THE LIME-ALUMINA SYSTEM

O — THIS INVESTIGATION AT 1550°C
+ — RECALCULATED FROM KALYANRAM (1500°C)
X — RECALCULATED FROM SHARMA AND RICHARDSON (1500°C)

LIME ACTIVITY (a_{CaO})

FIGURE-7

In fact a given gas composition gives a lower A value at $1,550^{o}C$ than at $1,500^{o}C$ (e.g. for a gas mixture of $CO/CO_2 = 10/1$ and $\%SO_2 = 1.6$, $A_{1500} = 3,000$; $A_{1550} = 2,100$). This will tend to offset the effect of the increase in the K value of reaction (5) and explains why the difference in sulphur content of the slags varies so little between $1,500^{o}C$ and $1,550^{o}C$.

The equilibrium in each of the four major reactions involved in the A value calculation, viz:

$$2SO_2 = S_2 + 2O_2$$
$$SO_2 = S + O_2$$
$$SO_2 = SO + \tfrac{1}{2}O_2$$
$$CO + SO_2 = COS + O_2$$
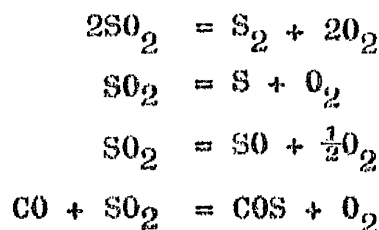
is displaced further to the right as the temperature increases and since this causes an increase in pO_2 as well as pS_2 the nett effect is to decrease the function $\left(\dfrac{pS_2}{pO_2}\right)^{\frac{1}{2}}$ which is the A value.

Since the present results were obtained at a higher temperature than those of the previous authors (9), (10) and (22) direct comparison cannot readily be made. The best basis for comparison would be that of the lime activity values obtained from each set of experimental results since it is probable that the variation of lime activity with temperature is small. Chipman (13) re-examined the results of Carter and Macfarlane in the light of recent information on the compounds formed in the lime alumina/

alumina system and concluded that a 50° change in temperature would have little effect on the activity of lime. A similar conclusion was reached by Sharma and Richardson (16) who investigated lime activities in the lime-silica system at $1,500^{\circ}C$ and $1,550^{\circ}C$.

Bell and Kalyanram calculated lime activity values from their results by the method used by Carter and Macfarlane viz, with reference to a standard slag with original composition such that the lime activity was unity.

a_{CaO} for any slag is given by:-

$$a_{CaO} = \frac{a_{CaS}}{K.A.}$$

When the standard slag was equilibrated with a suitable gas mixture,

$$a_{CaO} = \frac{a^{o}_{CaS}}{K.A.^{o}}$$

but $a_{CaO} = 1$ $\therefore$ $K = \dfrac{a^{o}_{CaS}}{A^{o}}$

$\therefore$ For any slag, $a_{CaO} = \dfrac{a_{CaS}}{A} \bigg/ \dfrac{a^{o}_{CaS}}{A^{o}}$, the superscript referring

to the standard slag. It was then assumed that for slags far removed from sulphide saturation, γ_{CaS} remained substantially constant and equal to that for the standard slag. The expression for a_{CaO} then became:

$$a_{CaO} = \frac{\%S}{A} \bigg/ \frac{\%S^{o}}{A^{o}} = \frac{(\%S).A^{o}}{(\%S).A.}$$

This technique of using a standard reference slag of unit lime activity was the only way in which these authors could calculate lime activities because there was no information available on the activity coefficient of calcium sulphide. Inherent in this technique is the assumption that γ_{CaS} is constant and equal to the γ_{CaS} of the standard slag, for every slag investigated. The present work, has however, yielded some information on γ_{CaS} and indications are that the above assumption is not valid. Therefore, as will be seen later, the results of Kalyanram and Bell, which are in good agreement with those of Carter and Macfarlane, have been recalculated using γ_{CaS} values derived here.

After the standard slag had been equilibrated with the gas mixture, some of the lime would have been converted to calcium sulphide and therefore the lime activity value would no longer be equal to unity. This was observed by Carter and Macfarlane who suggested that perhaps a_{CaO} would be reduced to 0.95. However, more recent data suggested that a_{CaO} could be reduced to 0.8.

Since the lime activity values of the previous authors (9),(10) and (22) have been calculated from experimental results where N_{CaS} was considerably lower than in the present work, before any comparison can be made with the present calculations some assessment of the probable effect of small amounts of CaS on lime activity values, must be attempted.

It will be noted however, from results of previous workers, that an increase of 1.0 N% on lime content makes only a slight increase in lime activity and a 1.0 N% increase in calcium sulphide content must make a smaller increase in the value of lime activity. On this basis, therefore, the assumption that lime activity remains constant over the range of N_{CaS} values being considered, seems justified.

From the equation:

$$K = \frac{a_{CaS}}{a_{CaO}} \left(\frac{pO_2}{pS_2}\right)^{\frac{1}{2}} = \frac{\%S\,\gamma_{CaS}}{a_{CaO}} \cdot \frac{1}{A}$$

a straight line relationship for a plot of $(\%S)$ against $\left(\frac{pS_2}{pO_2}\right)^{\frac{1}{2}} = A$ means that the function $\frac{\gamma_{CaS}}{a_{CaO}}$ must be a constant.

When a curved relationship is obtained for the plot of $(\%S)$ against A, the function $\frac{\gamma_{CaS}}{a_{CaO}}$ is no longer constant and since it has been shown that a_{CaO} may be considered to be constant, then any variation of $\frac{\gamma_{CaS}}{a_{CaO}}$ must be due to a variation in the value of γ_{CaS}.

As has already been mentioned, it is possible to recalculate the values of lime activity obtained by Kalyanram and Bell using the values of γ_{CaS} derived from the present work and obtained as follows:

From the equation: $CaO + \frac{1}{2}S_2 = CaS + \frac{1}{2}O_2$

$$K = \frac{a_{CaS}}{a_{CaO}} \left(\frac{pO_2}{pS_2}\right)^{\frac{1}{2}}$$

or $a_{CaO} = \frac{a_{CaS}}{K.A.}$ $\qquad \therefore a_{CaO} = \frac{\%S\,\gamma_{CaS}}{K.A.}$

However, since α_{CaO} is constant, the calcium sulphide activity coefficient for a slag sulphur content below saturation may be obtained from:

$$\frac{\dfrac{\%S \; \gamma_{CaS}}{A}}{\dfrac{\%S^0 \; \gamma^0}{A^0}} = 1$$

Where the superscript refers to the saturated slag.

Values of γ_{CaS} can be obtained directly from curves of the type shown in fig. 4. A convenient way of doing this is to draw a line from the origin through the point in question to the line representing calcium sulphide saturation. The reciprocal of the intercept which the line makeswith this saturation line gives the required value of γ_{CaS}. In this way, new lime activity values have been calculated using these values for the activity coefficient of calcium sulphide.

The actual experimental results (10) have been modified to take into account any difference in calcium sulphide free lime content and the A values have been recalculated to the same basis as those used in the present work. The discrepancy here was due to the use of different thermodynamic data for the reaction,

$$\tfrac{1}{2}S_2 + O_2 = SO_2$$
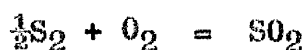
the A values of Bell and Kalyanram being between 50 and 150 lower than those used here.

It will be noted, that when the results of these workers are recalculated using the values of γ_{CaS} obtained from this investigation, the new lime activity values show excellent agreement with those of the present study (fig.7).

The experimental results of Sharma and Richardson (22) have been replotted as weight percent sulphur against $^{pH_2}/pCo_2$ rather than log weight percent sulphur against $^{pH_2}/pCo_2$ and are shown in figure 8. The compositions of slags A and B are such that, on losing lime in the form of calcium sulphide, the new compositions move into a two phase region and since the effect of calcium sulphide on the liquidus cannot be readily estimated, it was considered that no corelation with the results of the present work could be made.

Slags D and E, however, compare reasonably well from a composition point of view with slags CA1 and CA3 but for D and E it must be noted that the original composition has changed as sulphur is absorbed and also, the plot is on a basis of $\frac{pH_2}{pCo_2}$ which is proportional to $\frac{1}{pO_2}$. While this is approximately equivalent to A value, a slight correction would also be required here. It is difficult to assess the effect of these two factors on the position of the final points on the plot but it would seem that, for both these slags, saturation with calcium sulphide occurs between 1.5 and 2.0%S and this is in reasonable agreement with the present results.
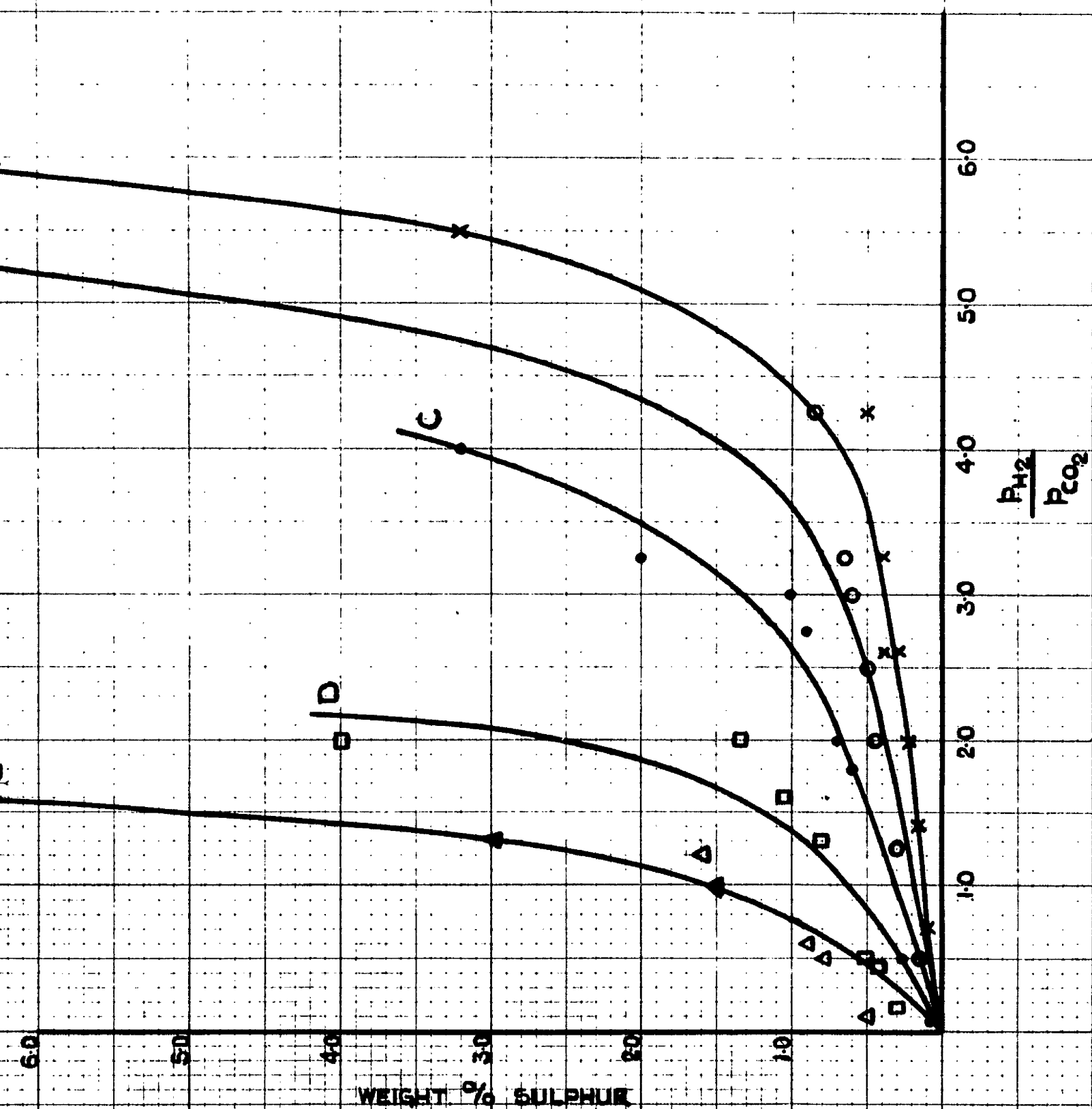
FIGURE-8

In table I of the publication by Sharma and Richardson, these authors indicate sulphide capacity (C_S) values calculated at CaS saturation for the slags investigated. Since

$$C_S = \%S \left(\frac{pO_2}{pS_2} \right)^{\frac{1}{2}}$$

an A value corresponding to an experimental point for D and E may be obtained, enabling these points to be plotted on graphs in fig.4 corrections being made to bring the compositions onto the same CaS free lime basis as those of this investigation. In a similar fashion to that already described for Bell and Kalyanram it is then possible to calculate a_{CaO} values using the present results for γ_{CaS}. As will be seen from fig.7, the values of lime activity so obtained, show excellent agreement with the lime activities calculated from the experimental results of this investigation.

Lime-alumina-silica system.

The results obtained for the slags investigated in this system, shown in table II, have been plotted and are shown in figs 9 to 15. As for the lime-alumina system, previously discussed and except for slag M, the calcium sulphide saturation level is clearly recognisable by the sudden increase in slag sulphur content corresponding to only a slight increase in the sulphurising potential of the gas with which it is in equilibrium. Again, a correction has been applied to take into account the alteration in composition of the slag as it gains or loses sulphur; this correction is in most cases small and probably within the limits of experimental error. It has already been explained that, because of the rapid decrease of lime activity as the lime content of the slags decreased and the consequent difficulty of saturating these slags with calcium sulphide with the sulphurising potential available, the range of slags investigated has been rather restricted.

The graphs plotted in figs. 9 to 15 show that the plot of $(\%S)$ against $(pO_2/pS_2)^{\frac{1}{2}}$ obtained for the less basic slags, shows a straight line relationship but for the slags of higher lime content, this plot tends to give a slightly curved line. Since it can again (as for the lime-alumina system) be reasonably assumed that the lime activity remains substantially constant as sulphur is absorbed by the slag, it must be deduced that, for the more basic slags, the calcium sulphide activity coefficient increases fairly rapidly at low slag sulphur contents.

SILAGE

(%) 4·0   3·0   2·0   1·0

A VALUE

500   1000   1500   2000

FIGURE-9

SLAG-F

SLAG-D

(%S)

(%S)

A VALUE

A VALUE

FIGURE-10

SLAG-H

SLAG-G

(%S)
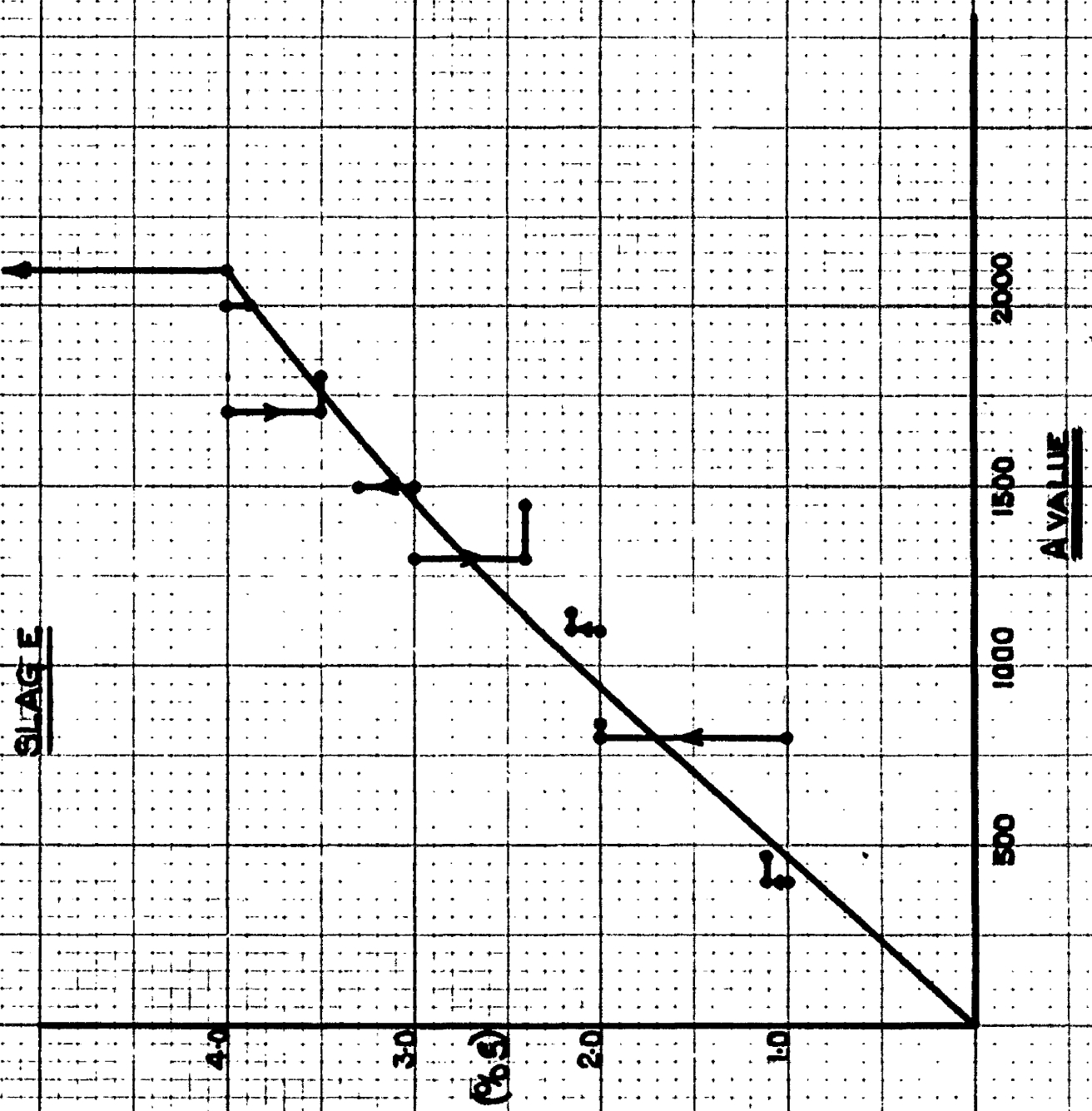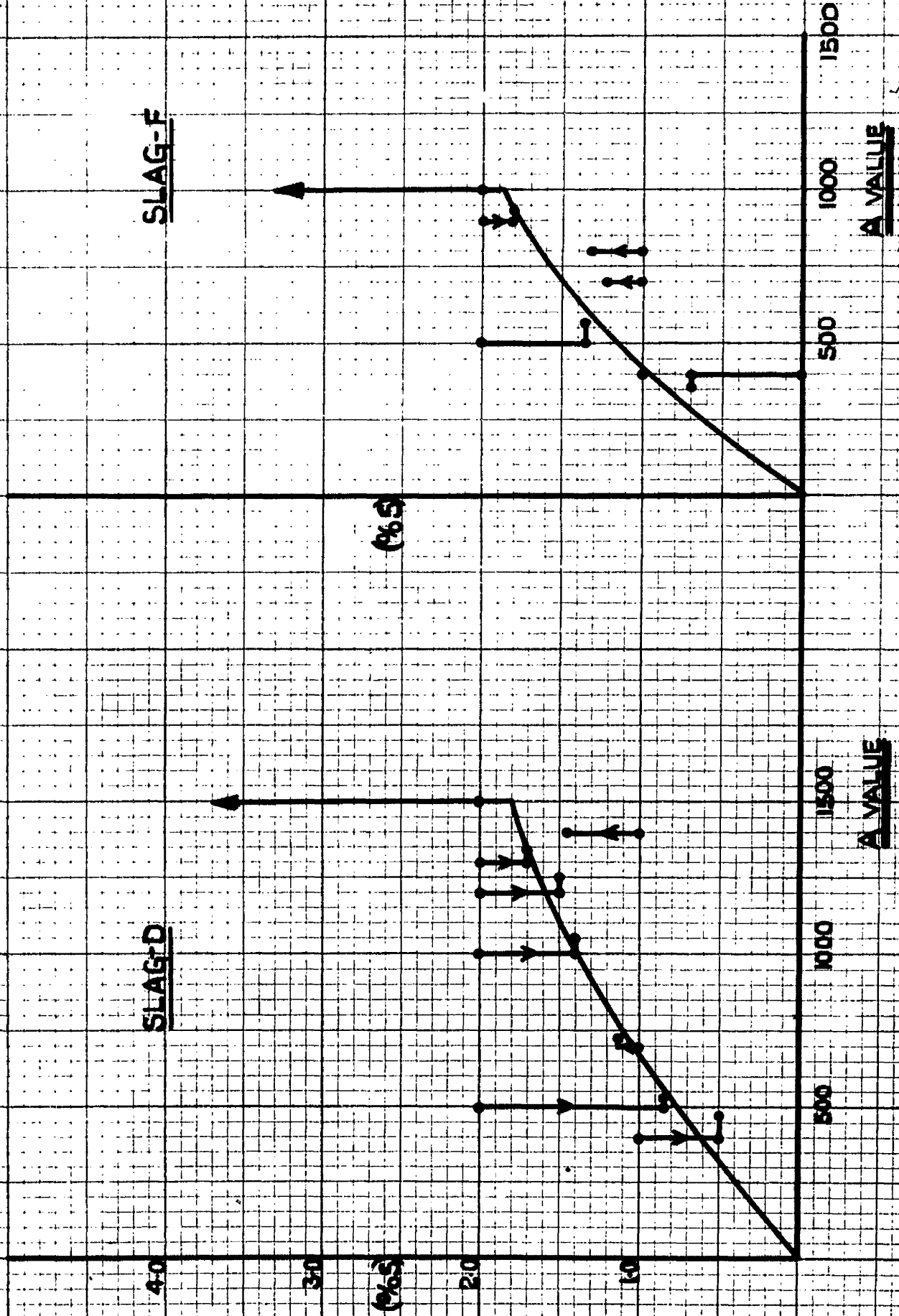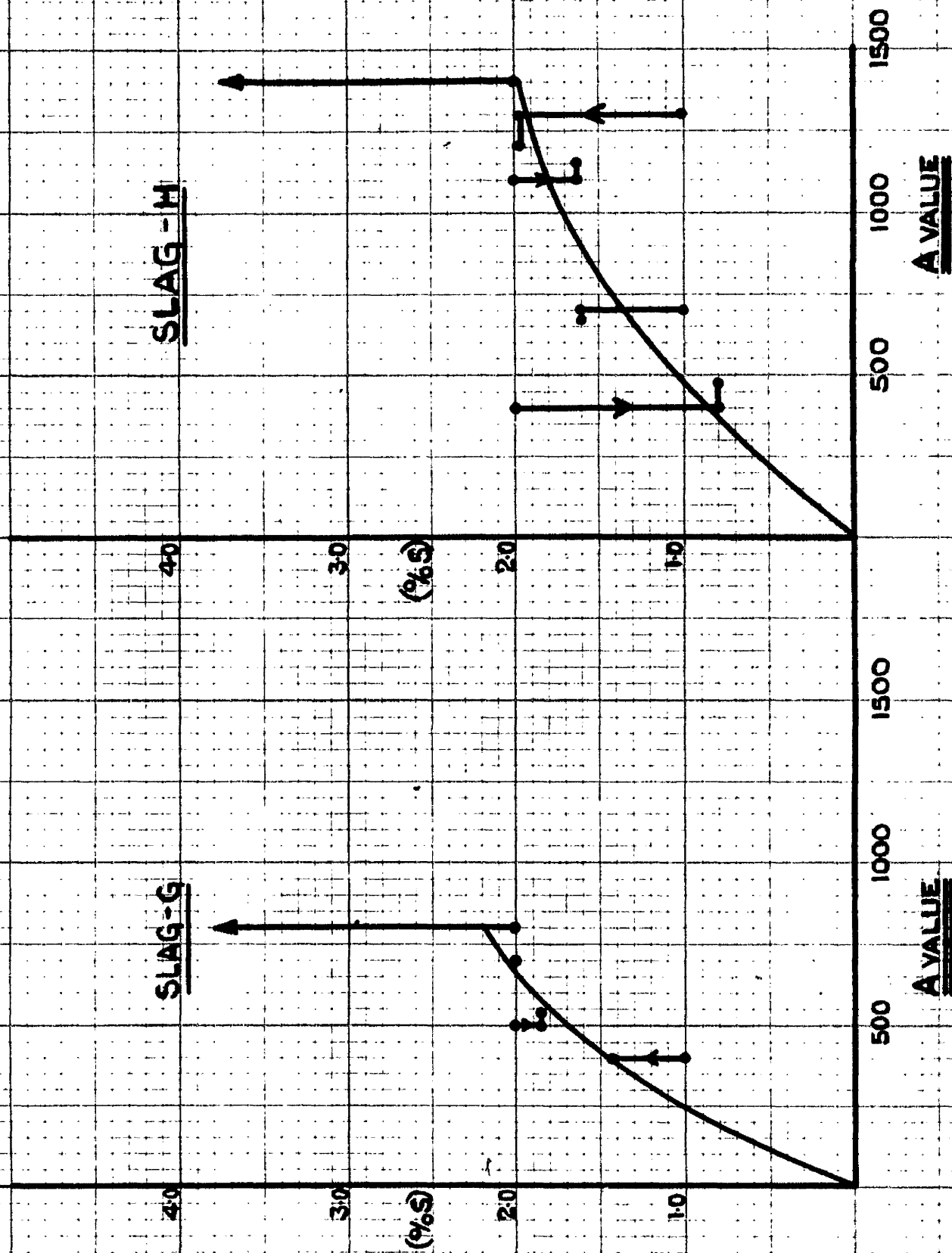
A VALUE
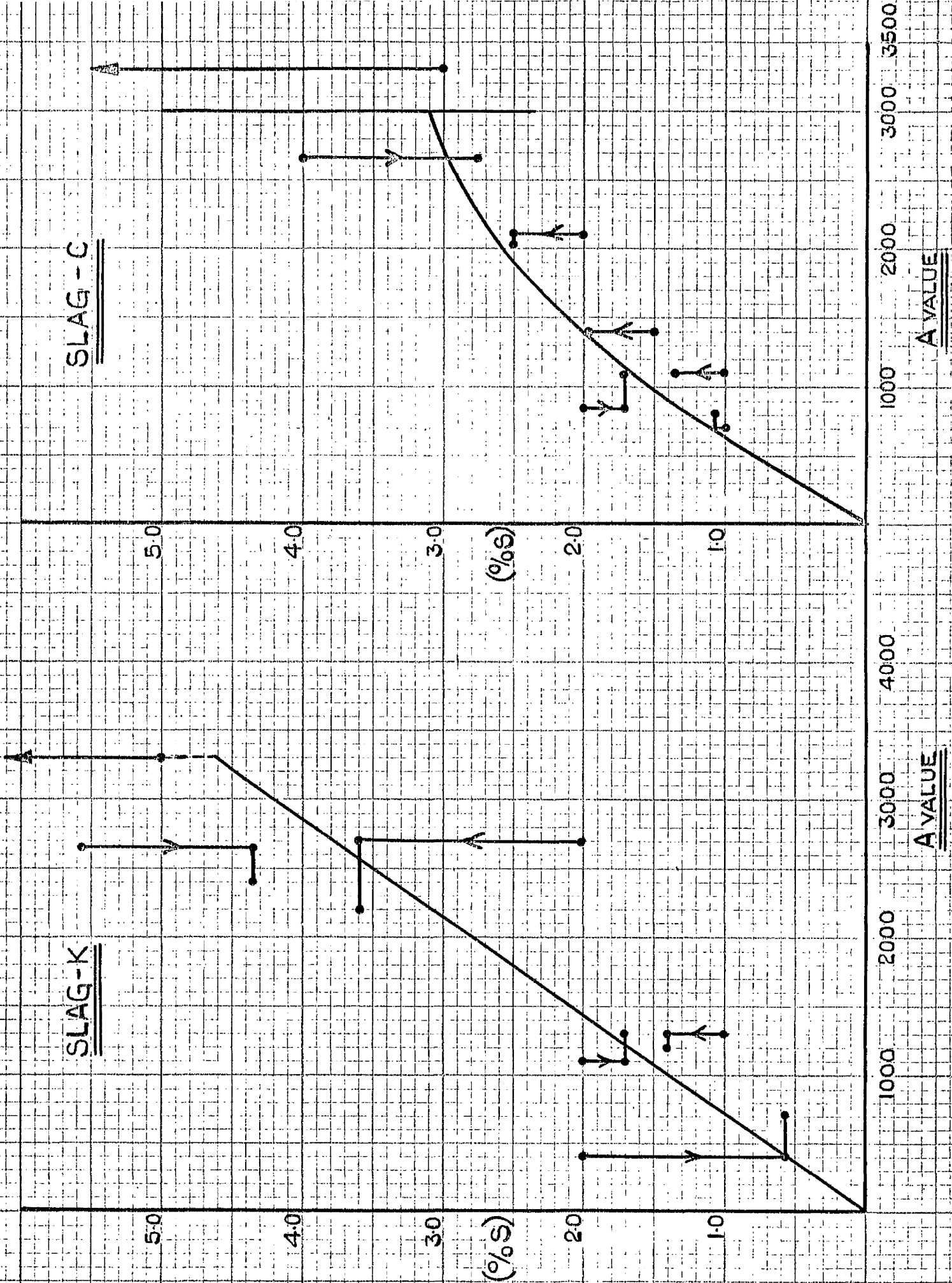
A VALUE

FIGURE-11

FIGURE-12
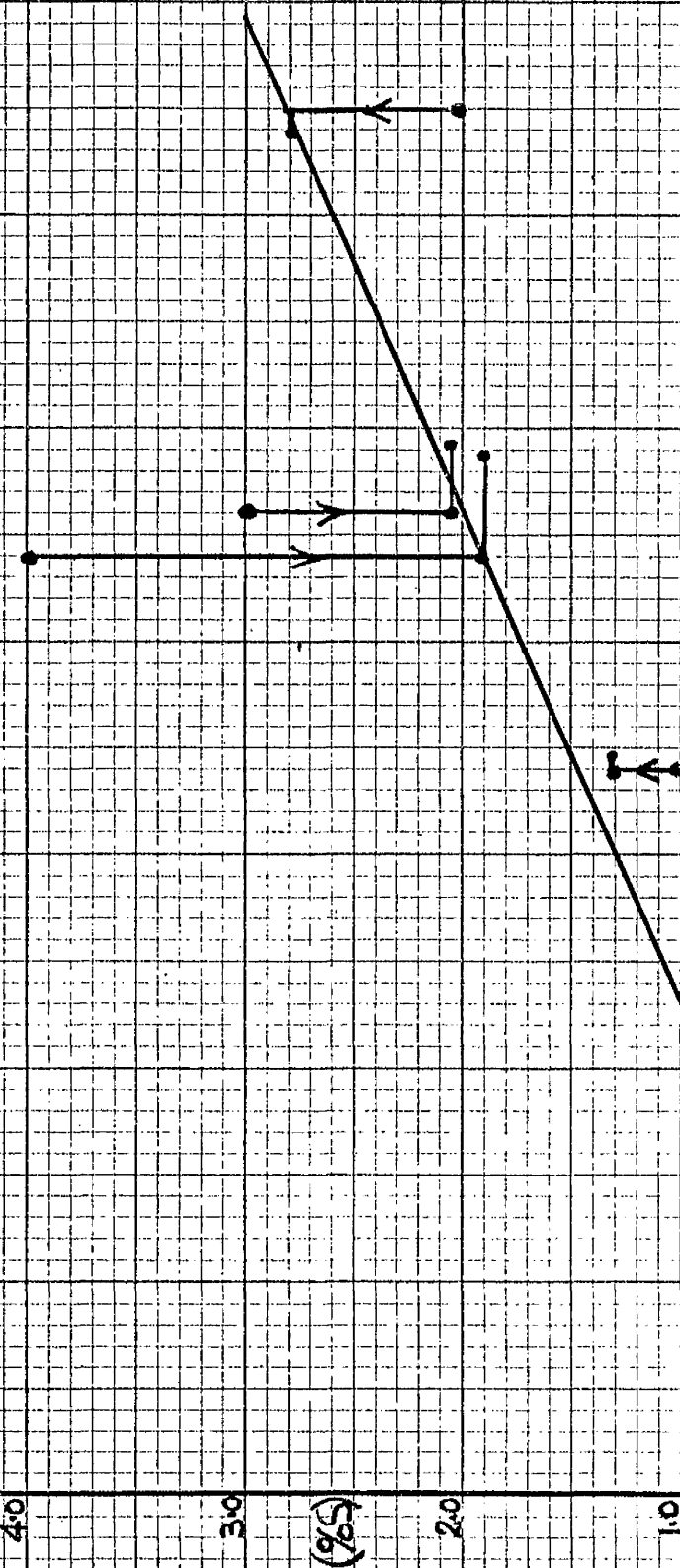
SLAG-L
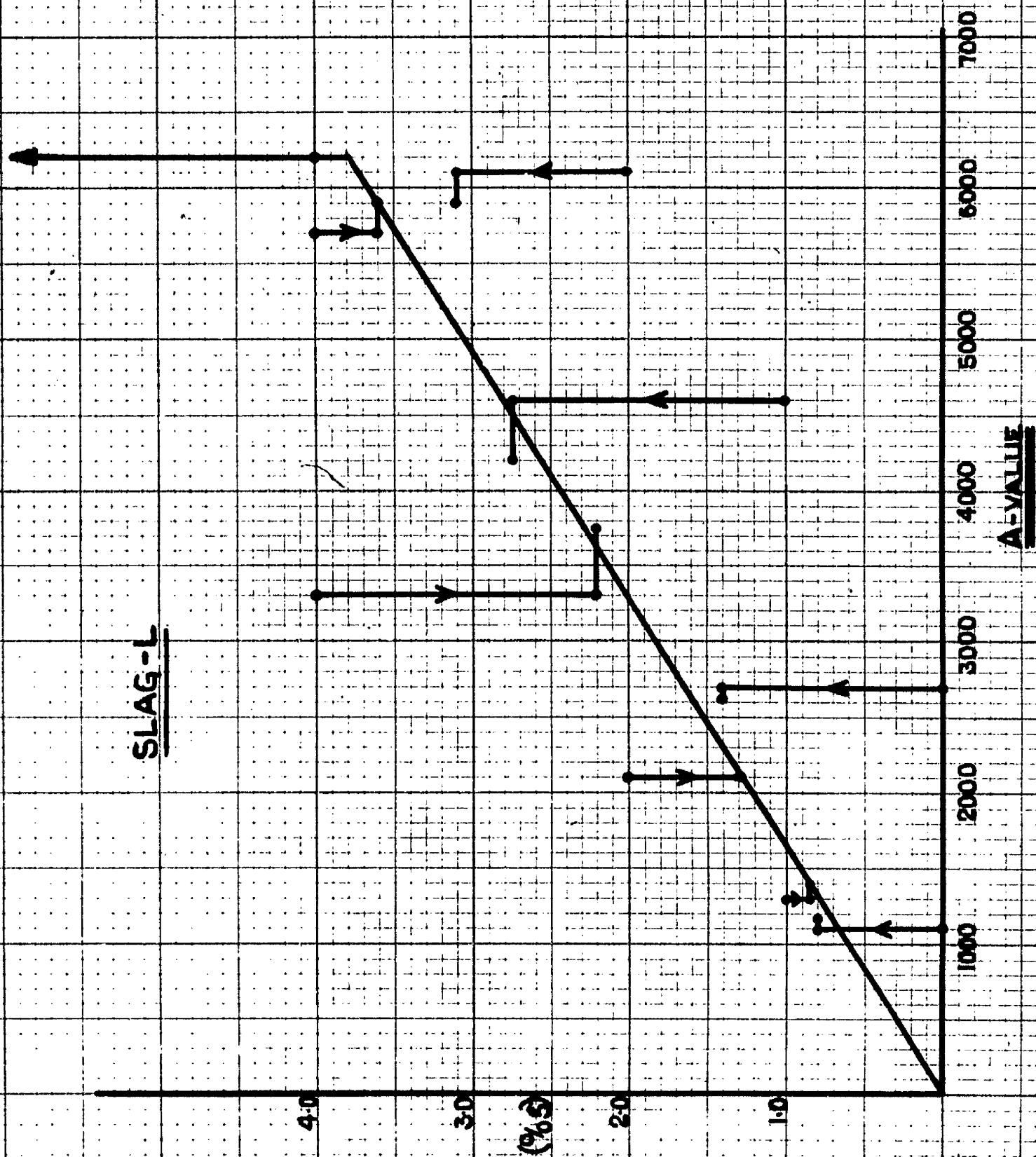
FIGURE-13

SLAG-N

A VALUE

FIGURE-14
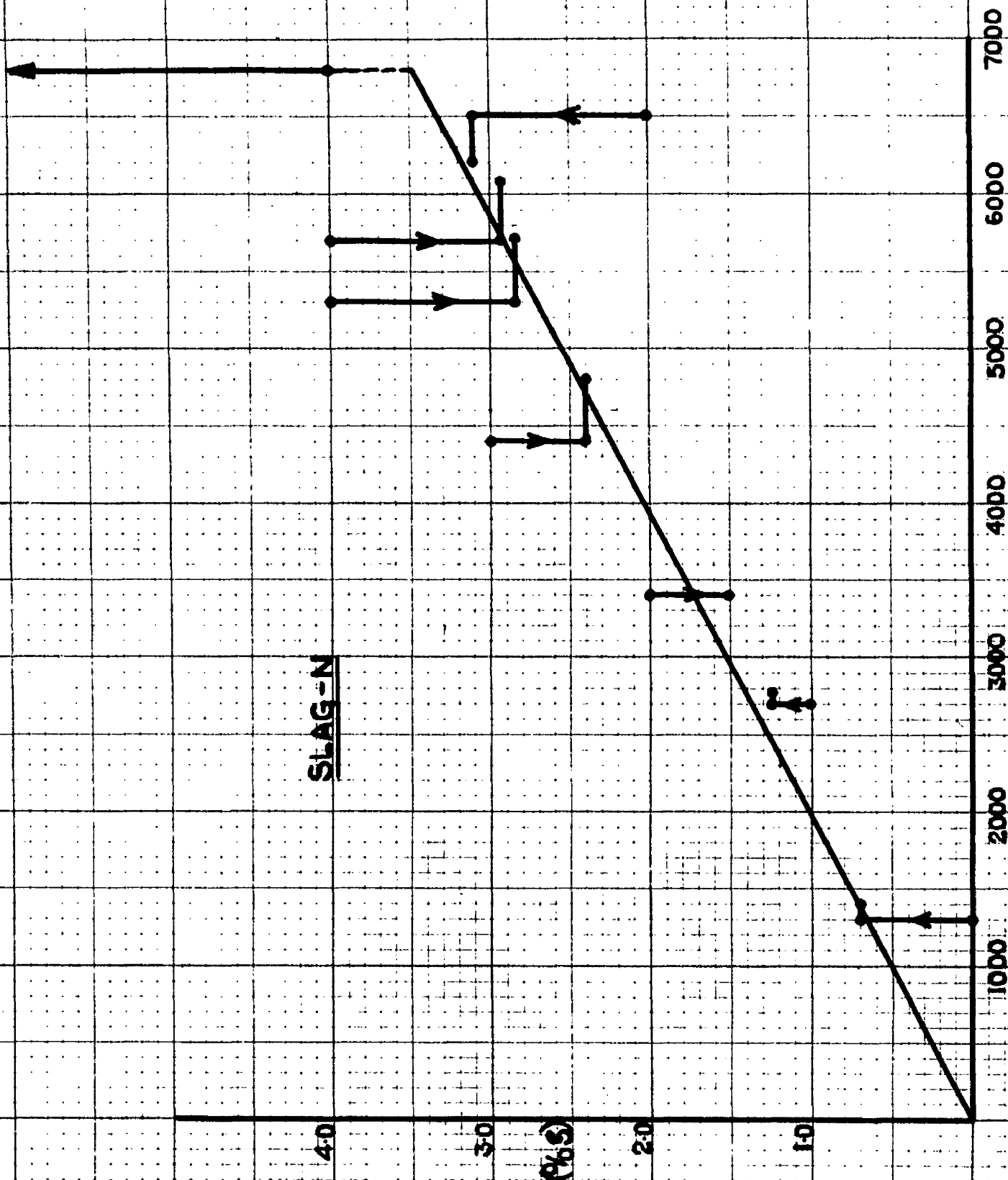
SLAG-M

FIGURE-15

A VALUE

(%S)

The percentage sulphur corresponding to calcium sulphide saturation for each slag, as read from figs. 9 to 14 has been plotted on a ternary diagram in figs. 17 and 18. In a paper on the solubility of calcium sulphide in the lime-silica system, Sharma and Richardson (16) quote a calcium sulphide saturation limit at 1500°C for a lime-alumina-silica slag of composition 58.5% lime, 7.6% silica and 33.9% alumina. Although the results of the present investigation disagree with those of Sharma and Richardson (22) for lime-alumina the same disagreement need not necessarily hold for the results in the lime-silica system since in this case the saturation levels were obtained in a different way. The calcium sulphide saturation level reported by these authors for the ternary slag mentioned above, has therefore been plotted in fig. 17 and found to be in reasonable agreement with the results of the present investigation.

From these saturation results, contour lines have been drawn representing constant sulphur levels corresponding to calcium sulphide saturation. Here, the lime-alumina results have been used to link up with the values noted in the ternary. For the binary system, the sulphur content corresponding to calcium sulphide saturation appears to be fairly constant until the lime-alumina ratio becomes less than 2 to 1. Thereafter a rapid increase occurs, a trend which appears to be continued with slag CA2.
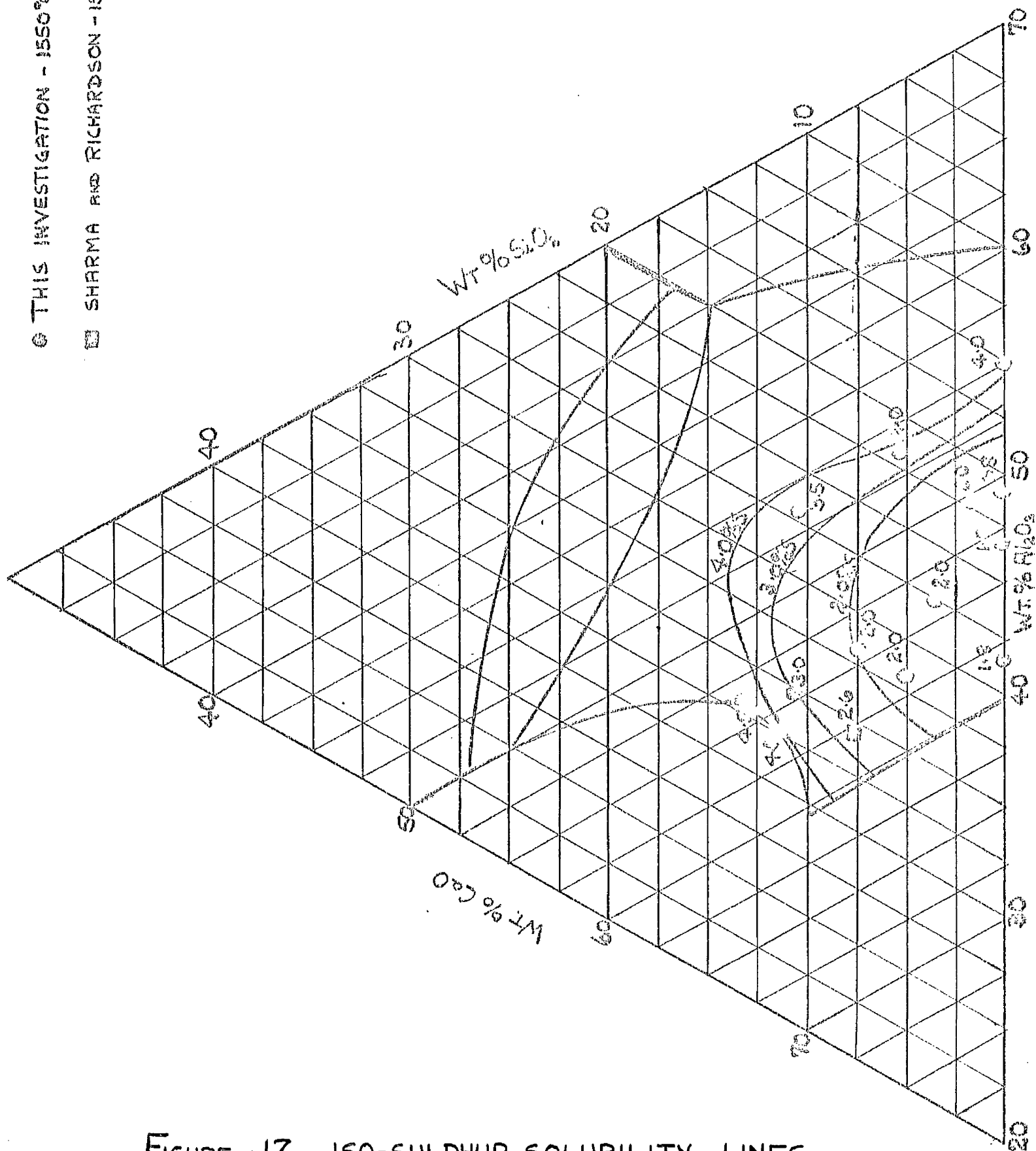
FIGURE - 17   ISO-SULPHUR SOLUBILITY LINES
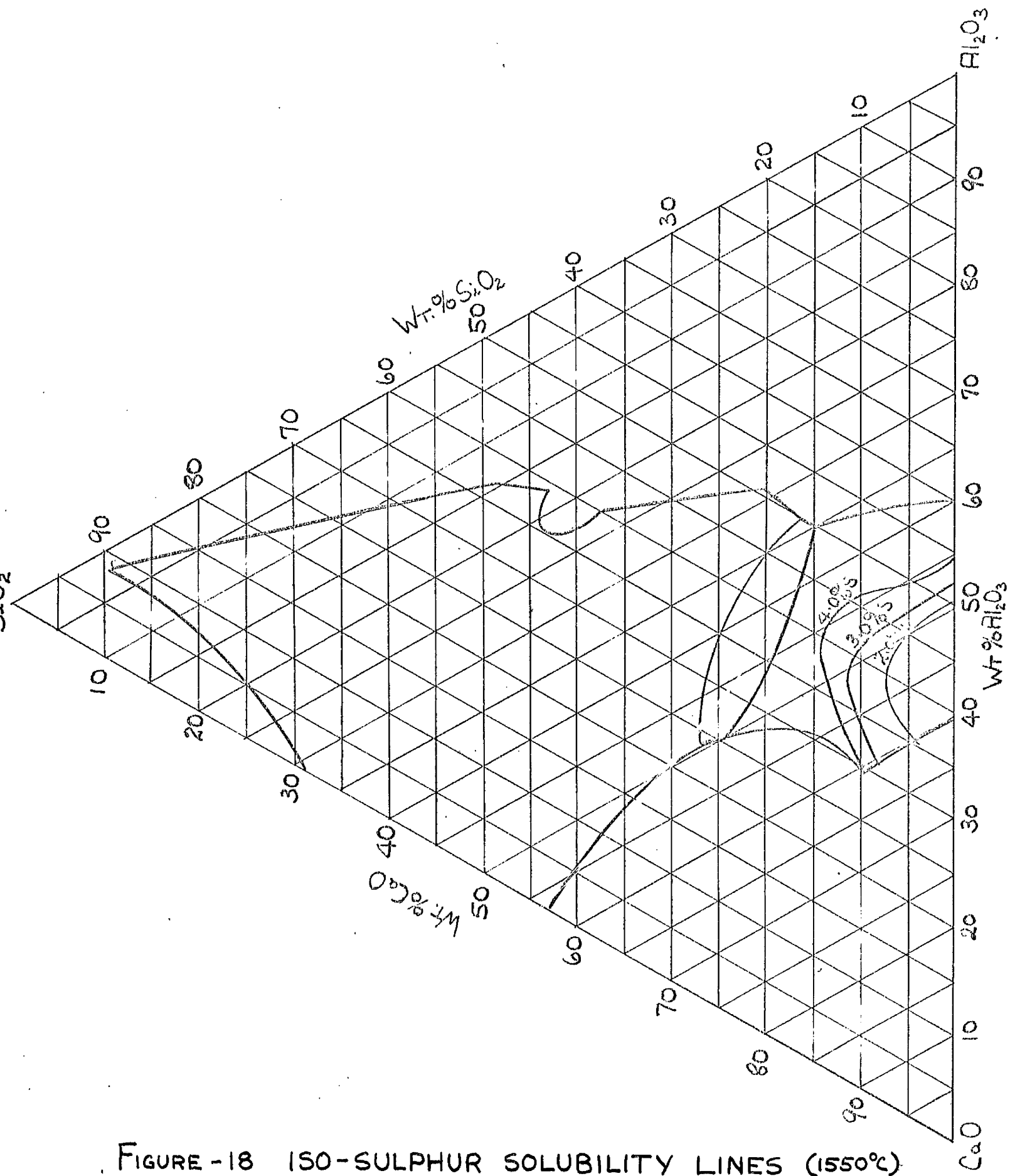
FIGURE -18   ISO-SULPHUR SOLUBILITY LINES (1550°C)
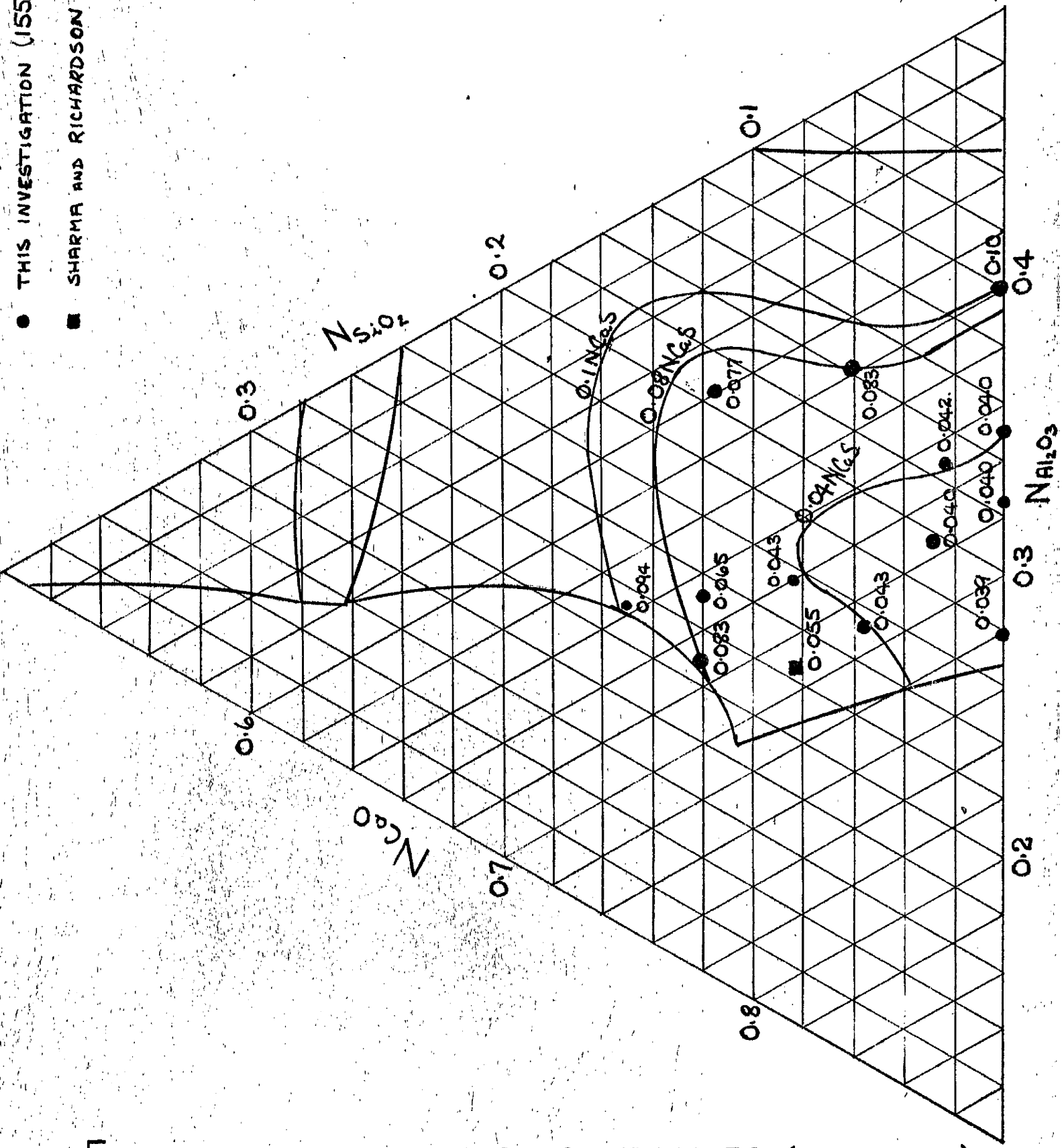
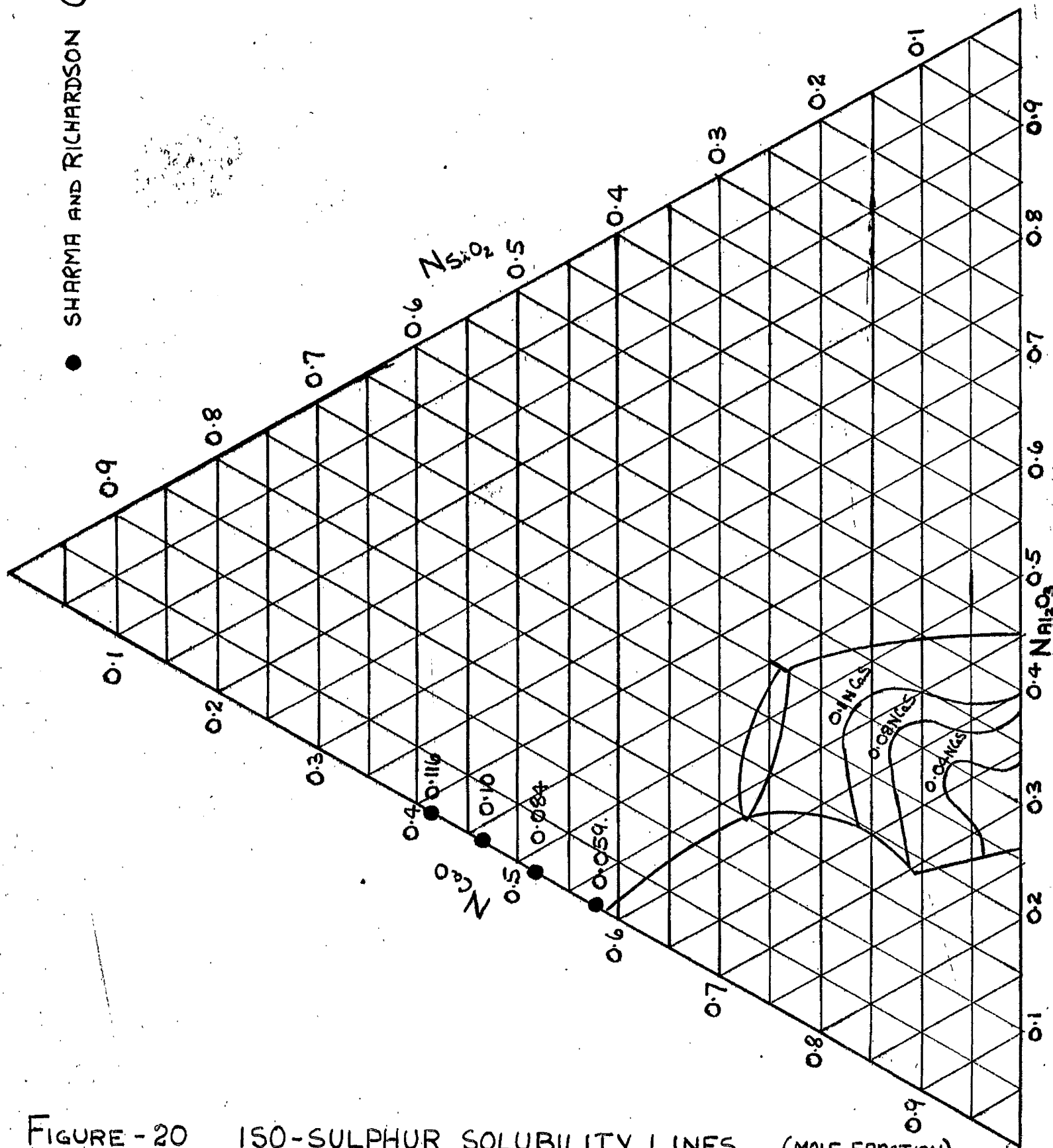FIGURE-19   ISO-SULPHUR SOLUBILITY LINES (MOLE FRACTION)
(1550°C)

FIGURE - 20   ISO-SULPHUR SOLUBILITY LINES   (MOLE FRACTION)
(1550°C)

These saturation values have also been plotted on a mole fraction scale and are shown in figs. 19 and 20. Here the calcium sulphide solubility level appears to increase as N_{CaO} decreases above a silica/alumina ratio of 3/1. For lower silica/alumina ratios the solubility appears to be more affected by the silica content of the slag and increases as N_{SiO_2} increases. The data obtained by Sharma and Richardson for the lime/silica binary are also shown in fig. 18. The unexplored region of the ternary system between the results in the lime silica binary and those obtained in this investigation is so large however, that it does not seem possible to relate the two sets of data.

From the equation:

$$CaO + \tfrac{1}{2}S_2 = CaS + \tfrac{1}{2}O_2$$

it has been shown that $a_{CaO} = \dfrac{1}{K.A}$ and values of the lime activity corresponding to the slag composition at calcium sulphide saturation (and therefore $a_{CaS} = 1$) have been calculated. These lime activity values have been plotted on a ternary diagram as shown in fig. 21 and iso-lime activity lines have been drawn on the basis of these results. Accurate location of these iso activity lines is not easy because of the paucity of data.
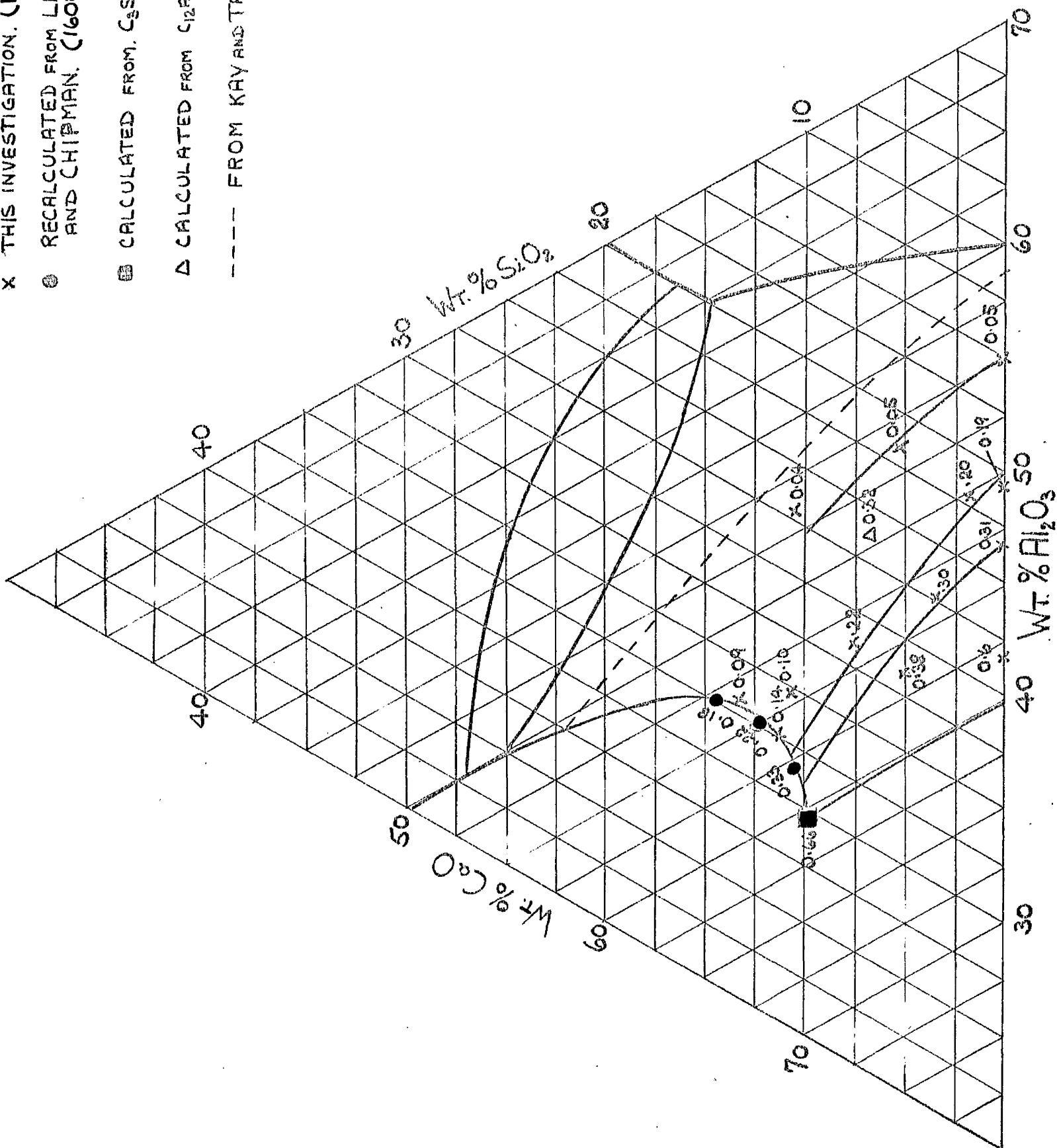
FIGURE - 21   ISO-LIME ACTIVITY LINES

Chipman (13) and Kay and Taylor (14) have published iso-activity contours for this region of the lime-alumina-silica system. These iso-activity lines have been obtained from a Gibbs-Duhem type integration using silica activity data. The actual lime activity values based as they were on the Carter and Macfarlane lime activities in the lime-alumina system cannot be expected to be in good agreement with the lime activities of the present study but comparison of the slopes of the iso-lime activity contours is of some value. To obtain iso-activity lines representing high lime activity values, the above authors extrapolated beyond the range of available silica activity data and for this reason, comparison is not very satisfactory at high lime activity values.

The dotted line in fig.21 is reproduced from the publication of Kay and Taylor and is in good agreement with Chipman's data. This line has been calculated without appreciable extrapolation and it will be observed that it is parallel to the iso-activity lines obtained here. Since the slope of the iso-activity contours obtained from the Gibbs-Duhem type integration is the same as those obtained in this investigation it follows that there is good general agreement between the two sets of data, at least so far as the shape of the line is concerned.

To give a crosscheck on the lime activity values calculated here, some independent measurement of lime activities was sought. Unfortunately, no experimental determinations of lime activity have previously been carried out in the region of the lime-alumina-silica ternary system studied in this investigation. However, if silica activity values are known along the C_2S saturation boundary, then lime activities may be calculated from the reaction

$$C_2S = 2C + S$$
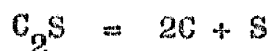
for which $$K = (a_C)^2 \times (a_S).$$

Langenberg and Chipman (23) have investigated the equilibrium of iron-carbon-silicon alloys in contact with slags containing silica, by observing the distribution of silicon between metal and slag. These experiments were carried out in graphite crucibles under a CO pressure of 1 atmosphere, so that for the reaction,

$$SiO_2(\text{crist}) + 2C(\text{graph}) = Si(1) + 2CO(g)$$

the equilibrium constant reduces to;

$$K = \frac{a_{Si}}{a_{SiO_2}}$$

From the silica activities so obtained along the C_2S saturation boundary lime activity values can be calculated from the equilibrium mentioned above. (viz. $C_2S - \underline{2C} + \underline{S}$)

It is necessary firstly however, to recalculate the silica activities obtained by Langenberg and Chipman because a recent determination of the free energy of formation of silica (24) indicates that the value used by these authors was in error by about - 8,000 cals; also, new values of γ'_{Si} are available (25). Unfortunately the data reported by in this publication (23) did not quite extend into the composition range used here and some extrapolation of the data was necessary. It should also be noted that the work was carried out at $1,600^{\circ}C$ but the higher temperature is probably of little significance.

The lime activity values, calculated from the new silica activity values along the C_2S saturation boundary are shown in fig. 21. It is perhaps fair to say that while these results are of the same order as those calculated here, the agreement is not outstandingly good. Difficulties of extrapolation may, in part, account for the discrepancies.

Further independent sources from which lime activity values may be calculated may be obtained from consideration of the lime, alumina, silica phase diagram; and if, in the first place, the effects of temperature are ignored the following data may be calculated.

At a temperature of $1,335^{\circ}C$, the phases, C_2S, C_3A and $C_{12}A_7$ and liquid are in equilibrium at the eutectic point represented by the composition, 52%lime, 41.3%alumina, 6.7%silica. These three phases can be arranged to give a reaction in which either lime or silica is formed in solution viz:

for silica $9C_2S + 2C_{12}A_7 = 14C_3A + 9\underline{S}$
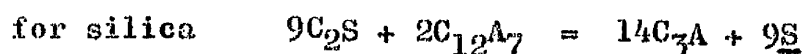
The free energy for this reaction may be obtained from the free energy values of the individual compounds and this gives a silica activity of 4×10^{-5}. Similarly the equation:
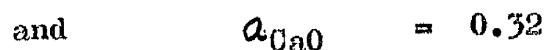
$$7C_3A = C_{12}A_7 + 9\underline{C}$$
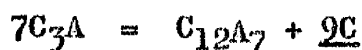
gives a lime activity of approximately unity. This latter value is obviously in error and casts some doubt on the thermodynamic data used in the calculation.

A second eutectic point is available at $1,335^{\circ}C$ and this corresponds to the composition, 49.6%lime, 43.7%alumina, 6.7%silica, where the phases C_2S, CA and $C_{12}A_7$ and liquid are in equilibrium. Here the equations,

$$5C_2S + 14CA = 2C_{12}A_7 + 5\underline{S}$$

and $C_{12}A_7 = 7CA + 5\underline{C}$

may be applied to give: $a_{SiO_2} = 4.16 \times 10^{-4}$

and $a_{CaO} = 0.32$

This result, quite apart from the fact that it is in better agreement with the values obtained from this investigation, seems much more credible and on comparing the data used in the calculations at each eutectic point, it would appear as though the free energy data for C_3A may be inaccurate.

Finally, the peritectic reaction at $1,380^\circ C$ and a composition of 48.4%lime, 47.0%alumina, and 9.6%silica where the phases, CA, C_2AS and CA_2 are in equilibrium, may be considered. In this case, however, there is some doubt about the thermodynamic data for Gehlenite (C_2AS). The free energy values for gehlenite quoted by Kelley (26) cannot be reconciled with the silica activity values reported by Kay and Taylor; these authors indicate a free energy value for gehlenite considerably higher than that mentioned by Kelley. When the data supplied by Kelley for gehlenite is used to calculate a lime activity value from:-

$$CA + C_2S = C_2AS + \underline{C}$$

the value obtained is very low and undoubtedly in error. Alternatively when the Kay and Taylor free energy value is chosen the lime activity calculated from the same equation is approximately equal to unity and again obviously in error. This gives cause to doubt the value of the gehlenite free energy used.

It should be noted that a difference of $\pm$ 2K cals in the free energy value for the reaction (i.e. gehlenite) alters the activity of lime by a factor of 2. Since the accuracy of the thermodynamic data used throughout for calculation of activities from these compounds is not greater than $\pm$ 2K cals then it is clear that these activities are of limited value as a crosscheck and can only be expected to furnish an approximate indication of the order of the activity which may be expected.

CHAPTER V.

CONCLUSION.

CONCLUSION.

It will be clear from what has gone before that the scope of this investigation has been more restricted than was intended in the first place. This restriction arose because such lime activity data as existed suggested that a substantial area of the lime alumina silica diagram could be explored using the sulphurising potential available from the gas mixture $CO/CO_2/SO_2$. In fact, the lime activity decreased much more rapidly than available data indicated, as the lime content of the slag decreased, and the sulphurising potential obtainable proved to be inadequate to saturate the less basic slags with calcium sulphide. A gas mixture of $H_2/H_2S/CO_2$ will allow an extension of the field of investigation but it is doubtful if this gas mixture would have been suitable for the whole slag range. This is because, for the highly basic slags, requiring only a low sulphurising potential to give CaS saturation control of the gas flow with this gas mixture becomes difficult.

The work has shown that the calcium sulphide saturation values vary more than had been suspected and so far as the lime-alumina system is concerned they vary in a different direction to that reported by other authors (22). However, the present results only indicate a trend over a narrow range of composition and obviously an extension of the field of investigation is necessary to determine how this/

this trend develops.

Similar remarks apply to the lime activity values determined here. In this case a wider range of investigation would give an overlap with experimentally determined silica data. Then by using binary equilibrium lines and ternary equilibrium points in the lime-alumina-silica system along with available data on the interoxide compounds, it would be possible to estimate to what extent the lime and silica activity data are compatible.

Although restricted, the results obtained suggest that this approach if extended, should be a valuable method of increasing the thermodynamic knowledge of the lime-alumina-silica system.

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APPENDIX.

CALCULATION OF SULPHURISING POTENTIAL.

The purpose of the gas mixture used for the experiments just described is to supply a sulphur partial pressure, to which the slag samples are submitted. At the same time, it is necessary to control the oxygen partial pressure of the system to ensure that all the sulphur combines with the slag as calcium sulphide. Furthermore, for maximum sulphur absorption from a given sulphur dioxide flow rate, the oxygen partial pressure should be as low as possible and hence careful control of the CO/CO_2 ratio is required if large amounts of sulphur are to be absorbed by the slag. To obtain a basis for comparison of the individual gas analysis results, quoted as sulphur dioxide percentages and CO/CO_2 ratios, a quantity known as the sulphurising potential must be calculated.

For the calculation of this quantity which is equal to $(\frac{pS_2}{pO_2})^{\frac{1}{2}}$ it is necessary to obtain thermodynamic data for the reactions between carbon monoxide, carbon dioxide, and sulphur dioxide at the operating temperature of $1,550^{o}C$. Carter and Macfarlane (9) have shown that under the conditions of the experiment, the amounts of S_6, S_8, CS, CS_2 and SO_2, formed could be ignored. Thus only the reactions involving SO_2, SO, COS and S_2 need be considered.

II.

It is the purpose of this chapter to discuss the choice of thermodynamic data for the present calculations and to assess the importance of the degree of accuracy of the various data.

Free energy data for the formation of the various gaseous compounds have been given by Kelley (27) and by Richardson and Jeffes (28). Equations for the standard free energy changes for the relevant reactions have been calculated by Kelley (27), Richardson and Jeffes (28) and St. Pierre and Chipman (29), while it is now accepted that the most reliable data for the formation of SO are those of Dewing and Richardson (30). The data of St. Pierre and Chipman along with Dewing and Richardson's data for SO have been used throughout in the calculations of sulphurising potential in the present work. The data of St. Pierre and Chipman, have been used in preference to the others because these are the most up to date data available, there being no reason for preferring any of the earlier information.

Calculation of the Sulphurising Potential, $A = (\frac{pS_2}{pO_2})^{\frac{1}{2}}$

Without the services of a computer, it is difficult to deduce the sulphurising potential from the composition of the gas mixture introduced into the furnace. It is more convenient to assume an equilibrium gas composition within the furnace i.e. the final composition/

Table IV — FREE ENERGY DATA (From St. Pierre & Chipman (29)).

Reaction	Free Energy Equation.	ΔG 1,500°C	K 1,500°C	ΔG 1,550°C	K 1,550°C
$2S(g) = S_2(g)$	$-86{,}500 + 29.2T$	-34.72		-33.27	
$\frac{1}{2}S_2 + \frac{1}{2}O_2 = SO$	$-18{,}300 - 1.26T$	-20.50	3.32×10^{2}	-20.60	2.88×10^{2}
$CO + \frac{1}{2}S_2 = COS$	$-20{,}300 + 18.07T$	11.70	3.63×10^{-2}	12.60	3.10×10^{-2}
$S_2 + 2O_2 = 2SO_2$	$-172{,}400 + 34.52T$	-111.20	5.01×10^{13}	-109.50	1.26×10^{13}
$SO_2 = S + O_2$	$129{,}450 - 31.86T$	75.00	10.0×10^{-9}	71.50	2.76×10^{-9}
* $SO_2 = SO + \frac{1}{2}O_2$	$42{,}250 - 2.4T$	38.00	2.12×10^{-5}	37.40	3.72×10^{-5}
$CO + SO_2 = COS + O_2$	$65{,}900 - 0.81T$	67.34	5.0×10^{-9}	67.38	8.35×10^{-9}
$2CO + O_2 = 2CO_2$	$-153{,}120 + 40.30T$	-61.65	3.98×10^{7}	-59.65	1.41×10^{7}

* Dewing & Richardson Date - free energy equation valid between 1,500 and 1,600°C.

composition obtained when the carbon monoxide, carbon dioxide and the various sulphur compounds have all reached equilibrium, and from the selected thermodynamic data the initial gas composition can be calculated. A series of calculation of this type must be completed, and by plotting the results as curves of CO/CO_2 ratios against 'A' value at certain percentage sulphur dioxide levels, the inlet gas composition may be related to sulphurising potential.

The calculations referred to above can best be illustrated by an example. The data used throughout in these calculations are shown in table IV.

Assume an equilibrium CO/CO_2 ratio of $19/1$ and a total partial pressure of sulphur compounds, pps = 0.008. The temperature is $1,550^{o}C$ and pressure = 760 mm.

Since $CO/CO_2 = 19/1$, pO_2 may be obtained from the reaction:-

$$2CO + O_2 = 2CO_2, \text{ for which } K_{1550^oC} = 1.41 \times 10^7$$

$$\therefore \quad pO_2 = \frac{10^{-7}}{1.41 \times 361} = 1.96 \times 10^{-10}$$

$$\therefore \quad pCO = 0.942 \text{ and } pCO_2 = 0.050.$$

Also by the above assumption, pps = $P_{SO_2} + Ps + Ps_2 + Pso + Pcos = 0.008$

If $Pso_2 = a$, Ps_2, Pso, and Pcos can be obtained in terms of a from the equilibrium constants for the relevant reactions:

$$pS = \frac{2.76 \times 10^{-9}}{0.196 \times 10^{-9}} a = 14a.$$

$$pS_2 = \frac{a^2}{1.26 \times 10^{13} (0.196 \times 10^{-9})^2} = 2,100,000a^2$$

$$pSO = \frac{3.72 \times 10^{-5}}{1.40 \times 10^{-5}} a = 2.65a.$$

$$pCOS = \frac{8.35 \times 10^{-9}}{0.196 \times 10^{-9}} a.pCO = 40.1a.$$

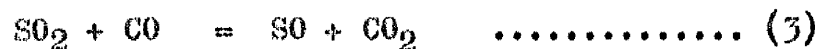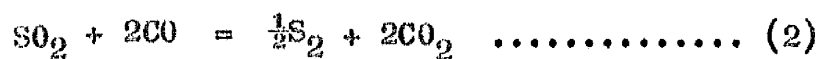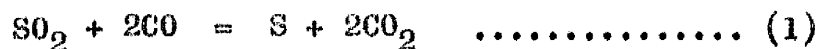$$\therefore \quad pps = 2,100,000a^2 + a(1+14+2.65+40.1) = 0.008$$

This is a simple quadratic equation which may be solved by the application of the well known formula and, rejecting the negative root, this solution gives:

$$a = 0.00005$$

and the partial pressures of the other sulphur compounds become:-

$$pS = 0.00070; \quad pS_2 = 0.00525; \quad pSO = 0.00013; \quad pCOS = 0.0020.$$

The final gas composition is controlled by the following reactions:-

$$SO_2 + 2CO = S + 2CO_2 \quad \dots\dots\dots\dots \quad (1)$$

$$SO_2 + 2CO = \tfrac{1}{2}S_2 + 2CO_2 \quad \dots\dots\dots\dots \quad (2)$$

$$SO_2 + CO = SO + CO_2 \quad \dots\dots\dots\dots \quad (3)$$

$$SO_2 + 3CO = COS + 2CO_2 \quad \dots\dots\dots\dots \quad (4)$$

From a consideration of the volume changes in these reactions it will be observed that the carbon dioxide content is increased at the expense of carbon monoxide, and sulphur dioxide, and hence, more sulphur dioxide and carbon monoxide and less carbon dioxide will be required in the initial gas mixture.

Hence, initial $\%SO_2 = 100 \; (\; pps + pS_2) = 1.33\%$

$$\%CO = 100 \; (Pco + 2Ps + 4Ps_2 + Pso + 3Pcos) = 97.1\%$$

$$\%CO_2 = 100 \; (Pco_2 - 2Ps - 4Ps_2 - Pso - 2Pcos) = 2.3\%$$

This composition would be required to obtain a CO/CO_2 ratio of $19/1$ and $pps = 0.008$ at equilibrium a $1550^{\circ}C$.

The sulphurising potential $A = (\frac{pS_2}{pO_2})^{\frac{1}{2}} = 5,200.$

The initial CO/CO_2 ratio $= 42/1.$

A series of these calculations was carried out for a wide range of CO/CO_2 ratios and for sulphur dioxide percentages between 0.9 and 1.6%. The results so obtained were then plotted as shown in fig.22 and this plot by interpolation could be used to obtain the sulphurising potential of any gas mixture used, provided the sulphur dioxide content was within the limits indicated above. The maximum CO/CO_2 ratio indicated on this plot was rarely used because of the experimental difficulty of controlling the very small flow rate of carbon dioxide required.

FIGURE-22

SULPHURISING POTENTIAL $= A = \left(\dfrac{P_{S_2}}{P_{O_2}} \right)^{1/2}$

(1550°C)
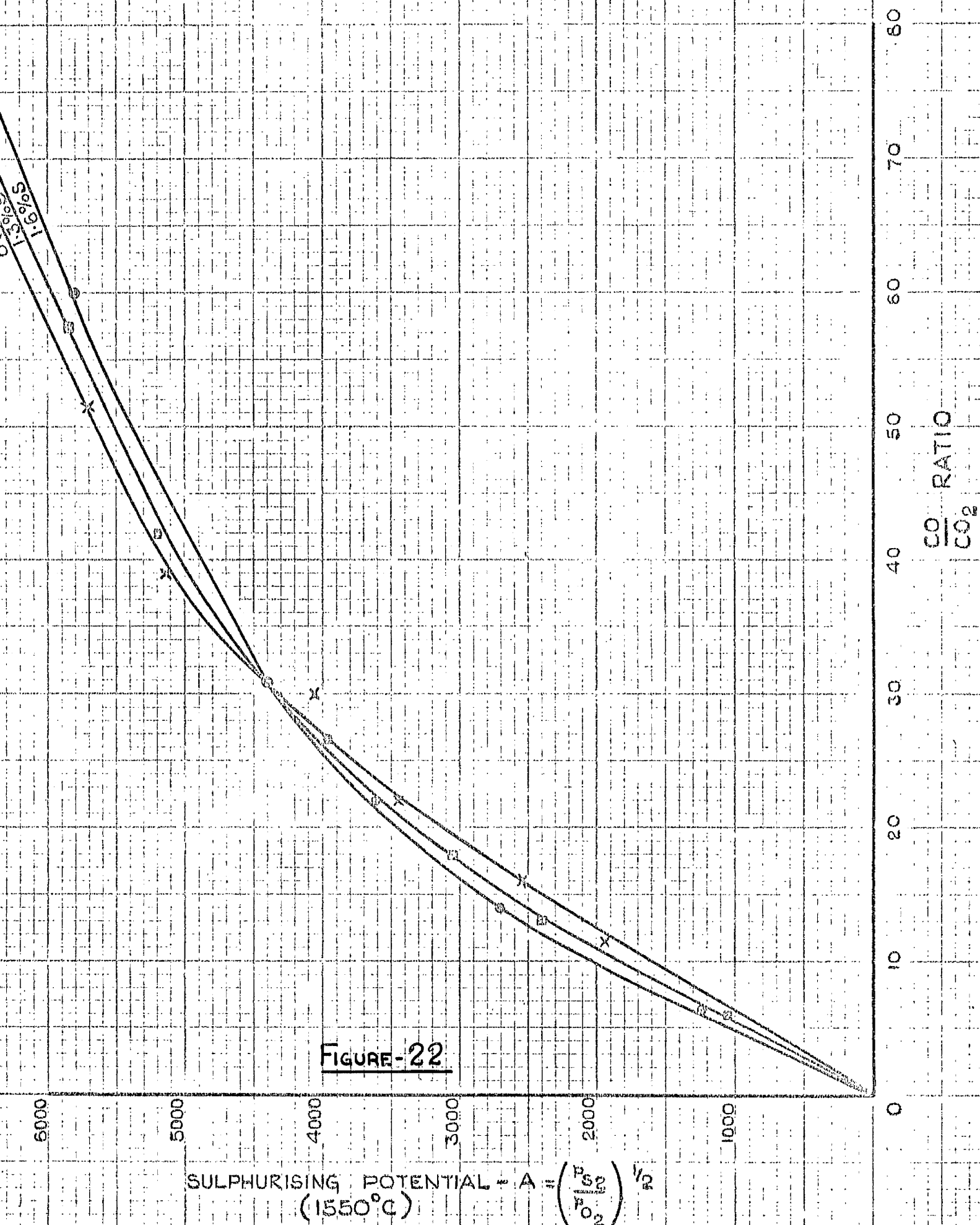
CO / CO₂ RATIO

VI.

An interesting feature of the curves in fig. 22 is the fact that when CO/CO_2 ratios are low (i.e. less than 30/1) increasing the sulphur dioxide content of the gas mixture increases the sulphurising potential as would be expected. However, as the CO/CO_2 ratio increases and becomes greater than 30/1, increasing the sulphur dioxide content lowers the sulphurising potential. This is because, sulphur dioxide, apart from being a source of sulphur is also a source of oxygen and this oxygen contribution becomes significant when the carbon dioxide content of the mixture is low. In short, a high sulphurising potential becomes more dependent on a low oxygen partial pressure than on a high sulphur partial pressure, and under these conditions the oxygen contribution of the sulphur dioxide is tending to cancel out any advantage obtained from the increased partial pressure of sulphur. For this reason, the gas mixture of sulphur dioxide, carbon dioxide and carbon monoxide is not entirely satisfactory for work where very high sulphurising potentials are required. By comparison, if hydrogen sulphide is used as a source of sulphur, along with hydrogen and carbon dioxide, the sulphur source is not at the same time a source of oxygen and much higher sulphurising potentials are possible. The experience gained from the present work has indicated that to saturate slags of high silica activities with calcium sulphide, this latter gas mixture, of hydrogen sulphide, hydrogen and carbon dioxide will be necessary.

Effect of Accuracy of the Thermodynamic data on the Sulphurising Potential Calculation.

It will be clear from the sample calculation shown above that since the partial pressures of S_2 and COS are considerably greater than those of S and SO, the two most significant reactions are those from which pS_2 and pCOS are calculated, viz:

$$S_2 + 2O_2 = 2SO_2 \quad \ldots\ldots\ldots\ldots (5)$$

$$CO + SO_2 = COS + O_2 \quad \ldots\ldots\ldots\ldots (6)$$
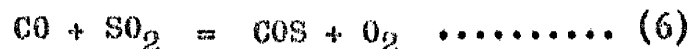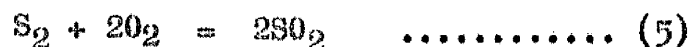
Also, it should be noted that the data for reaction (6) is derived from the data for reaction (5) along with that of the reaction:

$$2CO + S_2 = 2COS \quad \ldots\ldots\ldots\ldots\ldots (7)$$
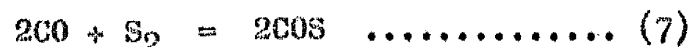
Thus, it is clear that reaction (5) is of considerable significance in the calculation affecting as it does, the two most significant partial pressures, particularly when it is realised that the value of the sulphur partial pressure directly affects the value obtained for the sulphurising potential $= \left(\dfrac{pS_2}{pO_2}\right)^{\frac{1}{2}}$ and although this quantity is equally affected by the value of pO_2, derived from the equation:

$$2CO + O_2 = 2CO_2$$

the thermodynamic data for this reaction are fairly well established and the free energy values calculated from the data of Kelley, St. Pierre and Chipman, and Dewing and Richardson, are in good agreement, the

maximum/

maximum difference being about 150 cals. Therefore, the accuracy of the data for the reaction:

$$S_2 + 2O_2 = 2SO_2$$

is a matter of cardinal importance.

When results obtained in the present investigation were compared with those of Bell and Kalyanram (10), it was apparent that there was some discrepancy in the sulphurising potentials calculated by that worker and those calculated here. The data used by the above authors (10) (and also by Sharma and Richardson (16) (22)), are those of Dewing and Richardson, i.e. Richardson and Jeffes combined with the SO information of Dewing and Richardson. The free energy values of St. Pierre and Chipman used here were the most recent available and to enable a closer comparison to be made between the two sets of data, several 'A' value calculations were carried out at 1,500°C for the St. Pierre and Chipman data used at 1,550°C in this investigation.

As a result of this exercise it became clear that the discrepancy lay with the slightly different free energy values quoted by the authors for the reaction:

$$S_2 + 2O_2 = 2SO_2$$
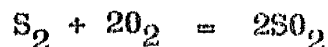
The calculated sulphurising potential of the gas mixture depends on the results obtained for sulphur partial pressure (as S_2) and oxygen partial pressure in the system. For the reaction:

For the reaction:

$$2CO + O_2 = 2CO_2$$

which controls the oxygen partial pressure, the data quoted by three groups of authors is in good agreement, as has already been mentioned. The reaction:

$$S_2 + 2O_2 = 2SO_2$$

controls the sulphur partial pressure of the/system and here again it would appear as though the difference between the individual sets of data was of little significance (see table V below.)

Table V.

Free Energy & Equilibrium constant values for reaction $S_2 + 2O_2 = 2SO_2$ at $1,500^\circ C$

Kelley.	Richardson & Dewing.	St. Pierre & Chipman
$\Delta G = -112.019$ $K = 6.461 \times 10^{13}$	$\Delta G = -111.88$ $K = 6.166 \times 10^{13}$	$\Delta G = -111.2$ $K = 5.01 \times 10^{13}$

The difference between the free energy values of St. Pierre and Chipman and Dewing and Richardson is 0.68K cals and although this would appear to be an insignificant factor it obviously has a considerable effect on the value of the equilibrium constant for the reaction. This effect is transmitted to the value of the sulphur partial pressure obtained and it was clear, on comparing the calculations using the two sets/

sets of data, that the discrepancy came from the uncertainties concerning the free energy data for this reaction.

To check the effect of this, calculations were carried out in which $\frac{1}{2}$K cal was added to the original St. Pierre and Chipman free energy data for this reaction. The new value of ΔG for $S_2 + 2O_2 = 2SO_2$, gave a new value for the partial pressure of S_2 in the system and the effect of this was indicated by the new value for the sulphurising potential of a given gas mixture, calculated therefrom. Examples of this are shown in table VI below.

Table VI.

| Temp.	Equilib. CO/CO_2	Equilib. pps.	A value for ΔG St. Pierre & Chipman.	A value for ΔG St. Pierre & Chipman.+ 500cal
1,500	1.5/1	0.008	435	407
1,500	3.0/1	0.007	1,113	1,060
1,500	2.5/1	0.007	880	844
1,550	19/1	0.008	5,200	5,000

It will be observed that the difference in sulphurising potential resulting from this very slight alteration to the free energy for this one reaction is considerable. Although this point has already been mentioned it will be further emphasised that the data for the reaction:

$$S_2 + 2O_2 = 2SO_2$$

is/

XI.

is combined with the data for

$$CO + \tfrac{1}{2}S_2 = COS$$
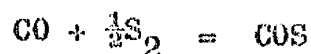
to give the data required for the reaction:

$$CO + SO_2 = COS + O_2$$

Thus the effect calculated above represents only part of the influence a slight alteration in the data for the reaction:

$$S_2 + 2O_2 = 2SO_2$$

will have on the calculated sulphurising potential. The difference in the A values of Bell and Kalyanram and those of the present investigation (these differences varied between 50 and 150 depending on the actual magnitude of the A value) may be attributed very largely to the different data selected for this reaction.

A further point emerges from this observation. Thermodynamic data is rarely accurate to $\pm \tfrac{1}{2}K$ cal and therefore the accuracy required for consistent calculations of sulphurising potentials is unlikely to be available.

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