A STUDY OF ACTIVITIES OF THE CONSTITUENTS OF MOLTEN SLAGS.

SUMMARY.

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February, 1959.

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The effect of Magnesia on the activity of lime in $CaO-Al_2O_3-SiO_2$ slags has been studied. The experiments consisted of equilibrating synthetic binary, ternary and quaternary slags with $CO-CO_2-SO_2$ gas mixtures at 1500°C, the slags being held in platinum crucibles. The slags, quenched at the end of the run, were analysed for sulphur by combustion in CO_2.

The reaction has been represented as :

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

Certain differences exist in the thermodynamic data available on the gaseous compounds of sulphur, carbon and oxygen at 1500°C. From a critical survey of these data, the data of Dewing and Richardson was selected for the calculation of the equilibrium partial pressures of S_2 and O_2. The activity of lime in these slags has been determined by comparison of the equilibrium sulphur contents of the various slags with the sulphur content of a standard slag of unit lime activity.

From these results the equivalence of CaO and MgO with respect to sulphur absorption has been determined. MgO would appear to increase the activity of lime due to its basic characteristics. In $CaO-Al_2O_3-MgO$ slags 1 mol of CaO was equivalent to 2 mols of MgO, and in the $CaO-SiO_2-MgO$ slags 1 mol of CaO was equivalent to 1.5 mols of MgO.

The activity of lime in slags containing silica was found to be considerably lower than that in slags containing equivalent Al_2O_3 contents.

Lime iso-activity lines have been drawn in the systems $CaO-Al_2O_3-MgO$ and $CaO-SiO_2-MgO$. The iso-activity lines in the $CaO-Al_2O_3-MgO$ system have been determined and reported in graph form.

The effect of basicity, as expressed by the molar ratio $\frac{CaO + \frac{2}{3} MgO}{Al_2O_3 + SiO_2}$ on lime activity in the quaternary system $CaO-Al_2O_3-SiO_2-MgO$ has been discussed in the light of the experimental results.

A STUDY OF ACTIVITIES OF THE CONSTITUENTS OF MOLTEN SLAGS

by

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CONTENTS.

CHAPTER I.

INTRODUCTION.

INTRODUCTION.

The need for very high quality iron and steel cannot be over emphasised in these modern times of rapid scientific advances. The increased production of iron and steel which has been taking place throughout the world has led to a rapid depletion of good quality raw materials including scrap. As a result the industry is being forced to use leaner ores of poorer quality requiring larger amounts of coke. As 90 per cent of the sulphur charged into the blast furnace comes from the coke used, there is a significant increase in the sulphur burden, due to the usage of larger quantities of coke of increasingly higher sulphur contents. As a result, in recent years, the problem of sulphur removal in iron and steel making has assumed great importance and urgency due to this increased sulphur burden.

Although differences may exist in the actual mechanism of desulphurization in the blast furnace and the open hearth furnace, the process is essentially a transfer of sulphur from metal to slag. The desulphurization of the metal has been found to depend upon a number of factors; e.g., temperature, total sulphur, composition of the slag, metal, and gas phases; and the degree of attainment of equilibrium among the various phases. The slag composition plays an important part in both the blast furnace and the Open hearth furnace, and an intimate knowledge of the thermodynamic properties of the slag components should be of assistance in the understanding of the reactions occurring. Several workers have attempted to study the complex sulphur transfer problem using works slag-metal data, but without much success due to the complexity of the slag-metal system. The thermodynamic properties of the slag components may be determined in the laboratory by establishing equilibrium conditions for the chemical reactions involving the slag. Unfortunately slag-metal studies tend to become rather complicated due to the corrosive action of the molten metal and slag on the containers which generally consist of graphite, magnesia, or alumina. Furthermore, interpretation of the results from such studies is difficult due to the non-ideal behaviour of the different components in solution. A simplification can be introduced by eliminating the metal phase and in its stead using a gaseous phase. The advantage of this procedure is two-fold. Metallic containers can be used for the molten slag, and ideal behaviour of the individual components of the gas phase can be reasonably assumed at the higher temperatures used. The partial pressures of the gas components calculated from the known thermodynamic data can then be equated to the activities of these components.

The present investigation is mainly concerned with slag-gas equilibria and it is proposed to study the sulphur pick up by synthetic blast furnace slags from a gaseous atmosphere containing SO_2, the slags being held in platinum crucibles. From a survey of the papers published on desulphurization it was found that the role of magnesia in blast furnace slag is not very clear, though most of the investigators agree that MgO is not a good desulphurizer. The present work deals with this particular aspect and an attempt has been made to assess quantitatively the effect on sulphur pick up of the addition of MgO to CaO-Al_2O_3, CaO-SiO_2, and CaO-Al_2O_3-SiO_2 slags.

CHAPTER II.

LITERATURE SURVEY.

LITERATURE SURVEY.

The papers published up to the present on the problem of desulphurization may be classified into three broad groupings.

1. Gas-Metal Investigations.
2. Slag-Metal Investigations.
3. Gas-Slag Investigations.

Though the present work is on Gas-Slag reactions it is proposed to make a general review of the work done on the other two types of investigations, as in practice the three types of reactions are taking place simultaneously. Most of the investigations referred to in this review have been carried out using slag and metal in the molten condition. The effect of the furnace atmosphere in the Open hearth furnace prior to the complete melting of the charge was summarised by Carter.(1)

Gas-Metal Investigations.

Several workers have determined the equilibrium between molten iron and hydrogen-hydrogen sulphide mixtures. Maurer and Bischof(2) observed a linear relationship between the sulphur content of the metal and the ratio of the partial pressures of H_2 and H_2S. The values of the equilibrium constant $K = pH_2S/pH_2.\%S$ were about 100 times these of Chipman and Ta Li(3) who investigated the same reaction and obtained a value of 0.00515 for the equilibrium constant at 1600°C. The latter suggested that the beryllia crucibles used by Maurer and Bischof may have been active in picking up sulphur, and that thermal diffusion was not taken into account. Because of this discrepancy between the results of the above workers, White and Skelly(4) repeated these experiments and taking special precautions against thermal diffusion. Their results showed the experiments of Maurer and Bischof to be considerably in error due to thermal diffusion. The equilibrium constant of 0.0025 of White and Skelly is about half that of Chipman and Ta Li. The metal used by White and Skelly picked up 2.65 per cent silicon and they suggested that the silicon in the metal may be the cause of this discrepancy between their results and those of Chipman and Ta Li. This is substantiated by the results of Morris and Williams(5) who showed that the silicon content of the metal influenced the sulphur absorption.

Assuming a standard state in which the metal contained 1 per cent sulphur, Morris and Williams obtained a value of 0.00256 (at 1615°C) for the equilibrium constant. For a given sulphur content the activity of sulphur increased with the addition of silicon. If the effect of silicon content of the metal on the activity of sulphur is taken into consideration and the results of White and Skelly corrected accordingly, their constant would be still lower than that of Chipman and Ta Li. They did not favour the idea that the added element (Si) formed a compound with the iron, thereby reducing the mole fraction of free iron and increasing the activity of sulphur. Morris and Buehl(6) found that carbon had a similar but greater effect on the activity of sulphur, which increased by as much as six fold between zero carbon and saturation. In the discussion of this paper Darken(7) stated that in a solution containing Fe, C, S, the affinity of carbon for iron is much stronger than that for sulphur. Making the reasonable assumption that each carbon atom is surrounded by six iron atoms he showed that at low concentrations each atomic per cent of carbon increased the activity coefficient of sulphur by 6 per cent which is in good agreement with the observed increase (6-7 per cent).

Sherman, Elvander and Chipman(8) reinvestigated the above reaction taking special precautions to avoid thermal diffusion and found the equilibrium constant $K = pH_2S/pH_2.\%S$ was not a true constant but varied with sulphur content. By graphical extrapolation of the values to zero sulphur the true equilibrium constant was obtained utilizing the infinitely dilute solution as a standard state. Making suitable allowances for the effect of silicon, they found that the results of White and Skelly(4), and Morris and Williams(5) were in good agreement with the extrapolated values.

Sherman and Chipman(9) investigated the activity of sulphur in iron solutions containing P, C, Si, Al, Cu, Mn, and found that P, C, Si, Al, increased the activity coefficient of sulphur, whereas Cu, Mn decreased it. It was found that in ternary and more complex systems the activity coefficient of sulphur could be expressed in the form

$$f_s = f'_s \cdot f^s_s \quad \ldots\ldots\ldots\ldots$$

where f_s is the overall activity coefficient of sulphur and f'_s is the activity coefficient in the binary iron-sulphur system, f^s_s is the coefficient representing the effect of the third element on the activity of sulphur and is equal to the ratio f_s/f'_s.

Maurer and Bischof(2), and Carter and Tahir(10), studied the equilibrium between molten iron and gas mixtures containing sulphur dioxide; the former used SO_2-O_2 mixtures and the latter workers SO_2-N_2, and SO_2+O_2-N_2 mixtures. Maurer and Bischof found that the final sulphur content was proportional to the ratio pSO_2/pO_2, and suggested that the reaction occurring was $Fe + SO_2 = FeS + O_2$. Chipman and Ta Li(3) showed from thermodynamic considerations that this reaction would not be expected to be the controlling reaction, since a high positive value was obtained for the free energy change. They therefore represented the reaction between iron and SO_2 by the equation

$$3Fe_{(Liq.)} + SO_2 = \underline{FeS}(\%) + \underline{2FeO}(\%)$$

for which the standard free energy change is

$$G^\circ = +1600 - 23.32\,T$$

This was confirmed by Carter and Tahir who observed no relationship at all between pSO_2 and pO_2. At constant pO_2 values they found per cent sulphur was proportional to pSO_2, although the values obtained were not equilibrium values as equilibrium was never attained in their experiments.

It was suggested that sulphur removal from the metal was much slower than the rate of absorption because no mechanism existed for the transfer of sulphur from metal to gas except via the slag. Since sulphur vapour was found in the exit gases the reaction was considered to occur in two stages.

$$2Fe + SO_2 = 2FeO + {}^1/_2 S_2$$

$$Fe + {}^1/_2 S_2 = FeS$$

The composition of the metal phase is affected by the amount of sulphur in the gas phase, but the reverse is not the case because the sulphur content of the metal cannot influence the sulphur content of the gas current which is continuously being renewed.

Slag-Metal Investigations.

Papers published under this heading may be classified into those pertaining to Open hearth practice, and those to blast furnace practice. These studies were carried out toe contribute to the understanding of the factors which affect the reactions occurring in these two furnaces. In the laboratory it is possible to isolate these reactions, and study them individually. The present survey is restricted to investigations of sulphur removal from the metal. Application of the results obtained from experiments on reaction equilibria in the laboratory, to furnace practice, is rather limited, due to the non-establishment of equilibrium between the reactants and products in actual practice, although in certain practices equilibrium may be approached very closely.

The desulphurizing power of the slags has often been represented by the ratio of sulphur in slag to that in the metal-(S)/[S] (where the round and square brackets denote concentrations in the slag and metal phases respectively). Wentrup(11), one of the earliest workers in this field represented this ratio in an Open hearth furnace, as

$$\frac{(\Sigma S)}{[S]} = \frac{(S)_{Ca} + (S)_{Fe} + (S)_{Mn}}{[S]}$$

where $(S)_{Ca,Fe,Mn,}$ is present as sulphur associated with Ca, Fe, and Mn as sulphides. According to Wentrup lime was effective in controlling the desulphurization only if FeO and SiO_2 contents were kept low. The important effect of slag basicity and lime additions to achieve desulphurization has long been recognised. But the concept of slag basicity in terms of the slag composition has been varied. According to Maurer and Bischof(12) basicity as represented by the ratio CaO/SiO_2 was not very useful in defining the phenomenon of desulphurization. Grant and Chipman(13) regarded it as the direct partitioning of FeS, the partition coefficient increasing with the "excess base" in the slag. The latter was calculated by assuming that CaO, MgO, MnO were equivalent bases, and that they combined with the acidic oxides such as SiO_2, P_2O_5, Al_2O_3 to form certain compounds. By plotting the "excess base" which is the excess of base remaining after allowing for any possible compound formation, against the sulphur distribution ratio, an almost linear relationship was obtained, indicating that CaO, MgO, MnO were equally effective as desulphurizers.

Carter(14) expressed the desulphurization ratio by the relationship.

$$(S)/[S] = K \frac{(\Sigma nMo)}{[O]}$$, where ΣnMo is the measure of excess base. A linear relationship between the two terms was obtained, by considering FeO as a base in addition to CaO, MgO and MnO. He also assumed the formation of certain compounds, not very different from those of Grant and Chipman. The desulphurization reaction was represented as

$$[S] + (O) = (S) + [O].$$

Harders, Grewe and Oelsen(15) suggested that a relationship existed between basicity and the ratio $\frac{(S).(Mn)}{[S].[Mn]}$, the basicity being expressed by the ratio CaO/SiO_2. The ratio (Mn)/[Mn] represented the state of oxidation; so that there is similarity between this expression and that used by Carter.

The MgO content in a basic slag is appreciably smaller than that of CaO, and being practically constant, its contribution to sulphur removal was generally overlooked. There has been much speculation on the effectiveness of MgO in desulphurization, and somewhat contradictory results have been reported. In certain cases addition of MgO improved the desulphurisation, in others there was no difference or even a slight deterioration. Maurer and Bischof(12) found that additions of MgO up to 10 per cent did not affect the desulphurization ratio. They suggested that higher percentages of MgO might impair desulphurization to a slight extent. When MgO crucibles or MgO lined basic furnaces are used, the MgO content of the slag ceases to be an independent variable, and increases with the amount of acid oxides present. According to Carter(16) the low sulphur distribution ratios attributed to MgO by Maurer and Bischof may be really due to the increased acid contents associated with high MgO contents.

The standard free energy changes for the desulphurization by the basic oxides at 1600°C are as follows.

$$\begin{aligned} CaO + \underline{S} &= CaS + \underline{O} & \Delta G &= 12{,}700 \text{ cals.} \\ FeO + \underline{S} &= FeS + \underline{O} & \Delta G &= 14{,}800 \text{ "} \\ MnO + \underline{S} &= MnS + \underline{O} & \Delta G &= 17{,}600 \text{ "} \\ MgO + \underline{S} &= MgS + \underline{O} & \Delta G &= 33{,}400 \text{ "} \end{aligned}$$

Rocca, Grant and Chipman(17) estimated that lime was about 1000 times a better desulphurizer than MgO. This was confirmed by Harders, Grewe and Oelsen(15) who found that $MgO.SiO_2$ slags, and pure MgO at sintering temperatures (1700°C) were unable to desulphurize molten iron containing sulphur, whereas basic $CaSiO_3$ and lime had appreciable desulphurizing powers. Of the four oxides CaO is shown to have the best desulphurizing ability, that of MnO being slightly lower. The desulphurizing ability of MgO is much less due to the low affinity of Mg^{++} for sulphide ions, so that the effect of MgO on desulphurization in an Open hearth furnace seems relatively unimportant. FeO in a basic slag, as pointed out by Richardson(18) causes an increase in the number of oxygen atoms replaceable by sulphur, at the same time as it increases the oxygen content of the metal, exerting thus a dual and conflicting effect on desulphurization.

The desulphurization is dependent on the basicity of the slag as well as on the oxygen potential of the system. Sulphur distribution ratios of about 10 have been obtained in the Open hearth furnace, while in the electric furnace(reducing period), and blast furnace much higher ratios are obtained, probably due to the lower oxygen potential in these furnaces.

The major constituents of a blast furnace slag may be considered to be CaO, MgO, Al_2O_3, SiO_2. Holbrook and Joseph(19,20), were the earliest to conduct laboratory investigations on the desulphurization of molten iron by synthetic slags made up from these four oxides. Their experiments were performed in graphite crucibles at 1500°C, each run lasting for half an hour. Although they studied neither the equilibrium nor the kinetics of the reaction, they obtained the relative desulphurizing powers of a range of $CaO-Al_2O_3-SiO_2$ slags containing 0-20 per cent MgO. It was found that for a given MgO content there was an optimum basicity beyond which the slags became very poor desulphurizers, basicity being calculated as the weight per cent ratio of basic oxides to acidic oxides ($= \frac{CaO+MgO}{Al_2O_3+SiO_2}$). The isodesulphurisation curves drawn showed that desulphurization was critically related to the slag composition at optimum and higher basicities and less so in the range of less basic slags. They found that the desulphurization increased regularly and rapidly as CaO replaces SiO_2, less rapidly as CaO replaces Al_2O_3, and slowly as Al_2O_3 replaces SiO_2.

Hatch and Chipman(21) carried out similar experiments, with the difference that the sulphur distribution ratio was measured after establishing equilibrium conditions in the system. As expected the distribution ratio was found to increase with basicity. They obtained lower ratios with slags containing more than 6 per cent MgO, and from this they assumed that MgO could not be as effective as CaO. According to Holbrook and Joseph, MgO and CaO should not be combined as total bases, nor Al_2O_3 with SiO_2 as total acids. Each oxide has its own effect and the degree of the effect is not constant for all ranges of compositions. Al_2O_3 being an amphoteric oxide may function as an acid or a base depending upon the oxide ion activity of the solution to which it is added.

Hatch and Chipman calculated the "excess base" by substracting the total acid oxides from total basic oxides, all quantities being expressed in molar concentrations. The best correlation between the sulphur partition ratio and the excess base was obtained when MgO was taken to be equivalent to two-thirds of a mol of CaO. According to them the difference between CaO and MgO may be due to the binding forces of

Mg^{++} and O^{--} being greater than those between Ca^{++} and O^{--}, and hence the replacement of one mol of CaO by one mol of MgO would result in lowering the O^{--} concentration of the slag. On a weight basis CaO and MgO were thought to be equivalent, but on a molar basis MgO was assumed to be equal to only $^2/_3$ of a mol of CaO.

Recently Negresco(22) carried out experiments with $CaO-Al_2O_3-SiO_2-MgO$ slags. According to him, Al_2O_3 exercised no direct influence on the sulphur distribution, and the desulphurizing ability of such slags was attributed to the proportion of "active lime" in a slag of a given composition, the active lime being calculated assuming that some of the lime was engaged by the silica in the slag forming inactive groups. It is difficult to compare this work with that of the previous workers because of the lack of data about the equilibrium sulphur content of the metal used by Negresco. His results only show the relative merits of slags used in the investigation. According to Negresco, in a $CaO-SiO_2-MgO$ slag the magnesia may combine with SiO_2 to set free CaO for the sulphur reaction according to the equation

$$C_3S_5 + 4MgO = M_4S_5 + 3CaO .$$

Although the exact nature of the combination in the molten state was not given, the idea of inert groupings being present in the melt was favoured by Negresco.

The effect of MgO in a blast furnace slag has still to be elucidated. On thermodynamic grounds it is unlikely to have any desulphurizing action relative to CaO, but as it is a fairly strong base, its influence may still be important.

Attempts have been made to apply ionic theory to the explanation of acid and basic Open hearth reactions. It is probable, that molten blast furnace slags are also ionic in nature, but knowledge about the ion species present in such slags is very meagre. While some investigators (23,24,25) proposed an ionic constitution for molten blast furnace slags, others (26,27,28), have stated that they are composed of minerals of definite composition and properties. A purely thermodynamic approach is more reliable, as it does not make any assumption of ionic or molecular constituents in the molten slag, even though the method may be slow and tedious.

They suggested the following equations to represent the reactions taking place between SO_2 and slags containing lime.

$$SO_2 + 3CO + CaO = CaS + 3CO_2$$

$$SO_2 + CaO + 3Fe = CaS + 3FeO$$

Under their experimental conditions sulphur was assumed to be present mostly as CaS since CaO is a much stronger base than FeO or MgO.

Assuming sulphur in silicate melts to be present in the form of sulphide and sulphate, Fincham and Richardson(32) represented the reactions for the partitioning of sulphur between melt and gas as follows.

$$\tfrac{1}{2} S_2 + (O) = \tfrac{1}{2} O_2 + (S) \qquad K_1 = \frac{(S).pO_2^{1/2}}{(O).pS_2^{1/2}}$$

$$\tfrac{1}{2} S_2 + (O) + \tfrac{3}{2} O_2 = (SO_4) \qquad K_2 = \frac{(SO_4)}{pS_2^{1/2}.(O).pO_2^{3/2}}$$

For a slag of constant composition (O) is constant, and at constant sulphur content of the gas, increase of oxygen partial pressure while favouring sulphate formation decreased the sulphide formation. It was found that at oxygen pressures less than $10^{-5} - 10^{-6}$ atm. the sulphide reaction was predominant, and at pressures greater than $10^{-3} - 10^{-4}$ atm. the sulphate reaction was more important. With 2% SO_2 in the gas, a slag containing 41% CaO, 52% Al_2O_3, 7% SiO_2 became saturated with CaS at an oxygen pressure of 10^{-9} atm. Still lower oxygen pressures resulted in the separation of CaS. At pressures above $10^{-2.5}$ atm. the formation of pyrosulphate becomes significant.

Fincham and Richardson studied the effect of temperature on the equilibria, and showed, that at a constant pO_2 and a constant SO_2 input, raising the temperature increased the sulphide content while decreasing the sulphate content. For the purposes of comparing the various slags a term sulphide capacity was introduced. It was represented as $C_S = (\%S).pO_2^{1/2}/pS_2^{1/2}$. Carter and Macfarlane(33) carried out similar work using $CO-CO_2-SO_2$ gas mixtures (Fincham and Richardson used $H_2-CO_2-SO_2-N_2$ mixtures). The ratio $pS_2^{1/2}/pO_2^{1/2}$ was termed the sulphurizing potential of the gas. As their experiments were confined to an oxygen pressure range of 10^{-8} - 10^{-9} atm. only the sulphide equilibrium was investigated. They used their results to calculate the activity of lime, alumina, silica in synthetic binary and ternary slags. The following assumptions were made by the above workers.

1. The activity of replaceable oxygen in the melt is not significantly altered by the substitution of small amounts of sulphur.

2. For low concentrations of sulphur in the slag the activity of sulphide is proportional to the sulphur concentration. Or in other words the activity coefficient of CaS does not vary appreciably in the range of low sulphur percentages found in the slags.

St. Pierre and Chipman(34) investigated the sulphur equilibria between SO_2 or SO_2-CO gas mixtures and CaO-FeO slags. Their investigations essentially consisted in using the ratio $Fe^{+++}/Fe^{+++} + Fe^{++}$ in the FeO slags in equilibrium with the gas mixture to determine the partial pressure of oxygen in the gas. The same authors, in a later investigation(35), used FeO slags containing CaO, SiO_2, and MgO. According to them, the substitution of CaO for FeO in CaO-FeO slags at constant atmospheric conditions decreased the sulphide content while increasing the sulphate content. It was also shown that the addition of SiO_2 to such slags lowered the sulphur content. As to the effect of MgO, it was regarded as contributing to the oxide concentration but not to the desulphurizing power of the slag. The addition of MgO results in an increase of the activity coefficient of the sulphide ion. This could be effected, according to these workers, by a portion of the magnesium ions taking a coordination number of four in silicate melts.

In order to have maximum efficiency in desulphurization, a slag must have as large a capacity for sulphur as possible or in thermodynamic terms the slag should be able to hold a high concentration of sulphur at a low chemical potential. The usefulness of any slag can be judged only by having an intimate knowledge of the thermodynamic properties of the various constituents present in that slag, and in particular of the activities of the metal oxides and sulphides.

The investigation of Fincham and Richardson into the equilibrium of the reaction $CaO + {}^1/_2 S_2 = CaS + {}^1/_2 O_2$ led to a value of

$K = 3.82 \times 10^{-3}$ at 1600°C for the equilibrium constant, assuming the standard states to be pure crystalline CaO and CaS. From this equilibrium constant and the lime activity values calculated from the free energies of formation of silicates, values for $a_{CaS}.pO_2^{1/2}/pS_2^{1/2}$ were calculated. By combining these with the corresponding values for sulphide capacity C_S ($= \%S.pO_2^{1/2}/pS_2^{1/2}$) values of a_{CaS} were derived.

Thus for a $CaO-SiO_2$ slag containing 56 mol per cent CaO, $\gamma_{CaS\,1600\,°C} = 5$ was calculated. A similar procedure was followed to obtain $\gamma_{MgS} = 2$ (1600°C), from results for the reaction $MgO + \frac{1}{2} S_2 = MgS + \frac{1}{2} O_2$. The activity of lime in $CaO-Al_2O_3$ melts was obtained by Fincham and Richardson, assuming that γ_{CaS} is the same as for a silicate melt. The basis for this assumption was that the ratio of γ_{CaS} to γ_{CaSO_4} is the same in the silicate and aluminate melts.

As mentioned earlier, Carter and Macfarlane(33) followed a different procedure in determining a_{CaO} in $CaO-Al_2O_3$, and $CaO-SiO_2$ slags. The equilibrium constant for the reaction is $K = a_{CaS}.pO_2^{1/2}/a_{CaO}.p.S_2^{1/2}$ If the desulphurizing potential of the gas is denoted by A, where $A = pS_2\ /p.O_2$, $K = a_{CaS}/a_{CaO}.A.$ for a standard slag of unit lime activity and activity of CaS = a°_{CaS} in equilibrium with a gas whose sulphurizing potential is A°, $K = a^{\circ}_{CaS}/A^{\circ}$. Now combining the equation for the standard slag and the other slag of lime activity a_{CaO}

$$a_{CaO} = \frac{a_{CaS}}{a^{\circ}_{CaS}} \cdot \frac{A^{\circ}}{A}$$

In the low sulphur concentrations encountered a_{CaS} was taken to be equal to per cent sulphur by weight. In using this procedure it was assumed that Al or Si atoms in the slag do not combine with sulphur to form aluminium or silicon sulphide. The finding of the investigations of Carter and Macfarlane, and Fincham and Richardson that replacement of lime by alumina or silica in the slags resulted in lowering the sulphur pick up provides ample justification for such an assumption. A weakness in these calculations is the assumption that γ_{CaS} is constant throughout the range of sulphur contents obtained in their experiments. However, by equilibrating a standard slag with gases of different sulphurizing potentials, Carter and Macfarlane observed a proportionality between the sulphur content of the melt and the sulphurizing potential, which suggested that γ_{CaS} was constant up to 1.8 per cent S. The equation of Carter and Macfarlane thus reduced to

$CaO = \%S.A^{\circ}/\%S^{\circ}.A$ where $\%S^{\circ}$ was the amount of sulphur picked up by the standard slag. The choice of a standard slag presented some difficulties. In order that lime activity may be unity, it is essential that the slag selected is all liquid at the working temperature and should be in equilibrium with solid lime. In the $CaO-Al_2O_3$ system no such slag could be found. It was found that a small part of the 1500°C isotherm in the $CaO-Al_2O_3-SiO_2$ system passed through the primary phase field of CaO. A composition on this part of the isotherm was chosen as the standard slag. The Gibbs-Duhem relationship was used in deriving the activities of alumina and silica in their respective binary slags, and approximate values obtained for the free energies of formation of binary aluminates and silicates from the oxide activities. In the case of ternary $CaO-Al_2O_3-SiO_2$ slags Macfarlane(36) made use of the Gibbs-Duhem relationship to evaluate a CaO and a SiO_2, assuming a Al_2O_3 on a constant Al_2O_3 line to be constant. The latter assumption leads to appreciable errors, and a more reliable method of dealing with activities in ternary systems has been given by Schumann(37). He derived a quantitative relationship between the tangent intercepts of iso-activity curves for the various components and used this relation to calculate the activities of SiO_2, FeO and O in ternary iron silicate slags.

Solubility of Sulphur in Slags.

Lime activities obtained as in the method of Carter and Macfarlane by comparing sulphur pick ups by different slags from similar gas mixtures are more likely to be correct if the sulphur contents are far removed from the saturation value, and if the sulphur solubilities are of the same order. Little accurate work has been carried out on sulphur solubilities in slags and most of this work had been confined to slags of the blast furnace type. McCaffery and Oesterle(38) determined the solubility of CaS in $CaO-Al_2O_3-SiO_2$ slags. According to them the effect of Al_2O_3 in blast furnace slags is to increase the solubility of the slags for CaS and that the chemical composition of the slag is of less importance than the temperature of the slag. They found the solubility of CaS in $CaO-Al_2O_3-SiO_2$ melts at 1500°C to correspond to about 8% S for acid melts and about 11% S for more basic melts. These values are thought to be rather high by Carter and Macfarlane. Glaser(39) found the solubility of CaS in liquid $CaSiO_3$ to be 5.5% S by weight at 1500°C. Filer and Darken(40) found the CaS saturation limit in blast furnace slags to be 3·5 - 4·5%. While Fincham and Richardson obtained a value of about 2% S, Carter and Macfarlane used a value of 2.7% S in their calculations.

It is clear from the above that considerable variations appear to exist in slag sulphide solubilities, and that there are indications that solubilities are greater in the more basic slags. This would correspond to a decrease in γ CaS with increasing basicity.

CHAPTER III.

EQUILIBRIA IN S-CONTAINING GASES AND CALCULATIONS.

EQUILIBRIA IN S-CONTAINING GASES AND CALCULATIONS.

In order that the sulphurizing potential as denoted by Carter and Macfarlane(33) may be obtained it is essential that the correct thermodynamic data are known for the various reactions taking place between CO, CO_2 and SO_2 in the gas mixture. Sulphur can exist in a gaseous atmosphere, e.g., Open hearth furnace gases - as H_2S, HS, SO_2, COS, SO, SO_3, S_2, S, etc. Free energy data for the formation of these compounds have been given by Kelley(41), and Richardson and Jeffes(42). The calculations of Carter and Macfarlane showed that within the range of compositions they used the amounts of S_6, S_8, CS, CS_2, SO_3 formed could be ignored.

Equations for the standard free energy changes for the relevant reactions have been derived by Kelley(41), Richardson and Jeffes(42), and St. Pierre and Chipman(34) and values of the free energy changes at 1773°K are given in Table I. It can be seen that there are significant differences between the three sets of data. The values of Kelley, and Richardson and Jeffes, and to a certain extent those of St. Pierre and Chipman, are based on spectroscopic measurements. These measurements have been interpreted differently by the various workers. The disagreements in the data lie in the choice of the correct dissociation energy of S_2 and SO into normal atoms.

There have been considerable discussions about the true value of the dissociation energy of S_2. According to Gaydon(43) the spectroscopic measurements indicate the possibility of three values -

TABLE I.

COMPARISON OF FREE ENERGY DATA.

Reaction	Kelley(41)		Richardson	Jeffes(42)	St.Pierre	Chipman(34)
	ΔG_{1773} °K K.cals.	K_{1773} °K	ΔG_{1773} °K K.cals.	K_{1773} °K	ΔG_{1773} °K K.cals.	K_{1773} °K.
1. $2S(g) = S_2(g)$	-54.38		-24.59 ± 10		-34.38	
2. $\frac{1}{2}S_2 + \frac{1}{2}O_2 = SO$	-8.945	1.268×10^{1}	$-26.768 \pm > 10$	1.995×10^{3}	-21.334	4.256×10^{3}
3. $CO + \frac{1}{2}S_2 = COS$	10.059	5.754×10^{-3}	10.29 ± 3	5.383×10^{-3}	11.70	3.614×10^{-3}
4. $S_2 + 2O_2 = 2SO_2$	-112.019	6.461×10^{13}	-111.88 ± 1	6.166×10^{13}	-111.78	6.026×10^{13}
5. $SO_2 = S + O_2$	83.199	5.309×10^{-11}	68.53 ± 5	3.565×10^{-9}	73.08	9.772×10^{-10}
6. $SO_2 = SO + \frac{1}{2}O_2$	47.062	1.578×10^{-6}	29.21 ± 5	2.512×10^{-4}	34.22	6.039×10^{-5}
				2.08×10^{-5} *		
7. $CO + SO_2 = COS + O_2$	66.068	7.162×10^{-9}	66.224 ± 2	6.855×10^{-9}	67.59	4.645×10^{-9}
8. $2CO + O_2 = 2CO_2$	61.52	3.849×10^{7}	-61.5 ± 1	3.819×10^{7}	61.614	3.855×10^{7}

* Value of Dewing and Richardson.

101 ± 3, 83, or 76 K.cals. - for the dissociation energy of S_2 into normal atoms. Nernst(44) and Wartenberg(45) determined the molecular weight of sulphur gas at 2000°C, and their results showed agreement with the lowest value. Dewing and Richardson(46) suggested that since iridium vessels were used by Nernst, and Wartenberg, they may be in error due to the formation of iridium sulphide in the hot part of their apparatus. Although it was not possible to decide conclusively between the three values, Gaydon himself favoured the highest value as being the most probable one. Basing his calculations on the corrected data of Montgomery and Kassel(47), Kelley derived a value which agreed with that of Gaydon. Recently Dewing and Richardson(46) determined the heat of formation of SO from S_2 and O_2 and used that value to calculate the dissociation energy of S_2. Although earlier, Richardson and Jeffes gave a value of 76 k.cals. these results seem to confirm the value of 83 k.cals.

According to Gaydon, the energy of dissociation of SO into normal atoms is either 119.5 or 92.3 k.cals., depending on how the spectroscopic measurements are interpreted. If the predissociation limit of 119.5 k.cals for SO is due to a $^3\Pi$ state arising from normal atoms, then it is the dissociation energy; however, if it goes to $O(^3p)+S(^1D)$, then the dissociation energy is 92.3 k.cals. Gaydon favoured the first interpretation while Herzberg(48) chose the latter. Richardson and Jeffes used Gaydon's higher value as being the most probable one, amd Kelley's calculations too agree well with Gaydon's choice.

As there are three probable values for the dissociation of S_2 there could be six different values for the heat of formation of SO from S_2 and O_2. These values are presented in Table 2, along with those for SO and S_2 from normal atoms. In order to determine the correct value of the heat of formation of SO, St. Pierre and Chipman(34) equilibrated CaO-FeO slags with SO_2-CO gas mixtures, the slags being held in platinum crucibles. The quenched slag was analysed for ferric iron, ferrous iron, calcium, and sulphur. Using sulphur, carbon, and oxygen balances, in the gas phase, the value of pO_2 determined from the slag composition, and the known equilibrium constants, the gas compositions resulting from the gas phase reactions of the gas mixture entering the furnace, was calculated. Their experimentally determined value of $\Delta H^\circ = -19$ k.cals. for the reaction $\frac{1}{2}S_2 + \frac{1}{2}O_2 = SO$, agrees with the value obtained by combining the intermediate ΔH° value for S_2 formation (= -83 k cals.) with -119.5 k cals. for the formation of SO from normal atoms.

Dewing and Richardson(46) studied the equilibria $S_2 + 2SO_2 = 4SO$, $2SO_2 = SO + SO_3$, at 1250°C and 1500°C respectively. In the first, the sulphur pressures developed in mixtures of SO_2 and S_2 were determined from the sulphur contents of beads of silver heated in contact with the gases. In the second, the SO_3 pressures developed in SO_2 were determined from the sulphate contents of a calcium silicate melt. From these results they obtained a value of -16 K.cals. for the same reaction $\frac{1}{2}S_2 + \frac{1}{2}O_2 = SO$. Though both St. Pierre and Chipman,

TABLE II.

CALCULATED VALUES FOR Ho FOR THE REACTION $\frac{1}{2}S_2 + \frac{1}{2}O_2 = SO$.

No.	$S+O=SO$ Δ Ho K.cal.	$2S = S_2$ Δ Ho K.cal.	$\frac{1}{2}S_2 + \frac{1}{2}O_2 = SO$ Δ Ho K.cal.	Investigations.
1.	-92.3	-76	+ 4.7	
2.	-92.3	-83	+ 8.3	
3.	-92.3	-101	+17.2	
4.	-119.5	-76	-22.5	Richardson and Jeffes.
5.	-119.5	-83	-19.0	St.Pierre and Chipman.
6.	-119.5	-101	-10.0	Kelley, Gaydon.

and Dewing and Richardson seem to agree on the choice of the dissociation energy of S_2 and SO, the difference in the ΔH° values is thought, by Dewing and Richardson, to be probably, due to the different gas mixtures used in the two investigations. This new value of Dewing and Richardson gives an additional set of data to the already existing three sets when it is combined with the values of Richardson and Jeffes for the other reactions (Reference Table I).

The correctness of the sulphurizing potential depends on the choice of the right values for the formation of the compounds S_2, SO, and COS. Carter and Macfarlane examined the data put forward by Kelley, and Richardson and Jeffes, in their calculations, and their results seemed to indicate better agreement with the data of Kelley. The intermediate values of St. Pierre and Chipman were not used in their calculations. The agreement of Carter and Macfarlane with Kelley could also mean that the data of the other two investigators may be in error. In this Chapter, therefore, all four sets are brought together for the purposes of comparison.

Calculation of the Sulphurizing Potential (A).

It is difficult to deduce A from the composition of the gas mixture introduced into the furnace. It is better to assume a final gas composition obtained inside the furnace after equilibrium has been attained between the various sulphur compounds and CO and CO_2, and from the known, or more correctly, the selected equilibrium constants calculate backwards to obtain the initial gas composition. By making a series of such calculations, curves relating the initial gas composition and the sulphurizing potential may be obtained. In the following illustration the equilibrium constants obtained from the data of St. Pierre and Chipman have been used, although curves obtained in this manner were derived from each of the four sets of data. The results of all the calculations on gas composition are shown in the Appendix. The calculations of Macfarlane(36) for the data of Kelley, and Richardson and Jeffes have also been used.

Let us assume an equilibrium CO/CO_2 ratio of 1.5 and a total partial pressure of $\sum PPS = 0.007$ for the sulphur compounds formed at 1500°C and 760 m.m. pressure. Then as $CO/CO_2 = 1.5$, $pO_2 = 1.164x10^{-8}$ $pCO = 0.5958$, and $pCO_2 = 0.3972$, and $\sum PPS = pSO_2 + pS + pS_2 + pSO + pCOS = 0.007$. If $pSO_2 = a$, pS_2, pSO, and $pCOS$ can be obtained in terms of 'a' from the equilibrium constants for the appropriate reactions in Table I.

Therefore,

$$pS = \frac{9.772x10^{-10}}{1.164x10^{-8}} .a \quad = \quad 0.08392a$$

$$pS_2 = \frac{a^2}{6.166x10^{13} \; x(1.164x10^{-8})^2} \quad = 119.6 \; a^2$$

$$pSO = \frac{6.039\times10^{-5}}{(1.164\times10^{-8})^{1/2}} = 0.5597a$$

$$pCOS = \frac{4.645\times10^{-9}}{1.164\times10^{-8}}.\ a.pCO = 0.2377a$$

$\therefore \Sigma PPS = 119.6a^2 + a(1+0.08392+0.5597+0.2377) = 0.007.$

Solving the above equation, $a = 3.106\times10^{-3}$, and the percentage composition of sulphur compounds is :-

$SO_2 = 44.39$, $S = 3.726$, $S_2 = 16.49$, $SO = 24.84$, $COS = 10.55$.

The final composition of the gas mixture is controlled by the following reactions.

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

$$SO_2 + 2CO = {}^1\!/_2\, S_2 + 2CO_2 \quad \dots\dots\dots\dots (2)$$

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

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

Considering the volume changes in the above reactions it can be seen that SO_2 and CO are expended while the CO_2 content increases. Hence more SO_2 and CO, and less CO_2 will have to be used in the initial gas mixture.

$\therefore$ Initial % SO_2 = $100 \times (\Sigma PPS + pS_2)$ = 0.813

Initial % CO = $100 \times (pCO+2pS+4pS_2+pSO+3pCOS)$ = 60.4

Initial % CO_2 = $100 \times (pCO_2-2pS-4pS_2-pSO-2pCOS)$ = 38.8

Total = 100.013

The above gas composition would have to be used to obtain the assumed CO/CO_2 ratio of 1.5 and $\sum PPS = 0.007$ in the gas mixture at 1500°C.

The sulphurizing potential $A = \frac{pS_2^{1/2}}{pO_2^{1/2}} = 314.8$, and

the Initial CO/CO_2 ratio $= 1.556$.

A series of calculations similar to that shown above was carried out for each of the four sets of data, and curves relating CO/CO_2 ratio to the sulphurizing potential for various SO_2 contents were drawn. The sulphurizing potentials obtained were designated A_K, A_{RJ}, A_{PC}, A_{DR}, where the subscripts refer to the investigators Kelley, Richardson and Jeffes, St. Pierre and Chipman, Dewing and Richardson, respectively. The four sets of curves are presented in Fig.1. The difference in the A values obtained from the same initial gas composition is readily seen. For instance for a gas of $CO/CO_2 = 1.5$, $\%SO_2 = 1.0$, the A values are $A_K = 400$, $A_{RJ} = 205$, $A_{PC} = 340$, $A_{DR} = 343$, and with $CO/CO_2 = 2.5$, and the same SO_2 content the A values are 770, 485, 710, 680, respectively. Thus for the same initial gas composition the highest A value is obtained using the data of Kelley and the lowest from those of Richardson and Jeffes. Those of the other investigators are intermediate, and also show the closest agreement. The slopes of the A_{PC} curves are greater than those of A_{DR}. The difference in the A values is largely due to the difference in the equilibrium gas composition. This is made clear in Table 3, in which the final gas compositions obtained from the same

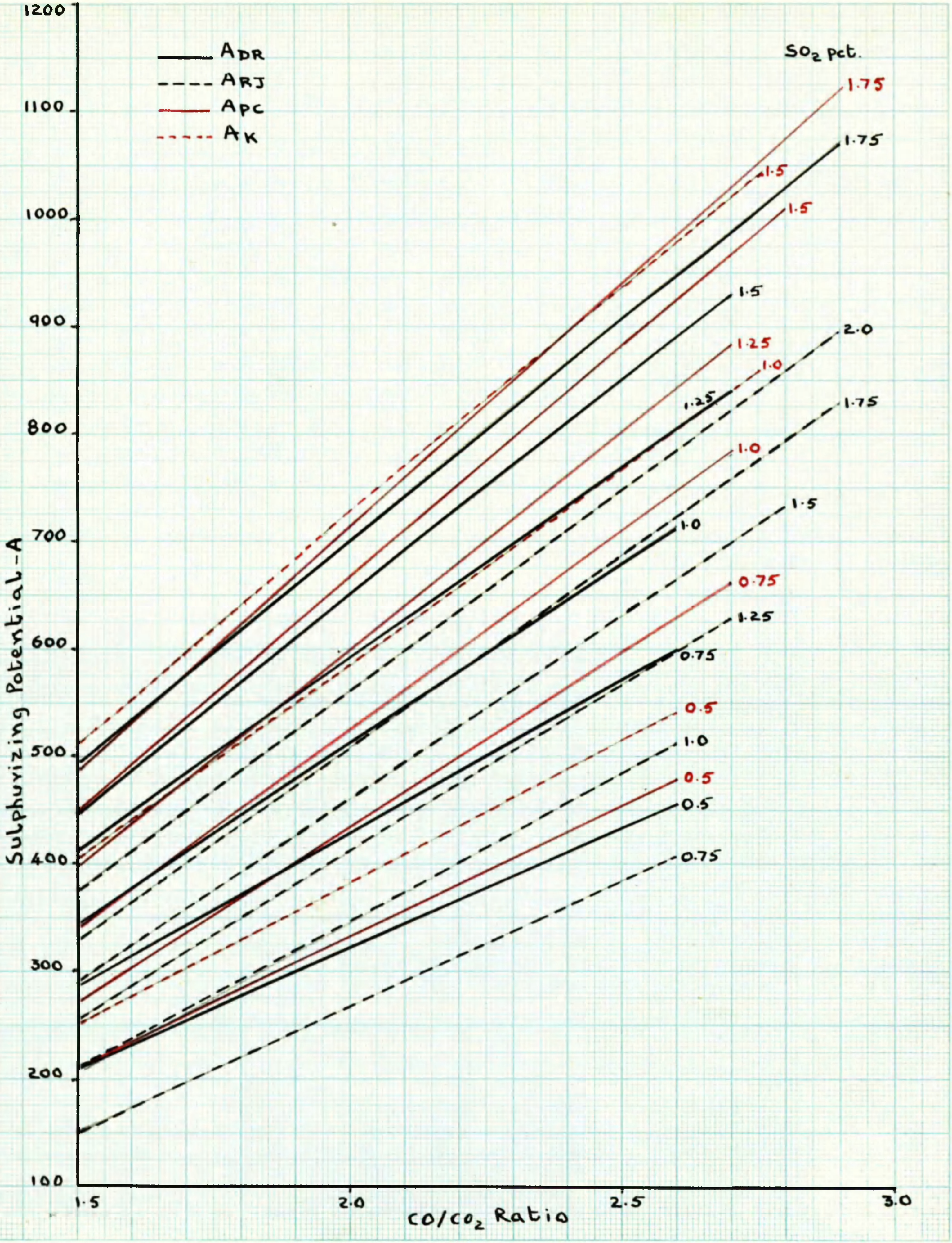


Fig. 1. Sulphurizing Potentials of CO-CO₂-SO₂ Gases at 1500°C

TABLE III.

CALCULATED GAS COMPOSITIONS AT 1500°C.

Initial CO/CO_2	Initial % SO_2	Final Gas Composition.							$\overset{A}{pS_2^{1/2}/pO_2^{1/2}}$	Investigators.
		CO/CO_2	pO_2	$\%S_2$	%S	%SO	%COS	$\%SO_2$		
1.5	0.77	1.448	1.239×10^{-8}	21.38	0.24	0.82	19.83	57.73	330	Kelley
1.5	0.77	1.451	1.244×10^{-8}	14.79	3.597	24.78	11.09	45.75	282	St. Pierre Chipman.
1.5	0.77	1.45	1.246×10^{-8}	4.84	7.79	54.34	8.07	24.96	168	Richardson Jeffes.
1.5	0.77	1.45	1.246×10^{-8}	15.32	14.55	8.5	15.08	46.56	285	Dewing Richardson.

initial gas mixture using the four sets of data are given.

In general there is little agreement to be observed between the four compositions, and at this stage no choice will be made between the four possibilities. Experiments will be described later in which an attempt was made to resolve this question.

CHAPTER IV.

EXPERIMENTAL.

EXPERIMENTAL.

Apparatus.

The experimental procedure consisted of three stages, and consequently the apparatus may be described under the following sections.

1. Gas preparation, Flow regulation and Mixing. (Fig.2).
2. Gas Analysis. } (Fig.3).
3. Reaction Chamber. }

Gas Preparation.

Three gases, namely, CO_2, SO_2, and CO, were used in the experiments. Cylinder CO_2 was used after being dried over anhydrone(A). The oxygen content of CO_2 which is about 0.04 per cent could be taken to have a negligible effect on the CO/CO_2 ratio at 1500°C.

SO_2 was used from a syphon. Before it entered the flowmeter it was passed through a H_2SO_4 bubbler(AB) and a U-tube filled with $Mg(ClO_4)_2$.

CO was prepared from CO_2 by passing it over dry powdered graphite held in a "Pythagoras" tube at 1150°C. The heating was carried out in a nichrome wound resistance furnace(G). At 1150°C the conversion of CO_2 to CO was as high as 99 per cent. Any unreduced CO_2 was removed by an absorption train consisting of a trap(T), a bottle containing 600-700 ml. of 20-25 per cent NaOH(SB), and a tower filled with 8-14 mesh soda asbestos and $Mg(ClO_4)_2$ (ST).

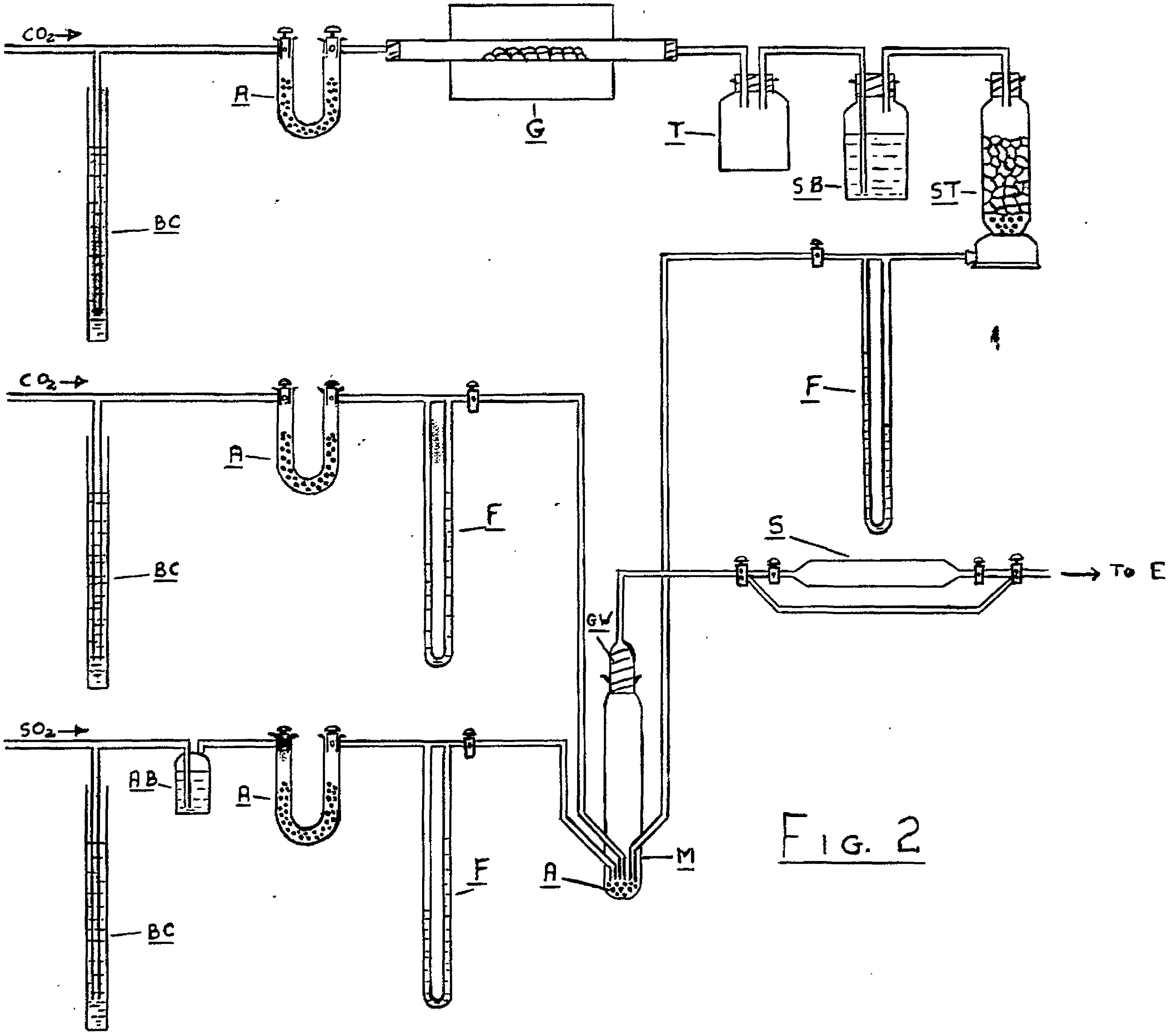


FIG. 2

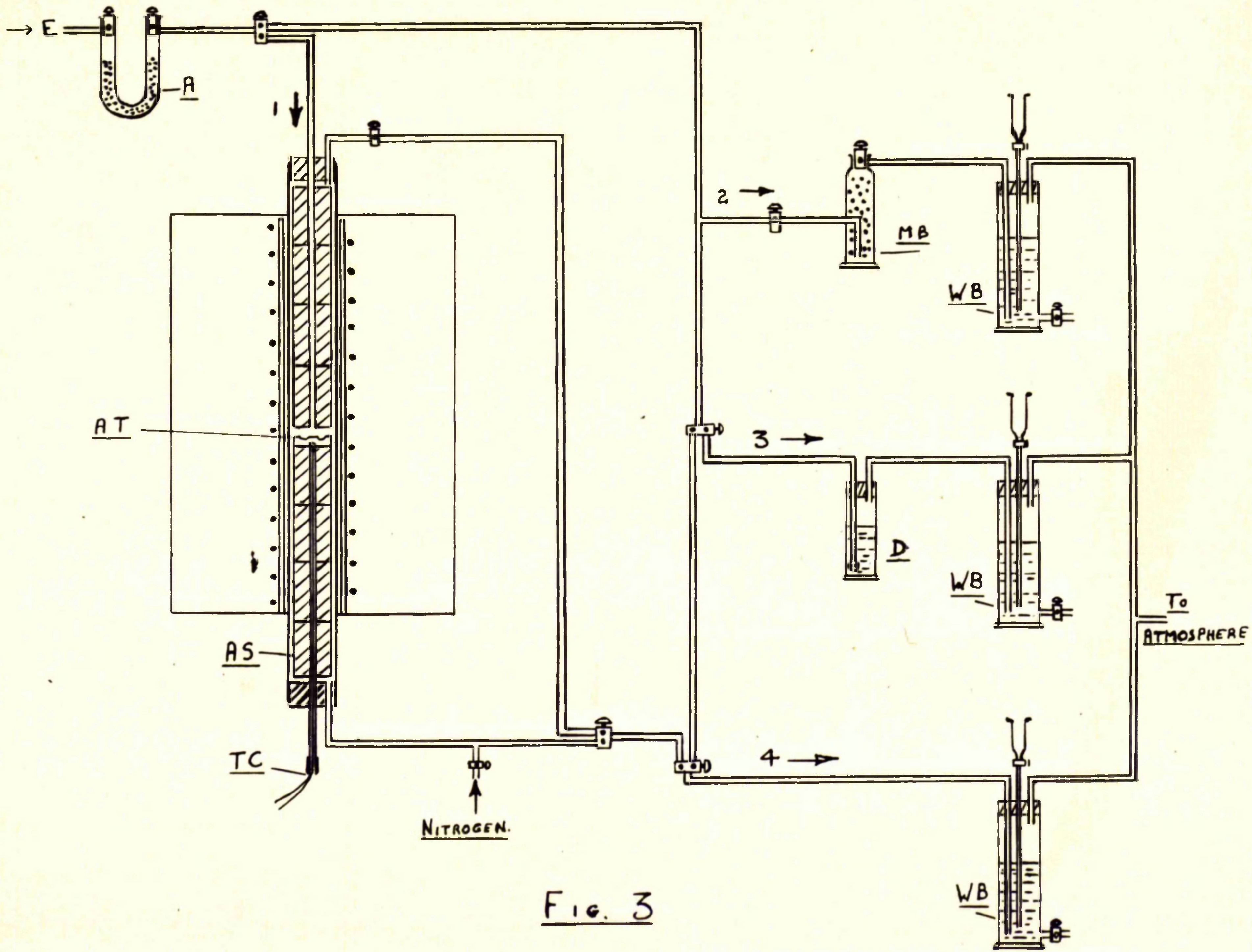


Fig. 3

Some difficulties were encountered during this part of the work. As far as the CO preparation went, at first no NaOH bubbler was used. The temperature of the furnace containing the graphite powder (hereafter termed the "Graphite Furnace") was hand controlled through an auto-variac transformer. Slight fluctuations in the temperature of the furnace increased the amount of unreduced CO_2 and this caused undue heating of the soda asbestos tower,. This difficulty was successfully overcome by the NaOH bubbler, which takes up most of the CO_2 coming through, leaving only small traces for the tower to cope with. A concentration of 20-25 per cent NaOH is about the limit as with higher concentrations the Na_2CO_3 formed during the absorption process tends to precipitate and sometimes choke the glass tubes. The trap serves a useful purpose by preventing the back suction of the alkali into the graphite furnace.

With regard to the SO_2 purification, the perchlorate U-tube was fitted, in the beginning, with rubber bungs. They were attacked by SO_2 and thus hardened with time. This made it difficult to make the appropriate points gas tight. Also, some fine liquid droplets were observed inside the glass tube leading up to the flowmeter. These droplets could be sucked right into the rather fine throat of the venturi, following sudden fluctuations in the gas flow, the consequence being stoppage of the gas flow. A new U-tube with ground-in glass stopcocks was used combined with a largely reduced number of rubber joints. This change proved beneficial and no liquid droplets were formed. A slight drawback was that the grease (silicone) used was attacked by SO_2 giving rise to a black substance. Contamination of the gas mixture by this substance was prevented by cleaning the tubes and regreasing these joints after every run. As this occurred before the gas is metered and analysed the possibility of its affecting the final gas analysis is negligible.

Flow Measurement and Regulation.

The flow rates were measured by means of venturimeters(F). A 2" long capillary tube with a constriction in the middle served as a venturi. The meter limbs were filled with "Griffin and Tatlock flowmeter" oil. The meters were calibrated by the water flow method. In this an aspirator bottle is connected to the outlet side of the meter, and the amounts of water, flowing out in known periods of time for various pressure differences across the venturi, were measured. Such measurements were considered to be approximate and were used only as a guide, the actual flowrates being obtained by analysis as explained later. The following ranges of flowrates were measurable with these meters.

SO_2-0.5-5 ml/min. CO-40-120 ml/min. CO_2-27-75 ml/min.

The problem of flow regulation was solved by Carter and Macfarlane by introducing bleeder columns. By adjusting the level of the tube dipping into the water column, the gas flow could be regulated to a fine degree. A similar set up (BC) was instituted in the present apparatus.

Mixing of Gases.

The three gases were led into a specially prepared gas mixer(M) which consists of a boiling tube (8" x $1^1/_4$") with three short glass tubes attached to it, 1" from the base. The gases impinge on a layer of $Mg(ClO_4)_2$ placed in the mixer. It is fitted with a standard B29 joint and a wad of glass wool(GW) is packed into the stopper part of the mixer. The large space in the mixer along with the glass wool packing at the exit ensured good mixing of the three gases.

Gas Analysis.

The gases after metering and mixing were analysed at this stage. A sampler(S) of 150 ml. capacity was connected to the outlet of the gas mixer. A bypass was provided at this point, to enable the withdrawal of the sampler(S), from the flow system for determining CO/CO_2+SO_2 volume ratio. This was followed by a drier containing $Mg(ClO_4)_2$ and four separate channels. Channelising is made possible by using 3-way stopcocks. The Channels indicated by numbers in Fig.3, were used for the following purposes.

1. To pass directly to the Reaction stage.
2. For the estimation of combined CO_2 and SO_2.
3. For the estimation of SO_2.
4. To the atmosphere.

The channel for the estimation of combined CO_2 and SO_2 consisted of a Midvale bulb (MB) packed with soda asbestos, and a water bubbler(WB) with an outlet to the atmosphere. Channel 3 is the same as 2, with the difference that the Midvale bulb was replaced by a bubbler(D), containing acidulated water for absorbing SO_2. The gas mixture may also be released directly into the atmosphere through Channel 4 which consists of a water bubbler. The water bubblers enabled the attainment of constant flow rates as denoted by the levels in the flowmeters. The height ofthe water in these bubblers could be adjusted according to requirements by attaching a thimble funnel at the top and a tap at the base of each of these bubblers. Once they were properly adjusted the flowrates remained practically constant when the gas flow was switched from one channel to another.

Reaction Stage.

Channel 1 led the gas to the reaction stage. This section essentially consisted of a vertical resistance furnace with a Mullite tube ($1\frac{1}{2}$" x 30") inside it. The heating element(H) was of 13 per cent Rh-Pt. wire (18 swg.) wound over a length of 12" on an alundum tube (2" i.d.). The current flowing through the coil was adjusted with a 20 amp. autovariac transformer, and a "Sunvic" energy controller was used to regulate the temperature. The winding gave a 2" long uniform temperature zone at 1500°C in the Mullite tube, the temperature being measured by a 13 per cent Rh-Pt.-Pt. thermocouple (TC). The Mullite tube was supported at the top with a clamp. When supported from the bottom the tube showed a tendency to bend with time, probably due to the weight of the materials inside it. The open ends of the Mullite reaction tube were fitted with rubber bungs. The top bung carried an 18" long alumina tube ($^1/_8$" i.d., $^1/_4$" o.d.) which extended into the hot zone of the reaction tube, and a short glass tube. The alumina tube carried a number of light weight alundum stools(AS). The lowest stool was cemented on to the alumina tube so as to act as a support for the stools above it. It was necessary to roughen the surface of the alumina tube before the stool was cemented on to it, since the stool, when cemented on to a smooth surface, slipped down on being fired at high temperatures. The bottom bung carried a Mullite thermocouple sheath containing the thermocouple, and a short glass tube. When the two bungs were fitted to the reaction tube the tips of the sheath and the alumina suspension lay within the uniform temperature zone and were separated by about an inch. This space formed the reaction chamber within which the crucibles containing the slags could be placed.

Platinum was found to be the most suitable crucible material for the types of slags used in the present investigation. Small discs (0.7" dia.) of sheet foil (0.0012" thick) were cut out, annealed, and pressed into crucibles. Annealing prevents tearing of the foil while being pressed. These crucibles can hold 0.25-0.4 gm. of slag. Use of larger quantities of slags involves difficulties in quenching.

Rapid cooling is highly desirable. With larger amounts of slag, involving the use of bigger crucibles, cooling is not so rapid, and this introduces the possibility of loss or gain of sulphur by the slag while cooling, depending upon the atmospheric conditions and rate of change of temperature in the reaction tube. An alundum tray (AT. 3/8" thick $1^1/4$" dia.) was prepared with four depressions in it for holding the crucibles. The thermocouple sheath fitted into a small depression at the base of the reaction tray. The dead space between the bottom bung and the tray was filled by fitting alundum stools round the sheath right up to the base of the tray, the stools thus supporting the tray. This arrangement is shown in Fig.3.

Requisite arrangements were made to introduce the gas mixture either at the bottom during the early stages of a run or at the top of the reaction tube in the later stages. The glass tube in the bottom bung could also be connected to a supply of purified nitrogen for flushing the system free of any oxygen. The outgoing gas from the top or the bottom of the reaction tube was connected to Channel 4, and thereby to the atmosphere.

Slag Preparation.

The experiments essentially consisted of equilibrating slags containing lime with SO_2-containing gases. The object of such experiments was to determine the effect of Al_2O_3, SiO_2, MgO on the pick up of sulphur by lime. In order that the slag composition may be effectively controlled, it is important that synthetic slags be used. These slags were prepared from the following materials.

1. Calcined analar $CaCO_3$
2. Analar Alumina.
3. Analar MgO heated to 1000°C.
4. Acid washed and ground Silica.

The melting was carried out in a graphite crucible heated by a high frequency induction coil. Usually the molten slags were poured out into small buttons, crushed, and remelted. This ensured a homogeneous melt. The slag was then crushed in a percussion mortar and finally ground in a mechanical agate mortar. Any carbon picked up by the slag was removed by igniting in a platinum crucible at 1000°C. Binary $CaO-Al_2O_3$, $CaO-SiO_2$, and ternary $CaO-Al_2O_3-SiO_2$ slags were prepared in the above manner. Most of the $CaO-Al_2O_3-MgO$ and $CaO-SiO_2-MgO$ slags were obtained by adding the required amount of MgO directly to the small platinum crucibles and thoroughly mixing before placing the crucible in the furnace. This method of addition was preferred to the addition of MgO-containing binary slags due to the difficulty of obtaining such binary melts with low enough melting points.

Analysis of Slags.

Silica. Silica was estimated in the slag-binary or ternary by fusing a known weight of sample with Na_2CO_3 in a platinum crucible. The water-leached fusion was acidified with HCl and a few drops of

HNO_3 and boiled. The silica was dehydrated with perchloric acid. On dense white fumes being obtained the solution was cooled, diluted, and filtered through paper pulp, and the residue washed alternatively with hot 1:4 HCl and water, and finally with water. The residue, weighed after ignition in a platinum crucible, was fumed with HF and H_2SO_4 and reweighed. The difference between the two weighings gives the amount of silica.

Alumina. Alumina in the ternary slag was determined in the filtrate obtained from the silica estimation. The $CaO-Al_2O_3$ slag was fused with Na_2CO_3 and the fusion leached with water, heated to boiling and dilute HCl added until just acid. The $Al(OH)_3$ precipitate, obtained by treating the solution with dilute NH_4OH in the presence of NH_4Cl, was dried, ignited, and weighed as Al_2O_3.

Lime. Lime was precipitated as calcium oxalate from the filtrate obtained from the determination of alumina. It was usually necessary to keep the solution overnight. Addition of a few grams of urea assisted in the formation of a coarse precipitate within 5 minutes. The precipitate was washed with 2 per cent NH_4NO_3 solution, dried, and ignited, the residue weighed as CaO.

Magnesia. Two master slags containing MgO were prepared by mixing CaO, SiO_2 and MgO in the required proportions. The melting procedure was as described earlier. The MgO in such slags was determined in the filtrate from the lime estimation by precipitating it as $MgHPO_4$ with Na_2HPO_4. On ignition the precipitate is converted to $Mg_2P_2O_7$. Using the appropriate conversion factor the percentage of MgO present can be obtained.

A complete analysis of a ternary slag is given below in duplicate.

	A	B	Average.
SiO_2	7.48	7.36	7.42
Al_2O_3	32.65	32.6	32.63
CaO	60.44	59.92	60.10
Total	100.57	99.88	100.16

The analysis obtained showed good agreement with the proportions in which the oxides were mixed, the greatest difference being about 1 per cent.

Experimental Procedure.

The alundum tray with the crucibles containing the weighed slags was introduced into the reaction tube. Purified N_2 was introduced at the bottom of the reaction tube and released to the atmosphere from the top through Channel 4. The reaction furnace and the graphite furnace were then switched on and left on overnight. By morning the temperaturesof the two furnaces were up to 1350°C, and 1100°C respectively. It took as much as two hours to obtain a gas mixture of constant composition, when all the three gas flows were started simultaneously. This may be due to the difference between the flow rates. The largest difference was between CO and SO_2, the gas flows of which were of the order of 100 ml./min. and 2-4 ml./min. respectively. The time taken to obtain the constant composition gas mixture could be reduced to an hour by the following procedure. The SO_2 flow was first started and let out into the atmosphere through Channel 3, as Channel 4 was being used for the nitrogen outlet, from the reaction furnace. A few mls. of KI-KIO_3 solution in the SO_2 bubbler will indicate the flow of SO_2. At this stage the CO_2 was started slowly. As the CO_2 flow rate was increased the CO was also admitted. In a few minutes the flowrates were up to the desired values. Small adjustments were made by means of the bleeder columns.

The gas was allowed to run to waste for an hour and was then analysed for SO_2. The absorbent in the SO_2 bubbler consisted of 100 ml. of distilled water + a few mls. of 1:4 HCl. The gas mixture was passed through this solution for a period of 2-4 minutes. The H_2SO_3 formed was then titrated against standard KI-KIO_3 solution using freshly prepared starch solution as an indicator. The nitrogen flow through the reaction tube was stopped before the SO_2 analysis was started. This was in order to divert the gas flow through Channel 4 while the absorbent in the SO_2 bubbler was being titrated. SO_2 absorption was complete and a second SO_2 bubbler was found to be superfluous. At least three estimations were carried out within a period of 15-20 minutes to determine any fluctuations in the SO_2 flow. During the second and later estimations it was found easier to add KI-KIO_3 solution (about 2 ml. short of the volume required in the first one) into the SO_2 bubbler and titrate as previously. In an alternative method a 5-volume H_2O_2 solution was used as the absorbent and the H_2SO_4 formed titrated against a standard NaOH solution using dimethyl yellow as an indicator. Difficulty was experienced in obtaining the same end point in each titration unless a standard coloured solution was kept for comparison. Carter and Macfarlane used the second method while the first one was used in the present work. The first method was considered to be more convenient and sharp end points could be obtained more easily.

When SO_2 was flowing at a steady rate the total $CO_2 + SO_2$ was determined by passing the gas for 6 minutes through the weighed Midvale bulb in Channel 2. CO_2 and SO_2 were both absorbed and thus the increase in the weight of the bulb gave the weight of $CO_2 + SO_2$ for that period. The gas sampler was now disconnected and analysed to obtain the CO/CO_2+SO_2 ratio by flushing the gas out with purified nitrogen through a weighed Midvale bulb containing soda asbestos. This absorbed CO_2 and SO_2. The CO was oxidised further on by Copper oxide held at 450-500°C in a small nichrome wound furnace. The CO_2 thus obtained was absorbed by a second weighed soda asbestos bulb. This estimation was completed in about 20 minutes.

The three determinations gave:-

1. Weight of SO_2 in gm./minute.
2. Weight of CO_2+SO_2 in gm./minute.
3. Weight ratio - CO/CO_2+SO_2.

The volumetric composition of the gas mixture can be obtained from the above three values.

The gas mixture was now introduced into the reaction tube from the bottom and withdrawn from the top to flush out all the nitrogen inside it. The flushing was carried out for half an hour. By this time the temperature of the reaction furnace had been brought up to 1500°C. The gas flow was momentarily switched to Channel 4, thereby by-passing the furnace. The top outlet was closed, and the gas reintroduced into the reaction tube through the central narrow bore alumina tube, and withdrawn from the bottom. Carter and Macfarlane using a similar set up found that the temperature in the reaction zone remained unaffected when the gas impinged on the slag in the crucibles, showing that the gas mixture was sufficiently preheated. Thermal diffusion effects were reduced to a minimum by having a small reaction chamber.

The direction of the gas flow within the reaction tube was subject to some changes before the above mentioned procedure was adopted. The gas mixture was, at first, introduced and withdrawn from the top. This method was found to be satisfactory only as long as the top suspension was very close to the crucibles (1/2"). If too close, the crucibles stick to the suspension, thus spoiling the entire run. If on the other hand, the suspension was too far away, lower sulphur pick-ups were obtained. For example a slag containing 49.6 per cent CaO, and 50.4 per cent Al_2O_3 absorbed 0.3 per cent sulphur instead of the expected value of 0.36 per cent sulphur from a gas whose A_K value was 245, when the distance was more than $3/4"$. The distance between the lower tip of suspension and the crucibles was not very critical in the method adopted for the present work which differed from Carter and Macfarlane in that the gas was withdrawn from the bottom instead of the top.

The gas flow through the reaction tube was continued for at least 4 hours after which the gas was switched to Channel 4, the reaction furnace switched off and the slags quenched by lowering the alundum tray quickly through the first 3" and then more slowly to prevent cracking the Mullite tube. The crucibles were out of the furnace in less than 2 minutes. The slags were then kept in desiccators. The SO_2 analysis was carried out every hour during each run; the variation in the titration reading did not vary by more than 0.2 ml. per minute (= 0.014 ml. of SO_2). The analysis of the gas mixture at the end of the run showed a similarly negligible difference from the earlier analyses.

The sulphur contents of the slags were determined by the method given by Fincham and Richardson.(49). The slag was broken up (with one single blow) into small pieces in a percussion mortar and then weighed into a pre-ignited alundum boat. The boat was introduced into a 13 per cent Rh-Pt. wound furnace held at 1425-1450°C. CO_2 was passed over the slag and the SO_2 evolved absorbed by acidulated water, and continuously titrated with $KI-KIO_3$ solution. The estimation was completed in half an hour for $CaO-SiO_2$ slags, whereas some $CaO-Al_2O_3$ slags took as much as one and a half hours. By adding small quantities of Na_2CO_3 to the slag in the boat, the time taken could be reduced to about half an hour. This procedure was adopted for all slags containing Al_2O_3.

CHAPTER V.

COMPARISON OF POSSIBLE THERMODYNAMIC DATA.

COMPARISON OF POSSIBLE THERMODYNAMIC DATA.

In Chapter III the differences in the thermodynamic data were discussed, but no conclusion was reached as to the best choice of data for use in the calculations of a CaO in the present investigation. In order to obtain further information a series of experiments was carried out in which a slag containing 45 per cent CaO, and 55 per cent Al_2O_3 was equilibrated with gas mixtures of different CO/CO_2 ratios and SO_2 contents at 1500°C. These results are presented in Table IV.

Lime activities were calculated in a manner similar to that used by Carter and Macfarlane. Thus for the reaction:

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

the equilibrium constant $K = \frac{a_{CaS}}{a_{CaO}} \cdot \frac{pO_2}{pS_2}$, and if $pS_2 / pO_2 = A$,

$a_{CaO} = a_{CaS}/K.A.$

Although the direct determination of absolute values of a CaO and a CaS is not possible from these experiments, the results obtained can be combined with the results of an experiment in which a standard slag of unit lime activity (i.e., saturated with lime) is equilibrated with a suitable $CO-CO_2-SO_2$ gas mixture. Hence the lime activity for any slag will be given by:

$$a_{CaO} = \frac{a_{CaS}}{A} \bigg/ \frac{a^{\circ}_{CaS}}{A^{\circ}}$$

where the superscript refers to the standard slag. If it is assumed that for slags far removed from sulphide saturation, percentage sulphur

TABLE IV.

CALCULATION OF α_{CaO} with A_K, A_{pC}, A_{RJ}, A_{DR}.

CO/CO_2	$\%SO_2$	A_K	A_{pC}	A_{RJ}	A_{DR}	Nature of Slag	% Sulphur	α_{CaO} K	α_{CaO} pC	α_{CaO} RJ	α_{CaO} DR
1.762	0.521				275	Glass	0.197				0.110
1.504	0.654	300	250	135	255	"	0.184	0.1109	0.1102	0.1251	0.1106
1.511	0.879	365	312	185	310	"	0.2295	0.1116	0.1103	0.1140	0.1136
1.778	0.658	395	330	190	330	"	0.2572	0.116	0.1169	0.1250	0.1198
1.675	1.148	500	440	285	445	"	0.3035	0.1086	0.1058	0.0977	0.1046
2.39	1.331	845	790	555	755	Glass + Y Spot.	0.559	0.1185	0.1069	0.0926	0.1137
2.242	1.769	900	83 5	605	810	Glass	0.5993	0.1192	0.1076	0.0911	0.1136
2.336	2.071	995	945	700	910	"	0.719	0.1293	0.1141	0.0945	0.1213
2.371	2.164	1040	975	730	950	"	0.714	0.123	0.1098	0.09	0.1153
2.272	2.354	1040	965	725	945	"	0.75	0.129	0.1166	0.0952	0.1218
2.491	2.024	1070	1010	750	975	"	0.79	0.132	0.1173	0.0968	0.1243
2.843	1.673	1130	1075	793	1031	"	0.821	0.130	0.1145	0.0923	0.1222
2.593	2.531	1215	1150	890	1112	"	0.8645	0.1263	0.1127	0.0893	0.1192
3.01	2.392	1375	1315	1030	1256	"	0.9835	0.128	0.1121	0.0878	0.1196
3.557	2.085	1555	1465	1160	1420	"	0.997	0.1147	0.1021	0.0790	0.1077
3.369	2.573	1580	1518	1235	1455	"	0.954	0.108	0.0943	0.0711	0.1008
3.411	2.685	1620	1555	1265	1500	"	0.9565	0.106	0.0923	0.0695	0.0978
3.405	2.717	1630	1562	1270	1503	"	0.9508	0.1044	0.0913	0.0693	0.0972

can be substituted for a_{CaS}, this expression becomes

$$a_{CaO} = \frac{\%S}{A} \Big/ \frac{\%S^{o}}{A^{o}}$$

A similar assumption was also made by Carter and Macfarlane. A standard slag (CaO = 60.0 per cent, Al_2O_3 = 32.6 per cent, SiO_2 = 7.4 per cent) was found to absorb 2 per cent sulphur from a gas mixture with sulphurizing potential - $A_K = 358$, $A_R = 185$, $A_{pC} = 300$, $A_{DR} = 307$, substituting these values in the above equation the lime activity values shown in Table IV were obtained. These values are plotted against sulphurizing potential in Fig.4 for each of the four sets of data. It can be seen that a_{CaO} values calculated using the data of St. Pierre and Chipman(34), and Dewing and Richardson(46) remain constant within the limits of experimental errors up to a sulphurizing potential of 1300, beyond which a decrease is observed. In the case of Kelley's data a_{CaO} shows a slight increase in the region of $A_K = 1100$ and decreases from 1400 onwards. The lime activity values derived from the data of Richardson and Jeffes show a decrease right through the range of A values.

Constancy in the calculated values for lime activity would be expected if:-

(a) the activity coefficient of CaS does not vary with sulphur content;

(b) substitution of oxide ions by sulphide ions does not affect the lime activity,

(c) the correct thermodynamic data have been chosen.

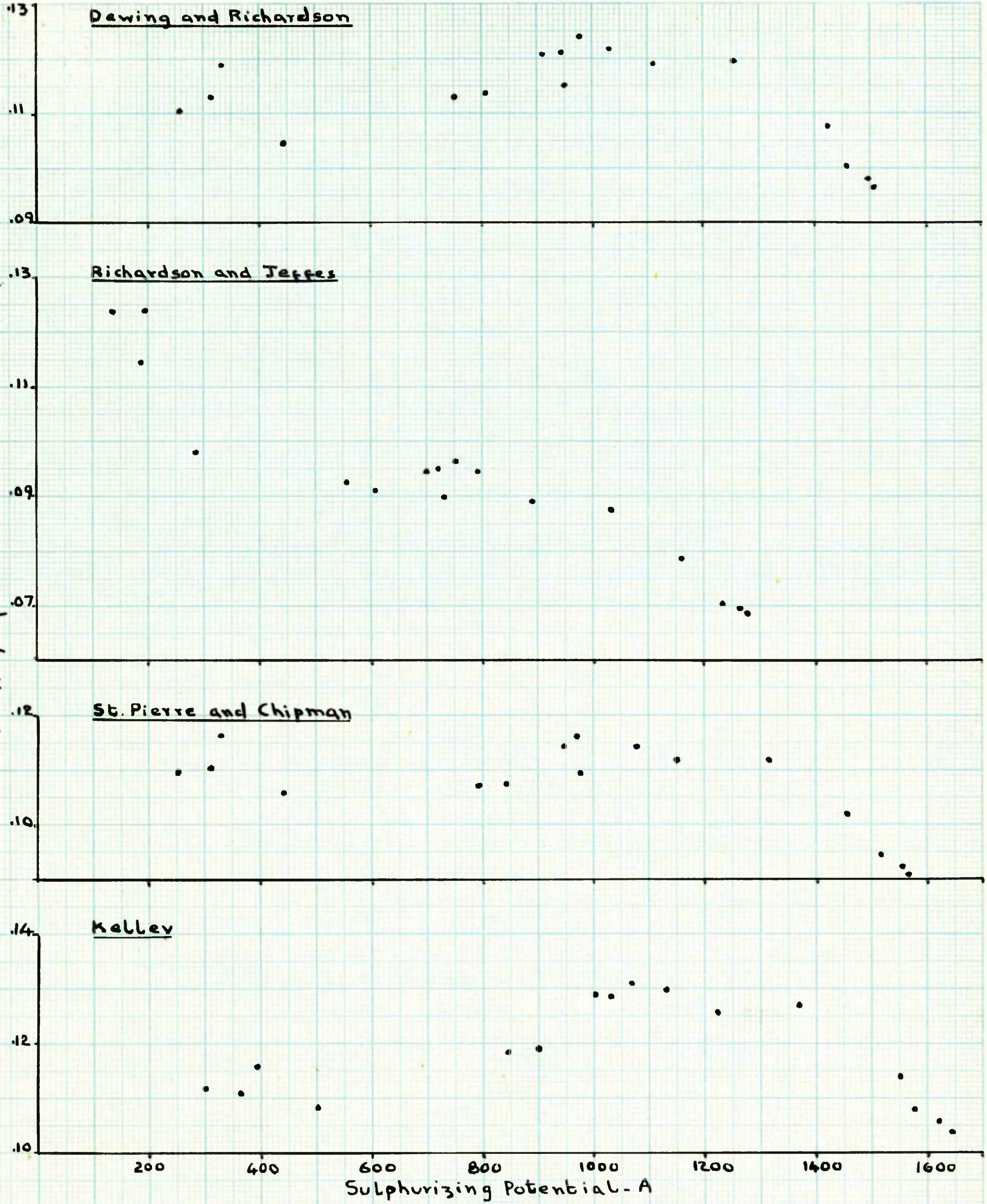


Fig. 4. Sulphurizing Potential against Activity of Lime

The data and the calculations of Rosenqvist(50) indicate that γ CaS decreases with increasing sulphur content in blast furnace type slags. However, the effect does not appear to be serious below about 2 per cent sulphur. A small decrease in γ CaS at high sulphur contents should show itself in the form of a decrease in a CaO and this may account for the small decrease observed, as shown in Fig.4, when the sulphur content exceeded about 1 per cent. On the other hand, it would seem probable that substitution of oxide ions by sulphide ions would cause some lowering of the oxide activity of the slag and this also may be the reason for the observed decrease in a CaO when the sulphur contents exceed 1 per cent. It would be difficult to calculate the quantitative effect of this substitution but some lowering of a CaO might have been expected at an earlier stage, i.e., at lower sulphur contents. It may be that in the early stages of the substitution sufficient further breakdown of the aluminate ions occurs, giving more oxide ions to counteract to a large extent the substitution of oxide ions by sulphide ions. It would be expected that eventually a stage would be reached when the breakdown of the aluminate ions would materially fall short of that required to compensate the loss of oxide ions caused by sulphide substitution. A marked fall in oxide activity should then occur and this is probably the main reason for the drop in a CaO shown in Fig.4 at high sulphur contents.

If this explanation is feasible, then some light might be thrown on the problem by re-calculating the slag compositions on a CaS-free basis. This has been done and the results plotted in Fig.5, which

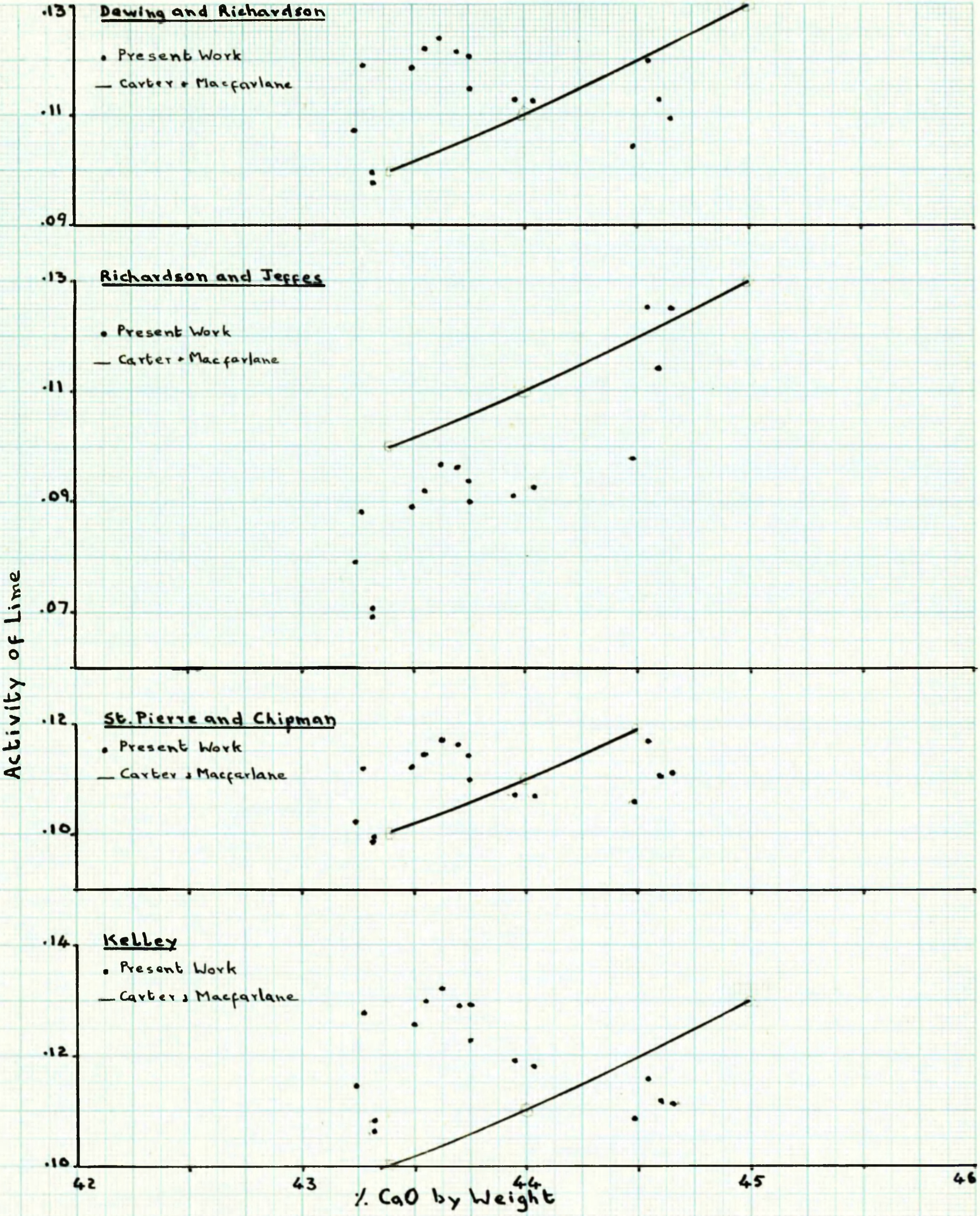


Fig. 5. Variation of aCaO with Slag Composition

also shows the variation of a CaO with composition given by Carter and Macfarlane. Apparently there is no agreement between the basic curve and the calculated results, and in fact in this line of argument the results of Richardson and Jeffes seem to fit the picture better than any of the others. However, it was shown by Carter and Macfarlane that a CaO is constant for low sulphur concentrations, and consequently the assumption made in using CaS-free slags has been fallacious.

It seems probable that at low sulphur concentrations the substitution of sulphide ions for oxide ions does not lower a CaO significantly. If this assumption is made, the results of the above experiments, recorded in Table IV, seem to rule out the possibility of the data of Richardson and Jeffes being correct. There is little to choose between the remaining three sets of data, although the slight rise in a CaO with sulphurizing potential shown by the data of Kelley seems improbable. The difference between the data of Dewing and Richardson, and St. Pierre and Chipman centres mainly around the value for the heat of formation of SO. The value put forward by Dewing and Richardson was obtained by two independent methods and hence one might expect that greater reliance could be placed on their values. Furthermore, the experimental results of St. Pierre and Chipman are more susceptible to errors caused by the presence of small amounts of oxygen which could enter the system either as an impurity in SO_2 or by a small leak. In their experiments the oxygen pressure in the gas (essentially pure SO_2) was calculated from the ratio $Fe^{+++}/Fe^{+++} + Fe^{++}$ in CaO-FeO slags with which the gas was in equilibrium. It was assumed that pSO would equal $\frac{1}{2}pO_2$. If oxygen has leaked into the system this assumption is not true and calculation indicates that less than 0.08 per cent O_2 would be sufficient to cause the discrepancy between Dewing and Richardson, and St.Pierre and Chipman. Since the SO data of Dewing and Richardson were obtained by two different methods which gave closely agreeing results, it is proposed to use their data in the remainder of this work.

CHAPTER VI.

RESULTS.

RESULTS.

The purpose of the present work is to determine the effect of addition of MgO on the sulphur absorption characteristics of slags containing CaO, Al_2O_3, and SiO_2. The general plan of work was to start with binary and ternary master slags and measure the equilibrium sulphur contents for these slags with and without MgO. In Table V, the compositions of the slags used in the present investigation are given. The method of preparation of these slags has been given earlier. The study of the master slags made it possible to compare the results of the present work with those of Carter and Macfarlane for slags of the same systems.

A detailed study of the effect of some variables like time, temperature, and gas rate has not been carried out during the present work. Fincham and Richardson(32) studied the effect of temperature, and showed that for a gas of constant equilibrium pO_2 and a given SO_2 content the equilibrium sulphur content increased with temperature. This was confirmed by Carter and Macfarlane. In the present investigation only 1500°C was used. As to the other variables Carter and MacFarlane's thorough investigation has been used as a basis for the present work. The equilibrium sulphur pick-up was attained in about three hours, and the flow rate did not greatly influence the sulphur pick-up. Hence in the present work the runs were carried out for a

TABLE V.

COMPOSITION OF SLAGS.

	Weight Per cent.				Mol. Fraction.			
Slag	CaO	Al_2O_3	SiO_2	MgO	CaO	Al_2O_3	SiO_2	MgO
CA1	40.3	59.7	-	-	0.551	0.449	-	-
CA2	41.6	58.4	-	-	0.564	0.436	-	-
CA3	45.0	55.0	-	-	0.598	0.402	-	-
CA4	49.6	50.4	-	-	0.642	0.358	-	-
CA5	53.8	46.2	-	-	0.679	0.321	-	-
CS1	35.14	-	64.86	-	0.367	-	0.633	-
CS2	40.25	-	59.75	-	0.42	-	0.58	-
CS3	45.94	-	54.06	-	0.477	-	0.523	-
CS4	49.2	-	50.8	-	0.509	-	0.491	-
CS5	52.0	-	48.0	-	0.538	-	0.462	-
CS6	56.0	-	44.0	-	0.577	-	0.423	-
CS7	56.8	-	43.2	-	0.59	-	0.41	-
CAS1	20.45	11.76	67.79	-	0.226	0.072	0.702	-
CAS2	29.66	11.14	59.2	-	0.326	0.067	0.607	-
CAS3	40.8	9.64	49.56	-	0.443	0.057	0.500	-
CAS4	23.88	14.87	61.25	-	0.268	0.092	0.64	-
CAS5	35.4	14.15	49.75	-	0.393	0.091	0.516	-
CAS6	41.38	14.34	44.28	-	0.457	0.087	0.456	-
CAS7	24.5	19.56	55.94	-	0.280	0.123	0.597	-
CAS8	36.2	16.34	47.46	-	0.405	0.100	0.495	-
CAS9	45.9	18.38	35.71	-	0.52	0.112	0.368	-
CAS10	60.06	32.56	7.38	-	0.708	0.211	0.081	-
CAM1	38.3	56.7	-	5.0	0.501	0.408	-	0.091
CAM2	37.9	56.1	-	6.0	0.492	0.400	-	0.108
CAM3	37.5	55.5	-	7.0	0.482	0.393	-	0.125
CAM4	37.1	54.9	-	8.0	0.473	0.385	-	0.142
CAM5	36.7	54.3	-	9.0	0.464	0.378	-	0.158
CAM6	36.3	53.7	-	10.0	0.453	0.372	-	0.175
CAM7	39.5	55.5	-	5.0	0.513	0.397	-	0.090
CAM8	39.0	55.0	-	6.0	0.503	0.390	-	0.107
CAM9	38.6	54.4	-	7.0	0.494	0.382	-	0.124
CAM10	37.8	53.2	-	9.0	0.475	0.368	-	0.157
CAM11	44.3	54.7	-	1.5	0.580	0.393	-	0.027
CAM12	43.7	53.3	-	3.0	0.566	0.380	-	0.054
CAM13	43.2	52.8	-	4.0	0.555	0.373	-	0.072
CAM14	42.8	52.2	-	5.0	0.546	0.366	-	0.088
CAM15	42.4	51.6	-	6.0	0.536	0.359	-	0.105
CAM16	41.9	51.1	-	7.0	0.525	0.353	-	0.122
CAM17	41.5	50.5	-	8.0	0.516	0.346	-	0.138

Slag	Weight Per cent.				Mol. Fraction.			
	CaO	Al_2O_3	SiO_2	MgO	CaO	Al_2O_3	SiO_2	MgO
CAM18	41.0	50.0	-	9.0	0.506	0.340	-	0.154
CAM19	47.1	47.9	-	5.0	0.586	0.328	-	0.086
CAM20	46.6	47.4	-	6.0	0.575	0.322	-	0.103
CAM21	46.1	46.9	-	7.0	0.565	0.316	-	0.119
CAM22	45.6	46.4	-	8.0	0.555	0.310	-	0.135
CAM23	45.1	45.9	-	9.0	0.545	0.304	-	0.151
CAM24	44.6	45.4	-	10.0	0.534	0.300	-	0.166
CAM25	51.0	44.0	-	5.0	0.621	0.295	-	0.084
CAM26	50.5	43.5	-	6.0	0.610	0.289	-	0.101
CAM27	49.9	43.1	-	7.0	0.599	0.284	-	0.117
CAM28	42.0	55.0	-	3.0	0.55	0.396	-	0.054
CAM29	41.0	55.0	-	4.0	0.534	0.394	-	0.022
CAM30	40.0	55.0	-	5.0	0.518	0.392	-	0.09
CAM31	48.1	50.4	-	1.5	0.618	0.356	-	0.026
CAM32	46.6	50.4	-	3.0	0.594	0.353	-	0.053
CAM33	45.6	50.4	-	4.0	0.578	0.352	-	0.07
CAM34	44.6	50.4	-	5.0	0.563	0.349	-	0.088
CAM35	43.6	50.4	-	6.0	0.547	0.348	-	0.105
CAM36	42.6	50.4	-	7.0	0.532	0.346	-	0.122
CAM37	41.6	50.4	-	8.0	0.517	0.345	-	0.138
CAM38	40.6	50.4	-	9.0	0.502	0.343	-	0.155
CAM39	39.6	50.4	-	10.0	0.488	0.341	-	0.171
CAM40	52.3	46.2	-	1.5	0.656	0.318	-	0.026
CAM41	50.8	46.2	-	3.0	0.632	0.316	-	0.052
CAM42	49.8	46.2	-	4.0	0.617	0.314	-	0.069
CAM43	48.8	46.2	-	5.0	0.601	0.313	-	0.086
CAM44	47.8	46.2	-	6.0	0.586	0.312	-	0.102
CAM45	46.8	46.2	-	7.0	0.571	0.310	-	0.119
CSM1	33.6	-	62.4	4.0	0.345	-	0.598	0.057
CSM2	32.3	-	59.7	8.0	0.326	-	0.562	0.112
CSM3	31.0	-	57.0	12.0	0.307	-	0.527	0.116
CSM4	29.5	-	54.5	16.0	0.288	-	0.496	0.216
CSM5	28.0	-	52.0	20.0	0.269	-	0.465	0.266
CSM6	2 6.7	-	49.3	24.0	0.252	-	0.434	0.314
CSM7	38.6	-	57.4	4.0	0.395	-	0.548	0.057
CSM8	37.0	-	55.0	8.0	0.372	-	0.516	0.112
CSM9	35.5	-	52.5	12.0	0.351	-	0.484	0.165
CSM10	34.0	-	50.0	16.0	0.331	-	0.453	0.216
CSM11	32.5	-	47.5	20.0	0.311	-	0.424	0.265
CSM12	30.7	-	45.3	24.0	0.289	-	0.397	0.314
CSM13	44.0	-	52.0	4.0	0.449	-	0.494	0.057
CSM14	42.6	-	49.4	8.0	0.427	-	0.462	0.111
CSM15	40.3	-	47.7	12.0	0.397	-	0.439	0.164

Slag	Weight Per cent.				Mol. Fraction.			
	CaO	Al_2O_3	SiO_2	MgO	CaO	Al_2O_3	SiO_2	MgO
CSM16	38.5	-	45.5	16.0	0.373	-	0.411	0.216
CSM17	36.6	-	43.4	20.0	0.349	-	0.386	0.265
CSM18	35.0	-	41.0	24.0	0.328	-	0.359	0.313
CSM19	47.3	-	48.7	4.0	0.481	-	0.462	0.057
CSM20	45.5	-	46.5	8.0	0.455	-	0.434	0.111
CSM21	43.4	-	44.6	12.0	0.427	-	0.409	0.164
CSM22	41.5	-	42.5	16.0	0.402	-	0.383	0.215
CSM23	39.5	-	40.5	20.0	0.376	-	0.359	0.265
CSM24	37.3	-	38.7	24.0	0.349	-	0.338	0.313
CSM25	31.14	-	64.86	4.0	0.32	-	0.623	0.057
CSM26	27.14	-	64.86	8.0	0.275	-	0.612	0.113
CSM27	23.14	-	64.86	12.0	0.230	-	0.604	0.166
CSM28	15.14	-	64.86	20.0	0.146	-	0.585	0.269
CSM29	11.14	-	64.86	24.0	0.106	-	0.576	0.318
CSM30	36.25	-	59.75	4.0	0.372	-	0.571	0.057
CSM31	32.25	-	59.75	8.0	0.326	-	0.562	0.112
CSM32	28.25	-	59.75	12.0	0.28	-	0.554	0.166
CSM33	24.25	-	59.75	16.0	0.237	-	0.545	0.218
CSM34	20.25	-	59.75	20.0	0.195	-	0.537	0.268
CSM35	16.25	-	59.75	24.0	0.154	-	0.529	0.317
CSM36	51.8	-	43.2	5.0	0.523	-	0.407	0.070
CSM37	47.8	-	43.2	9.0	0.475	-	0.400	0.125
CSM38	43.8	-	43.2	13.0	0.429	-	0.394	0.177
CSM39	39.8	-	43.2	17.0	0.384	-	0.388	0.228
CSM40	36.8	-	43.2	20.0	0.351	-	0.384	0.265
CSM41	33.8	-	43.2	23.0	0.319	-	0.380	0.301
CSM42	30.8	-	43.2	26.0	0.287	-	0.376	0.337
CASM1	19.42	11.18	64.4	5.0	0.210	0.066	0.648	0.075
CASM2	18.41	10.59	61.0	10.0	0.194	0.062	0.599	0.146
CASM3	17.38	10.0	57.62	15.0	0.178	0.056	0.552	0.214
CASM4	28.18	10.58	56.24	5.0	0.302	0.062	0.562	0.074
CASM5	26.69	10.03	53.28	10.0	0.279	0.057	0.519	0.145
CASM6	25.22	9.47	50.31	15.0	0.257	0.053	0.478	0.212
CASM7	38.77	9.16	47.07	5.0	0.41	0.053	0.464	0.073
CASM8	36.73	8.66	44.61	10.0	0.379	0.049	0.429	0.143
CASM9	34.68	8.20	42.12	15.0	0.349	0.045	0.396	0.21
CASM10	22.68	14.12	58.2	5.0	0.247	0.085	0.592	0.076
CASM11	21.49	13.39	55.12	10.0	0.228	0.078	0.546	0.148
CASM12	20.30	12.64	52.06	15.0	0.210	0.072	0.502	0.216
CASM13	33.62	14.11	47.27	5.0	0.364	0.084	0.477	0.075
CASM14	31.85	13.37	44.78	10.0	0.336	0.078	0.440	0.146
CASM15	30.09	12.62	42.29	15.0	0.309	0.071	0.406	0.214
CASM16	39.31	13.62	42.07	5	0.423	0.080	0.422	0.075

Slag	Weight Per cent.				Mol. Fraction.			
	CaO	Al_2O_3	SiO_2	MgO	CaO	Al_2O_3	SiO_2	MgO
CASM17	37.24	12.90	39.85	10.0	0.390	0.074	0.390	0.146
CASM18	35.18	12.19	37.63	15.0	0.360	0.068	0.389	0.213
CASM19	23.28	18.58	53.14	5.0	0.259	0.113	0.551	0.077
CASM20	22.05	17.60	50.35	10.0	0.238	0.105	0.507	0.150
CASM21	20.83	16.63	47.54	15.0	0.218	0.096	0.466	0.220
CASM22	34.39	15.52	45.09	5.0	0.374	0.093	0.457	0.076
CASM23	32.58	14.71	42.71	10.0	0.345	0.086	0.422	0.147
CASM24	30.77	13.89	40.34	15.0	0.318	0.079	0.388	0.215
CASM25	43.6	17.47	33.93	5.0	0.475	0.105	0.345	0.075
CASM26	41.3	16.55	32.15	10.0	0.438	0.096	0.318	0.147
CASM27	39.01	15.63	30.36	15.0	0.403	0.089	0.293	0.215

minimum of four hours with a flow rate of 140-150 ml./min.

No definite trend was noticeable from the nature of the slag at the end of each run. Slags varied from a glass to a milky coloured melt. Probably the differences are due to the quenching technique, the difference between the experimental temperature, the liquidus temperature and the slag composition. Osborn and Co-workers(51) determined the melting point of a number of slags using the quenching method. They found that liquids having a relatively low CaO + MgO content quenched to glasses, while those containing more than 60 per cent of CaO + MgO content do not quench to a glass but devitrify during quenching.

In each experiment the slags were weighed before and after the run, In almost every case a loss in weight was observed. In Tables VI, VII and VIII, the percentage loss in weight is tabulated against per cent MgO in $CaO-Al_2O_3$, $CaO-SiO_2$ and $CaO-Al_2O_3-SiO_2$ slags. Any increase in weight is denoted by a plus sign. In all three systems the loss in weight is found to increase with MgO content. This suggests that the loss may be due to volatilization of Mg from the slag. The agreement between the various sets is not particularly good. This may be due to the different CO/CO_2 ratios used in the various experiments, if the loss observed is assumed to be according to the reaction

$$MgO + CO = Mg + CO_2$$

$$\Delta G_{1773}^{\circ} = +58.16 \text{ K.cals.}$$

$$K_{1773}^{\circ} = 6.776 \times 10^{-8}$$

TABLE VI.

Per cent Loss in Weight in $CaO-Al_2O_3-MgO$ slags.

(a) MgO additions to slags of constant CaO/Al_2O_3 ratio.

Slag	CaO/Al_2O_3 Ratio.	% MgO									
		0	1.5	3	4	5	6	7	8	9	10
CA1	0.68	0.34	-	-	-	0.62	0.7	0.8	0.9	1.1	0.9
CA3	0.82	0.92	1.2	1.44	1.21	-	-	-	-	-	-
"	"	1.26	-	-	-	1.4	1.5	1.4	1.6	1.7	1.7
CA4	0.98	0.94	-	-	-	1.1	1.3	1.3	-	-	-
"	"	0.94	-	-	-	1.2	1.2	1.2	1.3	1.3	1.4
CA5	1.16	0.42	-	-	-	0.75	0.8	0.8	-	-	-

(b) MgO additions to slags of constant Al_2O_3 content.

Slag	Al_2O_3	% MgO									
		0	1.5	3	4	5	6	7	8	9	10
CA3	55.0	1.22	1.4	1.4	1.5	-	-	-	-	-	-
CA4	50.4	1.22	1.4	1.5	1.6	-	-	-	-	-	-
"	"	1.1	-	-	-	1.5	1.6	1.6	1.6	1.2	1.7
CA5	46.2	0.4	0.4	0.5	0.7	0.7	0.9	1.1	-	-	-

TABLE VII.

Per cent Loss in Weight $CaO-SiO_2-MgO$ Slags.

(a) MgO additions to slags of constant CaO/SiO_2 ratio.

Slag	CaO/SiO_2 Ratio.	% MgO 0	4	8	12	16	20	24
CS1	0.54	-	0.3	0.7	1.0	-	-	-
"	"	0.2	0.3	0.6	1.0	0.9	1.8	1.6
CS2	0.7	+0.1		0.4	0.8	1.0	1.4	1.6
CS3	0.9	-	-	0.4	0.5	1.3	1.1	1.4
CS4	1.0	-	0.3	0.6	0.8	1.2	1.0	1.0

(b) MgO additions to slags of constant SiO_2 content.

Slag	% SiO_2	% MgO 0	4	8	12	16	20	24	
CS1	64.86		0.2	0.4	0.7	1.1	1.2	1.9	
CS2	59.75	+0.2	0.2	0.5	0.6	0.8	1.0	1.3	
CS4	50.8	-	-	0.4	0.6	1.1	-	-	
CS7	43.2	-	(5) 1.0	(9) 1.1	(13) 1.4	(17) 1.7	-	(23) -	(26) -
"		-	1.0	1.2	1.7	1.7	1.7	1.8	2.3

TABLE VIII.

Per cent Loss in Weight in $CaO-Al_2O_3-SiO_2-MgO$ Slags.

MgO additions to slags of constant $CaO/Al_2O_3+SiO_2$ ratio.

Slag	$CaO/Al_2O_3+SiO_2$ Ratio.	% MgO. 0	5	10	15
CAS1	0.257	-	0.2	0.4	1.0
CAS2	0.422	-	0.3	0.6	0.9
CAS3	0.689	-	0.3	0.9	1.2
CAS4	0.314	-	0.3	0.6	1.0
CAS5	0.549	0.1	0.5	0.7	1.4
CAS6	0.706	0.7	0.8	1.3	1.5
CAS7	0.324	0.2	0.3	0.6	0.9
CAS8	0.567	-	0.3	0.7	2.0
CAS9	0.848	-	0.4	0.7	1.0

But for the lack of data, it would have been possible to determine the partial pressure of Mg over such melts and use these results to calculate a MgO. Absorption of moisture by the magnesia during the preliminary weightings cannot be overlooked. This would also result in a loss in weight. A 2 per cent loss in weight corresponds to a loss of 5 m.gm. in a 0.25 gm. sample. Some of the high losses obtained may also be due to the slag material being blown away by the gas impinging on the slag surface.

On comparing the two binary systems, it can be seen that the change in weight of $CaO-SiO_2$, and $CaO-Al_2O_3-SiO_2$ slags is small compared to that in $CaO-Al_2O_3$ slags. The activity of lime in $CaO-SiO_2$, and $CaO-Al_2O_3-SiO_2$ slags is low, resulting probably in smaller losses in weight, even though the silica activities may vary from 1.0 to 0.1. In the case of $CaO-Al_2O_3$ slags, the lime activities are much higher with the alumina activity varying from 0.2 downwards. The greater loss in $CaO-Al_2O_3$ slags may be due to this increased a CaO.

AN ESTIMATE OF EXPERIMENTAL ERRORS.

During a run, as described in the experimental procedure, several gas analyses are carried out. Variations in these analyses would affect the final a CaO values obtained from these measurements.

Slag Analysis : ± 0.5 %

Furnace Temperature : ± 2°C

SO_2 flow rate : ± 0.014 cc/min.

Total $CO_2 + SO_2$: ± 0.086 cc.

Sulphurizing Potential : ± 8 %

Sulphur estimation : ± 3 %

From this data the calculated Total Error is ± 12 %.

The effect of the change in weight of the slag must also be considered. As pointed out earlier, the loss cannot be ascribed to any particular cause, e.g., mechanical loss, moisture, volatilization of Mg, loss of CaO. If only MgO was lost, it would be possible to correct the slag composition. A maximum loss in weight of 2.3 per cent (Table VII) corresponds to a change in MgO content from 26 per cent to 24.3 per cent. If other factors were operative in the loss then the change in MgO content would be much less.

All the experimental results obtained during the present work are presented in Tables IX - XIV, and the graphs plotted from these results are presented in the appropriate sequence.

$CaO-Al_2O_3$ System.

The lime activity values of Table IX are plotted against per cent CaO by weight in Fig.6, where they are represented by open circles.

TABLE IX.

$CaO-Al_2O_3$ System.

Slag	CO/CO_2 Ratio.	$\%SO_3$	A_{DR}	Time in Hours	Nature of Slag	%Sulphur	α CaO	Mean
CA1	1.83	0.695	360	5½	Glass	0.119	0.050	0.052
CA1	1.83	0.511	285	5½	Cryst.	0.100	0.054	
CA2	1.91	0.48	300	4	Yellow	0.125	0.064	0.065
CA2	1.83	0.533	295	5½	White	0.127	0.066	
CA3	Mean of first 15 in Table IV.							0.116
CA4	1.937	0.76	420	5½	Glass	0.652	0.238	
CA4	1.981	0.596	360	5½	"	0.627	0.267	
CA4	1.837	0.599	325	5	"	0.542	0.256	0.257
CA4	1.681	0.624	292	5	"	0.483	0.254	
CA4	1.576	0.811	323	4½	"	0.543	0.258	
CA4	1.624	0.643	292	5	"	0.514	0.270	
CA5	1.67	0.597	275	5½	"	0.875	0.488	
CA5	1.526	0.773	293	5	"	0.944	0.494	
CA5	1.694	0.647	300	5	"	0.889	0.455	0.473
CA5	1.784	0.588	310	5	Glass + w spots	0.962	0.476	
CA5	1.746	0.734	350	5½	" "	1.057	0.463	
CA5	1.737	0.704	335	4½	" "	1.005	0.461	

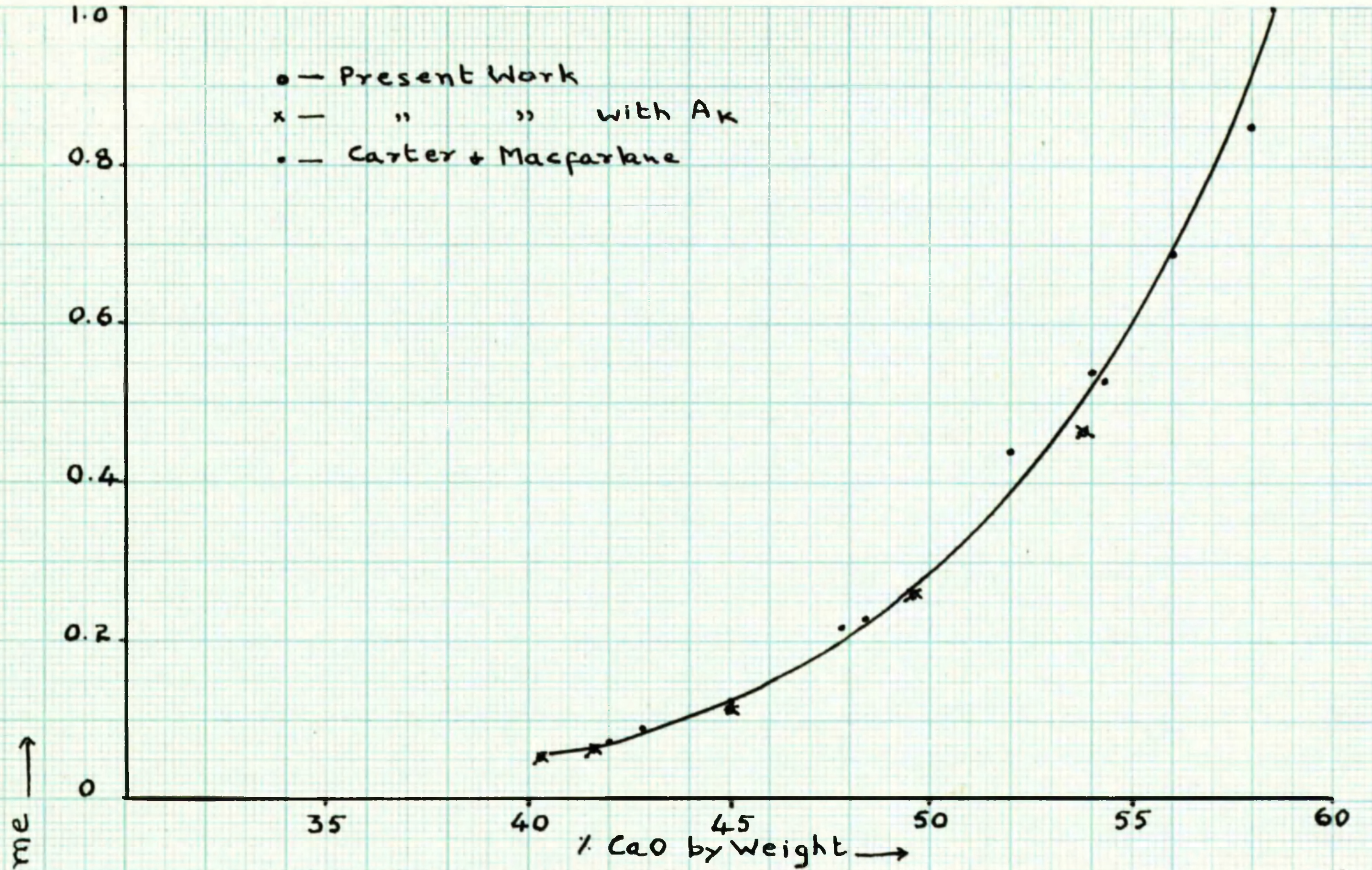


Fig-6. Activity of Lime in $CaO-Al_2O_3$ Slags at 1500°c

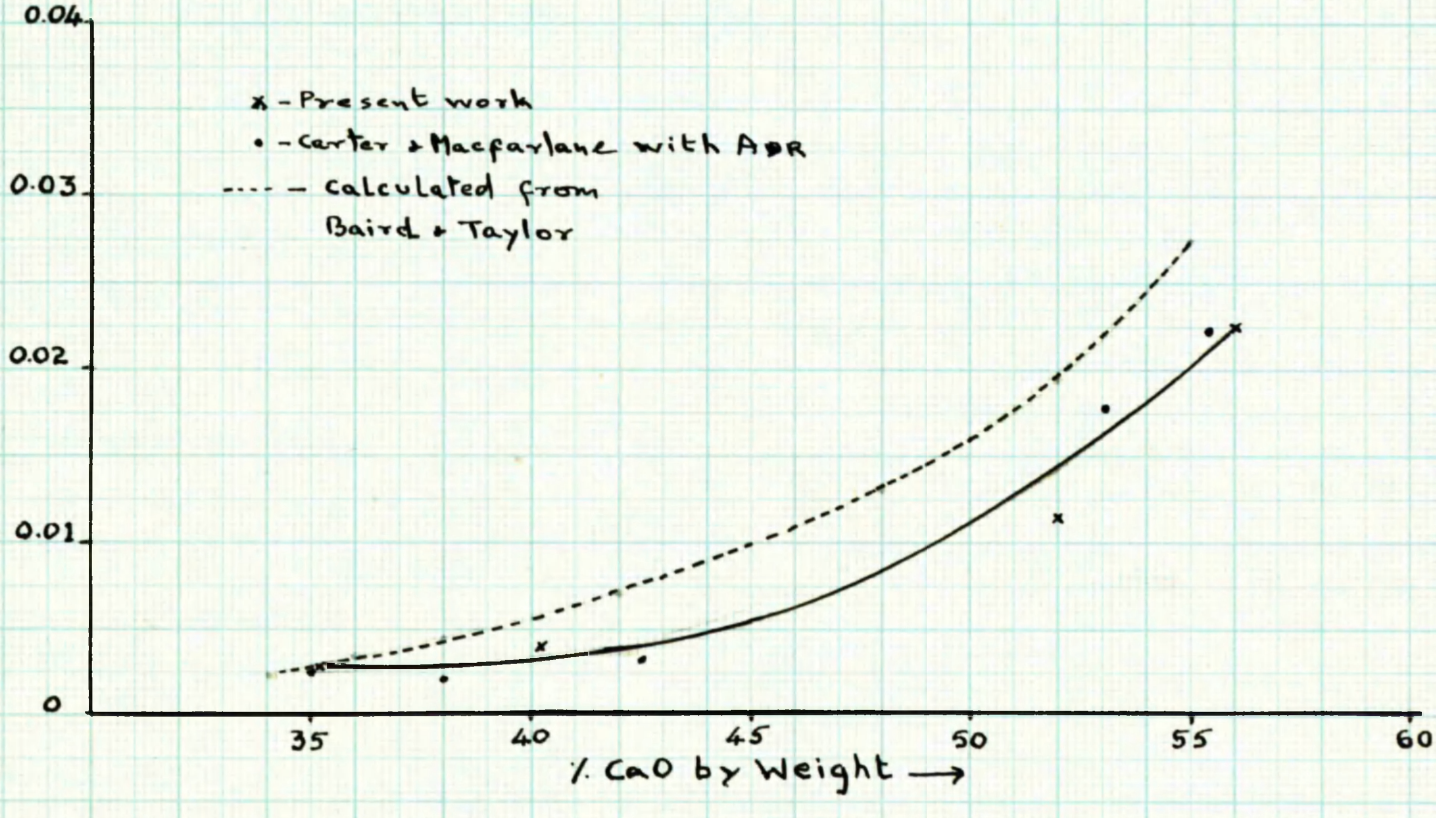


Fig-7 Activity of Lime in $CaO-SiO_2$ Slags at 1500°c

Lime activity values were also calculated using A_K values and these are shown in the graph as crosses. It can be clearly seen that the lime activity values presented here are independent of the thermodynamic data used for their calculations, when a narrow range of gas compositions is used in the experiments. (In the present work the A_{DR} values varied from 250 to 420 - Table IX). The experimental points of Carter and Macfarlane, obtained with gas mixtures having $A_K = 358 \pm 15$, are also plotted in the same graph. Due to the almost constancy of gas compositions used, their results should be independent of the thermodynamic data used. There is close agreement between the two investigations and it can be inferred that there is no significant difference in the experimental techniques followed by Carter and Macfarlane, and the author. The best curve through the combined sets of points has been drawn in Fig.6.

CaO-SiO_2 System.

In the calculation of a_{CaO} in this and other SiO_2 containing systems with low Al_2O_3, an error would be introduced if no account were taken of a possible difference in γ_{CaS} between these slags and the standard slags, as might, for instance, be expected if the sulphur solubilities were different in the two cases. It has been shown by Carter and Macfarlane that this change may be reasonably accounted for by using a correction factor of 0.75 (= 12/16), assuming that there is no appreciable change in γ_{CaS} over the range of CaO-SiO_2 slags investigated. In Tables X, XI, XIII, and XIV, a CaO values corrected by a factor of 0.75 are presented along with the uncorrected values.

The results for the CaO-SiO_2 system given in Table X are plotted in Fig.7. The lime activity values of Carter and Macfarlane were recalculated with A_{DR} and plotted in the graph. The activity values obtained with A_{DR} are slightly lower than those with A_K. A similarly close agreement, as in the CaO-Al_2O_3 system, may be observed here too. The best curve through the combined set of points has been drawn. In addition the lime activity curve obtained by calculation from a SiO_2 values of Baird and Taylor(52) using the Gibbs-Duhem relationship, is also drawn in Fig.7. Baird and Taylor's curve is seen to lie well outside the recommended ± 12 per cent error limit. The slags containing CaO between 42.4 and 52 per cent have melting points higher than 1500°C; as such this portion of the curve refers to a supercooled liquid condition.

In Fig.8, a SiO_2 values calculated from a CaO values of the present work using the Gibbs-Duhem equation, and those of Carter and Macfarlane, and of Baird and Taylor, are plotted against N_{SiO_2}. The silica activities of Carter and Macfarlane were calculated from a CaO with A_K. The present curve was obtained from a CaO with A_{DR}. Close agreement is indicated between the curves of the present work, and Carter and Macfarlane. Since, as pointed out by Carter and Macfarlane, the values of a CaO obtained using the various thermodynamic data are approximately in constant proportion to each other, the Gibbs-Duhem curves would differ only in their positions relative to the log γ CaO

TABLE X.

$CaO-SiO_2$ System.

Time 4 Hours.

Slag	CO/CO_2 Ratio.	$\%SO_2$	A_{DR}	Nature of Slag	%Sulphur	α CaO	Mean	α CaO (corrected
CS1	3.138	1.786	1175	White	0.031	0.004	0.0037	0.0028
CS1	3.151	1.84	1197	"	0.028	0.0036		
CS1	3.408	1.964	1332	"	0.028	0.003		
CS1	3.575	2.595	1552	"	0.040	0.004		
CS1	3.516	2.719	1550	"	0.041	0.004		
CS1	3.685	2.72	1625	"	0.036	0.0034		
CS2	2.818	2.292	1165	Glass	0.042	0.0056	0.0054	0.0041
* CS2	3.215	2.689	1412	"	0.051	0.0055		
CS2	3.516	2.719	1550	"	0.057	0.0056		
CS2	3.042	2.691	1340	"	0.050	0.0057		
CS2	3.118	2.721	1375	"	0.043	0.0048		
CS5	3.758	2.143	1525	"	0.153	0.0154		0.0115
CS6	3.758	2.143	1525	"	0.296	0.0298		0.0224

* $3\frac{1}{2}$ Hours.

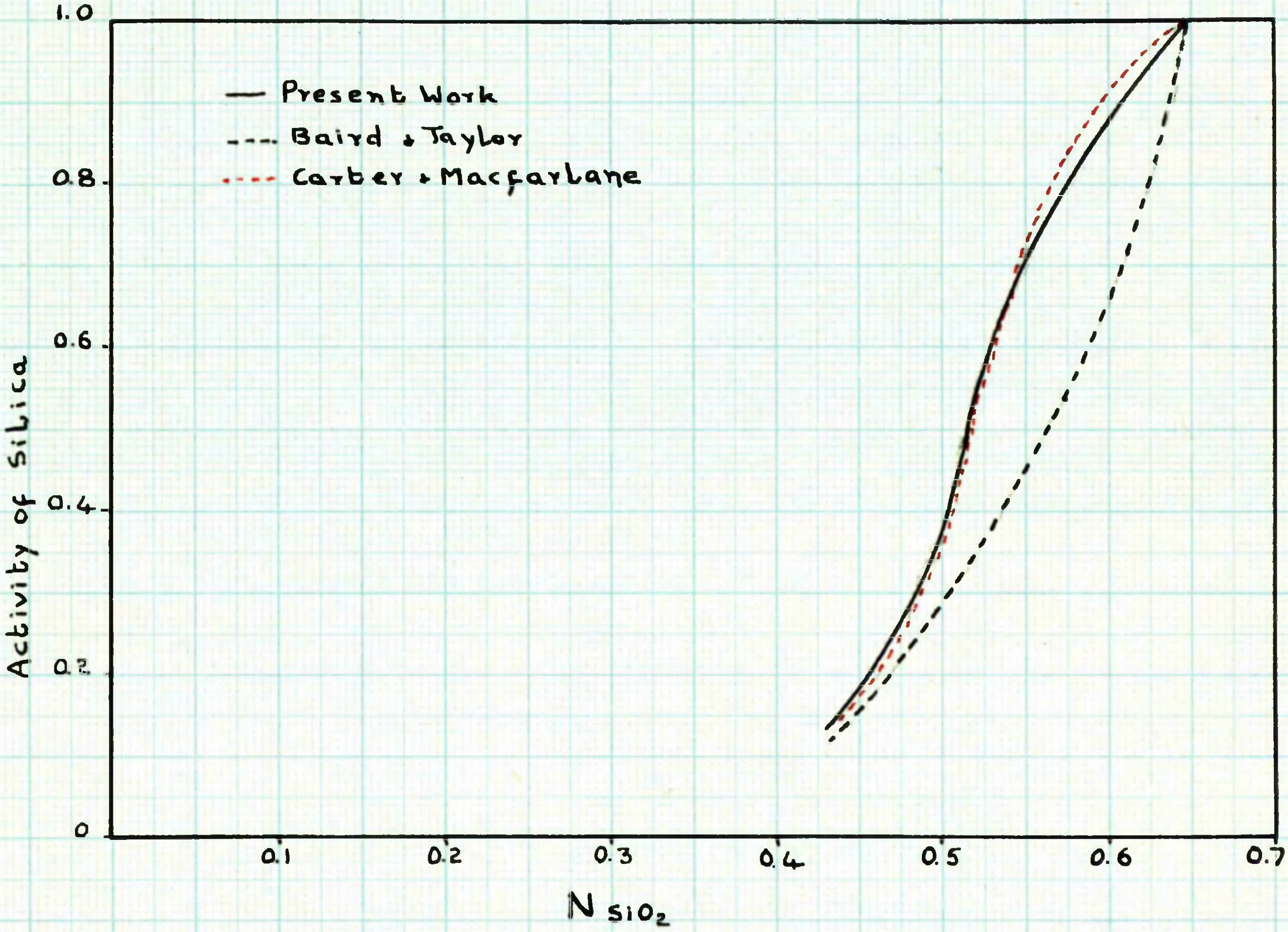


Fig. 8. Activity of SiO_2 in $CaO-SiO_2$ Slags at 1500°c

axis. Thus the derived $a\ SiO_2$ values would be expected to be identical and independent of the thermodynamic data used.

The curves obtained by Fulton and Chipman(53) and Fincham and Richardson(32), and others have not beeb presented for the sake of clarity in Fig.8. The difference between these and other investigations has been fully discussed by Carter and Macfarlane, and Baird and Taylor. Concordance has been indicated between the curves of Carter and Macfarlane, and Fincham and Richardson, and most of the investigators agree with the general trend shown by the present curve.

The greatest difference between Carter and Macfarlane, and Baird and Taylor lies at the high silica region. No inflexion as shown in the curve of Carter and Macfarlane is indicated by the curve of Baird and Taylor. The silica activity curve of the present work is the minimum, and if the increase of γ CaS with silica content is taken into consideration, the activity curve would be shifted even higher, thereby increasing the difference between the two curves. The curve obtained by the latter from the directly determined $a\ SiO_2$ values is less reliable due to the considerable scatter of the few experimental points. The activity determinations at the high silica side in the present work are considered to be more accurate, since at least four experiments were carried out with each slag.

As was pointed out by Carter and Macfarlane, increase of Al_2O_3 or SiO_2 in the binary slags tends to decrease the amount of sulphur absorbed, and $a\ CaO$ in a CaO-Al_2O_3 melt is much greater than that in a CaO-SiO_2 melt. Hence in the calculation of basicity of a slag,

Al_2O_3 and SiO_2 would have to be considered as acids of different strengths. The present experiments provide more evidence in support of the assumption that sulphur is not associated with either, Al or Si, in the slag.

<u>$CaO-Al_2O_3-SiO_2$ System.</u>

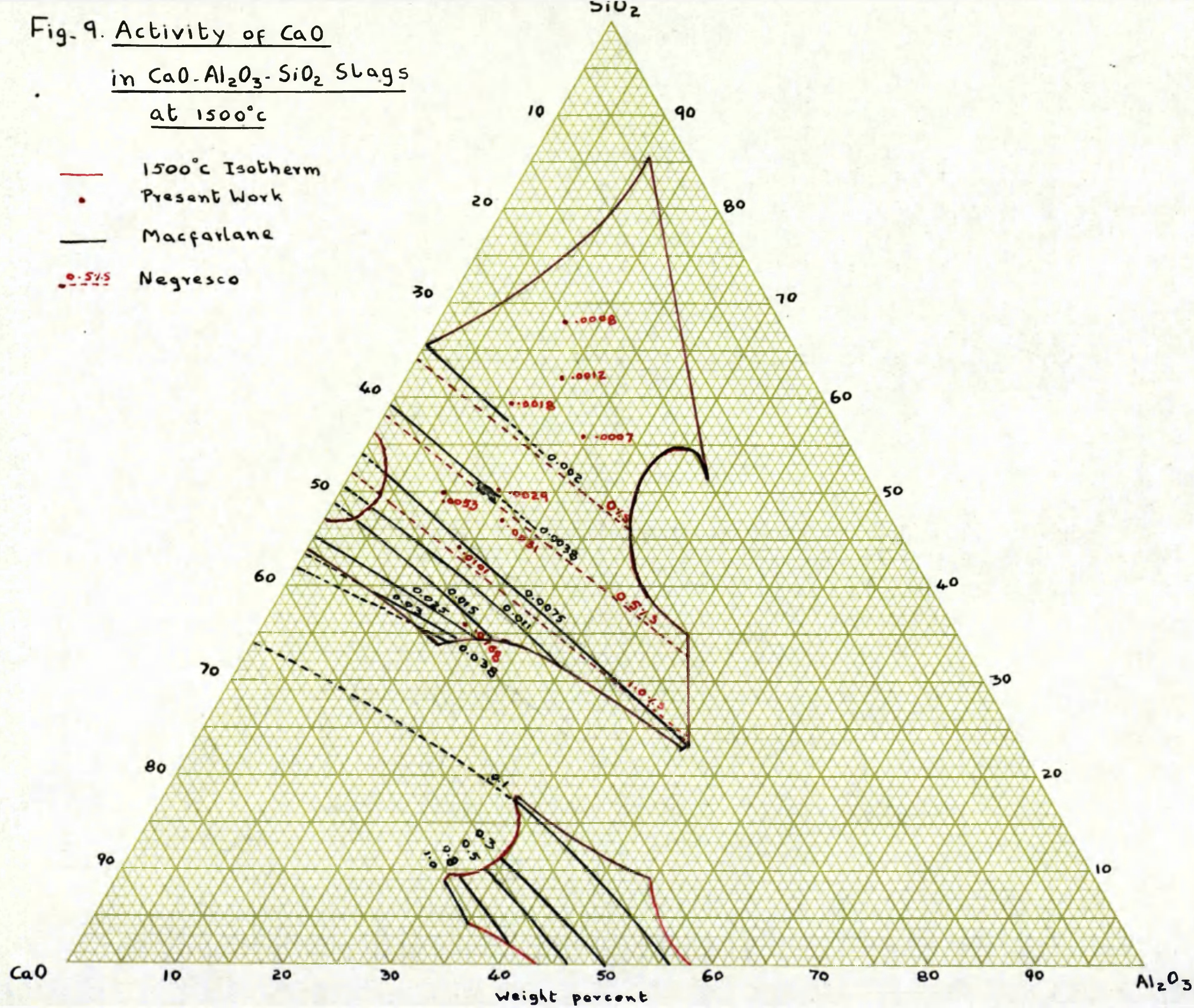
A series of 9 slags was used in these experiments and a CaO was calculated in a manner similar to that adopted for the binary $CaO-SiO_2$ slags, and the results presented in Table XI are plotted in Fig.9. The black solid lines in the graph refer to the iso-activity lines obtained by Carter and Macfarlane(36). In the high silica field his activity values have been corrected by a factor of 0.75. Though there are not sufficient results from the present work, to enable the drawing of iso-activity lines, the trend is noticeable and in agreement with the results of Macfarlane. On a constant CaO line, replacement of SiO_2 by Al_2O_3 increases the activity, which may be due to the lower affinity of CaO for Al_2O_3 than for SiO_2, in addition to the higher mol. fraction of CaO in low silica field. Negresco(22) presented his results in the form of iso-sulphur capacity lines, and in the graph three such lines have been reproduced. The numbers on the lines refer to grams. of sulphur absorbed by 100 gms. of slag. Although quantitative comparison of his results with those of Macfarlane(36) is not possible, the trend of the lines is similar.

TABLE XI.

$CaO-Al_2O_3-SiO_2$ System.

Slag	Ratio $C/_{A+S}$	CO/CO_2 Ratio	$\%SO_2$	A_{DR}	Time in Hours	Nature of Slag	%Sulphur	a_{CaO}	a_{CaO} Corrected
CAS1	0.257	3.722	2.762	1645	4	Glass	0.0117	0.0011	0.0008
CAS2	0.422	3.391	2.887	1527	$4^1/_2$	"	0.0239	0.0024	0.0018
CAS3	0.689	3.514	2.369	1475	4	"	0.0683	0.0071	0.0053
CAS4	0.314	3.598	2.425	1528	4	"	0.0159	0.0016	0.0012
CAS5	0.549	3.195	2.702	1400	$4^1/_2$	"	0.0356	0.0039	0.0029
CAS6	0.706	3.328	2.68	1458	4	"	0.1273	0.0134	0.0101
CAS7	0.324	3.397	2.672	1493	4	"	0.0098	0.0010	0.0007
CAS8	0.567	3.452	2.809	1535	4	"	0.0405	0.0041	0.0031
CAS9	0.848	3.157	2.821	1407	5	"	0.2054	0.0224	0.0168

Fig. 9. Activity of CaO in $CaO-Al_2O_3-SiO_2$ Slags at 1500°c



CaO-Al_2O_3-MgO System.

In the study of this (and also the CaO-MgO-SiO_2 system) two methods of obtaining the desired composition were followed.

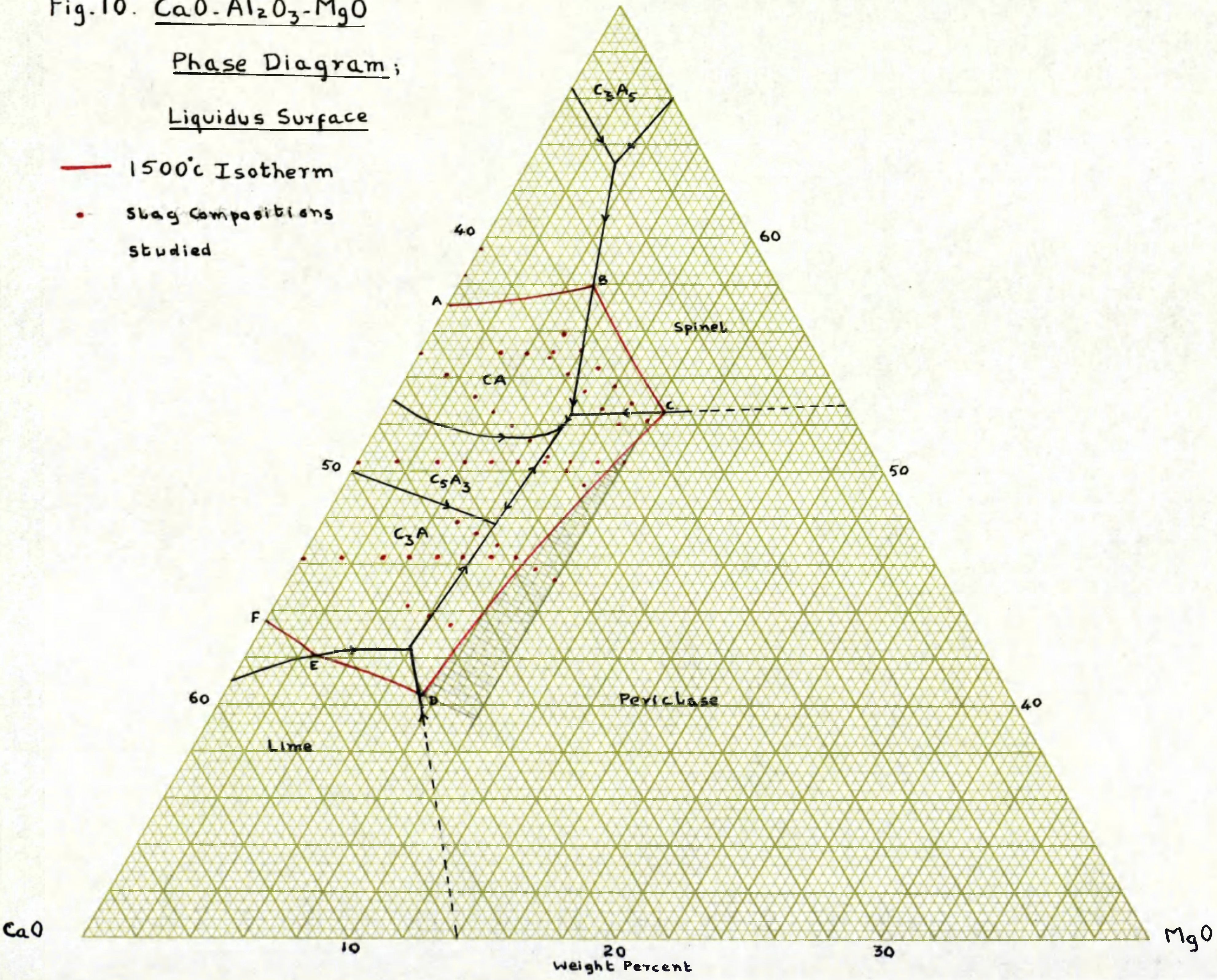
(a) Addition of MgO while maintaining the weight proportion of CaO to Al_2O_3 or SiO_2 constant, and

(b) Addition of MgO while maintaining the weight per cent of Al_2O_3 or SiO_2 constant.

The above methods were adopted in order to cover as wide a range of ternary slag compositions as possible with a minimum number of master binary slags. About 12 ternary MgO-containing slags were prepared from each binary slag. In each run three ternary slags and a master binary slag were used. The binary slag acted as a reference point or a check for each series of slags. In no case did the result for the binary slag vary, within the limits of experimental errors, from those given earlier for the binary systems. It may therefore be concluded that the results obtained for the ternary slags are consistent with the earlier work and that nothing untoward happened during these runs.

Figures 10 and 11 give the phase diagrams for CaO-Al_2O_3-MgO, and CaO-SiO_2-MgO systems, and the compositions studied are plotted in the diagrams. One or two slags which have melting points slightly above 1500°C were found to be molten at 1500°C, probably due to the absorption of sulphur.

Fig. 10. $CaO-Al_2O_3-MgO$ Phase Diagram; Liquidus Surface



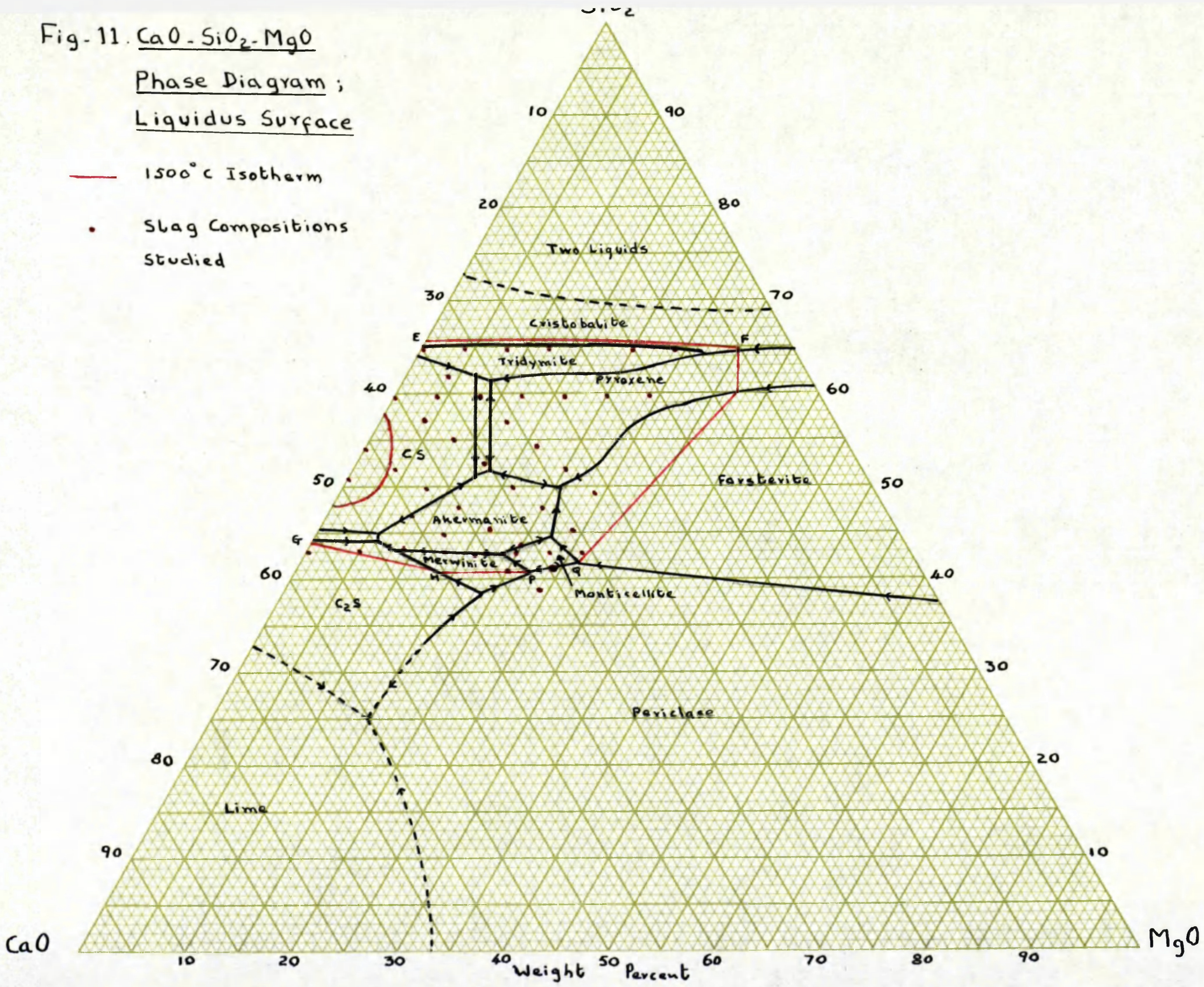


Fig-11. CaO-SiO$_2$-MgO Phase Diagram; Liquidus Surface

In ternary MgO-containing slags, MgO as well as CaO may play a part in the absorption of sulphur, but the extent to which the sulphur is combined as CaS or MgS is not known, due to the lack of clear understanding of the relative capacities for sulphur absorption. It is proposed to use the term "lime equivalent" for slags containing MgO, since a_{CaO} strictly can only be calculated when CaO is the only oxide present which can lead to sulphur absorption. The lime equivalent would therefore represent the combined effect of CaO and MgO.

The results of CaO-Al_2O_3-MgO experiments are presented in Tables XII A, B, and are plotted against weight per cent MgO in Fig.12a, b. From Fig.12a, it can be seen that as per cent MgO is increased there is a slight increase in the lime equivalent for each of the CaO/Al_2O_3 ratios. The slope of curves also increases at higher ratios. In Fig.12b, where CaO is replaced by MgO while per cent Al_2O_3 is kept constant, there is a decrease in the lime equivalent as per cent MgO is increased. It may be concluded that on a weight basis MgO is not as good a desulphurizer as CaO. The slope of the curves increases as per cent Al_2O_3 in the slag decreases, i.e., the deleterious effect of MgO is more pronounced at higher basicities.

CaO-SiO_2-MgO System.

The results of Tables XIII A, B, are plotted in Figs.13 a, b. The maximum amount of MgO that could be addedwas 24-28 per cent. Sulphur absorption data were obtained at 4 per cent intervals of MgO.

TABLE XIIA.

$CaO-Al_2O_3-MgO$ System.

(MgO addition maintaining CaO/Al_2O_3 wt.ratio constant)

Slag	%MgO	CO/CO_2 Ratio.	%SO_2	A_{DR}	Time in Hours	Nature of Slag	%Sulphur	Lime Equivalent.
C/A = 0.675								
CAM1	5.0	1.83	0.695	360	5½	Glass	0.128	0.055
CAM2	6.0	1.83	0.695	360	5½	"	0.154	0.066
CAM3	7.0	1.83	0.695	360	5½	"	0.178	0.076
CAM4	8.0	1.83	0.511	285	5½	"	0.156	0.084
CAM5	9.0	1.83	0.511	285	5½	"	0.148	0.079
CAM6	10.0	1.83	0.511	285	5½	"	0.168	0.090
C/A = 0.712								
CAM7	5.0	1.755	0.597	305	5½	"	0.158	0.079
CAM8	6.0	1.755	0.597	305	5½	"	0.159	0.080
CAM9	7.0	1.83	0.533	297	5½	"	0.182	0.094
CAM10	9.0	1.83	0.533	297	5½	"	0.196	0.101
C/A = 0.818								
CAM11	1.5	1.778	0.658	335	5	"	0.295	0.135
CAM12	3.0	1.778	0.658	335	5	"	0.322	0.147
CAM13	4.0	1.778	0.658	335	5	"	0.336	0.154
CAM14	5.0	1.762	0.521	275	5½	Glass + White	0.298	0.166
CAM15	6.0	1.706	0.513	257	5½	Glass	0.298	0.178
CAM16	7.0	1.762	0.521	275	5½	Glass + White	0.299	0.167
CAM17	8.0	1.706	0.513	257	5½	Glass	0.324	0.194
CAM18	9.0	1.762	0.521	275	5½	White	0.365	0.204
C/A = 0.984								
CAM19	5.0	1.618	0.862	345	5½	Glass	0.647	0.288
CAM20	6.0	1.618	0.862	345	5½	"	0.662	0.294
CAM21	7.0	1.618	0.862	345	5½	"	0.707	0.315
CAM22	8.0	1.937	0.76	410	5½	"	0.800	0.300
CAM23	9.0	1.937	0.76	410	5½	"	0.863	0.323
CAM24	10.0	1.937	0.76	410	5½	"	0.880	0.329
C/A = 1.165								
CAM25	5.0	1.67	0.597	275	5½	"	1.007	0.562
CAM26	6.0	1.67	0.597	275	5½	"	1.02	0.569
CAM27	7.0	1.67	0.597	275	5½	"	1.043	0.582

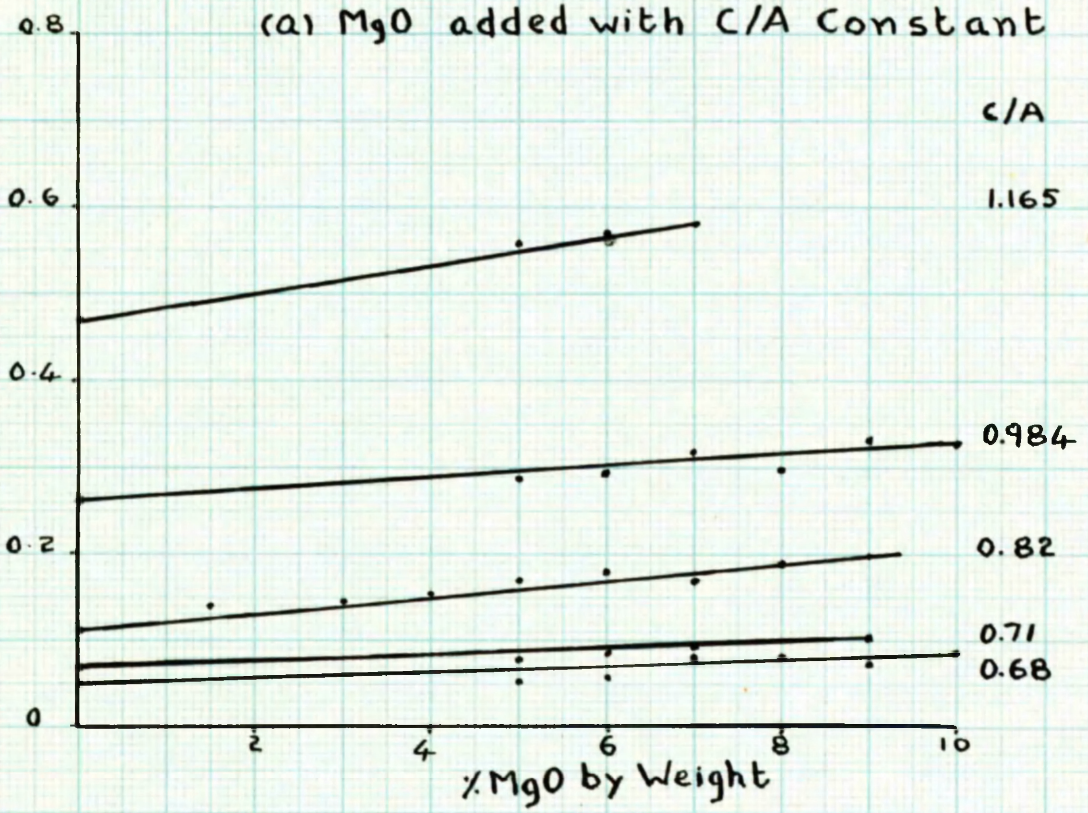
TABLE XIIB.

$CaO-Al_2O_3-MgO$ System.

(MgO addition maintaining % Al_2O_3 Constant)

Slag	%MgO	CO/CO_2 Ratio.	%SO_2	A_{IR}	Time in Hours	Nature of Slag	%Sulphur	Lime Equivalent
%Al_2O_3 = 55.0								
CAM28	3.0	1.618	0.657	285	5½	Glass	0.177	0.093
CAM29	4.0	1.61	0.657	285	5½	"	0.162	0.085
CAM30	5.0	1.618	0.657	285	5½	"	0.158	0.085
%Al_2O_3 = 50.4								
CAM31	1.5	1.62	0.643	285	5½	"	0.502	0.271
CAM32	3.0	1.62	0.643	285	5½	"	0.433	0.233
CAM33	4.0	1.62	0.643	285	5½	"	0.426	0.229
CAM34	5.0	1.576	0.811	323	4½	"	0.420	0.199
CAM35	6.0	1.576	0.811	323	4½	"	0.381	0.181
CAM36	7.0	1.576	0.811	323	4½	"	0.372	0.177
CAM37	8.0	1.681	0.624	290	5	"	0.306	0.162
CAM38	9.0	1.681	0.624	290	5	"	0.270	0.142
CAM39	10.0	1.681	0.624	290	5	"	0.225	0.119
%Al_2O_3 = 46.2								
CAM40	1.5	1.746	0.734	355	5½	"	0.948	0.410
CAM41	3.0	1.746	0.734	355	5½	"	0.933	0.404
CAM42	4.0	1.746	0.734	355	5½	"	0.858	0.371
CAM43	5.0	1.737	0.704	335	4½	"	0.816	0.374
CAM44	6.0	1.737	0.704	335	4½	"	0.750	0.344
CAM45	7.0	1.737	0.704	335	4½	"	0.705	0.323

Fig-12. Lime Equivalent of $CaO-Al_2O_3-MgO$ Slags


(a) MgO added with C/A Constant

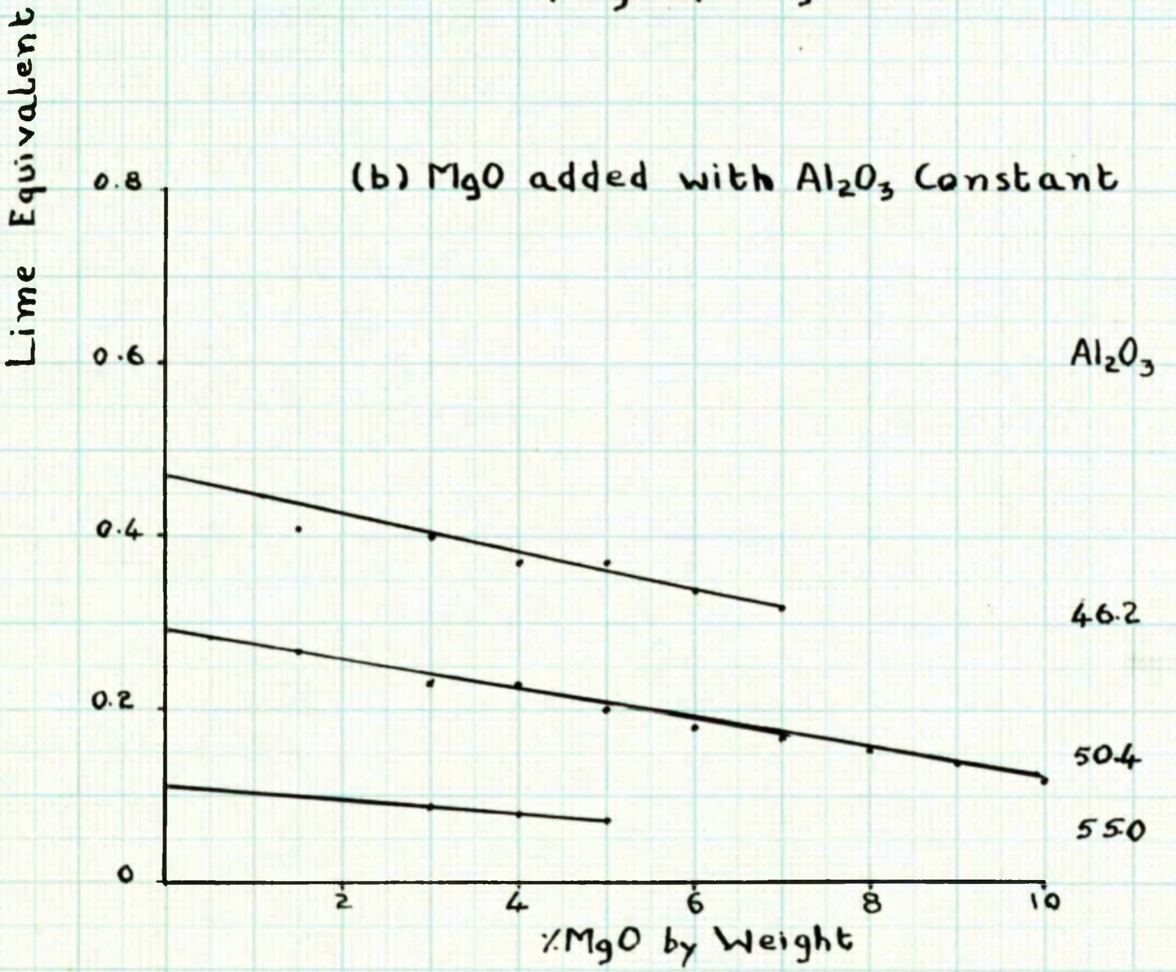

(b) MgO added with Al_2O_3 Constant

TABLE XIIIA.

$CaO-SiO_2-MgO$ System.

(MgO addition maintaining CaO/SiO_2 wt. ratio constant)

Time 4 Hours.

Slag	%MgO	CO/CO_2 Ratio.	$\%SO_2$	A_{DR}	Nature of Slag	% Sulphur	Lime Equiv- alent.	Lime Equivalent "corrected"
				C/S = 0.542.				
CSM1	4.0	3.138	1.786	1175	White	0.033	0.0043	0.0032
CSM2	8.0	3.138	1.786	1175	Glass	0.029	0.0039	0.0029
CSM3	12.0	3.138	1.786	1175	"	0.031	0.0049	0.0037
CSM4	16.0	3.151	1.84	1197	"	0.042	0.0054	0.0041
CSM5	20.0	3.151	1.84	1197	"	0.053	0.0069	0.0052
CSM6	24.0	3.151	1.84	1197	"	0.072	0.0098	0.0074
				C/S = 0.674				
CSM7	4.0	2.997	2.185	1220	"	0.056	0.0071	0.0053
CSM8	8.0	2.997	2.185	1220	"	0.062	0.0078	0.0058
CSM9	12.0	2.997	2.185	1220	"	0.065	0.0081	0.0061
CSM10	16.0	2.818	2.292	1165	"	0.077	0.0102	0.0077
CSM11	20.0	2.818	2.292	1165	"	0.095	0.0125	0.0094
CSM12	24.0	2.818	2.292	1165	"	0.128	0.0169	0.0127
				C/S = 0.85				
CSM13	4.0	3.522	2.456	1500	"	0.083	0.0085	0.0064
CSM14	8.0	3.522	2.456	1500	"	0.098	0.0100	0.0075
CSM15	12.0	3.522	2.456	1500	"	0.119	0.0123	0.0092
CSM16	16.0	3.522	2.456	1500	"	0.145	0.0149	0.0112
CSM17	20.0	3.376	2.478	1440	"	0.194	0.0207	0.0155
CSM18	24.0	3.376	2.478	1440	"	0.291	0.031	0.0233
				C/S = 0.968				
CSM19	4.0	3.515	2.396	1480	"	0.134	0.0139	0.0104
CSM20	8.0	3.515	2.396	1480	Glass + White	0.163	0.0169	0.0127
CSM21	12.0	3.515	2.396	1480	" "	0.239	0.0247	0.0185
CSM22	16.0	3.515	2.396	1480	White	0.329	0.0341	0.0256
CSM23	20.0	3.376	2.478	1440	Glass	0.542	0.0578	0.0434
CSM24	24.0	3.376	2.478	1440	Glass	0.645	0.0688	0.0516

TABLE XIIIB.

$CaO-SiO_2-MgO-$ System.

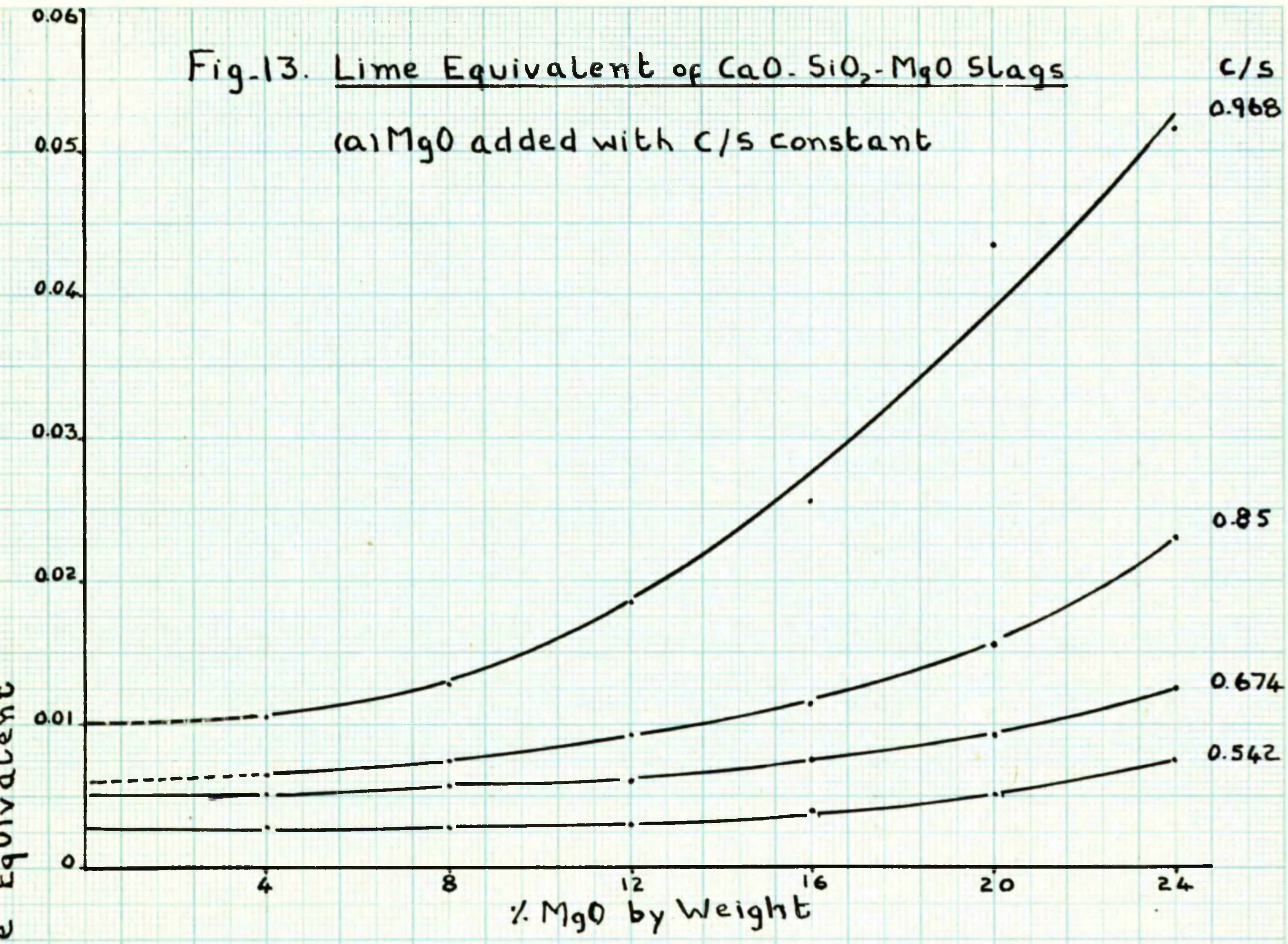
(MgO addition with $\%SiO_2$ constant)

Time 4 Hours.

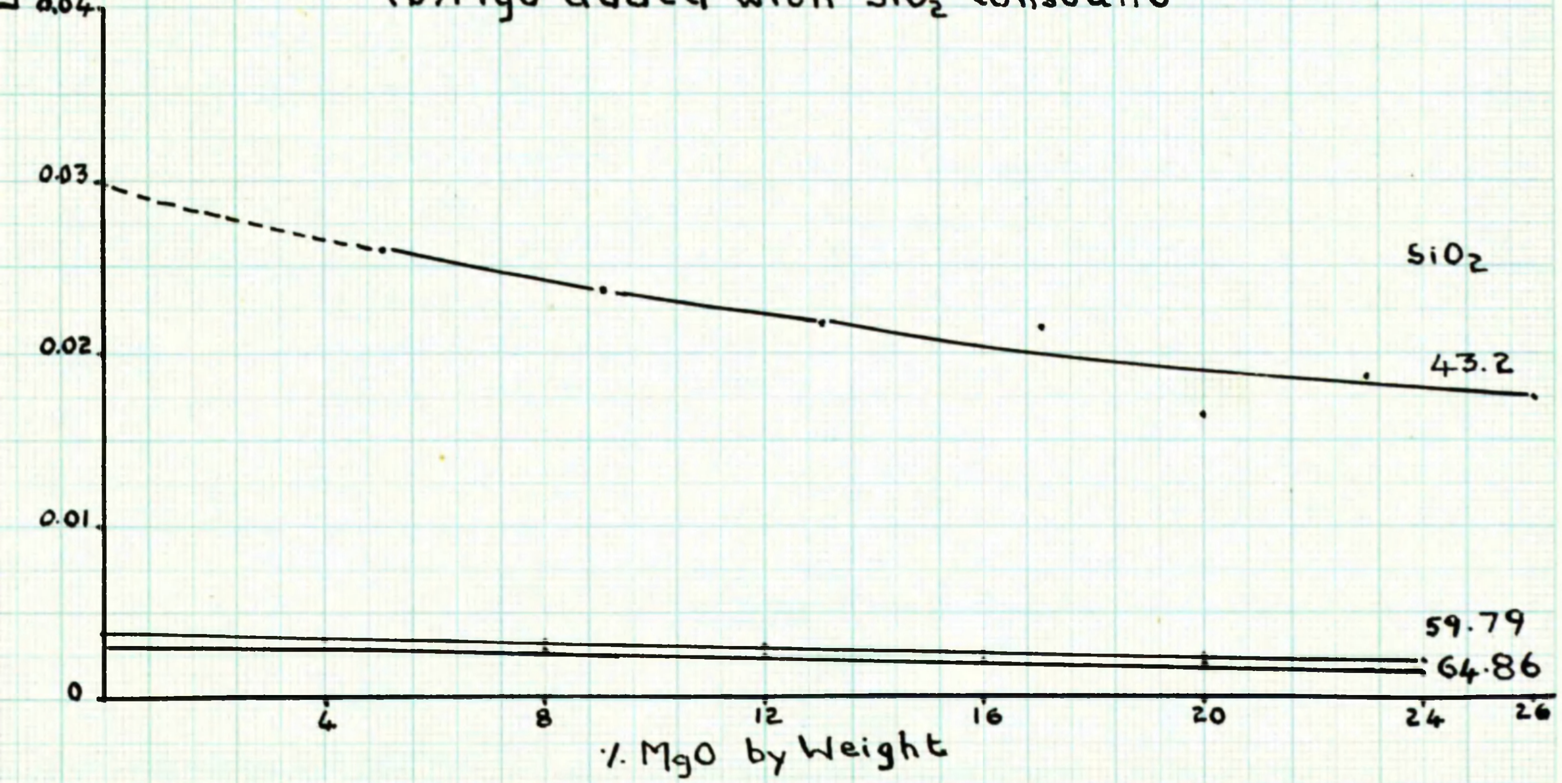
Slag	%MgO	CO/CO_2 Ratio.	$\%SO_2$	A_{DR}	Nature of Slag	% Sulphur	Lime Equivalent.	Lime Equivalent corrected
$\%SiO_2 = 64.86.$								
CSM25	4.0	3.575	2.595	1550	White	0.041	0.0041	0.0031
CSM26	8.0	3.575	2.595	1550	"	0.040	0.0040	0.0030
CSM27	12.0	3.575	2.595	1550	"	0.033	0.0033	0.0025
CSM28	20.0	3.685	2.72	1625	"	0.028	0.0026	0.0019
CSM29	24.0	3.685	2.72	1625	"	0.024	0.0023	0.0017
$\%SiO_2 = 59.75$								
CSM30	4.0	3.042	2.691	1340	Glass	0.042	0.0048	0.0036
CSM31	8.0	3.042	2.691	1340	"	0.039	0.0044	0.0033
CSM32	12.0	3.042	2.691	1340	"	0.038	0.0043	0.0032
CSM33	16.0	3.118	2.721	1375	"	0.029	0.0032	0.0024
CSM34	20.0	3.118	2.721	1375	"	0.02 8	0.0031	0.0023
CSM35	24.0	3.118	2.721	1375	White	0.028	0.0031	0.0023
$\%SiO_2 = 43.2$								
CSM36	5.0	3.098	2.909	1395	G+White	0.313	0.035	0.0259
CSM37	9.0	3.098	2.909	1395	" "	0.287	0.0316	0.0237
CSM38	13.0	3.098	2.909	1395	" "	0.265	0.0292	0.0219
CSM39	17.0	3.098	2.909	1395	" "	0.263	0.0289	0.0217
CSM40	20.0	3.227	2.77	1428	" "	0.203	0.0218	0.0164
CSM41	23.0	3.227	2.77	1428	" "	0.232	0.0249	0.0187
CSM42	26.0	3.227	2.77	1428	" "	0.217	0.0234	0.0176

Fig. 13. Lime Equivalent of CaO-SiO_2-MgO Slags

(a) MgO added with C/S constant



(b) MgO added with SiO_2 constant



Observations similar to those made in the $CaO-Al_2O_3-MgO$ system may be made here also, i.e., Lime Equivalent increased with increase of MgO when CaO/SiO_2 ratio was kept constant, and decreased when CaO was replaced by MgO. The increase in lime equivalent caused by additions of MgO is greater at higher CaO/SiO_2 ratios, and for constant SiO_2 contents the decrease is greater at higher basicities. In the more acid slags the effect of replacing CaO by MgO is very small. The amount of sulphur absorbed was much smaller than that by a $CaO-Al_2O_3-MgO$ slag.

$CaO-Al_2O_3-SiO_2-MgO$ System.

In these experiments 5, 10, 15 per cent MgO were added to each of the 9 ternary $CaO-Al_2O_3-SiO_2$ slags, thus giving in all 27 quaternary slags. As in the earlier experiments, in each run one ternary master slag and three different quaternary slags were used, the ternary slag acting as a check for each series. The results of these experiments are given in Table XIV. The 9 master slags are divided into three groups of slags containing approximately 10, 15, 20 per cent Al_2O_3 respectively. The actual compositions are given in Table V. The results have been plotted in Fig.14, where three sets of curves are shown, corresponding to 10, 15 and 20 per cent Al_2O_3 in the original master slag respectively. In each case lime equivalent is plotted against $CaO/Al_2O_3 + SiO_2$ (weight ratio). It can be seen that in any particular set of curves the lime equivalent increases with increase of MgO content from 0 to 15 per cent. Also, for the same MgO and similar

TABLE XIV.

$CaO-Al_2O_3-SiO_2-MgO$ System.

Slag	CO/CO_2 Ratio.	$\%SO_2$	A_{DR}	Time in Hours	Nature of Slag	% Sulphur	Lime Equivalent.	Lime Equivalent corrected.
CASM1	3.772	2.762	1645	4	Glass	0.013	0.0012	0.0009
CASM2	3.722	2.762	1645	4	"	0.016	0.0015	0.0012
CASM3	3.722	2.762	1645	4	"	0.015	0.0014	0.0011
CASM4	3.391	2.887	1527	4¼	"	0.026	0.0026	0.0019
CASM5	3.391	2.887	1527	4¼	"	0.033	0.0034	0.0025
CASM6	3.391	2.887	1527	4¼	"	0.047	0.0047	0.0035
CASM7	3.514	2.369	1475	4	"	0.085	0.0088	0.0066
CASM8	3.514	2.369	1475	4	"	0.114	0.0119	0.0089
CASM9	3.514	2.369	1475	4	"	0.159	0.0165	0.0123
CASM10	3.598	2.425	1528	4	"	0.020	0.0020	0.0015
CASM11	3.598	2.425	1528	4	"	0.024	0.0024	0.0018
CASM12	3.598	2.425	1528	4	"	0.034	0.0034	0.0025
CASM13	3.195	2.702	1400	4½	"	0.044	0.0048	0.0036
CASM14	3.195	2.702	1400	4½	"	0.054	0.0060	0.0045
CASM15	3.195	2.702	1400	4½	"	0.082	0.0089	0.0067
CASM16	3.328	2.68	1458	4	"	0.200	0.0211	0.0158
CASM17	3.328	2.68	1458	4	"	0.247	0.0259	0.0194
CASM18	3.328	2.68	1458	4	"	0.443	0.0466	0.0349
CASM19	3.397	2.672	1493	4	"	0.011	0.0012	0.0009
CASM20	3.397	2.672	1493	4	"	0.016	0.0016	0.0012
CASM21	3.397	2.672	1493	4	"	0.036	0.0041	0.0031
CASM22	3.452	2.809	1535	4	"	0.067	0.0066	0.0049
CASM23	3.452	2.809	1535	4	"	0.088	0.0088	0.0066
CASM24	3.452	2.809	1535	4	"	0.112	0.0112	0.0084
CASM25.	3.157	2.821	1407	5	"	0.275	0.030	0.0225
CASM26	3.157	2.821	1407	5	"	0.380	0.0394	0.0296
CASM27	3.157	2.821	1407	5	"	0.534	0.0583	0.0438

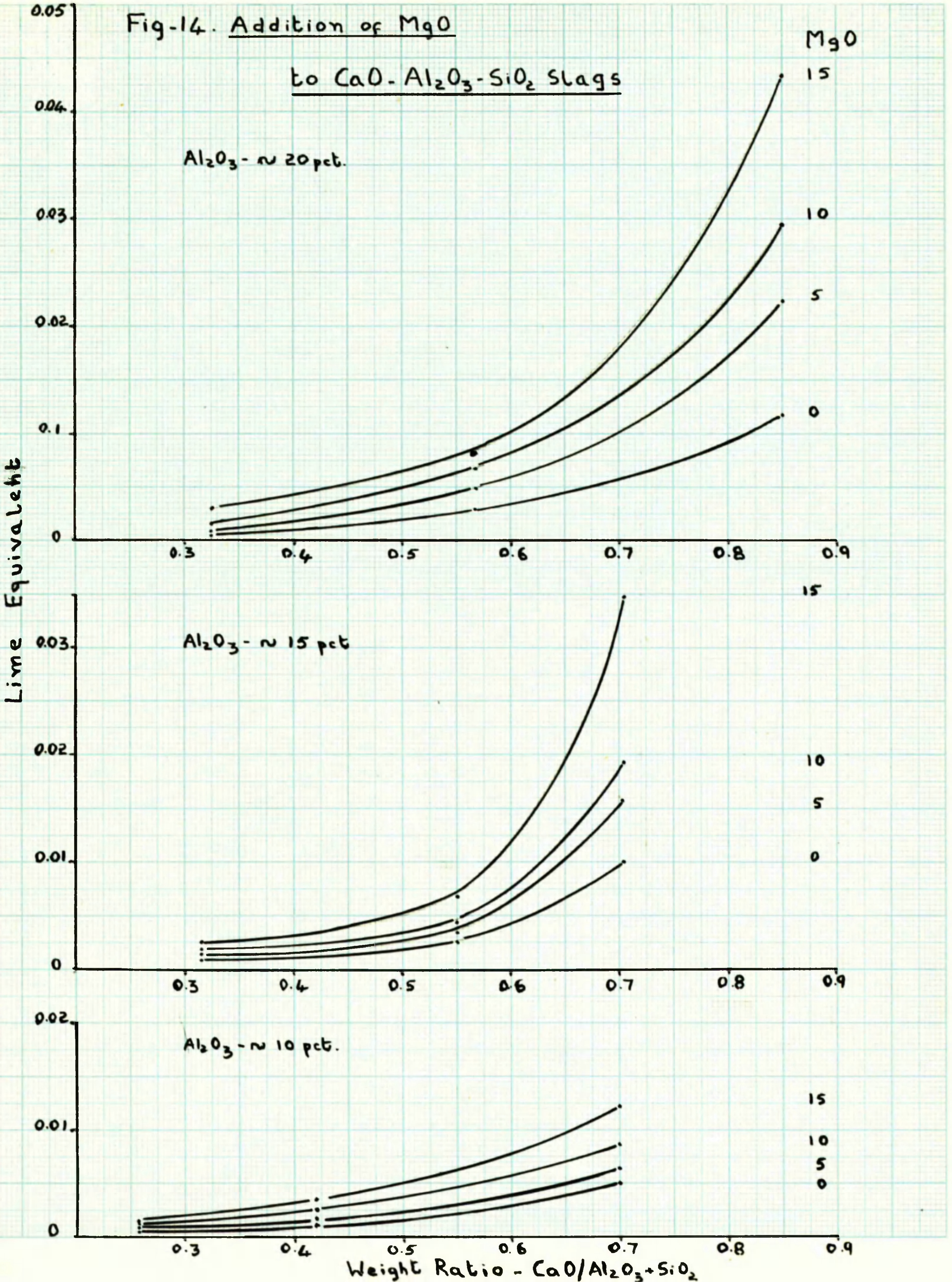


Fig-14. Addition of MgO to CaO-Al_2O_3-SiO_2 Slags

Al_2O_3 contents the lime equivalent increases when CaO replades SiO_2. It will be noted that for a given $CaO/Al_2O_3+SiO_2$ ratio lime equivalents are higher in the 15 per cent Al_2O_3 series than in either the 10 per cent or 20 per cent Al_2O_3 series. This indicates that an optimum desulphurizing power must exist in the region of 15 per cent Al_2O_3 in these slags.

Activity of Lime.

So far in this work on slags containing MgO, the term lime equivalent has been used. At this stage the validity of using lime activity in place of lime equivalent will be considered. Referring to the phase diagram of the $CaO-Al_2O_3-MgO$ system (Fig.10) it can be seen that the slag of composition 37 per cent CaO, 10.4 per cent MgO, and 52.6 per cent Al_2O_3 contains free MgO, and lies on the 1500°C isotherm. This slag, being in equilibrium with pure MgO will therefore have a MgO activity of unity. It was found that this slag absorbed 0.22 per cent sulphur under standard gas conditions, giving a lime equivalent of 0.11. This value of 0.11 corresponds to the additive effects of MgO ($a_{MgO} = 1$), and a_{CaO} of an uncertain value. It can be concluded that CaO is more powerful than MgO.

Further evidence of the low desulphurizing power of MgO as compared with CaO can be derived from a consideration of the $CaO-SiO_2-MgO$ system. It can be seen from the phase diagram shown in Fig.11 that the 1500°C isotherm almost coincides with the binary curve separating the monticellite and periclase fields. Compositions on this curve may therefore be regarded as having a magnesia activity of unity at 1500°C. The two extremes of compositions (P and Q) on this curve have lime equivalents of approximately 0.055 and 0.025 respectively. The contribution of MgO to sulphur absorption along the curve is constant and must be smaller than the total contribution of 0.025 for the composition Q.

For further evidence, a $MgO-B_2O_3$ melt containing 72 per cent MgO was equilibrated with a gas mixture of standard A_{DR} value. This system was selected because of the suitable melting range. This melt, which could be considered to have an α MgO nearly equal to one, was found to absorb 0.024 per cent sulphur. In terms of lime equivalent this would correspond to 0.012; whereas a melt of unit α CaO would absorb about 2 per cent sulphur. In this case, therefore, the absorption of sulphur by lime is about 100 times greater than that by MgO. These results are in agreement with the large difference in the equilibrium constants calculated for the reactions:

$$CaO + \underline{S} = CaS + \underline{O} - K_{1600\,^\circ C} = 0.04$$

$$MgO + \underline{S} = MgS + \underline{O} \quad K_{1600\,^\circ C} = 1.0 \times 10^{-4}$$

They are also of the expected order of magnitude. Exact agreement with the calculated constants could hardly be expected, since no allowances could be made for differences in activity coefficient of CaS and MgS in the slags concerned.

In view of the above results, it may be assumed that little error will be incurred if lime activities are substituted for lime equivalents in slags containing MgO as well as CaO, except in slags of relatively low basicities containing high percentages of MgO. This assumption has been made in the subsequent discussion.

CHAPTER VII.

DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS.

As the contribution of MgO to sulphur absorption is considerably smaller than that of CaO, lime equivalent values given in Table IX, X, have been taken to represent activities. These values are plotted against weight per cent CaO for various levels of MgO in Fig.15, 16. In extending the curves of Fig.15 to unit activity, the compositions on the part (DE) of the 1500°C isotherm in Fig.10 having a lime activity corresponding to one, have been used. The dotted portions of the curves shown in Fig.15 refer to slags in the super cooled condition, i.e., to compositions in the shaded area of Fig.10. It can be seen that at each MgO level lime activity increases as expected with lime content, and that for the same CaO content increasing MgO content increases the activity of lime.

It can be deduced from the relative positions of the curves in Fig.15, that in the $CaO-Al_2O_3-MgO$ system 1 gm. of CaO may be replaced by Approximately 1.5 gm. of MgO without affecting the activity of lime. This relationship holds with surprising constancy up to a_{CaO} of 0.7. At higher activities the MgO equivalent is very slightly lower. The comparison cannot be made over such a wide range of slag compositions in the $CaO-SiO_2-MgO$ system, but for the range shown in Fig.16 it can be deduced that CaO and MgO are almost equivalent on a weight basis. On a molar basis 1 mol. of CaO is equivalent to about 2 mols. of MgO

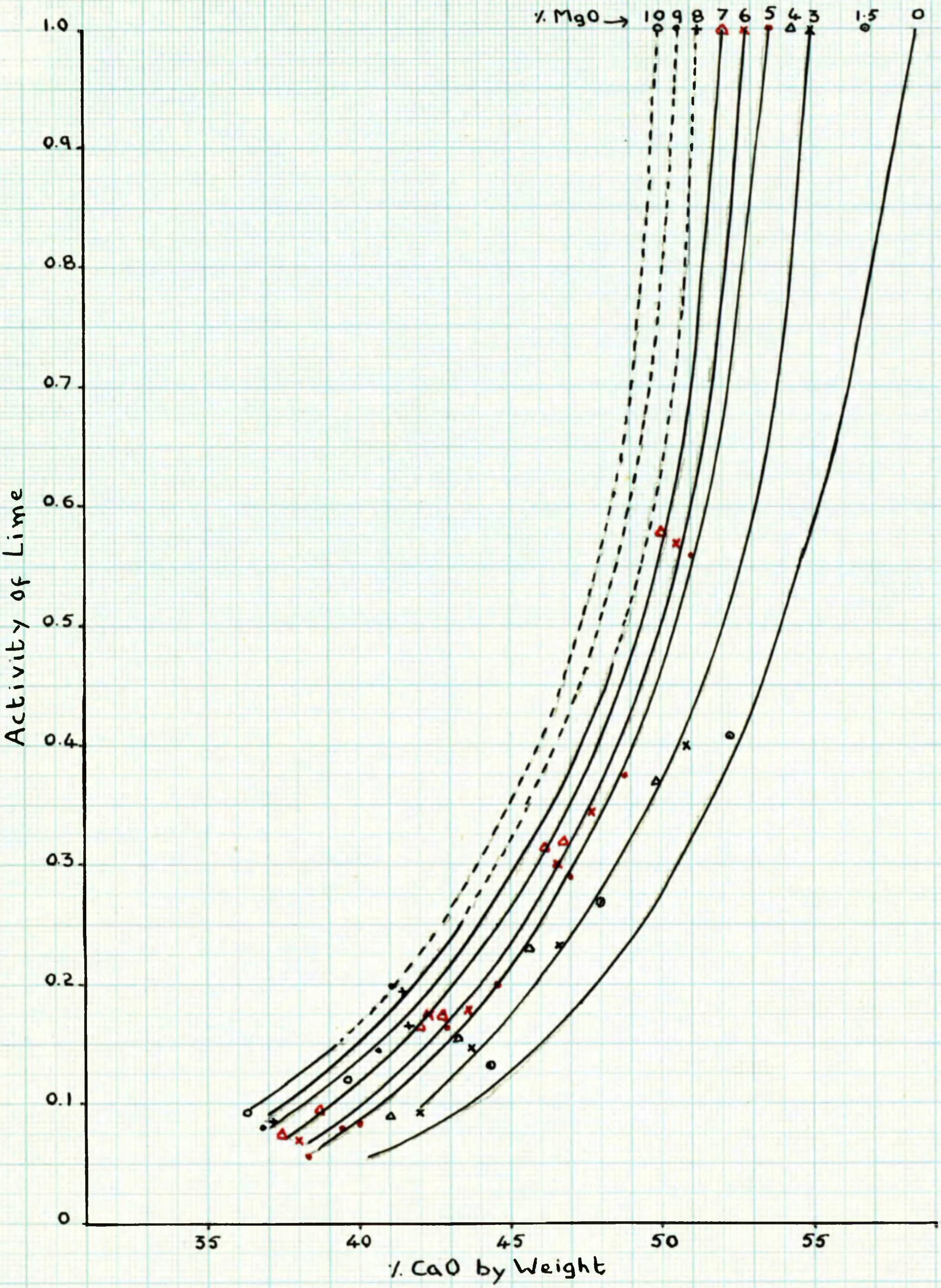


Fig. 15. Activity of Lime in $CaO-Al_2O_3-MgO$ Slags

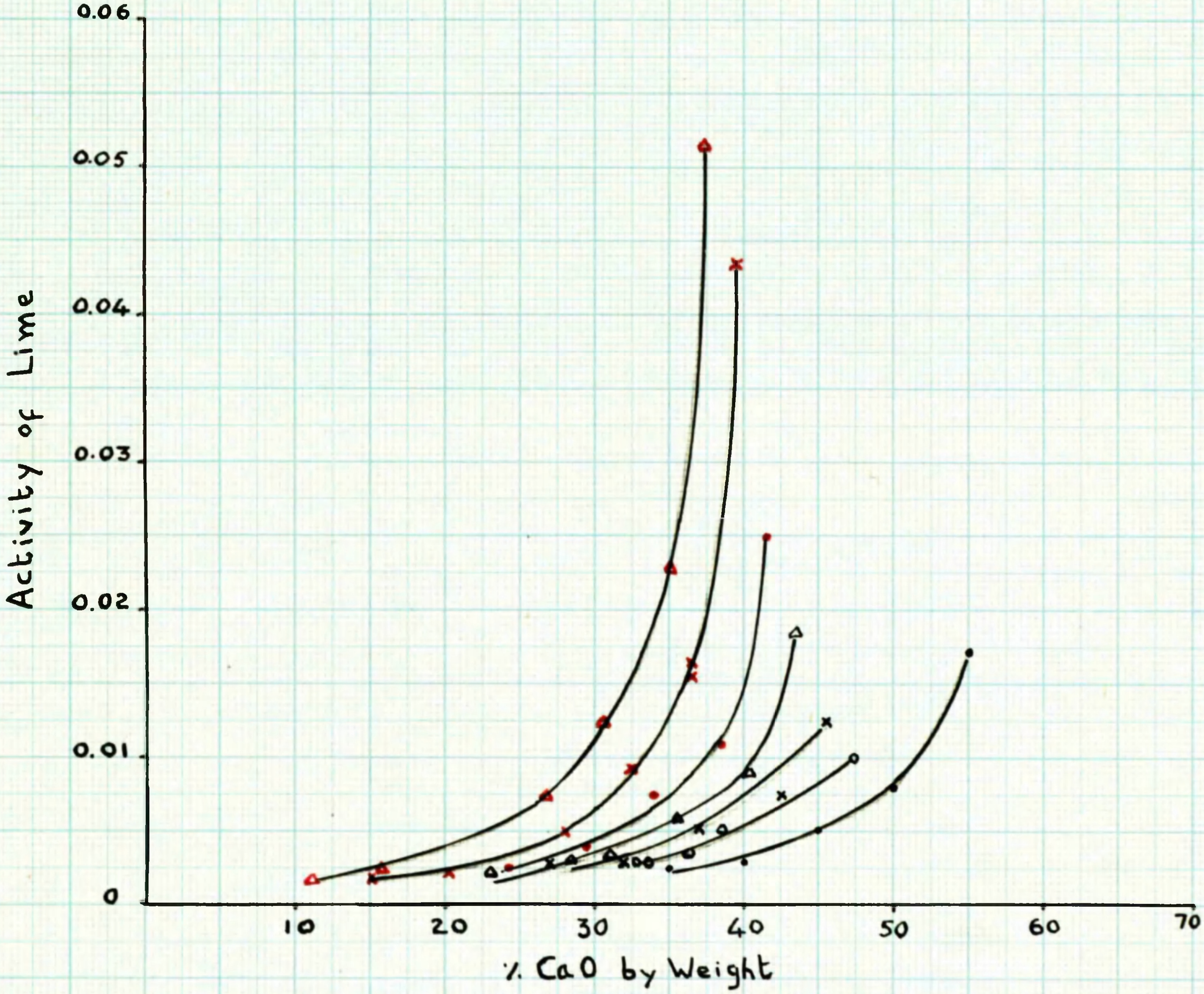


Fig. 16. Activity of Lime in CaO. SiO$_2$-MgO Slags at 1500°C

in the $CaO-Al_2O_3-MgO$ system and 1.5 mols. in the $CaO-SiO_2-MgO$ system.

In both systems it has been shown (Fig.12, 13) that when MgO is added to a binary slag while maintaining the ratio of the two constituents constant, the activity of CaO is increased, but when CaO is replaced by MgO (on a weight basis) the activity decreases. In the first case, MgO though by itself a poor desulphurizer, may increase the activity indirectly by combining with Al_2O_3 or SiO_2 of the slag thereby increasing a CaO. In the second case, as MgO is introduced into the slag at the cost of lime which is the sole desulphurizer, the lime activity would be expected to decrease.

The curves of Fig.15, 16, have been used to draw iso-activity lines in the $CaO-Al_2O_3-MgO$, $CaO-SiO_2-MgO$ systems, and these are given in Fig.17, 18, respectively. Very little is known about the thermodynamic properties of $CaO-Al_2O_3-MgO$ and $CaO-SiO_2-MgO$ slags. In view of the absence of activity data in these systems, it was therefore considered that even approximate calculations of activities of Al_2O_3, MgO and SiO_2 might be of some value. Referring to Fig.10 a part of the 1500°C isotherm (AB) traverses the $CaAl_2O_4$ field. Carter and Macfarlane obtained an activity of 0.2 for Al_2O_3 for the binary melt corresponding to point A, where the 1500°C isotherm meets the $CaO-Al_2O_3$ binary. The slag B is in equilibrium with $CaAl_2O_4$ at 1500°C. Since the activity of CaO and Al_2O_3 for point A, and the lime activity for point B (from the present work) are known, the alumina activity at

Fig. 17. Activities of CaO, Al_2O_3, MgO in CaO. Al_2O_3 - MgO Slags at 1500°c

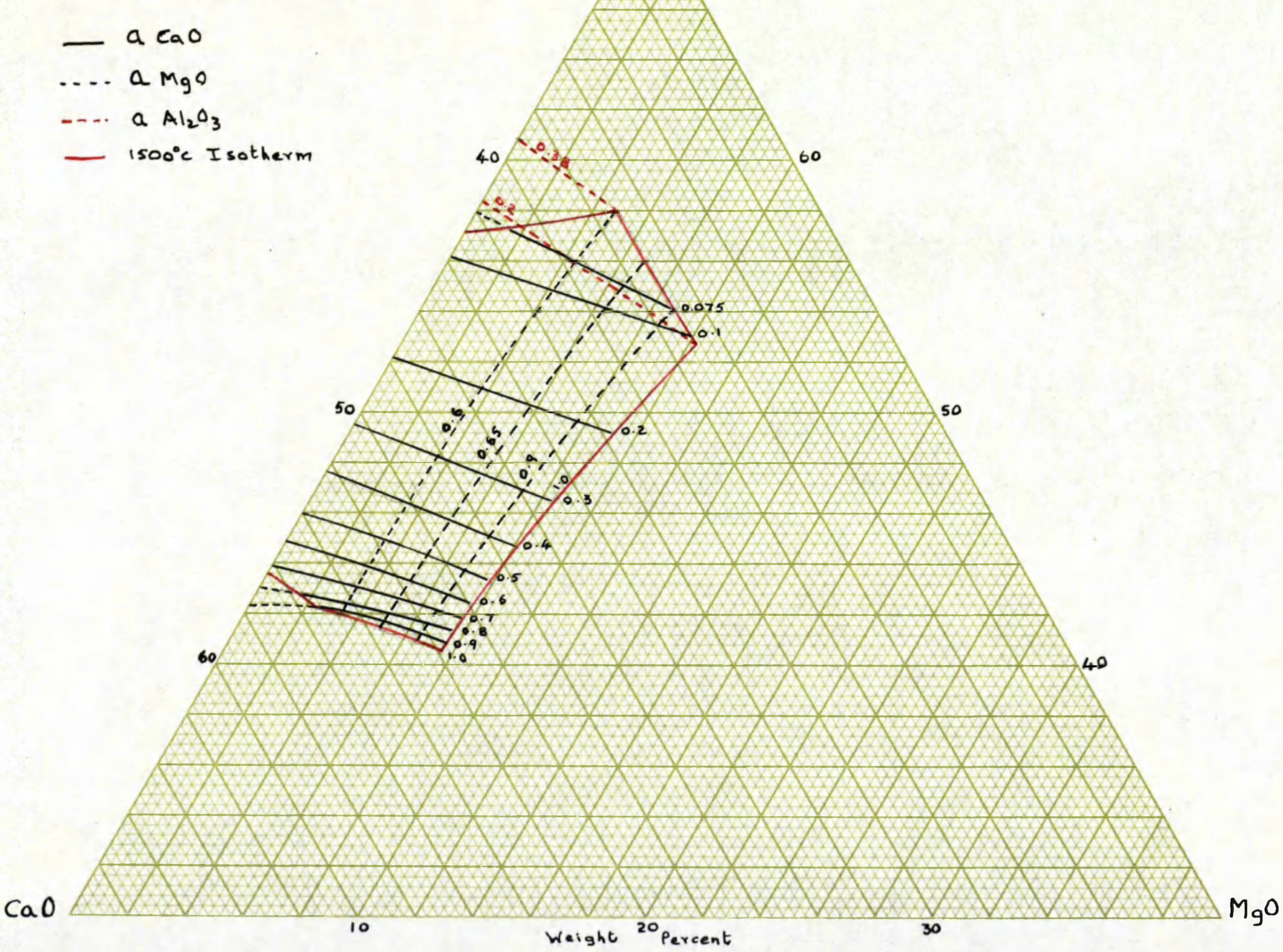
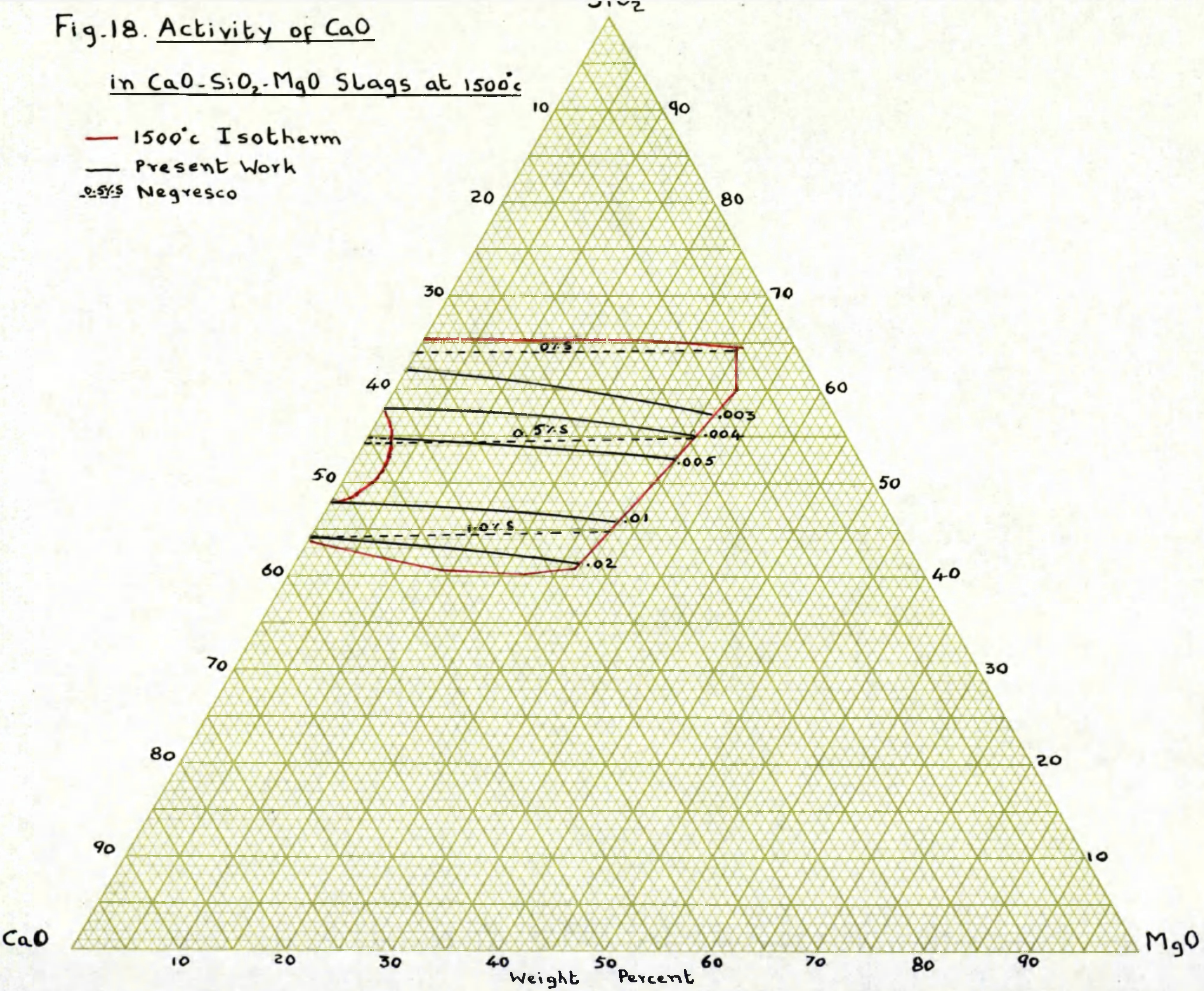


Fig.18. Activity of CaO

in CaO-SiO$_2$-MgO Slags at 1500°c



B can be calculated. This is found to be equal to 0.38. Now an alumina iso-activity line of 0.38 is obtained by joining point B with a point on the CaO-Al_2O_3 binary having the same alumina activity. $a_{Al_2O_3}$ at C could be obtained within a reasonable accuracy by drawing a line parallel to this known $a_{Al_2O_3}$ line, to meet the binary line at a point whose $a_{Al_2O_3}$ is also known. The point C corresponds to 0.22. Also, the a_{MgO} at C is 1.0. The activity of Al_2O_3 and MgO being known for composition C, the activity of MgO at B may be obtained, since the liquid slags at B and C are both in equilibrium with the spinel at 1500°C. By calculations this is found to be 0.6. The two limiting lines for a_{MgO} are the binary CaO-Al_2O_3 line having an a_{MgO} equal to zero, and the line CD where a_{MgO} is equal to one. Thus it is possible to obtain a corresponding point to B on the high CaO side. Similarly other lines were also drawn in Fig.17.

In Fig.18, in addition to the lime iso-activity lines from the present work, iso-sulphur capacity lines obtained by Negresco have also been drawn. The numbers on these lines refer to grams of sulphur absorbed by 100 gms. of slag. The curves of Negresco indicate the inter-changeability of CaO and MgO on a weight basis without any detrimental effect on sulphur absorption, and are seen to be in fair agreement with the curves of the present work.

In this system too, an attempt was made to determine the trend, of activity lines for SiO_2 and MgO. On the line EF (Fig.11) the slags are saturated with silica at 1500°C, and as such have unit silica activity. At the low silica end a part of the isotherm

(GH) traverses the dicalcium silicate field. From the known free energy of formation of this compound, and the lime activity obtained from the present work, the activity of silica for composition (H) may be calculated. By drawing a line through Q parallel to GH, a_{SiO_2} at Q is found to be 0.2. From the free energy of formation of forsterite ($2MgO.SiO_2$) given by Richardson, Jeffes and Withers(54), a value of 0.014 for a_{SiO_2} at Q, may also be obtained. This value is considerably smaller than 0.2 obtained from the present work. It could be that the thermodynamic data of Richardson et al is incorrect. On the other hand the constancy of γ_{CaS} with MgO content may be questionable. There is an obvious discrepancy which cannot be resolved here with the limited knowledge on the solubility of CaS and the variation of γ_{CaS} with composition in these slags.

CHAPTER VIII.

GENERAL DISCUSSION.

GENERAL DISCUSSION.

Application of the experimentally determined activity values to practical problems is severely limited because these results relate only to ideal conditions where equilibrium has been established. In the blast furnace there is no certainty of this occurring. Even then the activity values obtained here should serve as a pointer to the desulphurizing characteristics of the industrial slag.

A slag to have maximum desulphurizing capacity must have a high α CaO value. The results of the present work indicate that high Al_2O_3 slags possess such αCaO values. But they are not ideally suited for this purpose since their melting points are not low enough. On the other hand high silica slags, though having low melting points, are not suitable either due to their low αCaO values. Furthermore, these slags have been shown to be more viscous due to the presence in the melt of long polymerised silicate chains. An optimum slag should thus have moderately high α CaO value and fairly low melting point.

MgO which is invariably present in a blast furnace slag, though not directly taking part in the desulphurization, assists in this process indirectly by lowering the viscosity of high silica and alumina slags - by breaking down the long silicate and aluminate chains which are responsible for the increased viscosity. As pointed out by

Negresco, MgO may combine with Al_2O_3 and SiO_2 to form inactive groups and increasing α CaO. According to Holbrook and Joseph, the presence of MgO in the melt enables the use of higher CaO contents than would otherwise be possible.

The desulphurizing power of a slag is closely related to the basicity of the slag. In calculating basicity Hatch and Chipman considered CaO and MgO to be equivalent on a weight basis, and on a molar basis MgO is equivalent to two-thirds of a mol. of CaO. From the present work this equivalence is found to hold good only in the CaO-SiO_2-MgO slags, while in the CaO-Al_2O_3-MgO slags, MgO is only equivalent to half a mol. of CaO. This difference is probably due to the greater affinity of CaO for SiO_2 than for Al_2O_3. The amphoteric nature of Al_2O_3, as pointed out by Hatch and Chipman, may also cause this difference.

In quaternary slags an attempt was made to correlate αCaO and basicity as expressed by the ratio of basic and acidic constituents on a molar basis. The scatter of the points was greatly reduced when MgO was taken to be equivalent to 2/3 of a mol. of CaO, which is in accordance with the inferences of the present work on the CaO-SiO_2-MgO system and those of Hatch and Chipman. In Fig.19, α CaO is plotted against basicity, basicity being equal to CaO + $\frac{2}{3}$ MgO/Al_2O_3 + SiO_2 in molar ratio. Three sets of points, corresponding to approximately 10, 15 and 20 per cent Al_2O_3 in the original ternary slag, are plotted in the graph.

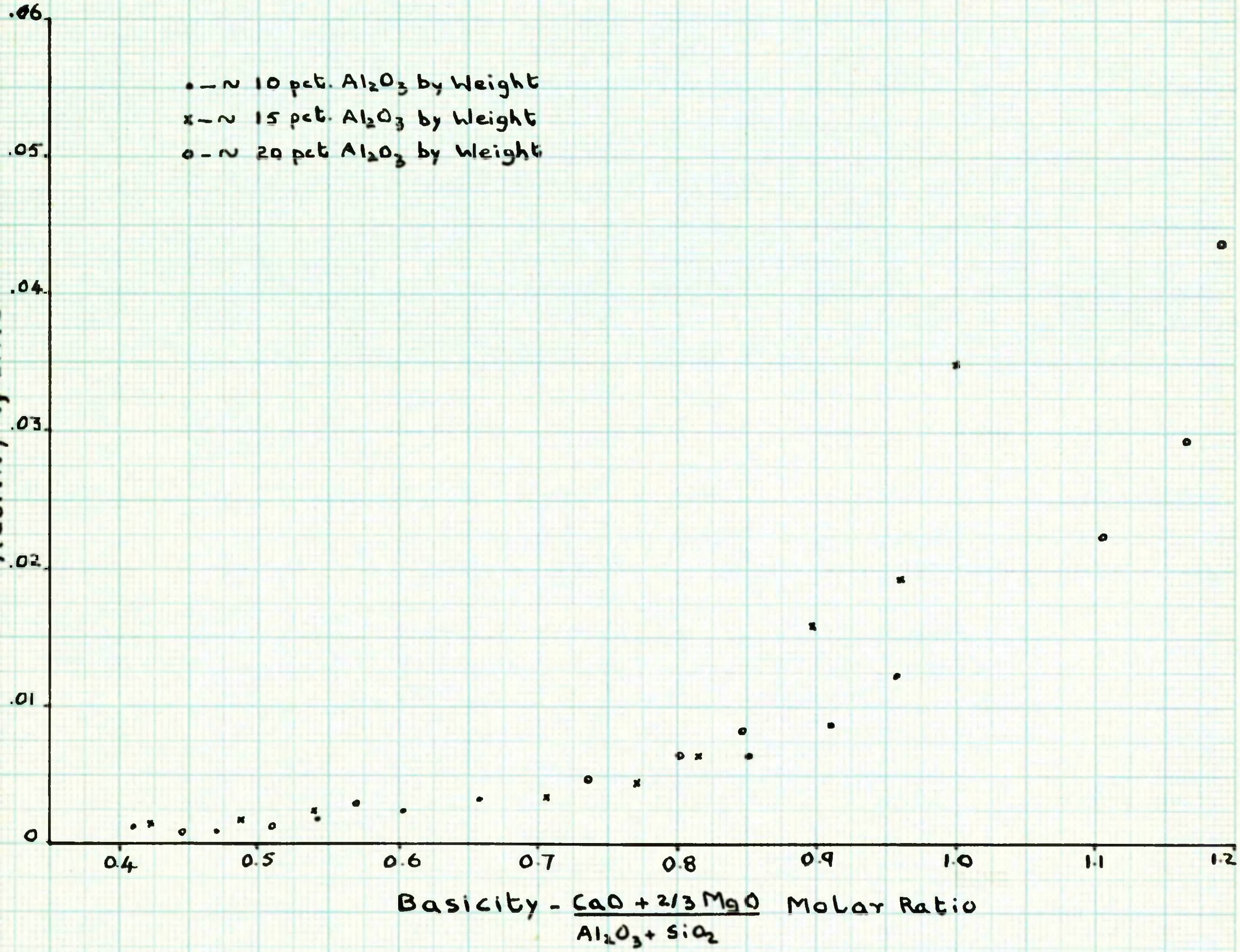


Fig. 19. Effect of Basicity on Activity of Lime at 1500°c

At basicities lower than 0.8 the scatter is very much less than that at higher basicities. The slope of the curves, which could be drawn through these points would change at basicity approximately equal to 0.8. Fig.19 suggests that at low basicities Al_2O_3 content has little or no effect on a CaO. At basicities higher than 0.8 the a CaO varies with the Al_2O_3 content, being higher in the 15 per cent Al_2O_3 slags than in the 10 per cent or 20 per cent Al_2O_3 slags for a given basicity. Unfortunately insufficiency of data on slags in this range of composition prevents the author from making any definite conclusions from this scatter. For the present a mean curve through all these points will be assumed to represent the lime activity-basicity relationship.

The quaternary slags investigated during the present work have melting points of 1300-1400°C. In slag-metal studies Hatch and Chipman, and others, have correlated the desulphurizing power $((S)/[S])$ with basicity, while in the present work basicity has been correlated with lime activity. It should be possible to correlate the three factors i.e., a CaO, basicity, and desulphurizing power. More activity data for a wider range of slag compositions may be advantageously used in combination with the melting point data given by Osborn and co-workers. Desulphurization in the furnace is also governed by the oxygen potential of the system. The FeO content of the slags encountered in practice will further modify the deductions to be made from the experimental results of the present work.

REFERENCES.

1. P.T. Carter, Iron and Steel, 1953, 26, July.
2. E. Maurer and W. Bischof, J.I.S.I., 1934, 129, 123.
3. J. Chipman and Ta Li, Trans. A.S.M., 1937, 25, 435.
4. J. White and H. Skelly, J.I.S.I., 1947, 155, 201.
5. J.P. Morris and A.J. Williams, Jr., Trans. A.S.M., 1949, 41, 1425.
6. J.P. Morris and R.C. Buehl, Trans. A.I.M.E., 1950, 188, 317.
7. L.S. Darken, Trans. A.I.M.E., 1950, 188, 1349.
8. C.W. Sherman, H.I. Elvander and J.Chipman, Trans. A.I.M.E., 1950, 188, 334.
9. C.W. Sherman and J. Chipman, Trans. A.I.M.E., 1952, 194, 597.
10. P.T. Carter and S. Tahir, J. West of Scotland I.S.I., 1951-52, 59, 133.
11. H. Wentrup, J.I.S.I., Carnegie Schol. Memoirs, 1935, 24, 103.
12. E. Maurer and W. Bischof, J.I.S.I., 1936, 133, 183.
13. N.J. Grant and J. Chipman, Trans. A.I.M.E., 1946, 167, 134.
14. P.T. Carter, Disc. Far. Soc., 1948, 4, 307.
15. F. Harders, H. Grewe, W. Oelsen, Stahl und Eisen, 1951, 71, 973.
16. P.T. Carter, Iron and Steel, 1953, 26, June.
17. R. Rocca, N.J. Grant and J. Chipman, Trans. A.I.M.E., 1951, 191, 319.
18. F.D. Richardson, Disc. Far. Soc., 1948, 4, 341.
19. W.F. Holbrook and T.L. Joseph, Trans. A.I.M.E., 1936, 1290, 99.
20. W.F. Holbrook, Trans. A.I.M.E., 1938, 131, 127.
21. G.G. Hatch and J. Chipman, Trans. A.I.M.E., 1949, 185, 274.
22. T.T. Negresco, Revue de Metallurgie, Acad. R.P.R., 1957, 2, 5.
23. M. Temkin, Acta Phys. Chim. U.R.S.S., 1945, 20, 411.

24. P. Herasymenko, Trans. Fara. Soc., 1938, 34, 1245.

25. A.E. Martin and G. Derge, Trans. A.I.M.E., 1943, 154, 104.

26. A.E. Martin, G. Glockler and C.E. Wood, U.S. Bur. Mines, Rep. Invest., 1941, No.3552.

27. R.S. McCaffery and J.F. Oesterle, Amer. Iron and Steel Inst., 1924, 285.

28. T.P. Colclough, J.I.S.I., 1936, 134, 547.

29. F.D. Richardson and G. Withers, J.I.S.I., 1950, 165, 66.

30. P.T. Carter, Disc. Far. Soc., 1948, 4, 342.

31. C.H. Herty, Jr., A.R. Belyea, E.H. Burkhart, C.C. Miller, Trans. A.I.M.E., 1925, 71, 512.

32. F.D. Richardson and C.J.B. Fincham, J.I.S.I., 1954, 178, 4.

33. P.T. Carter and T.G. Macfarlane, J.I.S.I., 1957, 185, 54-66.

34. G. St. Pierre and J. Chipman, J. Amer.Chem.Soc., 1954, 76, 4787.

35. G. St. Pierre and J. Chipman, J. Metals, 1956, 8, 1474.

36. T.G. Macfarlane, Ph.D. Thesis, 1955, Glasgow University.

37. R. Schumann, Jr., Acta. Met., 1955, 3, 219.

38. R.S. McCaffery and J.F. Oesterle, Trans. A.I.M.E., 1923, 69, 606.

39. O. Glaser, Zeitschrift fur Mineralogie, Geologie und Pataontologie, 1926, A, 81.

40. E.W. Filer and L.S. Darken, Trans. A.I.M.E., 1952, 194, 253.

41. K.K. Kelley, Bull. U.S. Bur. Mines, 1937, No.406.

42. F.D. Richardson and J.H.E. Jeffes, J.I.S.I., 1952, 171, 165.

43. A.G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", p.194, 1947, Chapman and Hall, London.

44. W. Nernst, Z. Elektrochemie, 1903, 9, 622.

45. H. Von Wartenberg, Z. Anorganische Chemie, 1908, 56, 320.

46. E.W. Dewing and F.D. Richardson, Trans. Far. Soc., 1958, 54, 679.

47. C.W. Montgomery and L.S. Kassel, J. Chem. Phys., 1934, 2, 417.

48. G. Herzeberg, "Molecular Spectra and Molecular Structure - Diatomic Molecules", p.1349, 1939, Prentice-Hall, New York.

49. C.J.B. Fincham and F.D. Richardson, J.I.S.I., 1952, 172, 53.

50. T. Rosenqvist, Trans. A.I.M.E., 1951, 191, 535.

51. E.F. Osborn, R.C. Devries, K.H. Gee and H.M. Kramer, J. Metals, 1954, 6, 33.

52. J.D. Baird, J. Taylor, Trans. Far. Soc., 1958, 54, No.424, 526.

53. J.C. Fulton and J. Chipman, Trans. A.I.M.E., 1954, 200, 1136.

54. F.D. Richardson, J.H.E. Jeffes, G. Withers, J.I.S.I., 1950, 166, 213.

APPENDIX.

APPENDIX.

Data used in A_{pc} v. Initial Gas Composition Graph.

No.	Initial Gas Composition.		A_{pc}	$-\log_{10} pO_2$
	$\%SO_2$	CO/CO_2		
1	0.5	1.27	148	7.7749
2	0.77	1.284	208	"
3	0.80	1.285	215	"
4	0.83	1.288	223	"
5	0.86	1.290	230	"
6	0.89	1.292	237	"
7	0.92	1.293	245	"
8	1.0	1.298	265	"
9	1.25	1.313	317	"
10	1.5	1.33	362	"
11	1.75	1.35	405	"
12	2.0	1.37	450	"
13	2.25	1.387	493	"
14	2.50	1.406	538	"
15	0.5	1.322	160	7.8099
16	0.77	1.338	232	"
17	0.80	1.340	238	"
18	0.83	1.342	245	"
19	0.86	1.344	252	"
20	0.89	1.346	260	"
21	0.92	1.348	266	"
22	1.0	1.353	285	"
23	1.25	1.369	340	"
24	1.50	1.387	390	"
25	1.75	1.406	435	"
26	2.00	1.425	482	"
27	2.25	1.445	528	"
28	2.50	1.463	576	"
29	0.50	1.374	173	7.8427
30	0.77	1.392	250	"
31	0.80	1.394	257	7.8427
32	0.82	1.396	265	"
33	0.86	1.398	273	"
34	0.89	1.400	280	"
35	0.92	1.402	287	"
36	1.0	1.406	308	"
37	1.25	1.425	366	"
38	1.50	1.446	417	"
39	1.75	1.468	467	"
40	2.00	1.49	511	"
41	2.25	1.512	560	"

No.	Initial Gas Composition.		A_{pc}	$-\log_{10} p_{O_2}$
	$\%SO_2$	CO/CO_2		
42	2.50	1.535	610	7.8427
43	0.50	1.427	187	7.8743
44	0.77	1.444	266	"
45	0.80	1.446	275	"
46	0.83	1.448	282	"
47	0.86	1.451	290	"
48	0.89	1.453	298	"
49	0.92	1.455	305	"
50	1.0	1.462	326	"
51	1.25	1.482	387	"
52	1.50	1.505	441	"
53	1.75	1.527	492	"
54	2.0	1.552	542	"
55	2.25	1.575	593	"
56	2.50	1.60	645	"
57	0.50	1.479	198	7.9045
58	0.77	1.499	283	"
59	0.80	1502	292	"
60	0.83	1.505	300	"
61	0.86	1.507	308	"
62	0.89	1.509	316	"
63	0.92	1.512	325	"
64	1.0	1.518	347	"
65	1.25	1.538	412	"
66	1.50	1.562	467	"
67	1.75	1.588	518	"
68	2.0	1.612	570	"
69	2.25	1.638	623	"
70	2.50	1.662	675	"
71	0.50	1.530	212	7.9339
72	0.77	1.552	300	"
73	0.80	1.555	308	"
74	0.83	1.557	318	"
75	0.86	1.560	327	"
76	0.89	1.563	335	"
77	0.92	1.565	345	"
78	1.0	1.572	367	"
79	1.25	1.591	435	"
80	1.50	1.617	495	"
81	1.75	1.643	552	"
82	2.0	1.672	607	"
83	2.25	1.70	660	"
84	2.50	1.73	712	"
85	0.50	1.795	277	8.0685
86	0.77	1.823	386	"
87	0.80	1.827	397	"
88	0.83	1.83	408	"

No.	Initial Gas Composition.		A_{pc}	$-\log_{10} p_{O_2}$
	%SO_2	CO/CO_2		
89	0.86	1.833	420	8.0685
90	0.89	1.837	430	"
91	0.92	1.842	441	"
92	1.0	1.855	470	"
93	1.25	1.887	548	"
94	1.50	1.922	631	"
95	1.75	1.958	700	8.0685
96	2.0	1.995	768	"
97	2.25	2.027	826	"
98	2.50	2.06	885	"
99	0.50	2.057	345	8.1840
100	0.77	2.1	481	"
101	0.80	2.103	496	"
102	0.83	2.107	510	"
103	0.86	2.112	525	"
104	0.89	2.117	535	"
105	0.92	2.121	547	"
106	1.0	2.132	577	"
107	1.25	2.168	671	"
108	1.50	2.206	760	"
109	1.75	2.255	840	"
110	2.0	2.305	908	"
111	2.25	2.355	991	"
112	2.50	2.406	1058	"
113	2.75	2.457	1126	"
114	0.50	2.325	412	8.2864
115	0.77	2.372	570	"
116	0.80	2.377	580	"
117	0.83	2.782	596	"
118	0.86	2.387	612	"
119	0.89	2.392	627	"
120	0.92	2.40	640	"
121	1.0	2.415	675	"
122	1.25	2.467	790	"
123	1.50	2.520	893	"
124	1.75	2.578	982	"
125	2.0	2.635	1070	"
126	2.25	2.691	1146	"
127	2.50	2.758	1225	"
128	2.75	2.827	1305	"
129	0.50	2.592	478	8.3779
130	0.77	2.652	650	"
131	0.80	2.66	668	"
132	0.83	2.665	685	"
133	0.86	2.67	702	"
134	0.89	2.678	720	"

No.	Initial Gas Composition.		A_{pc}	$-\log_{10} p_{O_2}$
	$\%SO_2$	CO/CO_2		
135	0.92	2.680	747	8.3779
136	1.0	2.695	786	"
137	1.25	2.737	905	"
138	1.75	2.898	1117	"
139	2.0	2.967	1216	"
140	2.25	3.042	1311	"
141	2.50	3.125	1395	"
142	2.75	3.26	1480	"
143	3.0	3.29	1565	"
144	0.5	2.857	545	8.4605
145	0.77	2.93	738	"
146	0.80	2.94	757	"
147	0.83	2.947	777	"
148	0.86	2.955	795	"
149	0.89	2.964	815	"
150	0.92	2.972	838	"
151	1.0	2.995	877	"
152	1.25	3.066	1020	"
153	1.75	3.225	1258	"
154	2.0	3.312	1360	"
155	2.25	3.40	1465	"
156	2.50	3.50	1560	"
157	2.75	3.60	1655	"
158	3.0	3.7	1750	"

Data of Dewing and Richardson.

1	0.5	1.483	202	7.9048
2	0.75	1.50	281	"
3	1.0	1.528	352	"
4	1.25	1.55	415	"
5	1.50	1.573	475	"
6	1.75	1.596	532	"
7	2.0	1.622	586	"
8	2.25	1.654	636	"
9	2.5	1.685	685	"
10	0.5	1.83	283	8.0854
11	0.75	1.86	388	"
12	1.0	1.892	480	"
13	1.25	1.93	565	"
14	1.5	1.967	641	"
15	1.75	2.02	712	"
16	2.0	2.045	782	"
17	2.25	2.086	847	"
18	2.5	2.132	907	"

No.	Initial Gas Composition		A_{PC}	$-\log_{10} pO_2$
	$\%SO_2$	CO/CO_2		
19	2.75	2.175	965	8.0854
20	3.0	2.222	1020	"
21	3.25	2.272	1075	"
22	0.5	2.606	452	8.3813
23	0.75	2.66	610	"
24	1.0	2.717	757	"
25	1.25	2.785	870	"
26	1.5	2.855	990	"
27	1.75	2.927	1080	"
28	2.0	3.0	1180	"
29	2.25	3.078	1270	"
30	2.5	3.165	1357	"
31	2.75	3.252	1442	"
32	3.00	3.345	1522	"
33	3.25	3.441	1600	8.3813
34	3.5	3.54	1680	"
	Data of Richardson and Jeffes.			
1	0.73	1.508	162	7.9048
2	2.22	1.62	430	"
3	2.3	2.037	620	8.0854
4	2.81	2.113	727	"
5	2.46	3.04	1072	8.3823
6	3.01	3.203	1238	"

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