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SULPHUR DISTRIBUTION

IN

GAS-METAL-SLAG SYSTEMS

THESIS

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TEXT
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SUMMARY

A study was made of the rate of absorption of sulphur in grams per minute from sulphur dioxide - nitrogen gas mixtures by molten iron and iron containing four per cent carbon. The maximum rate of nitrogen flow and partial pressure of sulphur dioxide was 350 ml/minute and 0·06 atmospheres respectively. The melts were contained in alundum and magnesia crucibles at 1400° - 1550°C, the gas being blown on to the surface of the metal and occasionally bubbled through the metal for mixing purposes by means of an alumina tube. Samples of metal were taken periodically and analysed for carbon and sulphur by combustion methods. In the iron - carbon melts the rate of carbon removal was also studied. The effect of up to three per cent silicon on the absorption of sulphur and on the removal of carbon was noted at 1400°C. The effect of sulphur on the solubility of carbon in iron - carbon - sulphur alloys was found at 1400° C and the limits of the miscibility gap at carbon saturation were determined in this system at 1300° and 1500°C.

The equilibrium sulphur distribution between iron oxide-silica-magnesia slags and molten iron at 1550°, 1600°, and 1650°C was obtained. The minimum ferrous oxide content of these slags was 55 mol per cent. The Fe_2O_3 content of the slag was converted to FeO on the iron basis, the slags being analysed

for FeS, FeO, Fe_2O_3, SiO_2, and MgO, the metal for S. The variation in the sulphur distribution ratio, $\frac{(\%S)}{[a_s]}$, with mol per cent FeO_T was found to be independent of temperature in the range studied and was given by the expression :

$$\frac{(\%S)}{[a_s]}_{1550^\circ - 1650^\circ C} = \cdot 078 \, (\text{mol } \% \, FeO_T) - 3\cdot 25$$

The effect of magnesia and silica on the distribution ratio of sulphur was noted, magnesia and silica being found to lower the ratio by approximately the same amount. Using the relevant thermodynamic data the sulphide capacities, $\frac{(\%S) . \, p^{\frac{1}{2}}O_2}{p^{\frac{1}{2}}S_2}$, of the slags in equilibrium with the molten metal were found to increase with increasing FeO_T concentration and with increasing temperature.

The absorption of sulphur from a 2 per cent sulphur dioxide - nitrogen gas mixture by molten iron oxide slags held in magnesia crucibles was studied at 1550°, 1605°, and 1620°C. The partial pressure of oxygen in the gas phase was calculated from the ferric oxide content of the equilibrium slag and the partial pressure of sulphur in the gas phase was calculated from the known thermodynamic data on the gaseous compounds of sulphur and oxygen. The sulphide capacity was used as a measure of the absorption power of the slags for sulphur. The sulphide capacities obtained from the gas - slag experiments differed from those obtained from the slgg - metal equilibrium experiments and reasons are given for the difference.

The absorption of sulphur from a 3 per cent sulphur dioxide-nitrogen atmosphere by molten iron oxide-silica slags in contact with molten iron was studied at 1550°C. Samples of slag and metal were taken almost simultaneously, and the variation in the sulphur distribution coefficient with percentage FeO_T throughout the run was obtained. The slag was found to be in equilibrium with the liquid metal and not with the gas phase. Reference has been made to the application of these results to the pick-up of sulphur by the metal in the open hearth furnace during the melt-down period.

CONTENTS

CHAPTER I

INTRODUCTION

INTRODUCTION

With the increased production of iron and steel and the demands of all industry for greater quantities of coal and fuel oil, the reserves of good quality raw materials used by the iron and steel industry are diminishing rapidly throughout the world. Perforce the industry must use ores, coal, and fuel oil of poorer quality each year, which places an increasing burden on the extraction and refining processes. As a result, in recent years, the problem of sulphur control throughout the production of iron and steel has assumed great significance and certainly in the near future will become of paramount importance.

The most important mechanism of sulphur removal in both the blast furnace and steel making furnace is the transfer of sulphur from metal to slag. The removal of sulphur from the molten metal has been found to depend upon a number of factors, e.g. composition of the slag, metal, and gas phases, contact area, temperature, total sulphur, time, and the degree of attainment of equilibrium among the various phases. The slag phase plays by far the most important part in sulphur removal in both the blast and open hearth furnaces and a thorough knowledge of the chemical and physical properties of the slags should go far to help our understanding of the reactions involved in the movement of sulphur in the furnaces. In the open hearth furnace numerous investigations have been carried out on slag-metal relationships with respect to sulphur, but with little success due to the complexity of the slag-metal systems studied.

In the laboratory, equilibrium conditions can be studied on much simpler slag and metal systems and the thermodynamic properties of the slag and metal obtained. Simplifications are adopted such as the study of only two phases, e.g. slag-gas or slag-metal. Even here complications arise as the study of chemical reactions at steelmaking temperatures is rather difficult. furthermore, molten metal and iron and steelmaking slags have a corrosive action on the containers and no refractory has been found which is completely resistant to this attack. Alumina, silica, zirconia, beryllia, thoria and magnesia are all attacked to a greater or less degree, while noble metals, which can be used for slags alone, are not always satisfactory. The interpretation of the results obtained from such studies are complicated by the non-ideal behaviour of most of the components in solution.

The role of the gas phase in iron and steelmaking reactions has up to the present been somewhat neglected, but more interest is now being shown, no doubt due to the introduction of the modern pneumatic processes of steelmaking where gas-metal reactions are assuming a new importance. The gas phase is of great significance in open hearth steelmaking, where the modern tendency is to use oil fired furnaces. Depending on the sulphur content of this fuel oil, appreciable quantities of sulphur can pass from the gas phase to the furnace bath. It has been established that the most dangerous time for pick-up of sulphur in an open hearth heat is during melt down when the metal is in direct contact with the gas phase and not protected by a slag layer as later on during the regining period. Experience has shown that a short, hot, oxidising flame, giving fast melt-down times, leads to less pick-up of sulphur by the melting metal than a long partially combusted flame.

Distinct advantages of using gases in laboratory experimental work are close control of composition, and more important the reasonable assumption that the individual components of the gas phase behave ideally at steelmaking temperatures. The thermodynamic properties of gases and their gaseous compounds are also reasonably well established at these temperatures.

The present investigation was concerned mainly with non-equilibrium conditions, and it was proposed to study the absorption of sulphur by molten Armco iron, high carbon iron, and iron oxide slags held in magnesia crucibles from a nitrogen atmosphere containing sulphur dioxide. As the published literature on the equilibrium of sulphur between molten iron and iron oxide-silica slags was found to be very scanty, a study was made of this equilibrium from 1550°C to 1650°C. A non-equilibrium study was also made of the three phase system Armco iron, iron oxide-silica slag, and nitrogen gas containing sulphur dioxide.

CHAPTER II

LITERATURE SURVEY

LITERATURE SURVEY

The literature pertaining to sulphur investigations on a laboratory as well as on a works scale is exceedingly voluminous. As far as is possible it is proposed to deal only with laboratory investigations and the published papers will be sub-divided roughly into three groupings :-

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

These three sub-divisions are of course flexible as many workers have carried out investigations on slag, gas, and metal equilibria at the one time. Almost all of the investigations referred to in this review have been carried out using slag and metal in the molten condition at temperatures ranging from 1300° to 1900°C, which covers both iron and steelmaking temperatures. Whiteley[1] and Carter[2] have summarised the effect of the furnace atmosphere in the open-hearth furnace prior to complete melting of the charge.

Gas-Metal Investigations

Several workers have investigated the equilibrium between molten iron and hydrogen-hydrogen sulphide gas mixtures. Knowledge of the thermodynamic properties of solutions of sulphur in molten iron have been obtained mainly from a study of the reaction

$$H_2(g) + \underline{S} = H_2S(g)$$

where $\underline{S}$ is sulphur in solution in iron. Maurer and Bischof[3] observed a linear relationship between the sulphur content of the metal and the ratio $\frac{pH_2}{pH_2S}$. Their melts, which covered a range of sulphur contents from 0 to 29·6 per cent sulphur, did not reach equilibrium as their crucibles were incapable of resisting chemical attack by the reacting substances for more than sixty minutes. Maurer and Bischof's estimated equilibrium constant $K = \frac{(pH_2S)}{(pH_2)\cdot[\%S]}$ was 100 times that of Chipman and Ta Li[4] who obtained a value of 0·00493 for the equilibrium constant at 1600°C. Chipman and Ta Li had used magnesia and beryllia crucibles initially, but had found a considerable pick up of sulphur by the crucible from the gas phase. They abandoned these basic crucibles and suggested the discrepancy between their work and that of Maurer and Bischof was due to the use of beryllia crucibles by the latter. White and Skelly[5] in the light of these discrepancies repeated the investigations, taking care to eliminate thermal diffusion by the use of a small reaction chamber entirely in the hot zone of the furnace and at a uniform temperature throughout. These workers obtained an equilibrium constant of 0·0025 at 1600°C, which although half the value of Chipman and Ta Li, seemed to prove that Maurer and Bischof's results were in error due to thermal diffusion. However, silicon pick-up from the alundum containers occurred, so that the results of White and Skelly really referred to iron containing 2·5 per cent silicon. They suggested that the difference between their equilibrium constant and that of Chipman and Ta Li was due to this silicon pick-up. Morris and Williams[6] showed that on increasing the silicon content of the iron, the sulphur absorbed by the metal from the hydrogen/hydrogen sulphide atmosphere decreased. Assuming a standard state in which the metal contained one per cent sulphur they obtained a value of 0·00256 at 1615°C for the equilibrium constant. When the effect of silicon on the activity coefficient of sulphur in molten iron is taken into consideration and the results of White and Skelly corrected accordingly, their corrected constant is even further below that of Chipman and Ta Li.

Kitchener, Bockris and Liberman[7] have reported on a preliminary study which shows that saturation of the melt with carbon approximately doubles the sulphur activity at 1560°C. Morris and Buehl[8] found that carbon had a similar but greater effect to silicon (on a weight per cent basis) on the activity coefficient of sulphur. At carbon saturation the activity of sulphur was increased six-fold in comparison with the two-fold increase of Kitchener et al. Reasons put forward for this increase in activity coefficient were that silicon and carbon formed a compound with iron in the melt, thus reducing the mol fraction of "free" iron and so increasing the activity of sulphur. Darken[9] also suggested that in a solution containing iron, carbon, and sulphur, the affinity of carbon for iron is much stronger than the affinity for sulphur. Making the assumption that each carbon atom is surrounded by six iron atoms it was shown that at low concentrations each atomic per cent of carbon increased the activity coefficient of sulphur by six per cent which is in good agreement with the observed increase of six to seven per cent.

Sherman, Elvander, and Chipman[10] investigated the effect of concentration on the activity coefficient of sulphur. The equilibrium constant, K $= \frac{(pH_2S)}{(pH_2)\cdot[\%S]}$, at different sulphur concentrations up to four per cent was found not to be a true constant but graphical extrapolation to zero sulphur gave a true value for this constant. The infinitely dilute solution was thus used as the standard state. Increase in sulphur concentration was found to decrease the activity of sulphur in the melt. These workers also showed that their work was in quite good agreement with the results of Morris and Williams[6] and the corrected results of White and Skelly[8]. The corrections to the results of White and Skelly were based on the data of Morris and Williams[6] on the effect of silicon on the activity of sulphur. It was also concluded by Sherman, Elvander and Chipman[10] that the work done by Chipman and Ta Li was in error due to thermal diffusion. Morris[11] found that manganese decreased the activity coefficient of sulphur in molten iron.

Sherman and Chipman[12] investigated from their own experiments and the data of others the effect of manganese, carbon, phosphorous, sulphur, aluminium, silicon, and copper on the activity coefficient of sulphur in molten iron solutions containing these elements. The data on copper was taken from the work of Rosenqvist and Cox[18]. It was found that phosphorous, aluminium, silicon and carbon increased the activity of sulphur, phosphorous having the least effect, and carbon the most, while copper, manganese and sulphur decreased the activity of sulphur, copper having the least effect and sulphur the most. All the elements were expressed in weight percentages. The method of combining activity coefficients for solutions of more than one component was developed in this paper. It was shown that in a multicomponent system the activity coefficient can be expressed in the form

$$f_s = f_s^{Fe} \cdot f_s^{C} \cdot f_s^{Si} \cdot \text{-------}$$

$$\text{or } \log f_s = \log f_s^{Fe} + \log f_s^{C} + \log f_s^{Si} +$$

where f_s = overall activity coefficient of sulphur.

f_s^{Fe} = activity coefficient of sulphur in the binary iron - sulphur solution

f_s^{C}, f_s^{Si} = coefficients representing the effect of carbon, silicon, etc., on the activity of sulphur.

Sherman and Chipman gave an alternative method for computing the overall activity coefficient based on an observation of Morris and Buehl[8] on the effect of carbon and silicon on the activity of sulphur. This method is to find the amount of solute B which has the same effect on the activity coefficient of sulphur as solute A. This equivalent amount of B is added to the actual amount of B in solution and the activity coefficient corresponding to this total represents the combined effect of A + B. This can then be repeated for a third solute and so on. This method gave better agreement with the experimental results than the first method of straight summation of log activity coefficients. Pig iron was shown to have an activity coefficient of sulphur approximately 5·5 times that of sulphur in mild steel, which stresses the importance of solute atoms, carbon in particular, on desulphurisation in the blast furnace.

In the solid state, low temperature studies at 900°C have been carried out on the reaction of solid iron sulphide with hydrogen to produce solid iron by Jellinck and Zakowski[14], and Britske and Kapustinsky[15]. Their results may be extrapolated to higher temperatures by the aid of the heat capacities and heats of fusion of the substances involved in the reaction, and are found to be in reasonable agreement with the high temperature data.

Under oxidising conditions, as in the open-hearth furnace, it would seem more appropriate to study the effect of sulphur dioxide on molten iron, but little work has been done on this aspect. Maurer and Bischof[3] circulated SO_2/O_2 gas mixtures over molten iron, withdrawing a portion of the gas periodically to see in which direction the equilibrium was proceeding. As in their

H_2/H_2S work equilibrium could not be attained due to failure of the crucibles. The results indicated that the final sulphur content was proportional to the ratio pSO_2/pO_2. Both Herty et al[16] and Maurer and Bischof suggested the following reaction to account for absorption of sulphur from gases:

$$Fe\ (liq) + SO_2 = FeS\ (in\ Fe) + O_2$$

Both their results and the steelworks data of Diehl[17] could be explained by this equation. Chipman and Ta Li[4], however, suggested that if this was the controlling reaction, then in a gas mixture of equal volumes of O_2 and SO_2 no sulphur pick-up beyond 0·0005% sulphur should occur at 1535°C. From practice this is known to be incorrect. Chipman and Ta Li therefore suggested that since the oxygen formed by the reaction would be absorbed immediately by the molten metal to form iron oxide, the effective reaction should be written[ø]

$$3\ Fe\ (liq.) + SO_2 = \underline{FeS}\ (\%) + \underline{FeO}\ (\%)$$

for which the standard free energy change is[18]

$$G^\circ = 1{,}600 - 23{\cdot}32T.$$

The equilibrium constant at the melting point is $8{\cdot}0 \times 10^4$, which signifies that sulphur dioxide in contact with molten iron would be absorbed almost entirely. In the open-hearth furnace the

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[ø] Round and square brackets throughout this review denote concentrations in the slag and metal phases respectively. Compounds or elements underlined, e.g. $\underline{O}$' refer to solution of the compounds or elements in liquid form.

function of excess air, therefore, is to prevent contact by sulphur bearing gases during melt down by the formation of a protective oxide skin.

Carter and Tahir[16], who studied the equilibrium between molten iron and gas mixtures of SO_2, N_2, and SO_2, O_2, and N_2, found no relationship between the sulphur content of the metal and the ratio pSO_2/pO_2. Using induction heating these workers found that considerable oxidation took place which eventually led to the separation of an oxide-rich phase. Due to the high frequency heating, this oxide-rich phase always moved to the periphery of crucible so that throughout each experiment the metal always appeared to be in contact with the gas. The "equilibrium" value of sulphur obtained was really the result of steady state conditions in which the rate at which sulphur entered the metal from the gas phase exactly equalled that at which sulphur entered the continuously forming oxide phase from the metal. The sulphur concentrations so found were proportional to the partial pressure of SO_2 in the gas phase and were greatest at low temperatures. The relationship between sulphur content of the metal, partial pressure of SO_2, and temperature was expressed quantitatively by

$$\log \frac{[\%S]}{pSO_2} = \frac{2{,}642}{T} + 0{\cdot}350$$

Carter and Tahir found sulphur vapour in the exit gases, and they considered that the reaction took place in two stages.-

$$2\,Fe + SO_2 = 2\underline{FeO} + \frac{1}{2}S_2$$

$$Fe + \frac{1}{2}S_2 = \underline{FeS}$$

followed by separation of the oxygen-rich phase when saturation was reached.

In two experiments the starting material contained more sulphur than that corresponding to the steady state condition. The sulphur content fell, but did not reach the expected value, showing that the rate of sulphur removal was much slower than the rate of absorption. It was suggested that this was because no mechanism existed for the transfer of sulphur from the metal to the gas phase except in the slag. An iron oxide slag, into which the iron sulphide could partition, must first be formed and the amount of this iron oxide is limited by the supply of oxygen from the SO_2 gas phase, making this method of sulphur removal a relatively slow process. As the magnitude of the sulphur pick-up seemed to be unaffected by one to six per cent oxygen, these workers suggested that their results might be applicable to the melting down stage, provided that the oxygen potential of the gas phase was high enough to bring about the formation of a separate oxide phase. Data on various gaseous fuels at different levels of excess oxygen were calculated and it was concluded that efficient mixing of gas and air is of greater importance in mixed gas, or other rich gas, firing of open-hearth furnaces, than when raw producer gas is used.

The reaction of solid iron with sulphur dioxide containing gases has been studied by Preece and Riley[19] at 1150°C, who found that the presence of sulphur dioxide in the furnace atmosphere caused increased rate of scaling, with the formation of a liquid FeO-FeS eutectic mixture which could penetrate the steel by intercrystalline means. No sulphur was picked up when the atmosphere contained more than 4 per cent oxygen.

Gas-Slag Investigations

As molten iron picks up sulphur from both reducing and oxidising furnace atmospheres, if the charge as a whole loses sulphur to the gases, then the slag must be responsible for the loss. While many investigations have been made on gas-metal, and slag-metal relationships less work has been done on gas-slag reactions especially those pertaining to sulphur due mainly to the corrosive properties of slags. Most metallurgical slags are extremely reactive substances, and difficulty is experienced in finding suitable containers to hold the slags at high temperatures. If a container material is found that will hold the slag without leakage as often as not the material is found to be slightly soluble in the slag. This gives rise to unwanted constituents in the slag which can alter its properties thus making the study of simple binary and ternary systems more complicated. Refractory oxides are normally used, e.g., alumina, magnesia, thoria, beryllia, silica, and zirconia. Noble metal containers of the platinum group can also be used in slag-gas investigations but, while inactive, are expensive and not so strong at high temperatures.

The importance of the furnace atmosphere in the blast furnace is difficult to assess but in the open hearth furnace the atmosphere above the bath is critical. According to Richardson and Withers[20] transfer of sulphur from slag to gas is accompanied by a simultaneous transfer of oxygen from gas to slag. Similarly transfer of sulphur from metal to slag is accompanied by a simultaneous transfer of oxygen from slag to metal. Thus the desirable transfer of sulphur from metal to gas is concurrent with an also desirable, especially early in the refining stage, transfer of oxygen from gas to metal, both elements passing via the slag. For conditions of complete combustion sulphur should be removed from the slag phase[21], but under less oxidising conditions the high basicity which favours transfer of sulphur from metal to slag also favours the passage of sulphur from gas to slag.

Herty[16], assuming most of the gaseous sulphur to be present as sulphur dioxide, suggested the following equations to represent the reactions between sulphur dioxide and lime-containing slags.

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

$$SO_2 + 3Fe + (CaO) = (CaS) + 2(FeO)$$

Qualitatively these equations show that reducing conditions and high gas sulphur contents favour pick up of sulphur by basic slags and vice-versa.

Fincham and Richardson[22], assuming that sulphur is present in slags as sulphide and sulphate, represented the reaction between gas and slag as

$$\frac{1}{2}S_2 + (O)_{melt} = \frac{1}{2}O_2 + (S)_{melt} \qquad K = \frac{(S).\,p^{\frac{1}{2}}O_2}{(O).\,p^{\frac{1}{2}}S_2}$$

$$\frac{1}{2}S_2 + (O)_{melt} + \frac{3}{2}O_2 = (SO_4)_{melt} \qquad K = \frac{(SO_4)}{(O).p^{\frac{1}{2}}S_2.p^{\frac{3}{2}}O_2}$$

The equilibria operated simultaneously but the sulphide equilibrium was important at oxygen pressures less thatn 10^{-5} - 10^{-6} atmospheres; while the sulphate equilibrium was important at oxygen pressures. greater than 10^{-3} - 10^{-4} atmospheres. Between these limits both sulphide and sulphate were thought to be present, while at oxygen pressures above $10^{-2\cdot5}$ atmospheres the formation of pyrosulphate occurred. The slags, which were held in platinum cups, were equilibrated with H_2, CO_2, SO_2 and N_2 gas mixtures. The capacity of a slag to hold sulphur was expressed as its sulphide capacity, $C_S = \frac{(\%S).p^{\frac{1}{2}}O_2}{p^{\frac{1}{2}}S_2}$, and the influence of slag composition on this capacity was obtained. An increase in temperature at a constant pO_2 and pSO_2 input, while raising the sulphide content of the slag, decreased the sulphate content. The majority of the slags used in the investigation were lime-alumina-silica slags, and increasing basicity favoured high sulphur contents at constant pO_2 and pSO_2 input. Magnesia was shown to be a less efficient retainer of sulphur than lime in binary silica slags of constant silica mol-fraction.

It was found impossible to study iron oxide-silica melts in iron cups because the slag crept out of them, a constant difficulty with iron oxide slags. Measurements were therefore made in silica cups, i.e. in equilibrium with silica, the equilibrium compositions being extrapolated from Michal and Schuhmann[23]. The same type of sulphide equilibrium was assumed to hold for these slags as in the lime-alumina-silica type.

Log C_S values obtained from the sulphur distribution data of Fetters and Chipman (24) and Winkler and Chipman (25), by application of the available data on $\frac{1}{2}O_2 = [O]$[26] and $\frac{1}{2}S_2 = [S]$[16], were found to agree quite closely with the theoretical points at pure FeO obtained from a consideration of the equilibrium constant for the reaction

$$FeO + \frac{1}{2}S_2 = FeS + \frac{1}{2}O_2$$

using the theoretical value of the activity coefficient of iron sulphide in ferrous oxide as calculated by Chipman[27].

Carter and Macfarlane[28] studied the equilibrium of lime-alumina-silica slags with $SO_2 - CO_2 - CO$ gas mixtures. The sulphurising power of the gas was denoted by the ratio of $\frac{p^{\frac{1}{2}}_{S_2}}{p^{\frac{1}{2}}_{O_2}}$, and only sulphide sulphur was formed as the experiments were conducted at oxygen pressures of $10^{-8} - 10^{-5}$ atmospheres. From their results the activities of lime, alumina, and silica in the binary and ternary synthetic slags were calculated, making the assumptions that the oxygen activity of the slag remained constant despite additions of small amounts of sulphur, and that the sulphide activity was proportional to the per cent by weight of sulphur in the slag.

White[20] studied the decomposition of ferric oxide into oxygen and the lower oxides of iron from 1000° to 1650°C under oxygen pressures of 2 cm. to 76 cm. of mercury. The effect of additions of lime and silica upon this reaction was also observed. The slag was suspended in a platinum crucible from one arm of an analytical balance, whereby the weight loss caused by the reaction

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

was obtained. The proportions of ferrous to ferric oxide could then be calculated. A side reaction of iron oxide with platinum

$$FeO = Fe\ (\text{in Pt}) + \tfrac{1}{2}O_2$$

involved a possible unsatisfactory correction procedure which may lead to errors.

Darken and Gurry[30] in a classical investigation determined the equilibrium pressures of oxygen over iron oxides of various oxygen contents. By suitable combinations of the gases, H_2, O_2, H_2O, CO, CO_2 and air, any partial pressure of oxygen could be obtained in the experimental system. A gas of a fixed composition, and hence of a fixed partial pressure of oxygen found from the pertinent thermodynamic data, was passed over molten iron oxide in a platinum crucible held at a constant temperature. After equilibrium was reached the slag was quenched and analysed for ferrous and ferric iron. Thus the relationship between partial pressure of oxygen and composition of liquid oxide expressed as the atom fraction ratio of oxygen to iron, $\frac{N_2}{N_1}$, was established. Darken and Gurry's results do not agree very well with those of White in the pure iron-oxygen system.

In a subsequent paper Gurry and Darken[21] made a less thorough investigation of the effects of additions of manganese oxide and lime on the composition of iron oxide melts. A few experiments were made and those in a narrower range of oxygen partial pressures and temperatures.

Krings and Schackmann[22] had studied the same problem before White[19], and Darken and Gurry[20] but by a different method. Ferric oxide was melted in an evacuated system and the oxygen pressure which resulted from its decomposition was measured at 1550°C, 1575°C, and 1600°C. As well as pure ferric oxide, ferric oxide + lime (2:1 and 1:1), and ferric oxide + silica (1:1) were also used. While their results for pure ferric oxide agree better with those of Darken and Gurry than do those of White, their results for ferric oxide + lime differ considerably from those of Darken and Gurry.

In order to extend the work of Gurry and Darken, Larson and Chipman[38] investigated by gas-slag equilibrium the ferrous and ferric oxide concentrations of various slags at 1550°C. The range of oxygen pressures used was from 10^{-1} to 10^{-9} atmospheres, and the ferrous and ferric oxide concentrations were expressed as a j-ratio where $j = \frac{Fe^{+++}}{Fe^{++} + Fe^{+++}}$. Additions of basic oxides, BaO, CaO, MgO, and MnO, were found to increase the j-ratio, while additions of acidic oxides, SiO_2 and TiO_2, had the opposite effect at a constant partial pressure of oxygen. Al_2O_3 had little effect on the j-ratio and seemed to act as an amphoteric oxide. Iron oxide was melted in magnesia crucibles, and in the course of a three to four hour experiment would become saturated with magnesia. The iron oxide penetrated the crucible wall to a depth of approximately $\frac{1}{32}$ of an inch. Several distinct layers could be noticed on cooling, a) the portion of the crucible penetrated by the iron oxide, b) a layer of magnesia-wustite solid solution, and c) the portion of the slag which was liquid at temperature. Difficulty was found in separating c) from b) which was necessary to obtain a correct j-ratio as c) is representative of the material which was liquid at the temperature. As barium oxide, lime and magnesia are ferrite formers these basic oxides raised the j-ratio, barium oxide the most, magnesia the least. From Gurry and Darken's work manganese oxide was expected to have a slightly less effect on raising the j-ratio than lime but Larson and Chipman found that manganese oxide had a much smaller effect than lime, roughly of the order of magnesia. Of the acidic oxides, silica lowered the j-ratio most, the effect of titania being slightly less. From the data for magnesia and silica it can be calculated graphically that at 1550°C these oxides are equivalent on a mol basis (i.e. 1 mol per cent SiO_2 plus 1 mol per cent MgO has no effect on the j-ratio). The results of Larson and Chipman differ considerably from White in the effect of lime and silica and also from Krings and Schackmann in the effect of lime, but there is excellent agreement with Darken and Gurry for pure iron oxide melts without additions. The relationship between the $\frac{N_2}{N_1}$ of Darken and Gurry and the $j = \frac{Fe^{+++}}{Fe^{++} + Fe^{+++}}$ of Larson and Chipman is given by $j = 2(\frac{N_2}{N_1} - 1)$.

St. Pierre and Chipman[34] used the data of Larson and Chipman to determine the partial pressure of O_2 in SO_2, and $SO_2 - CO$ gas mixtures in equilibrium with lime, iron oxide slags at 1550°C. The sulphur content of the slag was found to have no effect on the relation between the j-ratio and calcium content for a given pO_2, as might be expected due to the substitution of sulphur atoms for oxygen atoms. At 1550°C. the products of dissociation of SO_2 are principally SO and O_2 and the data lead to the choice of -19·4 kcal for the free energy of formation of SO from S_2 and O_2 at 298·16°K.

The same authors, in a later investigation[35], equilibrated

FeO slags containing additions of CaO, SiO_2, and MgO with atmospheres of SO_2 containing additions of CO and O_2. It was found that starting with an FeO - 12 atomic per cent Ca slag, containing no ferric iron, the sulphur content rose far above equilibrium then decreased. This was to be expected as the initial oxygen potential of this slag was low. Once the j-ratio of the slag had neared equilibrium with the sulphur dioxide atmosphere, the sulphur content decreased, probably in accordance with the increase in the j-ratio. St. Pierre and Chipman found that the substitution of lime for iron oxide produces a slight lowering of the sulphide sulphur content, while raising the sulphate content slightly. The activity coefficient of the sulphide ion seems to be independent of calcium content in lime-iron oxide slags. For conditions of constant oxygen pressure in the gas phase lime and iron oxide were approximately equal in desulphurizing power in these slags, whereas in slag metal relationships the substitution of iron oxide by lime raises the distribution coefficient due to the decreased oxygen pressure in the metal. Silica additions lowered the slag sulphur content, while a plot of log C_S against molar percentage silica gave a similar curve to Richardson and Fincham[22]. Addition of magnesia to iron oxide slags greatly lowered the sulphide sulphur, and it was shown that magnesia has about one half the effect of lime on the j-ratio, which is in agreement with Larson and Chipman[23].

Magnesia was said to contribute to the oxide ion concentration but not to the desulphurizing power of the slag.

Dewing and Richardson[35] obtained a value of $\Delta H^\circ_0 = -15{\cdot}4$kcal for the formation of SO from S_2 and O_2, using the equilibrium between molten calcium silicate and SO_2, O_2 gas mixtures. This disagreed with the value of -19·4 kcal given by St. Pierre and Chipman[34], the discrepancy being attributed to the greater complexity of gas mixtures made from SO_2 and CO than from SO_2 and O_2.

Rosenquist and Hynne[36] examined the reaction between sulphur dioxide, sulphur gas mixtures and iron sulphide, magnetite slags in the solid state at 700° to 1000°C theoretically and experimentally. It was found that the equilibrium sulphur content was very low at these temperatures.

The reactions between iron sulphide and iron oxide in the slag phase were studied up to 1300°C by Wohler, Martin and Schmidt[37], and Diepschlag and Horn[38], who found that ferric oxide reacted with ferrous sulphide in a nitrogen atmosphere to give ferrosic oxide and sulphur dioxide. This reaction commenced at 550°C and was complete at 800°C. The ferrosic oxide produced reacted slowly with any excess iron sulphide on heating between 900° and 1100°C to form ferrous oxide; the rate of reaction slowed down appreciably at higher temperatures.

Slag-Metal Investigations

Of the investigations pertaining to sulphur reactions in iron and steel making by far the greatest number have been carried out on slag-metal relationships.

Holbrook and Joseph[40] were among the first to investigate in the laboratory the distribution of sulphur between slag and metal. Interpretation of their results was difficult as this was neither an equilibrium nor a kinetic study of the reaction.

Bardenheuer and Geller[41] studied the distribution of sulphur between molten iron and molten iron oxide slags with additions of lime, alumina, silica, and manganese oxide. The melts were carried out in magnesia and alumina crucibles using a high frequency furnace. The atmosphere above the melt was not stated and it is presumed to be air. Sulphur was added to the molten slag as iron sulphide or calcium sulphide and after five to ten minutes when equilibrium was thought to have been attained, the slag and metal were cast into a copper chill mould "whereby a sufficient separation of metal and slag took place." Temperatures were measured by means of an optical pyrometer sighted on the slag layer. The effect of temperature on the distribution of sulphur between metal and pure iron oxide slags was given as

$$\log L_{FeS} = \frac{2390}{T} - 0{\cdot}714 \quad \text{where } L_{FeS} = \frac{(\%S)}{[\%S]}$$

This early work is open to many criticisms. temperatures as measured by the optical pyrometer in the thirties have in many cases been found to be too low[42], air being an oxidising atmosphere have an effect on the surface layers of the slag and hence on the distribution ratio, equilibrium may not have been attained, despite high frequency stirring of the metal, in the comparatively short time of ten minutes, the slag exposed to air and heated only by conduction from the metal may have been much colder than the metal, and finally separation of slag and metal may not have been perfect in the copper mould. While iron was removed by magnetic means from the slag, some slag may have been trapped in the metal and this could lead to lower distribution ratios.

In the light of these remarks it is surprising that this has been the only major investigation on the sulphur distribution between iron and slags high in iron oxide, and is the standard reference for work on these type of slags.

Bardenheuer and Geller came to the conclusion that lime was a better desulphurizer than iron oxide, as their sulphur distribution coefficient, L_{FeS} increased when lime was substituted for iron oxide. Additions of silica and magnesia together tended to lower the coefficient, but as both were always present in the slags no conclusions were drawn as to their separate functions.

According to Wentrup[45], who represented the distribution coefficient as

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

where $(S)_{Ca}$, $(S)_{Fe}$, and $(S)_{Mn}$ is the sulphur in the slag associated

Ca, Fe and Mn as sulphides, lime was effective in controlling the desulphurization only if the silica and iron oxide contents of the slag were kept low.

The importance of slag basicity and lime additions to achieve desulphurisation has long been realised, but the concept of slag basicity in terms of slag composition has been varied. The simplest concept of slag basicity is the V-ratio, $\frac{CaO}{SiO_2}$, of Maurer and Bischof[3], which is not very useful when using complex slags of the open hearth type. Hatch and Chipman[44] in their study of sulphur equilibrium between carbon saturated iron and blast furnace slags plotted their experimental distribution coefficients against various measures of slag basicity. The best correlation was found with a slag basicity of $\frac{CaO + \frac{2}{3} MgO}{SiO_2 + Al_2O_3}$. The $\frac{2}{3}$ factor shows that magnesia is not such an efficient desulphurising agent as lime. A more quantitative relationship might be evolved if the desulphurisation ratio was expressed as some function of excess base as in the manner of Grant and Chipman[47] who studied the distribution of sulphur between liquid iron and basic open-hearth slags. The best correlation was achieved by considering excess base to be $(CaO + \frac{2}{3}MgO) - (SiO_2 + Al_2O_3)$. The sulphur concentration of the metal was shown not to be directly proportional to the sulphur content of the slag, as increasing sulphur in the slag at constant excess base raised the distribution coefficient. A drop in temperature increased the equilibrium sulphur content of the metal.

The distribution coefficients obtained were considerably higher than those found in blast furnace practice, which means that in the blast furnace complete equilibrium between metal and slag, at least with respect to sulphur, is not attained. This was confirmed by Filer and Darken[45], who brought samples of blast furnace metal and slag to equilibrium in carbon crucibles.

Grant and Chipman[47] in a radically different approach to desulphurization from that normally accepted, showed the ability of oxides other than lime to take part in desulphurization. These workers made use of the data of Fetters and Chipman[24] on $CaO-MgO-FeO-SiO_2$ slags, the data of Winkler and Chipman[25], and their own experimental work which covered a greater slag range than the former wokkers and included the effect of MnO, P_2O_5, Al_2O_3 and CaF_2 on desulphurization. Grant and Chipman rejected the usual mechanism of desulphurization by the reaction

$$(CaO) + \underline{FeS} = (CaS) + (FeO)$$

and postulated instead a direct partition of iron sulphide between slag and metal, the partition coefficient being influenced by the excess base of the slag. The direct partition of iron sulphide between slag and metal has also been shown to occur in blast furnace slags by the work of Derge, Philbrook and Goldman[46] who found beads of iron in lime-alumina-silica slags in equilibrium with carbon saturated iron. These beads were shown to have come not by mechanical means into the slag but from reduction of the ferrous sulphide in the slag to iron.

The excess base of Grant and Chipman[47] was calculated assuming that CaO, MnO, and MgO were equivalent bases which neutralised the acid constituents of the slag forming the compounds $2MO.SiO_2$, $4MO.P_2O_5$, $2MO.Al_2O_3$ and $MO.Fe_2O_3$ where MO = basic oxide (CaO, MgO, or MnO]. FeO and CaF_2 were both considered neutral compounds. From the experimental data CaO, MgO, and MnO were found to be equivalent bases in desulphurizing power, while large variations in FeO, MnO, Al_2O_3 and temperature caused no appreciable changes in the distribution coefficient at a constant excess base.

Reasonable agreement was found between the experimental results and the steelworks data of Diehl[17], Darken and Larsen[48], and Tenenbaum and Brown[49], slight discrepancies being explained by Grant and Chipman as due to errors in sampling and analysis, failure to reach equilibrium in the open hearth, or the presence of carbon. Slags, however, as in the Perrin[50] process which have a V-ratio of 1, and are poorly oxidising give rise to much higher distribution ratios, about 50, than found by Grant and Chipman. Mowat[51] has also found high distribution ratios during the reducing period in electric steelmaking, and has concluded that for concentrations below 3 per cent, FeO plays an important role in desulphurization.

Carter[52] has shown that the experimental data of Grant and Chipman can be explained by the relationship

$$\frac{(S)}{[S]} = K\cdot\frac{(\Sigma nMO)}{[O]}$$

where ΣnMO is a measure of the excess base. Unlike Grant and Chipman, Carter assumed FeO was a base of equal desulphurizing power to CaO, MgO, and MnO, and also the compounds $3MO.P_2O_5$, and $3MO.Al_2O_3$ were formed instead of $4MO.P_2O_5$ and $2MO.Al_2O_3$. The scatter of points using this relationship was no worse than that obtained by Grant and Chipman.

The relationship of Carter corresponds to sulphur removal by the reaction

$$\underline{\underline{S}} + (O) = (S) + \underline{\underline{O}}$$

Harders, Grewe and Oelsen[33] suggested that a relationship existed between basicity and the ratio $\frac{(S).(Mn)}{[S].[Mn]}$, the basicity being expressed as the V-ratio. The ratio $\frac{(Mn)}{[Mn]}$ is a measure of the state of oxidation of the metal, thus there is a similarity between this expression and that of Carter.

The role of magnesia in desulphurization is somewhat obscure. The standard free energy changes for desulphurisation by the basic oxides are given by[8]

$$(CaO) + [S] = (CaS) + [O] \qquad \Delta G^{\circ}_{1600\,^{\circ}C} = 12,700 \text{ cals}$$

$$(FeO) + [S] = (FeS) + [O] \qquad \Delta G^{\circ}_{1600\,^{\circ}C} = 14,800 \text{ cals}$$

$$(MnO) + [S] = (MnS) + [O] \qquad \Delta G^{\circ}_{1600\,^{\circ}C} = 17,600 \text{ cals}$$

$$(MgO) + [S] = (MgS) + [O] \qquad \Delta G^{\circ}_{1600\,^{\circ}C} = 33,400 \text{ cals}$$

The desulphurizing ability of MnO is slightly less than that of CaO, while MgO is considerably less. Maurer and Bischof[8] found that additions of MgO up to 10 per cent did not affect the desulphurizing ratio, but Rocca, Grant and Chipman[54] estimated that CaO is about 1000 times a better desulphuriser than MgO. Harders, Grewe and Oelsen[55] found that $MgO.SiO_2$ slags, and pure MgO at sintering temperatures (1700°C) could not desulphurize molten iron containing sulphur, whereas basic $CaO.SiO_2$ and lime had an appreciable desulphurizing power. The experimental work to determine the extent to which magnesia can desulphurize in liquid slags is difficult as a basic crucible material other than magnesia is required in order to make magnesia an independent variable. In a magnesia crucible the magnesia content of the resultant slag is dependent on the acidic oxides in the slag, and low distribution ratios which might be attributed to the magnesia content are really caused by low slag basicity. Hatch and Chipman[44] gave an indication of the ability of MgO to aid desulphurization by neutralising excess acid oxides. MgO was regarded as equivalent to $\frac{2}{3}$ CaO on a mol basis when considering the equilibrium between metal and blast furnace slags.

In the studies of Rocca, Grant, and Chipman[54], when the distribution ratio was plotted against mol per cent FeO at constant slag basicity, a minimum distribution was found at 7·0 mol per cent FeO. The distribution ratio at 1600°C rose rapidly from this minimum as the FeO content fell below 1·2 per cent and as the FeO content increased to 3·6 (the value obtained by Bardenhëuer and Geller[61] for pure FeO slags at 1600°C). With increasing slag basicity, the minimum became less pronounced until at slag basicities corresponding to open hearth slags, the minimum disappeared. These workers regarded desulphurization as taking place by two reactions.

$$[FeS] = (FeS)$$

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

In highly reduced slags the first reaction was considered to control desulphurisation, but in high FeO slags, i.e. basic open hearth slags the second reaction was considered to be the controlling one. The apparent neutral behaviour of FeO in basic open-hearth slags has been explained by Richardson[88] as being due to the fact that addition of FeO to a basic slag of a fixed lime/silica ratio has two effects. It causes an increase in the number of oxygen atoms replaceable by sulphur in the slag, and also, due to the increased FeO activity in the slag, raises the oxygen content of the metal. At low FeO concentrations small additions of FeO have little effect on the number of replaceable oxygen atoms in the slag but increase considerably the oxygen content of the metal. At higher FeO contents (3-70 per cent) the two effects offset each other, and the net effect is small. Shanahan[86], who plotted the distribution ratio against mol per cent FeO in the slag at constant slag basicity, obtained a curve in the shape of a rectangular hyperbola which showed clearly that the distribution ratio remains substantially constant over a wide range of (FeO) concentrations but rises steeply when the (FeO) concentration falls below a certain value.

Of recent years the tendency to describe iron and steel making slags in terms of ionic concepts has come more to the fore. The ability of molten slags to conduct electricity has been demonstrated by many workers[57-60], showing that the normal concept of slags as a liquid solution of electro-neutral oxides and compounds should be replaced by the concept of an ionic solution. Several workers[61-66] have explained fairly successfully the reactions of sulphur, silicon, oxygen, phosphorous and manganese in basic steelmaking in the light of this ionic concept.

Both the theory of ionized compounds and the theory of non-ionized oxides and compounds can explain quite well the more important slag-metal relationships in iron and steel-making. The ionic theory, while no doubt being the more correct, is not so easily applied in actual practice as the more incorrect compound theory which involves much less calculation. Kheinman[66] has suggested that a compromise between the two theories might be effected by the use of partially ionized compounds. A purely thermodynamical approach is to be preferred to either theory as this makes no attempt to discover the nature of molten slags, but only gives the activity of a particular constituent of the slag.

The distribution of oxygen between carbon-free iron and simple acid slags of the FeO/SiO_2 type at 1600°C has been found by Korber and Oelsen[69,70] and Taylor and Chipman[67]. In order to obtain the distribution between carbon-free iron and basic slags the concept of ferrous oxide activity must be introduced. Both Korber and Oelsen[69] and Taylor and Chipman[67] have shown that in acid slags the mol fraction of FeO in the slag is approximately equal to its activity. The activity of FeO is found from the value of the oxygen content of the metal in equilibrium with the slag divided by the saturation value for oxygen at that temperature. Conversely if the mol fraction of FeO in the slag is known the oxygen content of the metal in equilibrium with that particular slag can be found. Values of the activity of ferrous oxide in the pseudo-ternary system (CaO + MgO) - SiO_2 - FeO are given by Fetters and Chipman[24] and Taylor and Chipman[67].

The solubility of oxygen in liquid iron is given by Chipman, Fetters, and Taylor[71,67] as

$$\log [\%O] = -\frac{6320}{T} + 2\cdot734$$

Floridis and Chipman[72] have investigated the activity of oxygen in liquid iron in the presence of various solutes. It was found that increase in oxygen decreases the activity of oxygen. However, the effect of sulphur on this oxygen activity was not obtained.

The effect of sulphur on the solubility of oxygen in liquid iron under pure iron oxide slags has been reported by Hilty and Crafts[73]. A minimum in the oxygen content was noted at 0·1 weight per cent sulphur. No minimum, however, was found in the work of Bishop, Grant and Chipman[74] on lime saturated-iron oxide slags. Hilty and Crafts found that sulphur up to one per cent had little effect on the oxygen solubility but with more than one per cent sulphur the oxygen solubility rose fairly steeply.

Fetters and Chipman[24] found that in ferrous oxide slags in equilibrium with molten iron appreciable quantities of ferric oxide existed, and that the normal assumption that all of the ferric oxide is reduced by contact with molten iron is wrong. The amount of ferric oxide increased with increase in MgO and CaO content, but decreased with increase in SiO_2 content as previously noted by McCance[75]. The effect of temperature was not accurately established, but increase in temperature seemed to lower the ferric oxide content. Bowen, Schairer, and Posnjak[76,77] at somewhat lower temperatures had also reported on appreciable quantities of ferric oxide found during their examination of the CaO - FeO - SiO_2 slag system. Fetters and Chipman[34] also gave the solubility of MgO in a pure FeO slag as

$$\log (\%MgO) = -\frac{6,600}{T} + 4\cdot 02$$

The solubility of magnesia increased with increasing silica content of the slag as expected, while increase in lime had little effect on the solubility in pure FeO slags.

Influence of dissolved elements on the solubilities of graphite in molten iron.

The solubility of graphite in pure iron has been well established by various workers[78-80]. Turkdogan and Leake[80] expressed the effect of temperature on the solubility as

$$\log N_c^c = -\frac{560}{T} - 0\cdot 375$$

where N_c^c is the atom fraction of dissolved carbon in the iron-carbon alloy.

Chipman et al[78] have investigated the effect of silicon on the solubility of carbon and their results as reported in the form of Turkdogan and Leake[80] are given by

$$N^c = N_c^c - 0\cdot 71\ N_{si} \quad \text{(for the range } 0\cdot 00-0\cdot 08\ N_{si}\text{)}$$

where N_c = the atom fraction of dissolved carbon in the iron-carbon-silicon ternary alloy.

N_c^c = as above

N_{si} = the atom fraction of dissolved silicon in the iron-carbon silicon ternary alloy.

The solubility of graphite in iron-carbon-silicon ternary alloys as reported earlier by Schichtel and Piwowarsky[81] gave values of graphite solubility 0·3 per cent lower than those of Chipman for the same silicon content.

The solubility of graphite in iron-carbon-sulphur alloys has been investigated by Turkdogan and Hancock[83] using their own results and those of Morris and Buehl[8] and is given by

$$N_c = N_c^c - N_s \text{ (for the range } 0{\cdot}00 - 0{\cdot}01\ N_s)$$

where N_c^c = as above

N_c = the atom fraction of dissolved carbon in the iron-carbon-sulphur ternary alloy.

N_s = the atom fraction of dissolved sulphur in the iron-carbon-sulphur ternary alloy.

From this equation it can be seen that at a given temperature for every atom of sulphur dissolved in carbon saturated iron, an atom of carbon is displaced from the solution. The results of Kitchener et al[79] are consistently 0·5 per cent lower than those obtained by Turkdogan and Hancock. Super-saturation of iron-carbon-sulphur melts is well known due to the stable nature of cementite in the presence of dissolved sulphur, but the consistency of Turkdogan's results seem to be against supersaturation as a possible source of error in his work.

The miscibility gap in the iron-carbon-sulphur system has been determined several times[63,64], and more recently by Norrö and Lundquist[65]. Turkdogan and Hancock[62] determined the boundaries of the miscibility gap at 1200°, 1350°, and 1500°C using carbon saturated iron. In this investigation the sulphur concentrations in the lower carbon rich layer were much less than those of Norrö and Lundquist, and it was suggested that the latter's sampling technique was at fault, thereby contaminating the bottom layer with sulphur rich material from the top layer.

CHAPTER III

EXPERIMENTAL

EXPERIMENTAL

Preparation of Crucibles

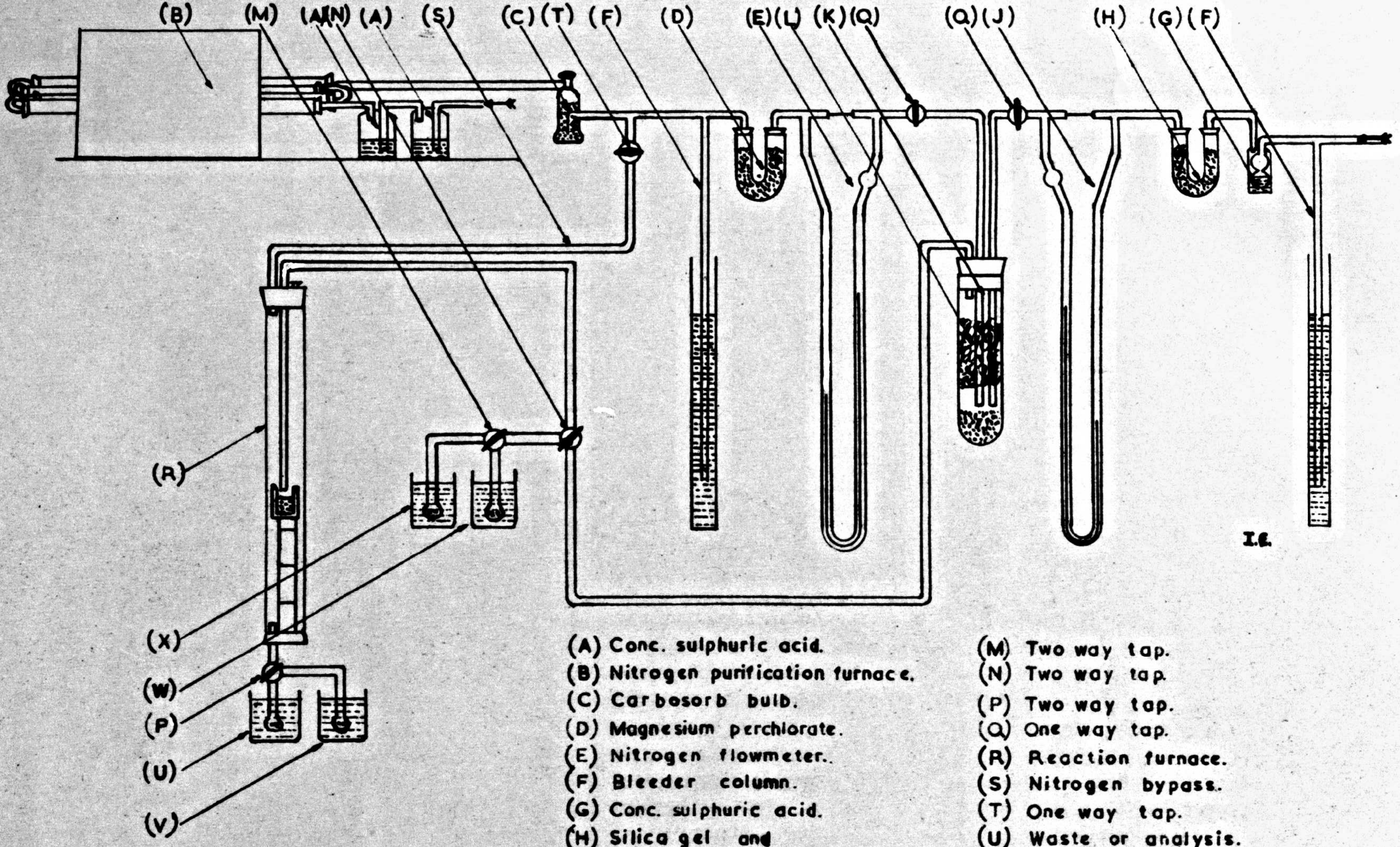
Magnesia and alundum crucibles were produced by casting a suspension of the finely ground refractory oxide into a plaster of Paris mould, the crucible being formed by adsorption of the suspending liquid by the plaster to leave a layer of refractory on the plaster surface[36]. The raw material used was fused magnesia granules and alundum powder.

To obtain a good non-porous crucible, alundum and magnesia should be fired above 1600° and 1800°C respectively. As this could not be carried out successfully in the department, the crucibles were fired to the appropriate temperature in an oil-fired furnace by courtesy of J.G. Stein and Co., Ltd., Bonnybridge. The crucibles after firing had a dense translucent appearance and were found, on the whole, resistant to the corrosive slags used in this investigation.

Reaction Gas Preparation

Nitrogen and sulphur dioxide were the only gases used throughout the experiments. As supplied cylinder nitrogen normally contains 0·2 to 0·4 per cent oxygen, which must be removed before the gas is passed into the reaction furnace.

The nitrogen purification furnace (B) Fig. 1, consisted of a 3.1/4" diameter alundum tube wound with Kanthal wire, controlled at 700°C by a "Sunvic" energy controller. In this furnace were placed four mullite tubes (1.1/4" diameter) containing respectively copper gauze(2),



(A)	Conc. sulphuric acid.
(B)	Nitrogen purification furnace.
(C)	Carbosorb bulb.
(D)	Magnesium perchlorate.
(E)	Nitrogen flowmeter.
(F)	Bleeder column.
(G)	Conc. sulphuric acid.
(H)	Silica gel and magnesium perchlorate.
(J)	Sulphur dioxide flowmeter.
(K)	Mixer tube.
(L)	Glass wool.
(M)	Two way tap.
(N)	Two way tap.
(P)	Two way tap.
(Q)	One way tap.
(R)	Reaction furnace.
(S)	Nitrogen bypass.
(T)	One way tap.
(U)	Waste or analysis.
(V)	Analysis.
(W)	Waste.
(X)	Analysis.

Fig. I.

iron wool, and small pieces of ferrosilicon. In the cooler (450°C) exit end of the fourth tube were packed some magnesium drillings. The nitrogen from the cylinder, after being dried in two concentrated sulphuric acid bubblers (A), passed through the four tubes, copper gauze first, magnesium last, Any carbon dioxide which might have been formed from the steel wool or ferro-silicon was removed by the "Carbosorb" bulbs (C). The nitrogen was then dried by magnesium perchlorate in a U-tube (D) before passing into the flowmeter (E). It was thought that at high rates of flow(i.e. 500 ml/min) the oxygen in the nitrogen might not be all removed and this was tested by passing the purified nitrogen at 500 ml/min over polished copper strip at 1000°C for 6 hours. No oxidation of the strip was noticeable at the end of this time. The copper gauze was renewed every 150 hours.

Sulphur dioxide was used from a siphon. Before it entered the sulphur dioxide flowmeter (J) it was passed through a sulphuric acid bubbler (G) and then through a U-tube (H) filled with silica gel and magnesium perchlorate to completely dry the gas. Difficulty was encountered with the sulphur dioxide as, after passing through the sulphuric acid bubbler, it carried with it a fine mist of sulphuric acid which was not removed when magnesium perchlorate alone was used in the U-tube. This mist eventually led to the blockage of the fine sulphur dioxide venturi during several runs. This blockage was not easily noticed as the gauge contined to register the correct positive pressure, although no sulphur dioxide was passing through the flowmeter. Choking of the venturi by this mist was detected when the known bubble rate through the sulphuric acid bubbler (G) dropped or ceased, thus the cause of the blockage was also the means of knowing when the blockage was taking place, a somewhat novel situation. As it was necessary to have a bubble check on the sulphur dioxide other liquids with low vapour pressures and containing no water were tried, e.g. butyl phthalate. This was to no avail, as reaction took place between the sulphur dioxide and all the liquids tried, the various reaction products coating the bubbler glass and making it opaque. As it was noticed that the mist always "condensed" on the low pressure side of the venturi, it was thought that a large empty bulb inserted after the sulphuric acid bubbler might help to precipitate this mist. The bulb was cooled in iced water to further the precipitation but without improvement as the venturi continued to block. Finally the inlet limb of the perchlorate U-tube (H) was packed with silica gel, which was exceedingly effective in removing this troublesome mist, although it took several hours to saturate the gel with sulphuric dioxide.

Another difficulty in using sulphur dioxide is that the silicone grease on the stopcocks was slowly attacked, giving rise to a black substance which sometimes choked the stopcocks. Contamination of the gas mixture by this substance was prevented by cleaning the tubes and regreasing the stopcocks after every run. As this occurred before the gas was metered and analysed it is highly unlikely that it will affect the final gas analysis.

Sulphur dioxide attacks and embrittles rubber very severely and all tubing along which sulphur dioxide flowed, either the pure gas or the nitrogen/sulphur dioxide mixture, was made of glass or polythene. Rubber had to be used at the venturi/flowmeter glass to glass connections for ease of dismantling and cleaning the venturi since polythene must be heated and melted on to the glass tubing to make a gas-tight seal.

Flow rates were measured by means of five foot high venturi meters (E,J). A 2" length of glass capillary tube drawn out in the centre was used as a fixed orifice, and the flowmeters were filled with "Griffin and Tatlock" flowmeter oil of low vapour pressure. Flow rates were adjusted by raising or lowering the bleeder columns(F), extremely fine adjustment being capable by this means.

From the flowmeters the two gases entered the mixer tube (K), which consisted of an upright closed tube, 8" x 1.1/4"diameter, with a layer of magnesium perchlorate at the foot. The two gases were led to the bottom of the mixer where they impinged on this perchlorate and mixed on their way up the tube while passing through at 6" packing of glass wool (L). From the mixer the gases could be led through polythene tubing to the furnace, to analysis (X), or to waste (W) by correct manipulation of the two-way stopcocks (M,N). After passing through the reaction furnace the gas could be passed to analysis (V) or to waste (U) by the two-way stopcock (P). Each gas side of the apparatus could be isolated by one-way stopcocks (Q,Q). The nitrogen/sulphur dioxide waste gas was passed into a strong solution of hydrogen peroxide and sodium hydroxide, which oxidised and neutralised the sulphur dioxide in the gas. Methyl red was added to this solution as an indicator. Both the sulphur dioxide bleeder folumn (F) and the waste beaker (U) were filled with a similar solution to prevent the passage of sulphur dioxide into the atmosphere.

A bypass for nitrogen (S) was also used, whereby the reaction furnace could be flushed with purified nitrogen during heating up, at the same time as the nitrogne/sulphur dioxide gas mixture was stabilising. The rate of flow of purified nitrogen through the furnace could be controlled by a stopcock (T).

Standardisation of Flowmeters

An accurate standardisation of the flow meters was necessary in order to find the exact partial pressure of sulphur dioxide in the nitrogen/sulphur dioxide gas mixture.

Nitrogen Flowmeter

As nitrogen is an inert gas, a physical means of calibration had to be found. Previous workers[57,58] had standardised their nitrogen flowmeters by displacing with a known volume of water an equal volume of air, which, after drying, passed through the flowmeter. The time for this to happen and the gauge reading were taken. After conversion of the gas volume to N.T.P. and using the formula

$$F_{N_2} = \frac{\sqrt{\rho_A}}{\sqrt{\rho_{N_2}}} \cdot F_A$$

where F_{N_2} = flow of dry nitrogen in ml/min at N.T.P.

F_A = flow of dry air in ml/min at N.T.P.

ρ_{N_2} = density of nitrogen at 0°C

ρ_A = density of air at 0°C

a graph of flow of nitrogen at N.T.P. against flowmeter gauge reading could be drawn. The errors involved in this method must have been considerable, especially at high rates of flow as the water under a pressure head of several feet must first compress the gas until the oil in the gauge has climbed to its correct position and drained down the glass tube for that particular rate of flow. Water flows into the calibrated vessel to do this and thus "compression water" was measured along with the remainder to give the flow rates, which must have been low.

Standardisation I

It was decided that a water meter offered the best accuracy and consequently a standard 2·5 litre gas measure was obtained and the meter standardised against this. The meter was found to be quite accurate, all volumes on the meter to be multiplied by 0·9976. The meter was connected to the exit end of the nitrogen flowmeter and dried compressed air was passed through the system. When conditions had stabilised after ten minutes with respect to gas flow, readings of the flowmeter gauge, water meter, temperature of the water meter, and ambient temperature were taken and the stop watch started. After twenty minutes all the readings were taken again, the flowmeter gauge having remained quite steady. From this the flow of saturated air in ml/minute could be calculated, hence the flow of dry air in ml/minute. It was assumed that complete saturation of the gas by water vapour had taken place, and the wet gas was accordingly corrected to dry gas at 23°C and 760 mm mercury using the tension of aqueous vapour (89). From the formula the nitrogen flow was found at 23°C and 760 mm mercury, and a graph of dry nitrogen flow rate versus flowmeter gauge reading was drawn. This arbitrary figure of 23°C was chosen for convenience since the apparatus was set up where the ambient temperature was 23°C ± 2°C.

Standarisation 2

In order to test the veracity of the formula impurified cylinder nitrogen was used instead of air and different results were obtained, assuming that the tension of aqueous vapour in nitrogen is the same as in air. At first this difference was thought to be due to the oxygen (0·4 per cent) in the cylinder nitrogen, but on removing this oxygen with pyrogallol very little improvement was noticed. The difference between the two results was consistent at 4-5 per cent.

Standardisation 3

A new, unused rotameter (guaranteed accuracy ± 2%) was obtained, which was graduated in ml/min of oxygen at 15°C and 760 mm mercury. The readings on the rotameter were converted to nitrogen at 23°C and 760 mm mercury by the following equation, which was derived from the data of Schoenborn and Colburn[90]

$$\frac{V_{O_2}}{V_{N_2}} = \frac{\mu_{O_2} \cdot \rho^{\frac{3}{2}}_{n_2}}{\mu_{n_2} \cdot \rho^{3/2}_{O_2}}$$

where V_{O_2} and V_{N_2} are flow rates/min of oxygen and nitrogen respectively, μ_{O_2} and μ_{n_2} are the viscosities of oxygen and nitrogen respectively, and ρ_{O_2} and ρ_{N_2} are the densities of oxygen and nitrogen respectively. This gave the volume rate of flow of nitrogen at 15°C which was then converted to volume rate of flow of nitrogen at 23°C and 760mm. mercury. The rotameter readings when plotted gave an unexpected result, in that they seemed to confirm the figures obtained by the compressed air standardisation.

The only obvious difference in the conditions between standardisation 2 and 3 was that 2 was conducted at a room temperature of 17°C while 3 was conducted at a temperature of 24·5°C. This was sought as an explanation since a rise in temperature expands the capillary venturi both in length and area, and also increases the viscosity of the gas. Calculation showed that the capillary expansion factor was negligible but that the viscosity factor increased the flow from 300 ml/min. at 24·5°C to 307 ml/min at 17°C for the same pressure head. To test this the venturi was cooled at 17°C and results with the rotameter showed the increase to be almost exactly as calculated. A possible exception to this idea may be the improbability of cooling the gas from 24°C to 17°C while it is moving at such rapid speeds through the short venturi, yet experimental results show the difference in flows. Using the rotameter, as the flow rate for the same pressure head had decreased, the venturi was cleaned in case it had been partially blocked but the same results were obtained. Data on the densities and viscosities of the gases were obtained from the Smithsonian Physical Tables[38].

Standardisation 4A

Due to the discrepancies between the results a simple system was set up to give a few check results, which might help in determining a choice between the previous standardisations. This involved the displacement of one litre of water from an upturned standard flask, a constant head device keeping the gas pressure inside the flask at atmospheric pressure. The gas outlet jet was situated in the water outside the neck of the flask at the same depth as it would occupy in the standardising position. This was done in order to keep conditions in the flowmeter gauge constant. The litre flask was filled with water, whose temperature was taken, the jet swivelled underneath the neck of the flask, and the time taken to displace one litre of water noted. This was done for various flow rates and the rate of flow of dry nitrogen at 23°C and 760 mm mercury plotted. The water temeprature for these tests was kept constant at 17°C. The gas was presumed to be saturated with water and the results obtained were in quite good agreement with the rotameter standardisation, especially at high rates of flow. At low rates of flow a tendency to drift to even lower rates of flow for a constant pressure head was noticeable. The ambient temperature was 24°C while that of the water was 17°C. A justifiable assumption was made during the calculations of dry gas flow that the litre flask and hence the gas temperature was 17°C as the displacement time was quite short (three minutes). At low rates of flow, however, displacement time was greater than ten minutes and the flask and gas inside it were no doubt heating up to room temperature. This may have caused the effect though it is not clear how as the expected change would be opposite to that obtained.

Standardisation 4B

To counteract this temperature effect the water was heated to 24°C so that all the apparatus was at room temperature. Seven determinations were made and the results were surprising. The points obtained were entirely different, the only explanation being that the gas was not saturated with water vapour at 24°C and an overcorrection had been made for this water vapour. The venturi was cleaned but the same results were obtained. Why the gas should be apparently saturated at 17°C and not at 24°C is inexplicable.

Later another new rotameter verified the results obtained by the original rotameter. With such diverse results it was difficult to feel confident at any particular choice of standardisation, but a combination of standardisation 3 and 4A seemed the best choice especially as a rotameter check could easily be made at any time in case of accidents to the venturi. The different results are plotted in Fig. 2, while the final choice is shown in Fig. 3, with the room temperature variations.

Standardisation of sulphur dioxide flowmeter

In contrast to the nitrogen flowmeter the standardisation of this flowmeter was quite simple. Unlike the physical standardisation of the nitrogen flowmeter a chemical standardisation was done.

Fig. 2. NITROGEN FLOWMETER STANDARDISATION.

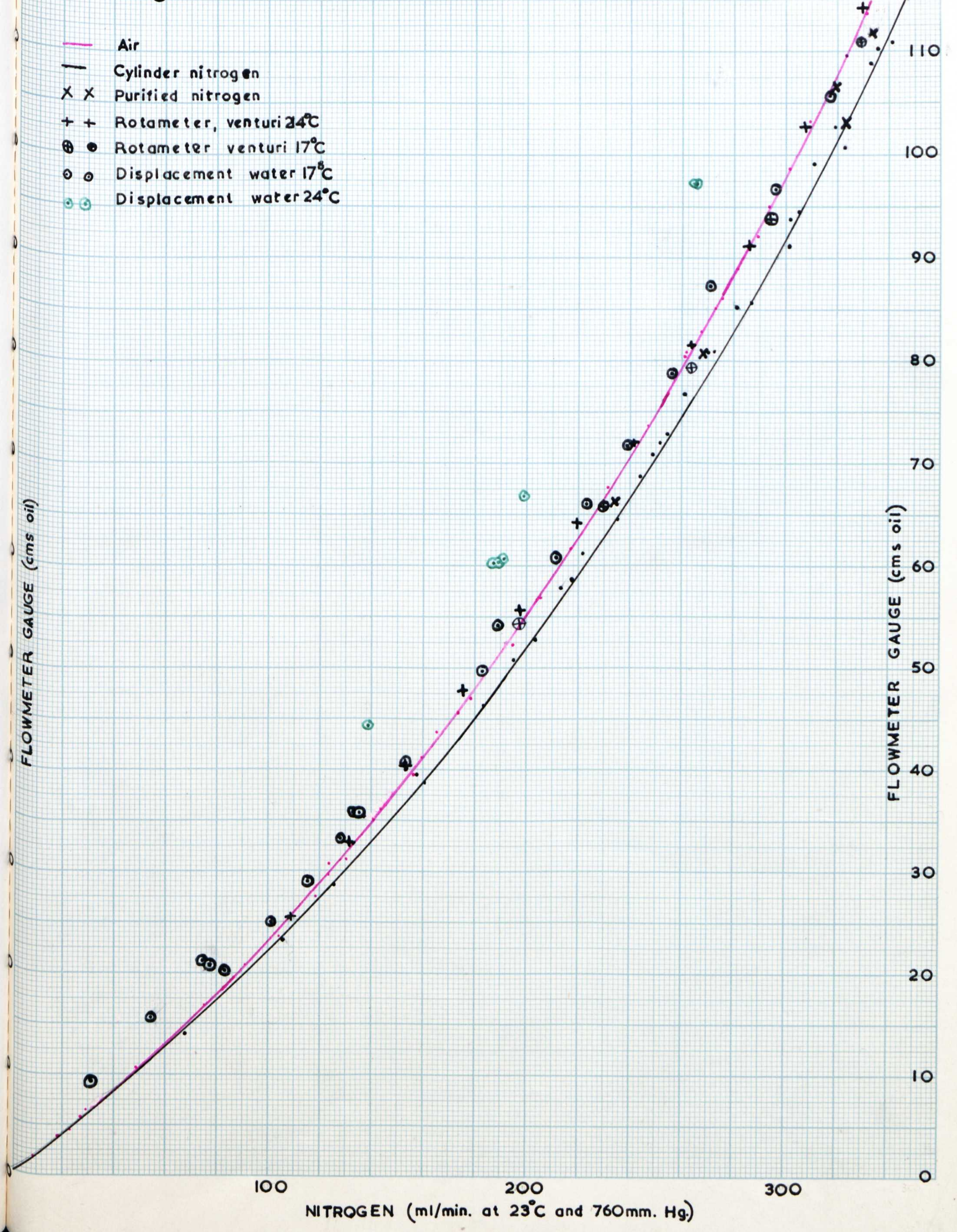
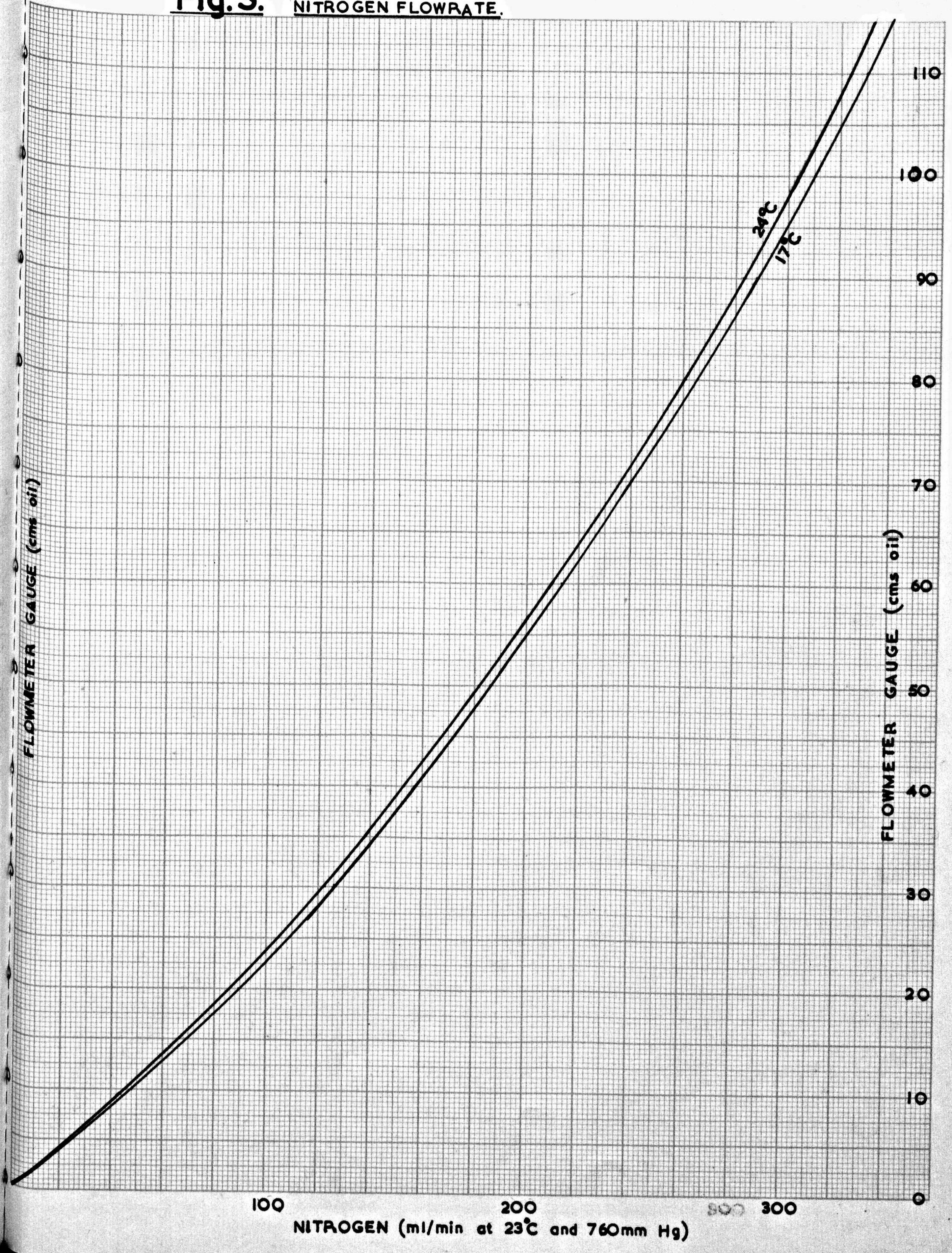


Fig. 3. NITROGEN FLOWRATE.



Sulphur dioxide from the flowmeter passed into the mixer and was diluted there with nitrogen. The thoroughly mixed gases were then passed into a neutral 4 volumes solution of hydrogen peroxide, where the sulphuric acid formed was neutralised by standard sodium hydroxide, using methyl red as an indicator. The mixed gas was passed for ten minutes through the solution and the volume of sulphur dioxide at 23°C and 760 mm mercury calculated and graphed for different gauge readings (Fig.4). Different flow rates of nitrogen were tried (50, 150, 350 ml/min) in case some of the sulphur dioxide was being carried out of the solution and not being oxidised, but it was found that for a fixed sulphur dioxide gauge reading the sulphur dioxide volume by this method of standardisation remained the same.

Absorption of the sulphur dioxide in acidulated water and titration with a standard KI/KIO_3 solution using starch as an indicator was also used and the two different chemical methods gave excellent agreement. The hydrogen peroxide method, however, was preferred due to the ease of standardising the decinormal sodium hydroxide.

This standardisation of the sulphur dioxide meter was only used as a rough guide to flow rates as the sulphur dioxide content of the gas was determined before, during, and after every run.

Reaction Furnace

The reaction furnace (R), Fig., 5, was a vertical resistance furnace would with 19 gauge molybdenum wire carrying a

Fig. 4. SULPHUR DIOXIDE FLOWRATE.

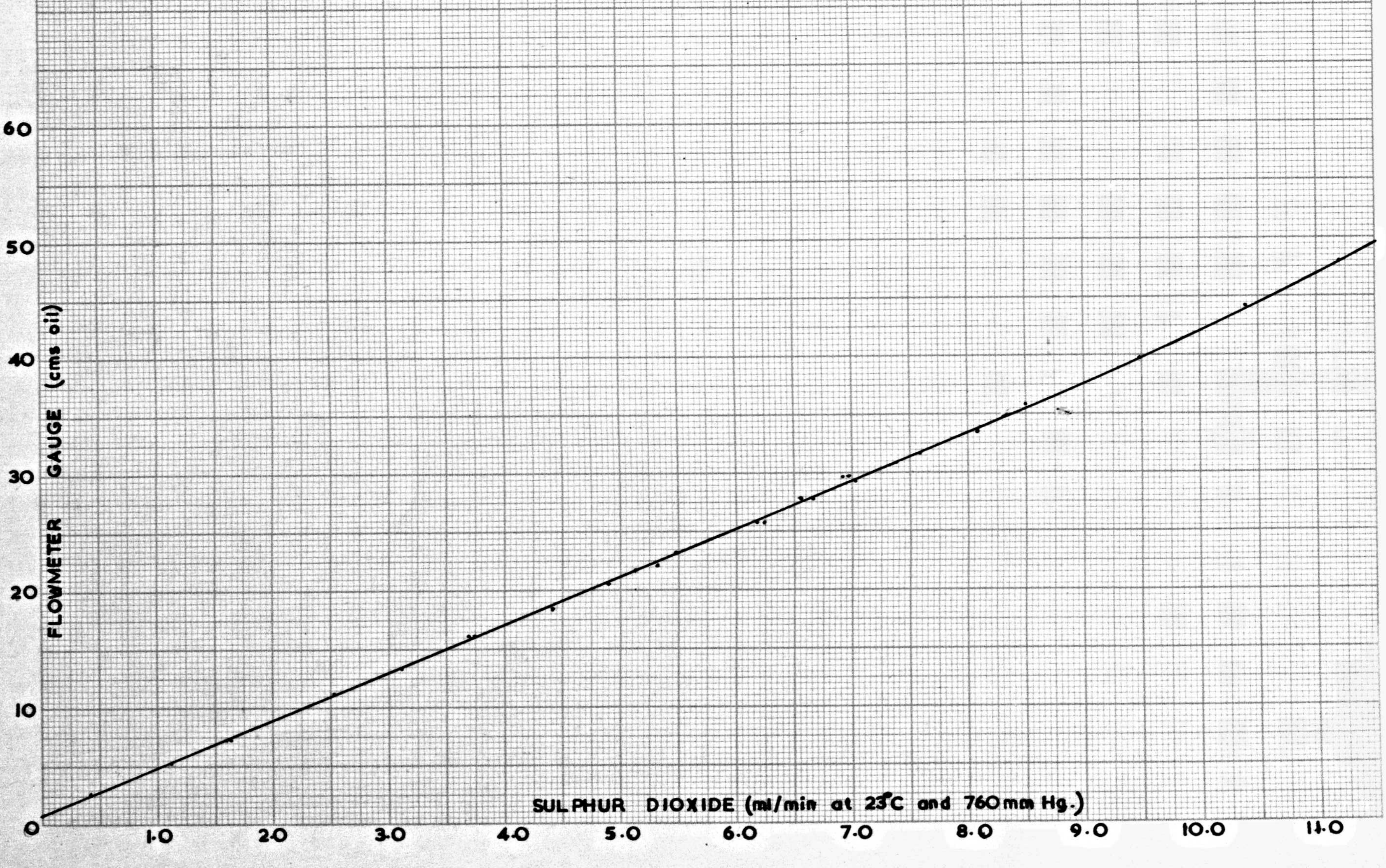
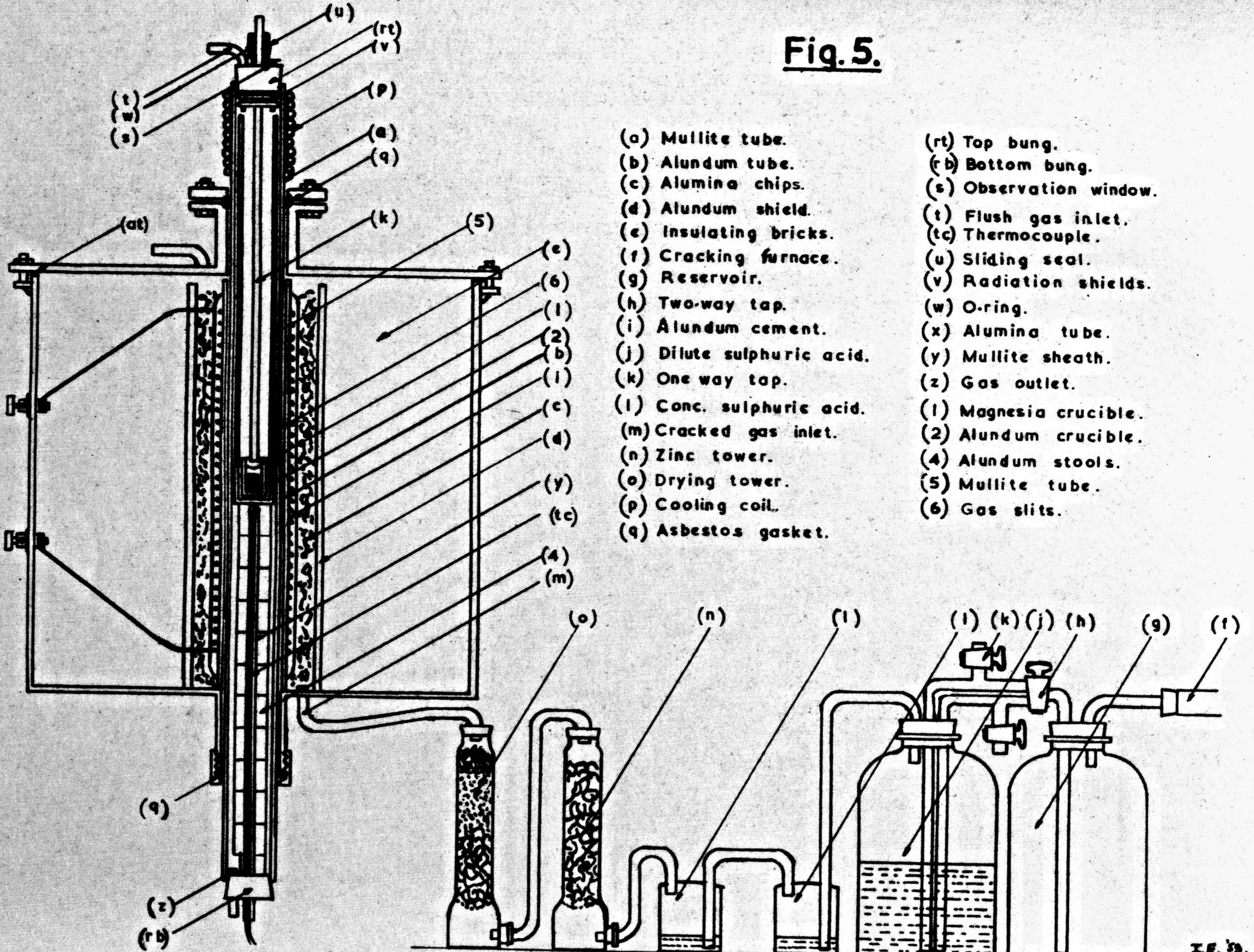


Fig. 5.


(u)
(rt)
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(t)
(w)
(s)
(p)
(a)
(q)
(at)
(k)
(5)
(e)
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(d)
(y)
(tc)
(4)
(m)
(q)
(z)
(rb)
(o)
(n)
(l)
(l)
(k)
(j)
(h)
(g)
(f)
(a) Mullite tube.
(b) Alundum tube.
(c) Alumina chips.
(d) Alundum shield.
(e) Insulating bricks.
(f) Cracking furnace.
(g) Reservoir.
(h) Two-way tap.
(i) Alundum cement.
(j) Dilute sulphuric acid.
(k) One way tap.
(l) Conc. sulphuric acid.
(m) Cracked gas inlet.
(n) Zinc tower.
(o) Drying tower.
(p) Cooling coil.
(q) Asbestos gasket.
(rt) Top bung.
(rb) Bottom bung.
(s) Observation window.
(t) Flush gas inlet.
(tc) Thermocouple.
(u) Sliding seal.
(v) Radiation shields.
(w) O-ring.
(x) Alumina tube.
(y) Mullite sheath.
(z) Gas outlet.
(1) Magnesia crucible.
(2) Alundum crucible.
(4) Alundum stools.
(5) Mullite tube.
(6) Gas slits.
I.E. '59.

mullite tube (a) (35" long, 2" i.d., 2·3" o.d.). The molybdenum wire was evenly wound over a length of 15" on an alundum tube (b) (18" long, 2·5" i.d.) the current to the coil being adjusted by means of a 40 amp Variac autotransformer. This winding gave in the mullite tube (a) a 3" long hot zone (± 5°C) at 1550°C, the temperature being measured by a platinum-platinum -13% rhodium thermocouple (tc). Temperature control was manual on the Variac, temperatures being easily kept constant at ± 5°C.

The molybdenum wire was covered by a 1/4" thick layer of alumina cement (i), which was protected from contamination from the insulating bricks (e) by broken lumps of alumina (c) held in place by an alundum tube (d), 6" in diameter. The space between this alundum tube and the steel outside body of the furnace was filled with insulating bricks (e). The protective furnace atmosphere round the molybdenum winding was nitrogen and hydrogen. This N_2 and H_2 was obtained from cylinder ammonia which was "cracked" by passing it through a furnace containing steel wool at 850°C. The "uncracked" ammonia was removed by dilute sulphuric acid followed by concentrated sulphuric acid. The gases were then completely dried by passing them over calcium chloride and magnesium perchlorate before being led into the bottom of the steel shell of the furnace. The nitrogen plus hydrogen exited from the top of the furnace via a steel tube into 4" of water, so that the gas inside the furnace shell was always above atmospheric pressure to prevent leakage of air, with its harmful oxygen, into the furnace shell. The removable steel top of the furnace was held in place by six nuts, the gas tight seal (at) being made of asbestos tape.

The mullite tube (a) was held in place by two asbestos rope gaskets (q.q), the lower one clamped very tightly, the top one fairly loosely to allow for expansion and contraction of the mullite tube during heating and cooling. The top end of the mullite tube was water cooled by a copper coil (p) to prevent melting of the rubber bung. (r) The open ends of the mullite tube were fitted with rubber bungs. The top rubber bung (r) carried an observation window (s), flush gas inlet (t), sliding seal (u), and two Sindanyo radiation shields. (v) Through the sliding seal, which consisted of a silicone greased O-ring clamped by a screw knob, passed a 24" dense sintered alumina tube (x) (1/4" o.d., 1/8" i.d.) which could be extended into the hot zone of the furnace at will. The bottom bung (rb) carried a 24" closed mullite thermocouple sheath (y) and a gas exit (z) which was connected to a two-way stopcock (p).

The magnesia or alundum crucible (1) (1.3/4" high, 1·1" o.d., 0·9" i.d.) was placed inside a protective alundum crucible (2) (1.1/2" high, 1·7" o.d., 1·4" i.d.), the two separated by a layer of powdered material (3) the same as the inside crucible. This powder acted as a sponge and soaked up the slag in the event of a crucible failure and so prevented the corrosive slag from attacking the mullite tube (a). The crucibles were supported by light alundum stools (4), which were slipped over the thermocouple sheath, whose closed end just touched the bottom of the outside crucible. A hot zone determination gave the relationship between the temperature at this point and the temperature of the metal in the crucible (3°C difference at 1550°C). On top of the outside alundum crucible was placed a mullite tube (5) (1·7" o.d., 1·4" i.d., 16" long) with gas slits (6) cut for three inches above the crucible. This mullite tube served the dual purpose of filling up dead space above the crucible in order to cut down fluctuations in the gauges and also to protect the outside mullite tube (a) from slag when "blowing" the gas into the slag and metal.

The thermocouple millivoltage was read on a Tinsley vernier potentiometer using a 36" galvanometer beam.

The train for removing the last traces of uncracked ammonia was redesigned in order to eliminate any moisture being carried through into the furnace shell. This train is shown in Fig.5. From the cracking furnace (f) the gas containing some uncracked ammonia passed into a 5 litre empty reservoir (g). This was to prevent a back suction of the liquids into the furnace in the event of an electrical fault in the cracking furnace.

Difficulty had formerly occurred in the train due to the choking of the inlet tube into the concentrated H_2SO_4 bottle with ammonium sulphate which is very insoluble in concentrated H_2SO_4. To eliminate this a two-way tap (h) led to a bottle (j) of 5 litres capacity, half filled with 25 per cent sulphuric acid containing methyl red as an indicator. If the inlet tube began to get blocked with ammonium sulphate the gas flow was switched to the other tube. The stopcock (k) on the blocked tube was gradually opened until sulphuric acid was forced up the tube by the gas pressure inside (j), and this dissolved out the blockages. Two or three washings were sometimes necessary before the blockage was completely cleared but at no time was air allowed into the system, and the gas flow was only momentarily interrupted when turning stopcock (h). Two concentrated sulphuric acid bubblers (e,e) removed most of the moisture picked up from the dilute sulphuric acid and the acid mist in the gas was removed by passing the gas through a granulated zinc tower (n). Finally the gas was completely dried by passing it through a tower (o), the bottom half filled with lump calcium chloride, the top half with magnesium perchlorate, before entering the furnace shell by (m). Another precaution which was taken was that the furnace was never allowed to become cold. The temperature of the furnace was kept at 150°C when not in use so that no moisture pick could occur, and the nitrogen and hydrogen flow was kept on all the time.

The alumina injection tube (x) which was lowered into the molten metal to give good mixing stood up well to this procedure, but when attempts were made to bubble high iron oxide slags, the iron oxide led to swelling and bursting of the tube. Magnesia, which has a much better resistance to iron oxide slags, was tried.

Magnesia tubes could only be supplied by the makers in 18" lengths maximum, and as the distance from the top bung to the melt was greater than 18" these lengths would have to be joined either together or to alumina tubes of the same diameter. In order to preserve the magnesia tubes it was decided to half them and join each 9" length to an alumina tube of similar diameter. Keyways were cut on the outside of both tubes, and the tubes butted together over a central wooden plug. An alundum covering 3" x 1/2" diameter was smeared over the join, allowed to dry thoroughly, and fired at 1000°C. The join was gas tight but when an attempt was made to lower the tube for the first time into the melt the magnesia broke at the edge of the covering. As the magnesia tube was extremely fragile it was though that it my have been knocked during the joining and partly fractured. The procedure was repeated and the same thing happened again, the fracture occurring at the same place. As the coefficients of expansion of alumina and magnesia are quite different it was thought that the expansion on heating to the high temperatures effects the fracture. A stainless steel tube with asbestos gaskets tightened by stainless steel nuts at either end of the tube was next used in an attempt to join the tubes. This after a few initial failures due to improper lubrication of the asbestos, provided an excellent if somewhat heavy join. On dipping the magnesia tube into the melt, however, no gas bubbles were observed. At a molten iron pressure head of 1/8" and blowing at 500 ml/min.

nitrogen, no bubbles were formed as all the gas was escaping through pores in the magnesia tube walls. An alchohol slip of magnesia powder was next used in order to fill up the pores but without success as at high temperature the tube was as porous as before. Evidently at high temperatures the magnesia grains must separate on expansion forming voids and the material inserted into the pores at room temperature is useless.

In view of these difficulties the use of magnesia tubes was abandoned and the less satisfactory alumina tubes used instead. No attempt was made to heat these alumina tubes in order to pre-heat the gas as it was thought that the long hot zone in the furnace plus the relatively high velocity of the gas through the tube would prevent any thermal diffusion. The relative densities and percentages of the gases are also against any thermal diffusion occurring.

Metal and Slag Preparation

The experiments essentially consisted of the sulphur pick-up by iron, iron-carbon, and iron-carbon-silicon alloys from sulphur dioxide-nitrogen atmospheres, the pick-up of sulphur by iron oxide slags from sulphur dioxide-nitrogen atmospheres, and the equilibrium distribution of sulphur between iron and iron oxide-silica slags. In order that the experimental conditions might be stabilised synthetic materials had to be used throughout and their preparations are described below.

4% Carbon-Iron Alloy

Stock Armco iron (C, 0·10 per cent, Mn,0·013 per cent P, 0·005 per cent, S, 0·035 per cent, Si, trace) was melted in a graphite crucible using high frequency heating. When the melt was quiescent the temperature was lowered to 1200°C and held there for ten minutes. The "kish" was skimmed off and the metal cast into 3/4" diameter iron moulds. The metal was broken up by hammer blows into small pieces. The carbon content was 4·3 per cent.

Iron-carbon-sulphur alloy

The 4 per cent carbon-iron alloy was melted in a magnesia crucible under a nitrogen atmosphere and enough lump ferrous sulphide added to give a 1 per cent sulphur alloy. The "kish" was removed and the alloy cast into 1/2" diameter iron moulds. The carbon and sulphur contents of this alloy were 3·7 and 1·27 per cent respectively.

Armco iron

Stock armco iron (3/4" diameter) was cleaned with emery cloth to remove all grease and rust, then sawn into 1" lengths.

Iron-sulphur alloy.

Stock Armco iron was melted in a magnesia crucible under nitrogen and encough lump ferrous sulphide added to give a 1 per cent sulphur alloy. The metal was cast into 1/2" diameter iron moulds, and sawn into 1/2" lengths.

Silicon

Silicon metal as supplied analysed 98·8% silicon, 0·4 per cent iron.

Ferrous oxide

Although there were various methods of preparing pure ferrous oxide, the method adopted was to heat ferrous oxalate under vacuum at 1000°C. The ferrous oxalate was packed into a steel tube and dried overnight at 150°C before the temperature was raised to 1000°C and held there for four hours under vacuum. The steel tube, still evacuated, was then quenched horizontally in cold water. The clinkered, black ferrous oxide was removed and stored under nitrogen to prevent oxidation. The yield by this method was small and several lots had to be made.

Analysis by total iron gave 101·2% FeO, and by ferrous iron 101·4% FeO, showing that a little metallic iron was present and that ferric iron was absent.

Silica

Fine white silica sand was ground in an agate mortar for eight hours, then boiled with dilute hydrochloric acid for a further twenty-four hours. The silica was filtered off, washed several times with water, dried and stored. No analysis was determined.

Ferrous sulphide

Ferrous sulphide was made by the direct heating together of iron powder and sulphur. Electrolytic iron (-70 B.S.S.) was mixed carefully with flowers of sulphur 1% in excess of the stoichiometrically required amount. The mixture in 15g. lots was placed in a glazed silica crucible with a fine layer of sulphur on top to prevent oxidation and the crucible covered with a silica lid. After ignition the ferrous sulphide button was scraped to remove any oxidation products, crushed to -60 B.S.S. and stored.

The analysis of the ferrous sulphide presented some difficulty as by total iron a good indicator end point with diphenylamine sulphonate could not be obtained. Gravimetric estimation of the sulphide involved some loss as H_2S when dissolving the sulphide in an oxidising acid solution. This H_2S was absorbed in alkaline cadmium chloride and added to the total sulphur found by the $BaSO_4$ precipitation.

The average of the two methods gave a ferrous sulphide purity of 96 ± 4%.

Preparation and Analysis of Metal Samples

The high carbon (above 1%) sulphur, silicon and iron samples were all crushed in a percussion mortar to pass a 22 mesh B.S.S. The iron and sulphur alloy samples were milled down to give fine turnings. The sulphur in both these alloys was helpful in giving small pieces of metal.

Carbon . Carbon was estimated by the standard combustion method[91]. Oxygen was passed over the alloy millings for half an hour at 1100°C and the carbon dioxide evolved was absorbed in a "Carbosorb" bulb. Tin powder was used as an accelerator and two extra potassium permanganate gas scrubbers were placed in the train to remove all traces of sulphur gases, as the alloy normally contained above 0·5 per cent sulphur. British Chemical Standard iron carbon alloys, or a synthetic standard were used as checks on the method every ten analyses.

Sulphur : Sulphur was also estimated by the standard combustion method[91]. Oxygen was passed over the alloy millings at 1300°C and the sulphur dioxide evolved was absorbed in acidulated water and titrated with KI/KIO_3 solution using starch as an indicator, the estimation normally taking twenty minutes. As no high sulphur, high carbon British Chemical Standard was available two synthetic standard alloys were made up by melting Armco iron and iron sulphide in a graphite crucible as above. These alloys were crushed to pass 60 B.S.S. and the $<$ 60 but $>$72 B.S.S. portion taken as the standard iron. The sulphur content of these irons was obtained by oxidation of the sulphur and precipitation as $BaSO_4$, (B.S. 1121, Part IA : 1957). The sulphur was also obtained by combustion analysis using as standard the British Chemical Standard iron as close to the synthetic standard compositions as possible. The evolution method for sulphur analysis was also tried with little success. The results by the first two methods were within the limits of analytical error and the final analyses of the two standard irons were

	S by $BaSO_4$ pptn	S by combustion	S by evolution	Carbon
Standard 1	1·01^{2}%	1·08^{4}%	0·94%	4·07%
" 2	2·21^{3}%	2·23^{1}%	2·00%	

It was noticeable that the British Chemical Standards and the new standards gave virtually identical results for the strength of the KI/KIO_3 solution. These new standards were also used as carbon standards when determining the carbon contents of high carbon, high sulphur alloys.

No synthetic standard was made up for the low carbon, high sulphur alloys, a high sulphur British Chemical Standard being used instead.

Silicon : Silicon was estimated by a standard procedure[93]. The metal was dissolved in concentrated hydrochloric acid, the solution evaporated to dryness and baked. The residue was dissolved in hydrochloric acid, boiled and the silica filtered off on an ashless paper pad. The residue, weighed after ignition in a platinum basin, was fused with HF and H_2SO_4 and reweighed. The difference between the two weighings gave the amount of silica ~~which was converted to silica~~ which was converted to silicon.

Preparation and Analysis of Slag Samples

The slags were crushed to pass a 60 mesh sieve. The method of crushing is important in order to prevent oxidation of the ferrous oxide to ferric oxide and the loss of sulphur by oxidation. The slag was crushed in a percussion mortar with a single blow, then sieved ; the oversize was crushed again with a single blow, then sieved. This single blow then sieving technique was carried out until all the slag was sieved. The slags were all treated this way in order to prevent as much as possible the production of fines which are very easily oxidised. After crushing a weak magnet was drawn across the slag to remove any metal globules which might have been picked up in sampling.

Sulphur : Sulphur was analysed by the standard technique of Fincham and Richardson[98]. A prefired boat containing the slag was introduced into a 13% rhodium/platinum wound furnace at 1450°C. Carbon dioxide at a fixed rate was passed over the slag and the sulphur dioxide evolved was absorbed in acidulated water and continuously titrated with KI/KIO_3 solution using starch as an indicator. The estimation normally took twenty minutes. A synthetic iron oxide, iron sulphide slag was melted under nitrogen and ground to pass a 72 mesh sieve. This slag and a blast furnace slag were analysed for sulphur by the $BaSO_4$ method. The synthetic slag was also analysed by combustion using the blast furnace slag as standard and the sulphur content by this method agreed closely with the result obtained by the $BaSO_4$ method, viz.-

	By $BaSO_4$ pptn	By Combustion
Blast furnace slag	1·34%	-
Synthetic iron oxide slag	1·14%	1·13%

This showed that either slag could be used as the standard.

Silica : Silica was estimated in the slags by fusing a known weight of sample with sodium carbonate in a platinum crucible.

The water leached fusion was acidified with hydrochloric acid and a few drops of nitric acid. Perchloric acid was added to dehydrate the silica. The solution was evaporated to dense white fumes, cooled, diluted, and filtered through paper pulp, the filtrate being washed alternatively with dilute hydrochloric acid and cold 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 gave the amount of silica.

Total Iron. If the slag contained under 10 per cent silica, the slag was dissolved in hydrochloric acid with a few drops of hydrofluoric acid added to aid dissolution. If over 10 per cent silica the slag was fused with sodium carbonate in platinum, the fusion leached with water and acidified with hydrochloric acid. The solution was evaporated almost to dryness, then concentrated hydrochloric acid added in order to obtain the correct concentration of acid for the reduction of ferric iron to ferrous iron by stannous chloride. Excess stannous chloride was removed by the addition of mercuric chloride. Phosphoric/sulphuric acid was added and the solution titrated with standard decinormal potassium dichromate using diphenylamine sulphonate as an internal indicator.

As several of the slag samples taken from the melt were not very heavy (1·0 - 1·5g) an alternative procedure was adopted for analysing for total iron in these samples. This involved finding the total iron from the silica filtrate. The filtrate from the silica estimation contained large amounts of perchloric acid which interfered with the oxidation-reduction reaction using potassium dichromate. To the almost boiling silica filtrate dilute ammonia (1 : 1) solution was added until the precipitation of iron as hydroxide was complete. This precipitate was washed by decantation several times using ammonium chloride (2%) as washing agent. The filtered precipitate was redissolved in hot concentrated hydrochloric acid and the total iron in this solution determined as above. This was a somewhat lengthy procedure but had to be resorted to as there was not always enough slag to do a separate total iron analysis.

Ferrous Iron : The ferrous iron in solution was analysed volumetrically by potassium dichromate using diphenylamine sulphonate as an internal indicator. As ferrous iron oxidises readily in solution in contact with air a closed system was used. Hydrochloric acid was saturated with carbon dioxide by boiling the hydrochloric acid in a closed vessel and continuously bubbling carbon dioxide through the acid not only as it cooled but also on standing in the cold. The slag plus a few marble chips was placed in a wide mouthed 600 ml conical flask fitted with a rubber bung through which carbon dioxide could be admitted by glass tubing to the bottom of the flask. A stoppered thistle funnel and a burette were also led into the flask through the bung. The gas exited by a glass tube in the bung into a beaker containing ammoniacal cadmium chloride. With carbon dioxide from a cylinder passing vigorously the thistle funnel stopcock was opened for a few minutes then closed. The gas was passed for five minutes until all the air was flushed from the flask. Carbon dioxide saturated hydrochloric acid plus a few drops of 40% hydrofluoric acid (into which marble chips had been dropped) were added to the thistle funnel. The carbon dioxide supply to the flask was turned down and most of the acid admitted by opening the thistle funnel stopcock, 5 ccs remaining in the thistle funnel to act as a seal. The acid reacted with the marble chips and kept a carbon dioxide atmosphere in the flask. On heating the slag was dissolved with the evolution of hydrogen sulphide which was swept out of the flask by the carbon dioxide flow and into the ammoniacal cadmium chloride solution where cadmium sulphide was precipitated. After purging for five minutes the acid solution was cooled in a cold water bath, carbon dioxide still passing. Phosphoric/sulphuric acid and sodium diphenylamine were added via the thistle funnel and the ferrous iron titrated by decinormal potassium dichromate. The cadmium solution was acidified with hydrochloric acid and titrated quickly with KI/KIO$_3$ using starch as an indicator. Blank determinations on the reagents were also carried out periodically and found to be negligible.

As sulphide ions reduce ferric iron to ferrous iron forming elemental sulphur a correction has to be made for this excess ferrous iron. The difference between the combustion sulphur analysis and the hydrogen sulphide analysis by cadmium chloride gives the amount of elemental sulphur formed in .

gives the amount of elemental sulphur formed in the flask and hence the correction for the ferrous iron. This excess ferrous iron normally amounted to one to two per cent of the true ferrous content of the slag.

The synthetic pure ferrous oxide analysed by this method gave 101·4% FeO as against 101·2% FeO by the total iron method, these results showing the accuracy of this ferrous iron procedure.

Magnesia . By the time that duplicate or more sulphur, silica, ferrous iron, and total iron analyses had been carried out there was often little or no slag left to analyse for magnesia. The classical methods of magnesia analysis are simple but above all exceedingly time consuming, especially in the presence of silica and iron oxide which must be removed before any magnesia analysis is attempted.

A shorter method was sought and a possible solution was found in the work of Bennet[93] and of Archer[94] on silliceous materials and coal ash deposits. This involved the use of ethylene diamine tetra-acetic acid (E.D.T.A.) for the analysis of magnesium, iron, aluminium, and titanium being complexed with triethanolamine. O-cresolphthalein complexone screened with methyl red and a green dye (paramine green BH) was used as an indicator. This method, however, had not been used for the types of slags formed in this investigation, the highest iron oxide contents previously investigated being sixty per cent. The effect, therefore, of 80 - 95 per cent iron oxide was not known. Three slags were analysed by the classical method ($Mg_2P_2O_7$ precipitation) and by the new method, the results shown below

	S	FeO	Fe_2O_3	SiO_2	MgO (Classical)	MgO New
Run 37 Final Slag	8·69	58·0	12·0	0·8	5·4	5·2
Run 42 8.20p.m.	·78	65·7	23·8	1·0	7·6	7·6
Run 42 10.05p.m.	·66	65·5	22·8	1·2	8·7	9·1

This seemed to indicate that the method was applicable to the slags used in this investigation.

0·25 g. of the powdered slag were dissolved by a sulphuric/hydrofluoric acid mixture in a platinum basin. The residue was dissolved in dilute hydrochloric acid and made up to 250 ml. 50 ml of this solution was taken and the iron complexed by the addition of triethanolamine and ammonia. The solution was titrated by the standard E.D.T.A. solution using O-cresolphthalein as indicator. The titrations were carried out in daylight as the purple to grey end point is extremely difficult to see under artificial light. The E.D.T.A. was standardised against a magnesium sulphate solution of known magnesium content.

By this method as many magnesia analyses as there were platinum basins could be carried out in four hours.

Experimental Procedure

In the gas/metal investigations approximately 70 g. of the metal were accurately weighed into a tared crucible. The iron-carbon alloy was in the form of lumps, and Armco iron in the form of 1.1/4" x 3/4" diameter cylinders. In the iron-carbon-silicon runs silicon in powdered form was added to the lump iron carbon alloy before melting.

In the gas/slag investigations the powdered slag constituents were thoroughly mixed and placed in the crucible.

In both the slag metal and gas/slag/metal investigations Armco iron crucibles were made to fit inside the magnesia crucibles. The powdered slag constituents were thoroughly mixed and placed in this metal crucible so that on melting at approximately 1300°C the molten slag was kept away from the magnesia crucible walls, until the iron crucible, which was part of the metal charge, itself melted at 1535°C. In the slag/metal equilibrium runs the equilibrium value for the distribution coefficient was approached from both sides as some of the charged slag sulphur contents were above the equilibrium value and some of the charged metal sulphur contents were above the equilibrium value.

The reaction furnace having been set up, and the system tested for leaks, purified nitrogen was admitted for ten minutes into the furnace via the mixer and the alumina tube (x) in order to flush out the air in the tube and then via the by-pass (s) for a further half hour. The furnace current was now switched on and the cooling water started through the coil. The nitrogen flow was then cut back to 25 ml/min., this flow rate persisting until the furnace temperature reached the experimental value. With molybdenum wound furnaces the resistance of the winding increases some seven times between room temperature and 1600°C. It was necessary, therefore, to start with a low voltage across the winding and increase this progressively as the temperature rose, keeping the furnace current as constant as possible. In this way the time taken to reach 1550°C from room temperature was seven to eight hours.

Two to three hours before the estimated time at temperature, the nitrogen and sulphur dioxide gas flows were started as it sometimes took this length of time before the sulphur dioxide content of the mixed gas reached its stable value especially if new perchlorate had been added to the mixer. The normal procedure was to start the sulphur dioxide flow first, the gas exhausting to waste (w). After half an hour when sulphur dioxide had filled all the gas tubes the nitrogen flow was started slowly and built up to its full value over ten minutes. Small adjustments to the bleeder columns gave the desired value for the flow of both gases. The mixed gas was allowed to run to waste for a further hour before the first ten-minute analysis was made at (x) using 4 vol. hydrogen peroxide and decinormal sodium hydroxide. Analyses for sulphur dioxide were carried out every fifteen minutes until a stable sulphur dioxide content was obtained. The ideal situation of both gas mixture and furnace temperature being correct at the same time was seldom realised as one nearly always lagged behind the other. On the charge melting, the sliding alumina tube (x) was moved into position 1/4" above the melt. This distance could be judged quite clearly by the reflection of the end of the tube on the molten surface and also by the depth from the top of the inner crucible.

When the furnace temperature and sulphur dioxide content of the gas were stable at the desired values, tap (T) was closed, and tap [N] turned so that the mixed gas was passing into the furnace with tap (P) open to analysis (V). The clock starting time was noted. Every fifteen minutes the alumina tube (x) was lowered into the melt and the gas bubbled through the melt for 15 seconds to ensure thorough mixing. Attempts to blow the gas into the melt all the time had to be abandoned because of the erratic surging of the gauges due to irregular bubbling in the melt. Fine bore alumina tubing also gave this erratic surging and was no improvement. Any erratic surging in the gauges could not be tolerated as an exact knowledge of the inlet gases had to be obtained, and this was impossible with fluctuating gauges.

At the end of a certain period of time and after a 15 second bubble mix the top bung was opened and a metal and/or slag sample taken. Tap (P) was switched to analysis (U) (formerly waste) and the bung replaced. From this after-furnace analysis (U,W) the volume of sulphur dioxide passing through the furnace, and therefore taking no part in the reactions with the melt, between samplings was obtained.

Metal samples were taken by a silica tube (30" long, 3/8" i.d.) attached to a partially evacuated rubber bulb. The tube was grounded on the bottom of the crucible and on releasing the clip slowly a 3" long metal sample was sucked up the tube. Care had to be taken as a hollow sample resulted if the clip was released too suddenly. The tube abd sample were quenched immediately into cold water, the silica broken away and the metal sample broken or sawn into several pieces to test its soundness. No slag was ever found entrapped in the metal specimens by this sampling technique. After weighing the metal was prepared for analysis. Metal sampling time was less than 10 seconds.

Slag samples were taken by dipping a 1/4" diameter Armco iron rod into the slag in the exact centre of the crucible. A blob of slag solidified in the cold metal and this was quenched in mercury. Slag samples taken at the same time and quenched in water showed an identical analysis to those quenched in mercury, which was, however, preferred due to the possible oxidation of the slag by steam from the water although a few slag samples were quenched in water. The position of sampling in the crucible was important as ferrous oxide-magnesia solid solutions were formed at the crucible walls and this material was not representative of the slag in equilibrium or in contact with the molten metal. After weighing, the slag specimen was prepared for analysis. Metal and slag sampling time was less than 20 seconds. By this method fairly small samples of slag were obtained (1·0-2·0g) which led sometimes to lack of material for analysis. In the equilibrium studies of slag and metal, after slag sampling the molten metal was sometimes uncovered and more slag was added by means of a silica tube (24" long, 1/2" i.d.) placed in the furnace 1/2" above the slag surface.

In this way metal and/or slag samples were taken over a period of time, the actual time at temperature being about five hours during which four to six slag and metal samples were obtained. Between samples the gas was normally analysed once to see if the sulphur dioxide flow was remaining constant, the drift usually being found negligible, or rising slightly due to the increased density of the bleeder column liquid. This rise in density was due to the absorption of sulphur dioxide from the bleed-off. At the end of the run the gas was analysed again, the furnce switched off and tap (T) opened to admit purging nitrogen to the system. The furnace cooled overnight with nitrogen flowing through the mullite tube (a) at 25 ml/min. The sulphur dioxide was turned off first, and nitrogen allowed to flow through the tubes and mixer to waste (W) in order to remove the sulphur dioxide before closing tap Q_2.

The procedure for carrying out the equilibrium runs involved the use of nitrogen only throughout the runs, metal and slag sampling as before. Metal was sometimes added to the melt by caging the piece of metal in Armco wire, the cage being quickly lowered into the furnace on an Armco wire, until the metal entered the crucible. After 1 second the remaining wire could be withdrawn.

In the slag/gas investigations the exit furnace gas was analysed every five minutes in order to find when equilibrium was attained, i.e. exit sulphur dioxide equalled inlet sulphur dioxide.

In all the investigations ideally it would have been advisable to analyse the samples for sulphur as soon as they were taken, but this was found impossible with only one pair of hands. In consequence all the runs were done "blind", and in a few cases longer experimental times would have been advisable.

Temperatures were measured by the millivoltage generated by a platinum/platinum-13% rhodium thermocouple (tc). This thermocouple was calibrated every 40 hours above 1000°C at the melting point of palladium (1552°C) and less frequently at the melting point of gold (1063°C) for the experiments up to 1550°C. After each run at 1600°C or 1650°C, three inches of couple were removed and a new join made. The calibrations were conducted in the molybdenum wound furnace, a palladium wire being laid across the ends of the two thermocouple wires, 3/16" apart, and welded to each wire by an oxy-coal gas flame. The melting point of this wire then corresponded to the E.M.F generated by the thermocouple at break. It was found that the variation in E.M.F. generated at 1552°C was very little from standardisation to standardisation of one thermocouple and from bathh to batch of thermocouple wire. The variations from B.S. 1826 : 1952 were also very small.

CHAPTER IV

THERMODYNAMIC DATA

Thermodynamic Data

The oxides and sulphides of iron are non-stoichiometric in behaviour, the precise compositions depending on temperature. Calculations on the ferrous oxide, ferrous sulphide equilibrium reactions are complicated by this behaviour, especially as the thermodynamics of the non-stoichiometry of ferrous sulphide have not been established. Normal procedure when working with these compounds, especially in the liquid state, is to treat them as stoichiometric compounds assigning to them the formulae 'FeO' and 'FeS', the inverted commas symbolising that in fact they are non-stoichiometric. Throughout this work however the compounds will be designated FeO and FeS.

The free energy change in the formation of liquid ferrous oxide from liquid iron and oxygen gas at 1 atmosphere pressure is given by[95]

$$Fe(\ell) + \tfrac{1}{2}O_2(g) = FeO(\ell) \quad \Delta G^\circ_{1808-2000\,^\circ K} = -55{,}620 + 10{\cdot}83T \ldots\ldots\ldots (1)$$

The free energy change in the formation of liquid ferrous sulphide from liquid iron and sulphur gas at 1 atmosphere pressure has not been directly measured at steelmaking temperatures but may be calculated from the free energy data at lower temperatures. Kelly[96] gives the free energy change in the reaction

$$Fe(\gamma) + \tfrac{1}{2}S_2(g) = FeS(\ell) \text{ as } \Delta G^\circ_{1300-1600\,^\circ K} = -30{,}260 + 8{\cdot}3T$$

This FeS equation was extrapolated beyond the melting point of iron by introducing the heat of transformation of γ-iron to δ - iron, the heat of fusion of δ-iron to liquid iron and the changes in heat capacities of the various elements and compounds from 1300° to 2000°K[27]

This gives

$$Fe(\ell) + \tfrac{1}{2}S_2(g) = FeS(\ell) \quad \Delta G^{\circ}_{1808^{\circ}-2000^{\circ}K} = 27{,}108 - 50{\cdot}44T + 18{\cdot}79T\log_{10}T - 2{\cdot}33 \times 10^{-3}T^{2}$$

A simplified form of this equation, neglecting the change in heat capacities is

$$Fe(\ell) + \tfrac{1}{2}S_2(g) = FeS(\ell) \quad \Delta G^{\circ}_{1808^{\circ}-2000^{\circ}K} = 34{,}170 + 10{\cdot}21T \quad \ldots.(2)$$

Combining equations (1) and (2) gives

$$FeO(\ell) + \tfrac{1}{2}S_2(g) = FeS(\ell) + \tfrac{1}{2}O_2(g) \quad \Delta G^{\circ}_{1808^{\circ}-2000^{\circ}K} = 21{,}450 - 0{\cdot}62T \quad \ldots.(3)$$

The estimated error in the free energy change of this equation is ± 2,000 cals.

A confirmation of the free energy change for this reaction can be obtained from the data of Grant and Chipman[67] on the sulphur equilibria between liquid iron and slags containing about ^{90} per cent FeO, 4 per cent Fe_2O_3, and 6 per cent MgO. The activity coefficient of FeS in these melts is assumed to 1·5, the value calculated by Chipman[27] from the 'FeO-FeS' phase diagram, the heats of fusion FeO and FeS, and the sulphur distribution data of Bardenheuer and Geller[41]. This activity coefficient combined with the sulphur in the slag, and the values of pO_2 and pS_2 in equilibrium with the liquid iron at the appropriate oxygen and sulphur contents of the metal respectively, gives the equilibrium constant for reaction (3) and hence the free energy change for the reaction.

The values of pS_2 are obtained from the equation of Cordier and Chipman[96]

$$\tfrac{1}{2}S_2 = \underline{S} \qquad \Delta G^\circ = -\ 28{,}180 + 3{\cdot}44T$$

using the activity of sulphur from the relationship obtained by Sherman, Elvander and Chipman[10] that

$$\log f_s = -0{\cdot}0278\ [\%S] \quad \text{where } f_s = \text{activity coefficient of sulphur}$$

The values of pO_2 are obtained from the equation of Dastur and Chipman[36]

$$\tfrac{1}{2}O_2 = \underline{O} \qquad \Delta G^\circ = -27{,}930 - 0{\cdot}57T$$

using the activity of oxygen from the data of Floridis and Chipman[78] that

$$\log f_o = -\ 0{\cdot}20\ [\%O] \quad \text{where } f_o = \text{activity coefficient of oxygen}$$

Using the above method the data of Grant and Chipman[47] leads to values for the change in free energy of equation (3) of + 19,550 cals and + 18,930 cals at 1796°C and 1670°C respectively. These values compare favourably with + 20,170 cals and + 20,250 cals. at 1796°C and 1670°C respectively obtained from $\Delta G^\circ_{1808^\circ - 2000^\circ K} = 21{,}450 - 0{\cdot}62T$ for equation (3). The difference between the values lies well within the estimated error.

<u>Sulphur bearing gases</u>

In order to obtain sulphur capacities of slags as denoted by Richardson and Fincham[22], it is essential to know the correct thermodynamic data for the breakdown of sulphur dioxide at elevated temperatures. At steelmaking temperatures sulphur can exist in a gaseous atmosphere of pure SO_2 as SO_2, SO, S_2, S_8, SO_3, S_6, and S. In such an atmosphere O_2 and O are also present. Free energy data for the formation of these compounds have been given by Kelley[96], Richardson and Jeffes[99], and St. Pierre and Chipman[34,35], significant differences being found between the three sets of data as shown in Table I.

Kelley, Richardson and Jeffes, and to a lesser extent St. Pierre and Chipman, have based their values on spectroscopic measurements. These measurements, however, have been interpreted differently by each worker, with the result that the main disagreement between them lies in the choice of the correct dissociation energy of S_2 and SO into normal atoms. Table I gives the free energy changes and equilibrium constants for the relevant reactions at 1550°C. Calculations show that the amounts of S_8 and S_6 in the gas can be ignored.

The data of St. Pierre and Chipman[35] is preferred on the grounds that these authors used iron oxide slags, similar to the slags which were used in this investigation. By means of the data, gas compositions at elevated temperatures can be calculated in terms of the partial pressures of SO_2 and O_2 in the

TABLE 1

Comparison of Free Energy Data at 1550°C.

Reaction	Kelley[96]		Richardson and Jeffes(99)		St. Pierre and Chipman (35)	
	$\Delta G^\circ_{1823°K}$ Kcal.	$K_{1823°K}$	$\Delta G_{1823°K}$ Kcal.	$K_{1823°K}$	$\Delta G^\circ_{1823°K}$ Kcal.	$K_{1823°K}$
$2SO_2(g)=S_2(g)+2O_2(g)$	110·29	$5{\cdot}971\times10^{-14}$	110·13	$6{\cdot}241\times10^{-14}$	109·48	$7{\cdot}467\times10^{-14}$
$SO_2(g)=S(g)+O_2(g)$	81·60	$1{\cdot}64\times10^{-10}$	66·62	$1{\cdot}028\times10^{-8}$	71·37	$2{\cdot}771\times10^{-9}$
$SO_2(g)=SO(g)+\frac{1}{2}O_2(g)$	46·15	$2{\cdot}928\times10^{-6}$	28·29	$4{\cdot}055\times10^{-4}$	34·17	$7{\cdot}998\times10^{-5}$
$SO_2(g)+\frac{1}{2}O_2(g)=SO_3(g)$	16·60	$1{\cdot}023\times10^{-2}$	16·34	$1{\cdot}098\times10^{-2}$	16·22	$1{\cdot}136\times10^{-2}$
$\frac{1}{2}O_2(g) = O(g)$	-	-	-	-	31·87	$1{\cdot}514\times10^{-4}$

gas phase viz.- using the data of St. Pierre and Chipman.

At 1550°C if $a = pSO_2$ and $x = pO_2$

$$pS_2 = \frac{7{\cdot}467 \times 10^{-14} . a^2}{x^2}$$

$$pS = \frac{2{\cdot}771 \times 10^{-9} . a}{x}$$

$$pSO = \frac{7{\cdot}998 \times 10^{-5} . a}{x^{\frac{1}{2}}}$$

$$pO = 1{\cdot}514 \times 10^{-4} x^{\frac{1}{2}}$$

$$pSO_3 = 1{\cdot}136 \times 10^{-3} . ax^{\frac{1}{2}}$$

But $pSO_2 + pO_2 + pS + pS_2 + pSO + pO + pSO_3 = 1{\cdot}000$ atm.

$$\therefore a + x + \frac{2{\cdot}771 \times 10^{-9} . a}{x} + \frac{7{\cdot}467 \times 10^{-14} . a^2}{x^2} + \frac{7{\cdot}998 \times 10^{-5} . a}{x^{\frac{1}{2}}}$$

$$+ 1{\cdot}514 \times 10^{-4} . x^{\frac{1}{2}} + 1{\cdot}136 \times 10^{-3} . ax^{\frac{1}{2}} = 1{\cdot}000$$

For any particular value of $x = pO_2$, this quadratic equation can be solved for $a = pSO_2$, and hence the composition of the gas phase with that particular partial pressure of oxygen can be calculated. At 1550°C and $pO_2 = 1 \times 10^{-4}$, with inlet gas of pure sulphur dioxide at 1 atomosphere pressure, the partial pressures of the gas components as calculated are

$pS = 2{\cdot}75 \times 10^{-5}$ atm.

$pS_2 = 7{\cdot}35 \times 10^{-6}$

$pSO = 7{\cdot}93 \times 10^{-3}$

$pO = 1{\cdot}51 \times 10^{-6}$

$pSO_3 = 1{\cdot}13 \times 10^{-4}$

$pO_2 = 1{\cdot}00 \times 10^{-4}$

$pSO_2 = 0{\cdot}992$

Graphs can thus be drawn of the partial pressures of diatomic sulphur gas in equilibrium with particular partial press ures of oxygen at various temperatures as in Fig.18, which shows the results of Kelley, Richardson and Jeffes, and St. Pierre and Chipman.

CHAPTER V.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The purpose of the present work was to investigate some of the factors affecting the sulphur absorption characteristics of various slags and metals from sulphur dioxide bearing atmospheres. A simple gas system of sulphur dioxide and nitrogen was chosen in order to facilitate the experimental work. The general plan was to start with high carbon iron, with and without additions of silicon, and proceed to Armco iron finding the effects of as many variables as possible. It was originally intended to use lime, silica, and alumina slags in this investigation but constant crucible failures made this impossible and iron oxide slags were used instead. As data on sulphur distribution coefficients between molten iron and iron oxide slags was very scanty, it followed that work had to be done on this aspect as well. Finally the effect of the sulphur bearing gas on iron oxide slags in the absence of molten iron was investigated.

In order to make reference easier it is intended to report the experimental work in four sections:-

1, Gas - metal.
2. Slag - metal.
3. Gas - slag.
4. Gas - slag - metal.

1. Gas-metal

In any investigation involving gas and liquid metal there are a great number of variables which must be investigated before a comprehensive picture of the reactions taking place can be obtained. In this investigation only a few of these variables were considered due to the length of time required for a single run and its attendant analyses. The variables considered were temperature, carbon, and silicon concentration of the metal, partial pressure of sulphur dioxide, and the mechanisms of the process.

As none of these gas-metal runs attained equilibrium with the gas phase the investigation was of necessity a dynamic one. The weight of metal in the crucible was known and from the change in composition with time the rates of carbon removal and sulphur absorption could be calculated. The reaction between liquid iron containing carbon and sulphur dioxide can be written as

$$Fe + SO_2 + 2\underline{C} = \underline{FeS} + 2CO \qquad \ldots\ldots\ldots(4)$$

This reaction can be subdivided into three component parts as follows:

$$2\,Fe + SO_2 = 2FeO + \tfrac{1}{2}S_2 \qquad \ldots\ldots\ldots(5)$$

$$Fe + \tfrac{1}{2}S_2 = \underline{FeS} \qquad \ldots\ldots\ldots(6)$$

$$2\underline{FeO} + 2C = 2Fe + 2CO \qquad \ldots\ldots\ldots(7)$$

Reactions (6) and (7) are of course controlled by reaction (5) and therefore cannot proceed at a faster rate than reaction (5), which is the rate controlling step in the reactions. The reaction rate of (5), however, cannot easily be measured in high carbon irons but the rate of sulphur absorption and of carbon elimination, i.e. rates of (6) and (7) respectively, can be obtained from a knowledge of the change in sulphur and carbon contents of the metal over a period of time. It follows from reaction (4) that for every 1g. of sulphur dioxide reacting with molten iron, 0·5g. of sulphur should be deposited in and 0·375g. of carbon eliminated from the metal at 100 per cent efficiency of reactions (6) and (7). From the experimental data this 100 per cent is rarely attained, for a variety of reasons, e.g. the nitrogen sweeping over the metal may remove the gaseous sulphur before it has time to react with the molten metal or concentration gradients may be set up in the metal, leading to parts of the melt being high in unreacted iron oxide in solution in the iron.

The experimental data on the gas-metal reactions is given in Tables II - IV. The efficiency factor, η, is calculated as the ratio of the actual change in carbon and sulphur weights calculated from the metal analysis to the theoretical change in carbon and sulphur weights calculated from the gas analysis, over the same period of time. The efficiency is reported as a percentage. The theoretical change in carbon and sulphur weights obtained from the gas analysis has been calculated from the inlet minus exit sulphur dioxide and not from the inlet sulphur dioxide alone. In most of the experimental runs an appreciable quantity (0 - 15%) of the inlet sulphur dioxide passed through the furnace without reacting. It follows that the efficiency factor, η,

TABLE II

Iron-Carbon Alloys

Run	Increment time of SO_2 flow mins.	$\eta\% = \frac{\text{Actual}}{\text{Theoretical}}$		Actual from metal analysis		Temp. °C	Charge Metal	Nitrogen flow 200ml/min. p_{SO_2} atm.	Remarks
		Carbon lost	Sulphur gained	$-\frac{d[C]}{dt}$ g/min.	$\frac{d[S]}{dt}$ g/min.				
1	15	780·0	52·0	·00935	·00082	1400	4%C	·0055	Fixed alumina tube
	34	150·0	52·0	·00176	·00082				
	109	97·5	62·3	·00101	·00085				
	99	73·0	52·1	·00083	·00082				
			Average (3)	·00105	·00084	Average (4)			
2	51	52·0	53·0	·00334	·00457	1380	4%	·0287	"
	79	30·1	33·1	·00190	·00285				
	134	24·0	17·1	·00157	·00146				
	129	2·9	1·8	·00018	·00016				
			Average (3)	·0020	·00248	Average (3)			
3	35	25·0	27·7	·00312	·00470	1400	4%	·0540	
	105	25·4	19·0	·00324	·00329				
	75	gauges unstable-			"				
	50	27·6	22·6	·00350	·00384				
			Average (3)	·00329	·00370	Average (3)			
7	46	43·0	33·3	·00087	·00090	1400	4%C	·01026	
	54	65·7	59·7	·00132	·00159				
	58	59·5	60·0	·00107	·00144				
	40	43·1	66·5	·00090	·00185				
	36	117·0	32·5	·00156	·00058				
			Average (5)	·00113	·00131	Average (5)			

TABLE II

Iron-Carbon Alloys (cont'd)

Run	Increment time of SO_2 flow mins.	η = % $\frac{\text{Actual}}{\text{Theoretical}}$ Carbon lost	Sulphur gained	Actual from metal analysis $-\frac{d[C]}{dt}$ g/min.	$\frac{d[S]}{dt}$ g/min.	Temp. °C	Charge Metal	Nitrogen flow 200ml/min. p_{SO_2} atm.	Remarks
10	57	86·5	55·4	·00088	·00075	1400	4%C	·0055	"
	49	83·0	54·2	·00088	·00076				
	30	77·8	87·5	·00074	·00110				
	35	111·0	66·5	·00114	·00091				
		Average (3)		·00085	·00085	Average (4)			
14	79	137·0	10·4	·00070	·00007	1400	4%C	·0103	Gas leaking at seal
15	20	127·0	113·0	·00750	·00850	1400	4%C	·0590	Gauges fluctuating very badly due to continuous bubbling
	23·5	180·0	169·0	·01240	·01541				
	24	189·0	188·0	·01521	·02022				
	37·5	138·0	110·0	·01040	·01091				
		Average (4)		·00114	·0137	Average (4)			
17	32	131·0	83·8	·00260	·00221	1400	4%C	·0106	Bubbled every 15 mins for 15 secs. Gauges fluctuating
	44	114·0	101·0	·00238	·00282				
	51	109·0	118·0	·00230	·00332				
	25	162·0	132·0	·00340	·00370				
	29	135·0	138·0	·00286	·00388				
		Average (5)		·00261	·00314	Average (5)			
18A	40	96·5	78·1	·00137	·00207	1400	4%C	·0100	gauges steady

TABLE II

Iron-Carbon Alloys (cont'd)

Run	Increment time of SO_2 flow mins.	% Actual/Theoretical Carbon lost	Sulphur gained	Actual from metal analysis $-\frac{d[C]}{dt}$ g/min.	$\frac{d[S]}{dt}$ g/min.	Temp. °C	Charge Metal	Nitrogen flow 200ml/min. p_{SO_2} atm.	Remarks
20	58	91·0	89·7	·00181	·00238	1250	4%C	·0103	gauges steady
	53·25	97·2	93·7	·00197	·00254				
	47·75	73·6	89·0	·00149	·00240				
	17	88·8	89·2	·00176	·00235				
	25	83·0	83·0	·00168	·00224				
		Average (5)		·00176	·00241	Average (5)			
21	58	113·0	72·5	·00224	·00193	1550	4%C	·0099	"
	53·5	107·0	78·2	·00205	·00200				
	32·5	99·5	71·8	·00178	·00172				
	33·5	62·1	72·2	·00122	·00189				
		Average (2)		·0015	·00191	Average (4)			
25	51·75	-	78·8	-	·00207	1400	4%C	·0098	Graphite Crucible
	56·75	-	93·5	-	·00243				
	40	-	78·9	-	·00205				
	40·75	-	74·0	-	·00193				
		Average			·00214	Average (4)			
26	69·25	-	94·4	-	·00537	1400	4%C, ½%S	·0210	Graphite
	55	-	96·4	-	·00547				Crucible
					·00542	Average (2)			

TABLE III -Iron-carbon-silicon alloys.

Run	Increment time of SO_2 flow mins.	η: % $\frac{\text{Actual}}{\text{Theoretical}}$ Carbon lost	Sulphur gained	Actual from metal analysis $-\frac{d[C]}{dt}$ g./min.	$\frac{D[S]}{dt}$ g./min.	$-\frac{d[Si]}{dt}$ g./min.	Temp. °C	Charge Metal	Nitrogen flow 200ml/min. P_{SO_2} atm.	Remarks
8	47	170·0	57·0	·00351	·00157	- ve	1400	4%C		
	57	25·44+	12·1+	·00053	·00033	- ve		1½% Si	·0106	Fixed alumina
	59	72·8-	55·2-	·00099	·00099	- ve				tube
	45	104·0	55·0	·00155	·00110	- ve				Silicon resul
	19	98·4	58·7	·00147	·00117	+ ve				erratic
			Average (3)	·00103	·00120	Average (4)				
9	44	23·1	43·6	·00046	·00114	- ve	1400	4%C	·0100	"
	58	— ve	49·8	-·00026	·00128	- ve		3% Si		
	60	30·8	34·8	·00055	·00083	+ ve				
	30	46·1	51·5	·00084	·00124	+ ve				
			Average (3)	·000582	·00110	Average (4)				
18B	56	111·0	98·7	·00214	·00263	·00008	1400	4%C	·0100	Bubbled
	46	117·0	119·0	·00222	·00313	·00007		1 ½%Si		every 15 mins.
	49	130·0	140·0	·00208	·00372	·00046				for 15 secs.
			Average (3)	·00215	(3) ·00313	·00020	Average (3)			
19	41	64·3	73·0	·00132	·00200	·00000	1400	4%C	·0104	"
	44	122·0	78·8	·00159	·00218	·00011		3% Si		
	43·5	76·8	92·5	·00138	·00255	·00032				
	41·5	94·5	91·2	·00168	·00250	·00031				
	16	316·0	97·8	·00119	·00268	·00200				
			Average (2)	·00142(5)	·00234	·00049	Average (5)			

TABLE IV

Armco Iron.

Run	Increment time of SO_2 flow mins.	? $\frac{\%\text{Actual}}{\text{Theoretical}}$ Sulphur gained	Actual from metal analysis $\frac{d[S]}{dt}$ g/min.	Temp. °C	Charge metal	p_{SO_2} atm.	Nitrogen flow ml/min.	Remarks
5	18	11·2	·00021	1550	Armco	·0104	200	Metal partially covered by 48/52 silica/limeslag
	20	18·0	·00034					
	20	25·6	·00048					
		Average(3)	·00034					
22	56·5	109·0	·00276	1550	Armco	·0099	200	
	60·75	110·0	·00254			·0091		Difficulty with SO_2 venturi blocking
	43·25	116·0	·00254					
	30	131·0	·00300					
	30	108·5	·00277			·0102		
		Average (5)	·00270					
24	20·8	104·0	·0135	1550	Armco	·0302	340	
	29·9	88·4	·0113					
	43	52·1	·0065					
	28	37·3	·0047					
		Average (4)	·0085					

should never be above 100 per cent but in several cases this has been exceeded, particularly in the amount of carbon oxidised.

This can be explained by the fact that air entered the furnace during the sampling of the metal and oxidising some of the carbon in the melt. As the weights of carbon lost (Appendix Table IIA) are very small a little air could change this efficiency appreciably, raising it above 100 per cent. Runs 1 - 14 were conducted with a fixed alumina inlet tube while from Run 15 onwards a sliding alumina tube was used in order to bubble the gas through the melt. This bubbling complicated matters as the flowmeters fluctuated wildly during this blowing time and it was difficult to obtain a constant sulphur dioxide flow. With blowing, an additional factor was the splashing of the metal out of the crucible on to the walls of the mullite protecting tube. This loss lessened the weight of metal in the crucible and thus raised the efficiency, η, as the weight of metal in the crucible for calculations was obtained from the charge weight minus the sample weights. Checks at the end of each run indicated that this loss was small (0 - 2g.) in the runs with blowing every 15 minutes. In Run 15 the gas was blown continuously into the metal causing the gauges to fluctuate, and the calculated efficiencies were all above 100 per cent. The total metal loss from the crucible was 13g. and correcting for this in the last period of time altered the efficiency from 210 to 138% for carbon, and from 167 to 110% for sulphur, as the estimated metal weight in the crucible for this last period of time was 38·0g.

while the actual weight was 25·0g. The fluctuating gauges and themetal loss from the crucible were the reasons for abandoning continuous bubbling. In all the other runs the metal loss was divided proportionally among the periods of time depending on the number of blows per period of time but in most cases the effect was almost negligible.

The rates of carbon drop, $-\frac{d[C]}{dt}$, and sulphur pick-up, $\frac{d[S]}{dt}$, were obtained from the actual metal analysis (Appendix) and are reported as grammes lost or gained per minute. The average values of the rates were obtained from the total sum of the losses or gains during the run divided by the total time of sulphur dioxide flow. Obviously erroneous results, those over 100% , were neglected in the calculation of these averages, the figures in parenthesis denoting the number of periods of time taken to arrive at the value. The average values are thus not the average of the rates of carbon loss or sulphur gain. In Runs 8 and 9, silicon in powdered form was added to the cold charge and from the erratic silicon analyses obtained it is obvious that thorough mixing of the silicon in the molten metal did not take place until late in the run. For this reason no rates of silicon removal are given for these runs only whether the silicon increased or decreased. In Runs 18B and 19, however, thorough mixing was accomplished by bubbling the gas through the melt every 15 minutes and the rates of decrease of silicon are reported. As the change in weight of the charge associated with the simultaneous removal of carbon and deposition of sulphur is very small (0·1g. max) the decrease in silicon content of the metal is due to oxidation of the silicon to silica and not to a dilution effect.

Fig. 6 shows the effect of various partial pressures of sulphur dioxide on the rate of carbon removal and sulphur absorption at 1400°C with a constant nitrogen flow of 200 ml/min. The points marked are the rate of carbon removal and the rate of sulphur absorption for each time increment of sulphur dioxide flow. Each run was carried out at a constant partial pressure of sulphur dioxide, and the run numbers are included in the figures for ease of reference. The theoretical efficiency of 100 per cent is given for comparison. It can be seen that the rates are approximately proportional to the partial pressure of sulphur dioxide in the gas but that the values are well below the maximum value. This is no doubt due to the sweeping away of the oxygen and sulphur gases by the nitrogen flow before they have an opportunity to react with the metal surface. Run 17 is plotted on this figure to show that bubbling of the nitrogen/sulphur dioxide gas mixture through the metal raises the rates to the theoretical value. This bubbling gives a more intimate contact between gas and metal as opposed to the stagnant layer of gas and metal as opposed to the stagnant layer of gas formed on the surface of the metal as the gas is blown on to the metal. It follows from this that the actual mechanics of the impingement of the gas on the metal are

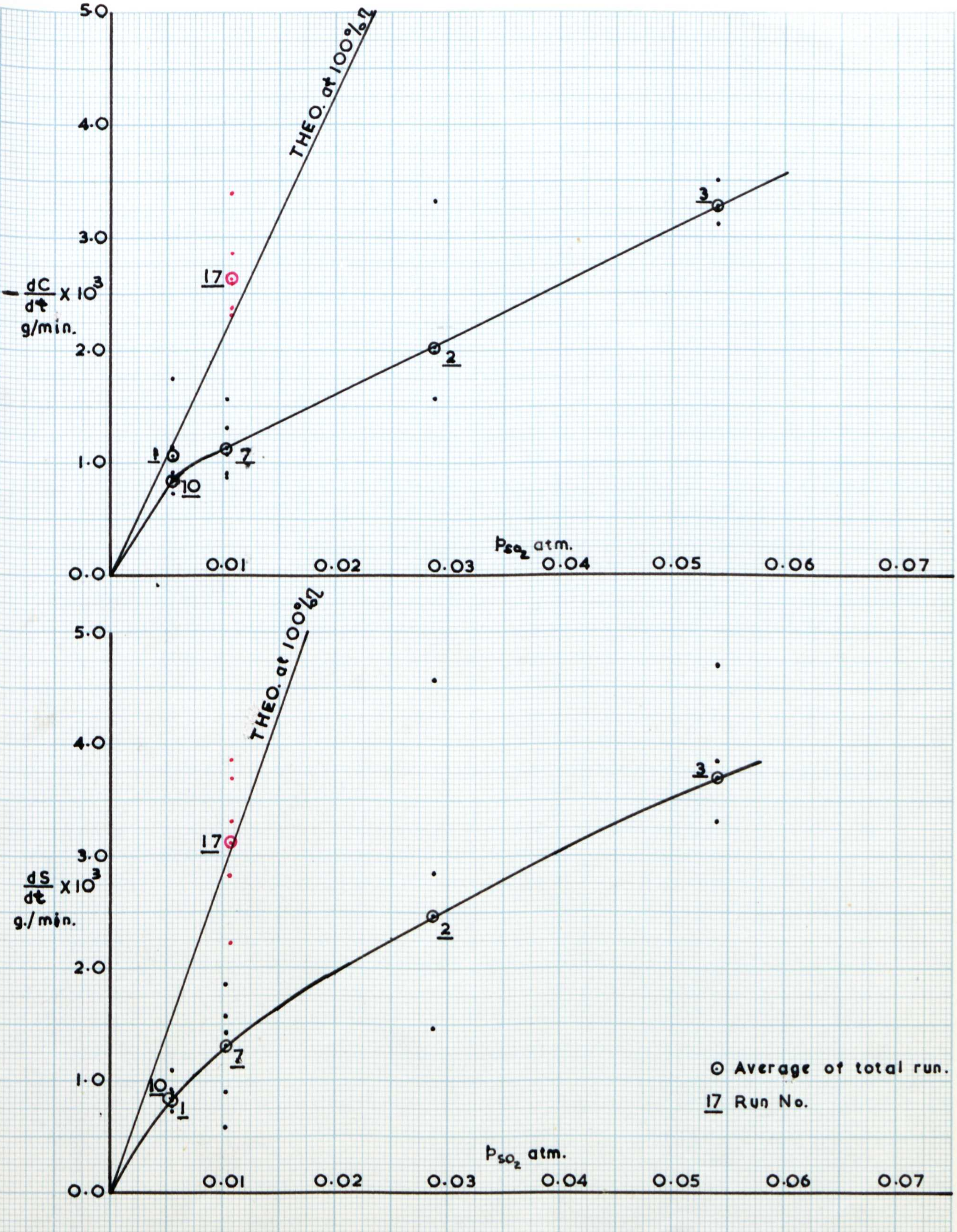

Fig. 6. EFFECT OF p_{SO_2} AT 200 ml/min. NITROGEN ON RATE OF CARBON REMOVAL AND SULPHUR ABSORPTION AT 1400°C.

important in these rate studies, and as far as was possible identical procedures were carried out in the experimental runs. The average values of each run are also plotted as circles, this being done throughout the gas-metal graphs.

The effect of temperature on the rates of carbon removal and sulphur absorption is shown in Fig.7, increase in temperature decreasing the sulphur rate and having little effect on the carbon rate. This reduction of pick-up of sulphur from an SO_2/H_2 atmosphere could be due to an increase in the activity of sulphur with increasing temperature. High temperature would be expected to raise the rate of carbon removal and although a tendency to raise it is noted the effect is very slight. The scatter of points in the carbon rate is much greater than in the sulphur rate, although all three runs were of the bubbled type.

There are two series of results plotted in Fig. 8, one series with the gas merely passed over the melt and the other with the bubbling technique. As also shown in Fig. 6 the bubbling technique raises both the rate of sulphur absorption and carbon removal; both series, however, show that increasing silicon lowers the rate of sulphur absorption while also lowering the rate of carbon removal. It is well known that silicon raises the activity of sulphur in molten iron-carbon alloys and it would be expected that increase in silicon would tend to lower the rate of pick-up of sulphur from a gaseous atmosphere containing sulphur.

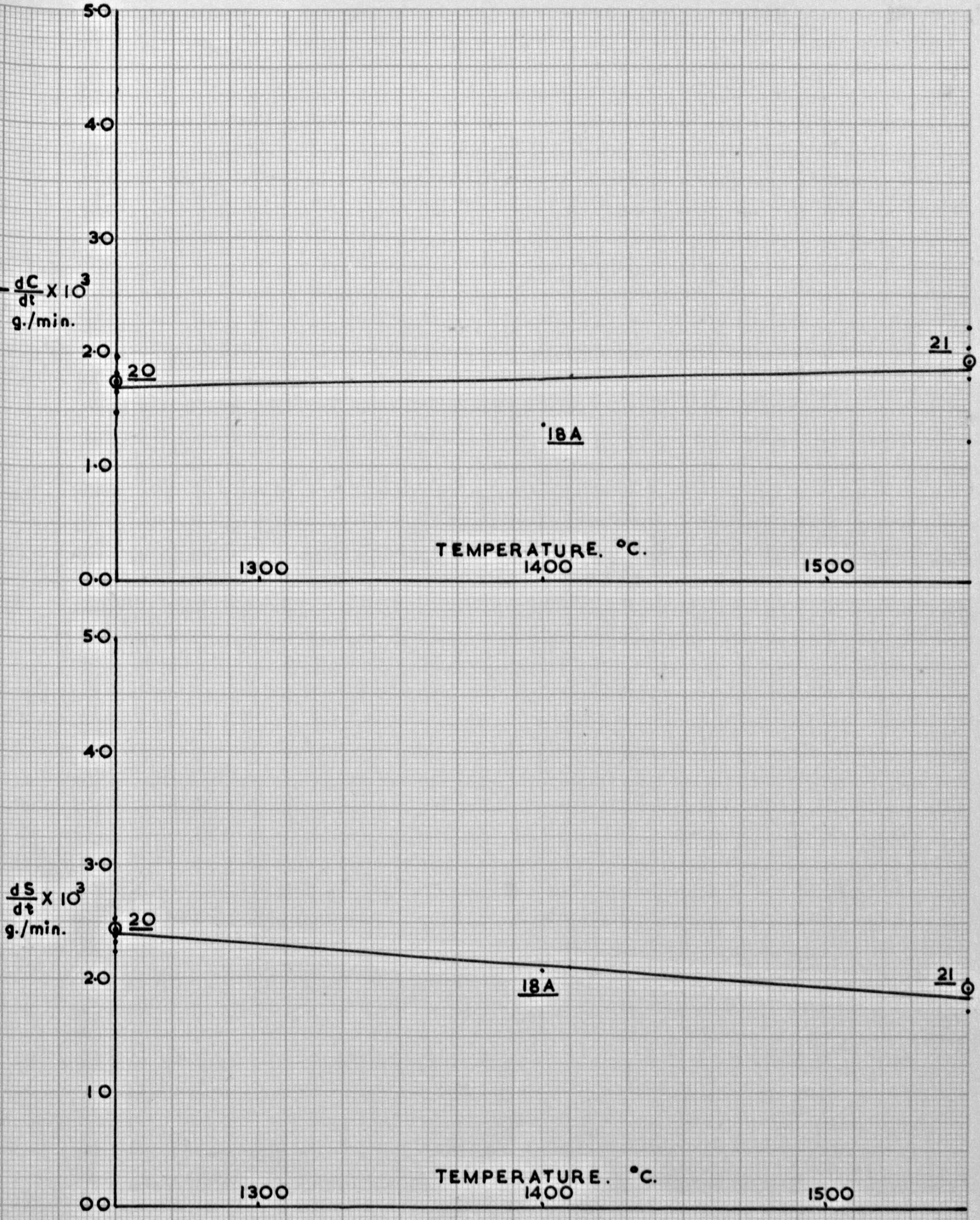

Fig. 7. EFFECT OF TEMPERATURE ON RATE OF CARBON REMOVAL AND SULPHUR ABSORPTION AT p_{SO_2} = 0·01 atm. NITROGEN FLOW = 200 ml./min. HIGH CARBON IRONS.

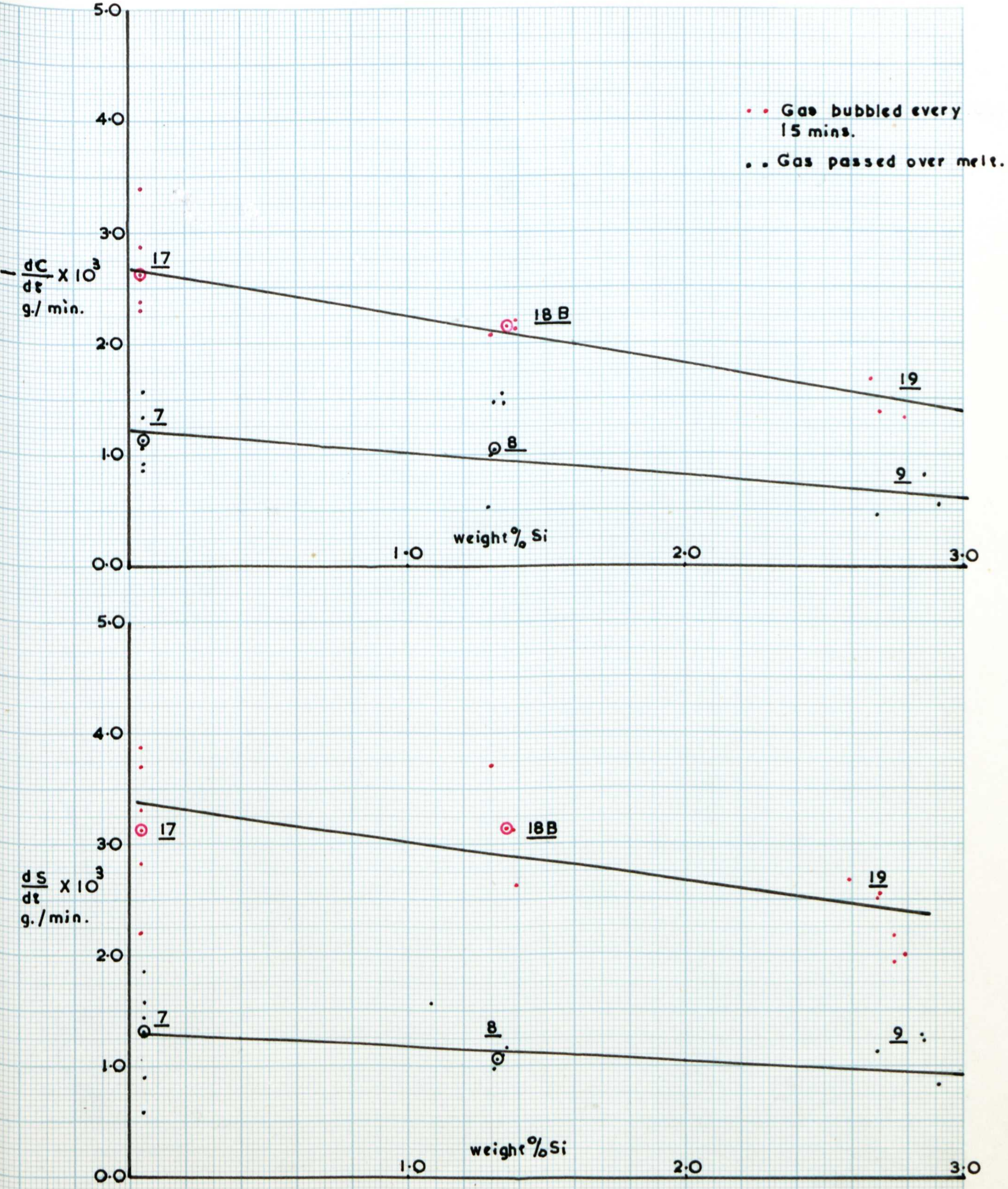

Fig.8. EFFECT OF SILICON ON RATE OF CARBON REMOVAL AND SULPHUR ABSORPTION AT 1400°C. NITROGEN FLOW = 200 ml./min. $p_{SO_2} = 0.01$ atm.

The change in the rates with silicon content is slightly greater in the case of the bubbled melts due no doubt to the mechanics of the process. In these iron-carbon and silicon runs the theoretical weight of carbon removed was calculated from the gas analysis by assuming that the gas reacted with the silicon first at 100% efficiency, any remaining oxygen then reacting with the carbon in the metal. No overall efficiency of carbon and silicon removal was calculated. It can be seen that the rate of carbon removal, $-\frac{d[C]}{dt}$, is much greater than the rate of silicon removal, $-\frac{d[Si]}{dt}$, in these experiments, but not enough experimental data is available to say more. The carbon contents of these runs were well below the amount of graphite which would be soluble in iron-carbon-silicon alloys as given by Turkdogan and Leake[80] although in Run 9 "kish" was observed on the surface after melting but this was thought to be due to inequalities in the silicon content of the molten metal. This "kish" was slow to disappear but did not interfere with the run as it was at the periphery of the crucible and the metal was exposed to the gas all the time. A little "kish" which disappeared before the first sample was taken, was also noticed on the metal surface in Run 19, probably for the same reason as above.

The effect of carbon content on the rate of sulphur deposition is shown in Fig. 9 at 1550° and 1400°C. No runs containing between 4 per cent carbon and Armco iron were attempted. The carbon contents plotted are the mean of the carbon contents at the beginning and end of an increment of sulphur dioxide flow.

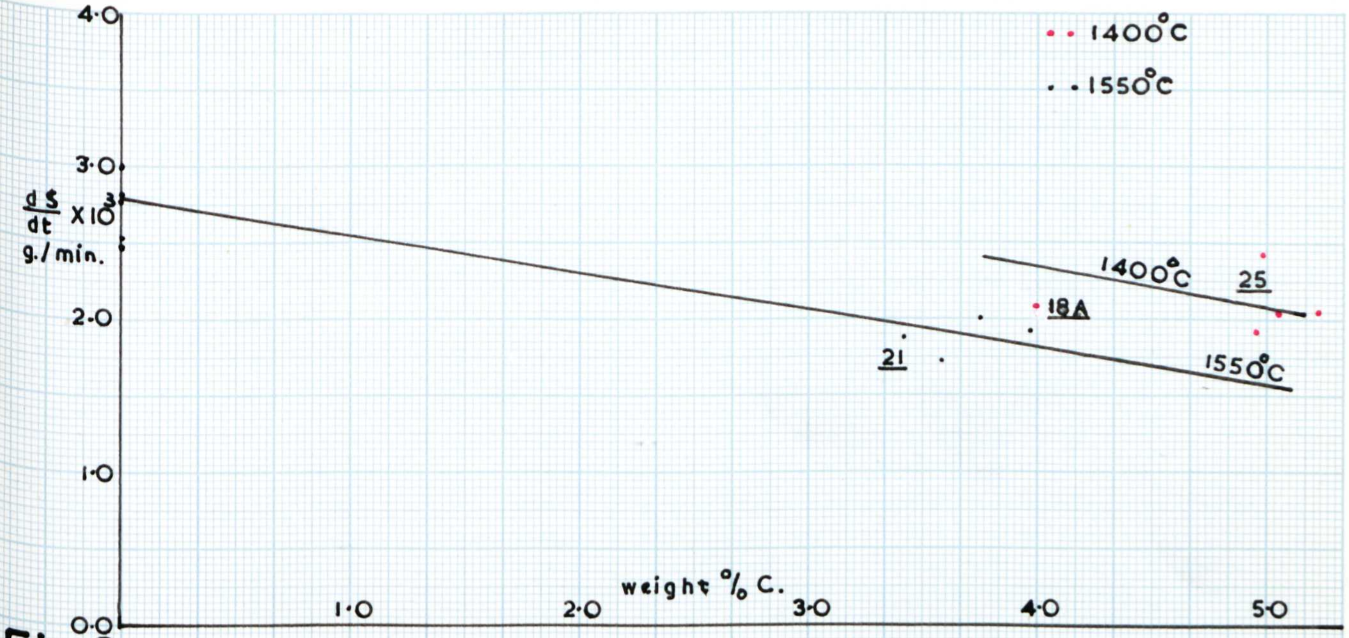

Fig. 9 EFFECT OF CARBON CONTENT OF METAL ON RATE OF SULPHUR ABSORPTION

p_{SO_2} = 0·01 atm. NITROGEN FLOW = 200 ml./min.

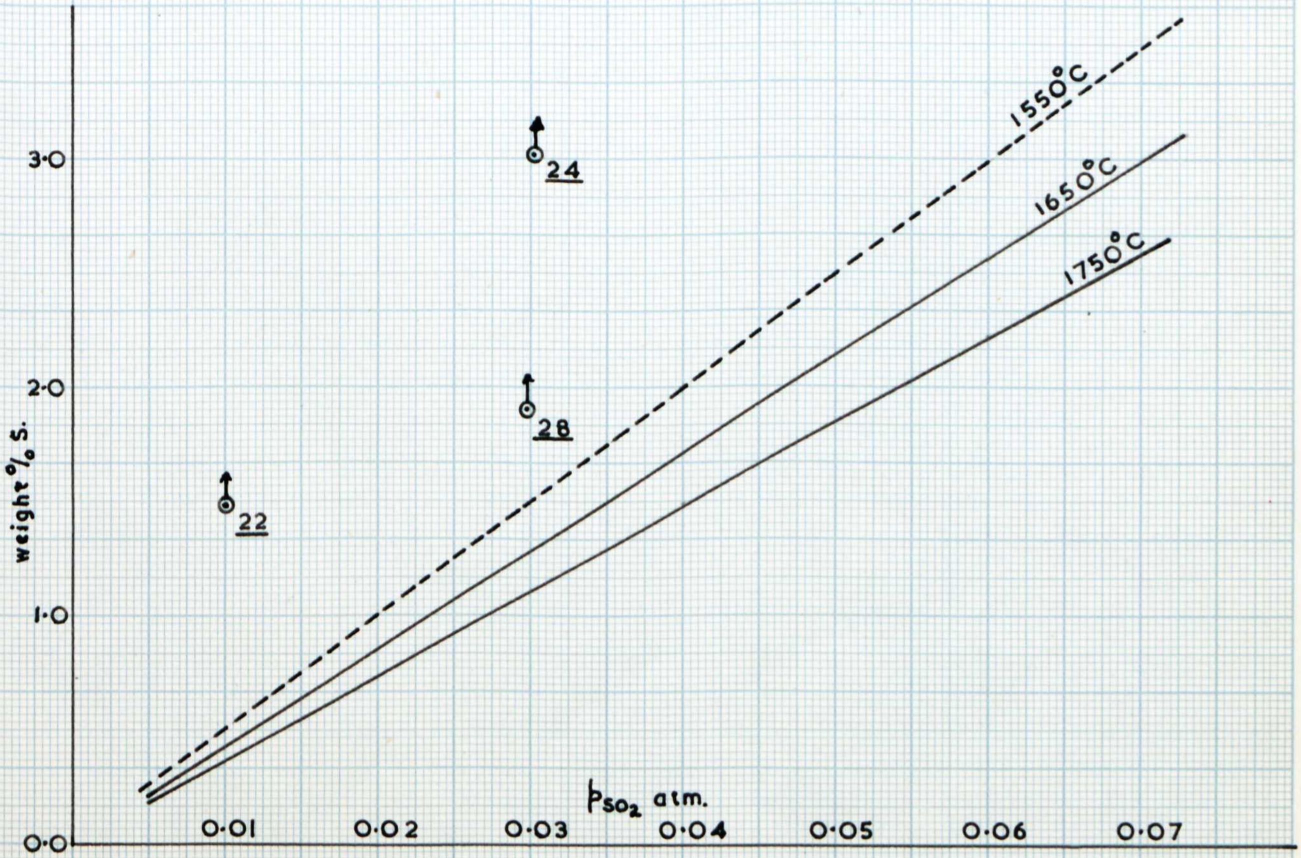

Fig 10. RELATIONSHIP BETWEEN FINAL SULPHUR CONTENT OF METAL AND p_{SO_2} OF SULPHUR DIOXIDE NITROGEN GAS MIXTURES (CARTER AND TAHIR[18])

Run 25 was conducted in a graphite crucible at 1400°C, hence the higher carbon content of the metal. An increase in carbon content lowers the rate of sulphur pick-up probably due to the increase in activity of sulphur with increasing carbon content. As already discussed raising the temperature lowers the rate of sulphur pick-up.

Previous work on the reactions between sulphur dioxide, nitrogen gas mixtures and molten Armco iron has been published by Carter and Tahir[18]. These workers obtained an "equilibrium" sulphur content in the metal depending on the partial pressure of sulphur dioxide above the melt as shown in Fig. 10. As the calculated equilibrium sulphur content of Chipman and Ta Li was twenty to thirty times that experimentally obtained, Carter and Tahir postulated that their constant sulphur contents were due to the rate of absorption of sulphur by the metal from the gas phase equallying the rate of absorption of sulphur from the metal by the slag phase. No such "equilibrium." sulphur contents were found in this investigation in Runs 22, 24, and 28. In these runs the charge metal was stock Armco iron, the experimental temperature 1550°C, and the experimental technique as in the 4%C runs. In Run 22 a separate oxide phase begun to be visible at 9•40, appearing in the form of a rim round the melt due to the convexity of the surface of the molten iron. Due to the small volume of this oxide phase, however, it could not be sampled. At no time during the run did this oxide phase cover the metal completely.

In Run 24 due to the greater concentration and rate of sulphur dioxide passing over the melt a separate oxide phase was observed one hour after commencement of the sulphur dioxide gas over the melt. Ninety minutes later this oxide phase had completely covered the melt and a sample was taken (Tables IX and VIIA). In Run 28 a separate iron oxide slag was added to the melt in order to saturate the molten iron with oxygen and so make conditions approximate to those of Carter and Tahir early in the run.

In all three runs commencing with Armco iron the sulphur content of the metal was still increasing at shut down, when the concentrations of sulphur in the metal were well above the constant values of Carter and Tahir as shown in Fig. 10.

The crucibles of Carter and Tahir were made from porous magnesia bricks which absorbed large quantities of slag. It is thought that the iron oxide slag was formed continuously, it picked up sulphur and was then absorbed by the crucible. Fresh iron oxide was formed and the process repeated. This is borne out by the fact that the distribution ratios of Carter and Tahir are all low, $\frac{(\%S)}{[\%S]} = 1{\cdot}6$ average and the slag never had time to come to near equilibrium with the metal. This constant removal of slag plus sulphur into the crucible walls always left the metal uncovered and also kept the metal sulphur fairly constant. In this investigation, however, little absorption of the slag occurred, the distribution ratio of 3·83 was near equilibrium and as the sulphur content of the slag rose so did the sulphur content of the metal and no equilibrium value was found.

In Run 2 it was noticeable that there was a very abrupt drop in the rate of pick-up of sulphur and loss of carbon. It was thought that as the carbon content of the melt had remained higher than normal at that sulphur content, the metal might have reached the composition where two liquid layers are formed in the iron-carbon-sulphur system. From the data of Turkdogan and Hancock[82] this appeared unlikely but no other explanation could be given. Two determinations were made in graphite crucibles to recheck the limits of the miscibility gap. The crucible was held at temperature for three hours with occasional mixing of the melt and then quenched into water. The two layers separated quite easily and analysis gave

	Top Layer		Bottom Layer	
1300°C	27·7%S,	< 0·02%C	2·20%S,	3·57%C
1500°C	26·8%S,	0·2%C	1·80%S,	4·10% C.

The sulphur analyses for the top layer are subject to error as the combustion method was used and it is doubtful if this method can be used successfully for such high sulphur contents. The results for the bottom metal layer are plotted on Fig.11, with those of Turkdogan and Hancock[82], Darken and Larsen[46], and Norrò and Lundquist[85]. The limit of the miscibility gap and its temperatures are from the work of Vogel and Ritzau[84]. The agreement between the various results is seen to be quite good except those of Norrö and Lundquist. The isothermals must be roughly parallel to the limit of the miscibility gap and it is obvious that at 4 per cent carbon the isothermals must be crowded very closely together, and that temperature has little effect on the composition of the carbon rich layer.

Turkdogan and Hancock[28] have also investigated the solubility of graphite in iron-sulphur-carbon alloys and although it was not the object of Runs 25 and 26 to determine the effect of sulphur on the graphite solubility in iron at 1400°C it can be obtained from these runs. As sulphur was added to the metal phase from the gas the graphite solubility decreased, Fig.12, the excess graphite over the solubility limit being thrown out of solution. The data from Run 25 is in excellent agreement with that of Turkdogan and Hancock. In Run 26 the partial pressure of sulphur dioxide was double that in Run 25 at the same nitrogen flow and thus the absorption of sulphur in Run 26 was proceeding at roughly double the rate than in Run25. Due to this faster pick-up of sulphur it is possible that the metal might be supersaturated with carbon because of the rate of precipitation of graphite being less than the rate of pick up of sulphur. This could explain the small discrepancies between Turkdogan's line and two of the experimental points in Run 26. The other point in this run lies on the line and from the position of this point and its neighbour from Run 25, it would seem that the inflection of the solubility line as given by Turkdogan might be too great, and should be slightly less, as shown by the dotted line in Fig. 12.

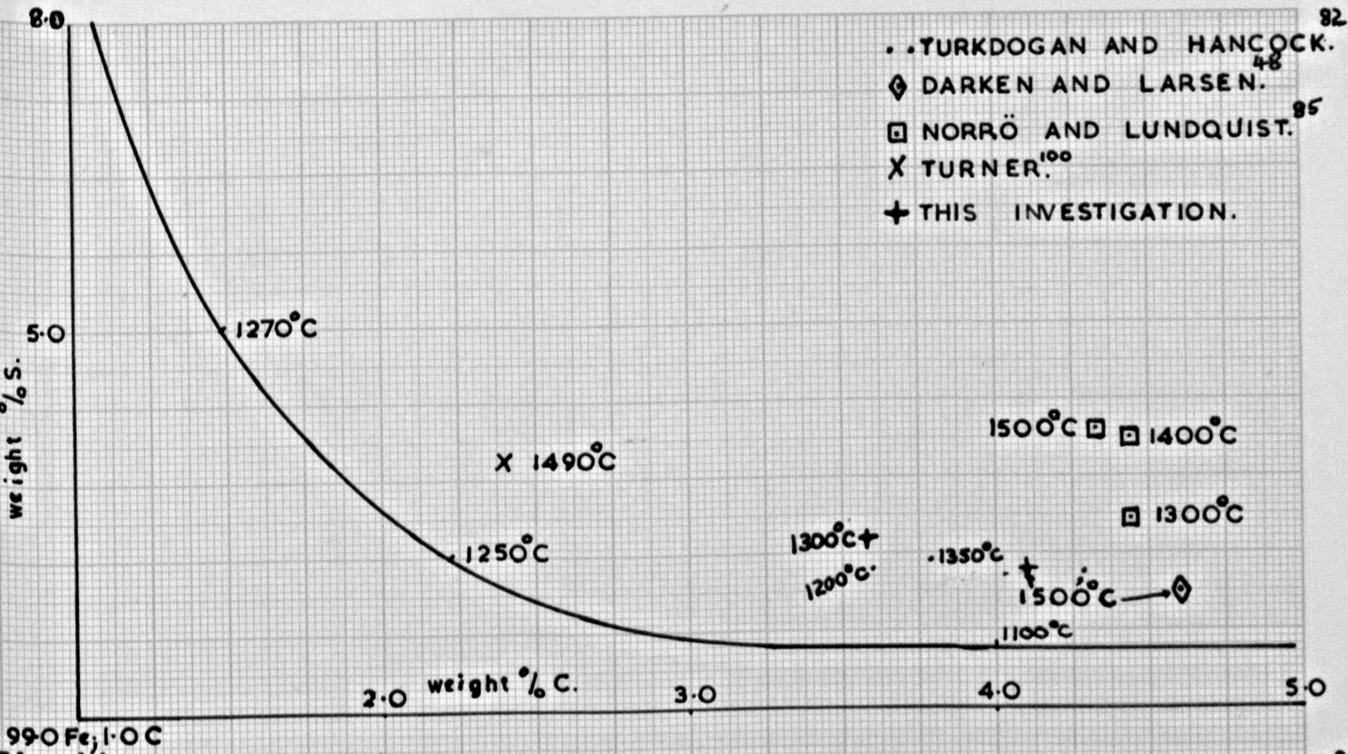

Fig.11. MISCIBILITY GAP IN IRON-CARBON-SULPHUR ALLOYS (VOGEL AND RITZAU[84])

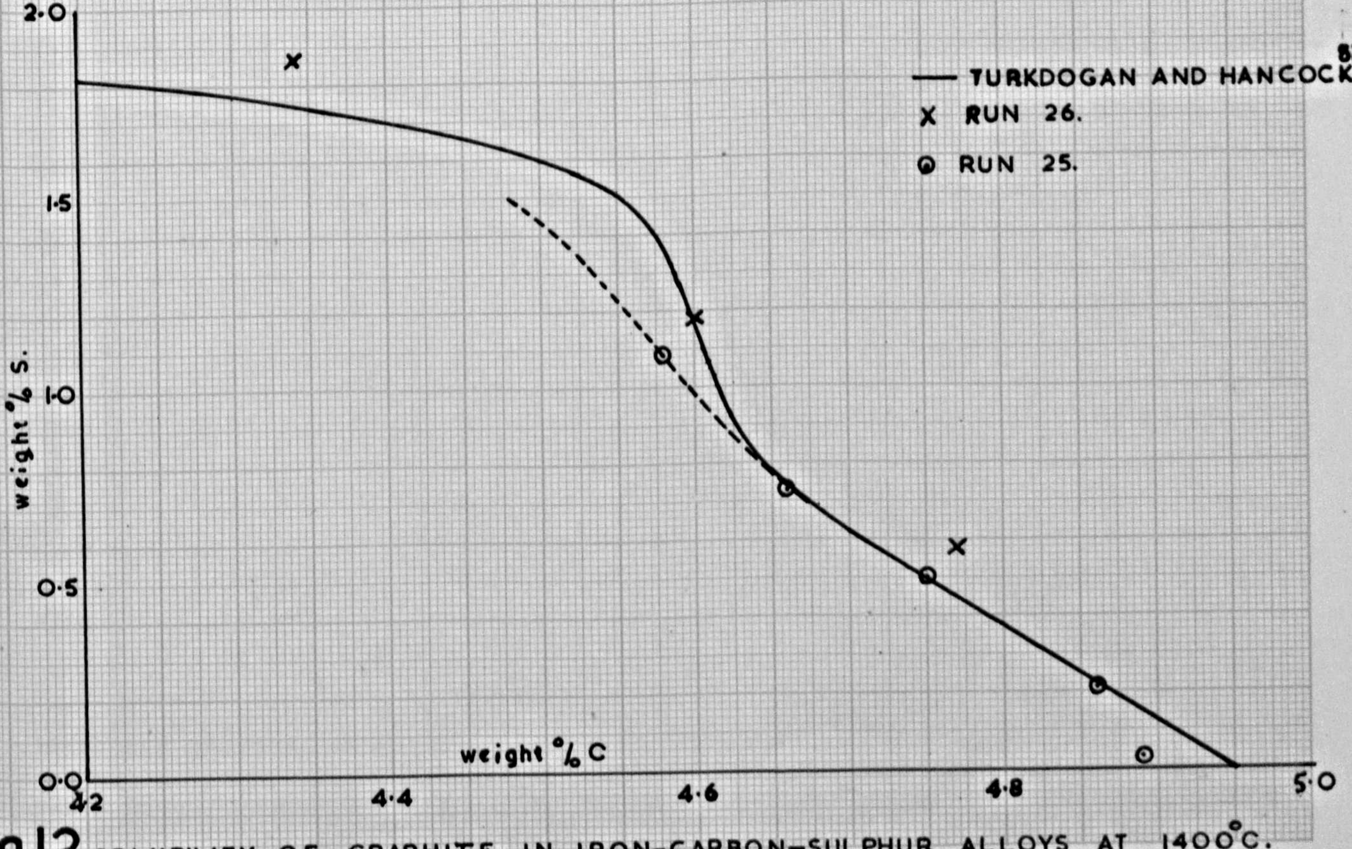

Fig.12. SOLUBILITY OF GRAPHITE IN IRON-CARBON-SULPHUR ALLOYS AT 1400°C.

In the early experiments with high carbon iron it was noticed that a carbon monoxide bubble was nucleated every twenty to thirty seconds, giving a good mix to the metal. However, in the runs with Armco iron it was obvious that as there was little or no carbon in the metal evolution of bubbles would not be available to help distribute the sulphur throughout the melt. The metal was at a temperature from top to bottom of ± 1°C and it was also unlikely that convection currents would play any part in mixing the metal. It was not known if the diffusion of sulphur was fast enough at 1550°C to even out the gradients in composition from top to bottom of the melt (3/4" deep). Experiments were carried out at 1550°C to determine not only if segregation took place but its extent.

A 1% sulphur dioxide-nitrogen gas was passed over molten Armco iron held in a magnesia crucible for two hours, then the crucible was cooled in the furnace under nitrogen. Quenching the crucible by drawing it down into the cold part of the furnace tube would have been more satisfactory but this was thought inadvisable due to the danger of cracking the mullite tube and consequent risk of a furnace burn out. Solidification was complete ten minutes after shut down with a rapid evolution of gas from the ingot a few seconds before final solidification. Theingot when sawn in two was blown at the top and analysis of the metal from three places gave

Distance from bottom of ingot	% Sulphur
0·78"	0·674
0·47"	0·171
0·16"	0.068

Saw cuttings made on halving the ingot analysed 0·384%S. From these figures it seemed that hardly any sulphur managed to diffuse to the bottom of the metal pool in two hours, as the original sulphur content of the iron was 0·04%. The sulphur segregation might have been due to the effect of solidification and to test this the ingot was remelted under nitrogen and stirred with a silica tube. The metal was cooled in the furnace as before and analysis of the half ingot showed a uniform sulphur content from top to bottom showing that no segregation had taken place.

No gas evolution was observed on cooling the metal in this experiment and so conditions were not quite the same as in the previous segregated run. A further experiment was carried out by passing a 1% sulphur dioxide-nitrogen gas over molten Armco iron and sampling the melt by two parallel silica tubes held together and connected at the top to a partially evacuated bulb by a T-piece. One tube was 3/4" longer than the other so that two samples could be drawn from the melt simultaneously but 3/4" apart vertically. By this method a sample from the bottom and top of the melt was drawn at the one time, the only mixing taking place when the sampling tubes were pushed into the melt. The samples were in the form of rods two inches long, 3/8" diameter, and the sample from the top of the melt was halved, the top half being the first metal to enter the silica tube, the bottom half of the sample being the last metal to enter the silica tube. The analyses of the samples were

Bottom of melt	0·178%S
Top of Melt (top half of sample)	0·264%S
Top of melt (bottom half of sample	0·189%S

The gas was passed for a further two hours and the melt cooled in the furnace under nitrogen. Gas evolution occurred as before and on halving the ingot segregation was again marked.

It was obvious from these experiments that,as expected, segregation was taking place in themelt, dueto the play of sulphur bearing gas on to the surface of the melt and the non-transfer of this sulphur at the surface to the interior of the melt. For this reason the experimental procedure had to be modified, and a sliding alumina tube replaced the fixed one, so that the gas could be bubbled into the melt to aid mixing.

An attempt was made to find if iron sulphide had any "floating" action in the melt, which could be a cause of segregation 60 g. of metal from previous segregation experiments (approx. 0·4%S) and 10 g. of Armco iron stock were melted, stirred vigorously and held at 1550°C in a platinum wound furnace for two hours, the metal then being quenched by lowering the crucible down the furnace tube. Solidification, with vigorous gas evolution, was complete in one minute. On halving the ingot the metal was very badly blown and a sulphur print showed two very distinct parts to the ingot. A layer 1/10" thick on the top of the ingot being high in sulphur (0·74%S), while the metal below was of uniform composition (0·29%S). The top layer was of a cindery appearance but could be drilled quite cleanly and it was thought to be an iron oxide slag. It is known from the work of Hilty and Crafts[78] that increase in sulphur above 2 per cent considerably increases the solubility of oxygen in molten iron. On diluting the sulphur content of the metal with the Armco iron stock, which is itself high in oxygen, an excess of oxygen must have been present which separated as a ferrous oxide slag phase. Sulphur partitioned into this slag phase from the metal, but the partition coefficient, $\frac{(\%S)}{[\%S]}$, = 2·6, was lower than normal.

2. Slag - metal

Owing to the lack of data on the distribution of sulphur between iron oxide slags and molten iron several experiments were carried out to determine the effect of silica and of temperature on the distribution coefficient.

All the experimental work was carried out in magnesia crucibles and the data is given in Table V, with the complete slag analyses in Table VA. There are various ways of reporting slag compositions when sulphur, ferrous iron and ferric iron occur together in slags. The ferric oxide can be reported as ferrous oxide on the basis of either its iron content or its oxygen content. Ferrous iron can be reported as being all ferrous oxide or divided between ferrous oxide and ferrous sulphide. The slag analysis in this investigation gave a closer approach to 100 per cent total when the sulphur was assumed to be present as ferrous sulphide, the remaining ferrous iron being reported as ferrous oxide. The analysed ferric oxide was converted to ferrous oxide on the iron basis, the total ferrous oxide being designated FeO_T. It was not always possible to analyse for magnesia due to insufficient weight of slag sample and the magnesia content by difference in the Tables is denoted by an asterisk. This method of slag designation is somewhat unsatisfactory, a better method would have been the atomic per cent of all the atom species present in the slag. This would have meant, however, a determination of the oxygen content of the slag which is a difficult analytical procedure especially in the

TABLE V - Distribution Coefficients of Iron Oxide Slags.

Run	Clock Time H.M.	Metal Sulphur wt.%	Metal sulphur activity $[a_S]$	Slag sulphur wt.%	$\frac{(\%S)}{[a_S]}$	(FeO_T) mol %	(SiO_2) mol %	(MgO) mol %	(FeS) mol %	Temp °C.
29	9·44	1·87	1·659	2·89	1·74	63·7	6·4	24·0∅	5·9	1550
30	9·35	2·60	2·201	3·93	1·79	67·5	11·0	13·1	8·4	1550
31	7·25	0·351	0·343	0·688	2·01	71·3	13·4	13·9∅	1·5	1550
	8·30	0·370	0·361	0·659	1·83	65·3	13·4	20·0	1·3	1550
32	7·15	0·372	0·363	0·495	1·36	57·2	18·1	23·6	1·0	1550
	8·44	0·396	0·386	0·426	1·10	55·8	18·3	25·0	0·9	1550
33	6·30	0·313	0·307	1·24	4·04	95·4	1·2	0·5∅	2·8	1550
	8·00	0·326	0·319	1·17	3·67	89·0	2·3	6·1	2·5	1550
	9·35	0·710	0·678	2·24	3·30	84·4	2·3	8·5	4·9	1550
34A	6·15	0·364	0·356	1·15	3·23	82·9	4·6	10·0∅	2·5	1550
	7·50	0·324	0·317	1·10	3·47	86·9	4·8	5·9	2·4	1550
	9·45	0·280	0·275	0·689	2·51	74·6	4·8	19·1	1·5	1550
39	4·49	0·328	0·321	1·155	3·60	86·8	0·9	9·8∅	2·5	1600
	5·50	0·427	0·415	0·909	2·19	68·4	7·4	22·4∅	1·8	1600
	6·25	0·443	0·431	0·867	2·01	66·8	8·5	23·0	1·7	1600
	7·30	0·513	0·496	1·37	2·76	78·4	3·6	15·1	2·9	1650
40	6·15	0·295	0·289	1·16	4·01	90·4	0·9	6·1∅	2·5	1600
	7·15	0·312	0·306	1·12	3·66	85·2	2·3	10·1	2·4	1600
	8·17	0·304	0·298	0·941	3·16	82·0	3·9	12·0	2·1	1600
	9·05	0·242	0·238	0·699	2·94	77·3	3·7	17·6	1·5	1650

∅ By difference

presence of sulphur.

In Table V the sulphur concentrations in the metal vary quite considerably, with a maximum of 2·6 weight per cent. Instead of the normal distribution coefficient, $\frac{(\%S)}{[\%S]}$, being used it was decided a better comparison of the distribution ratios could be made if the activity of sulphur in the metal was used in place of [%S] in the ratio. The conversion used was obtained from the work of Sherman, Elvander, and Chipman[10], who found that

$$\log f_s = -0{\cdot}0273[S]$$

where f_s = activity coefficient of sulphur in the binary iron-sulphur alloy

and [S] = percentage sulphur in the metal.

The activity of the sulphur is then obtained as $[a_s] = f_s \cdot [S]$, giving the new distribution coefficient $\frac{(S)}{[a_s]}$. An even better distribution coefficient would be obtained by using the activity of sulphur in the slag but no data were available for this.

The equilibrium distribution coefficient is plotted against mol % FeO_T in Fig.13. Equilibrium was approached mostly from the high slag sulphur side although a few points were obtained from the low slag sulphur side. It was impossible to obtain experimentally the distribution coefficient for a pure iron oxide slag held in a refractory crucible due to the dilution of the iron oxide by the crucible material, in this case magnesia. As well as pick-up of magnesia, silica was also fluxed from the crucible by the iron oxide slag. This silica was an impurity in the magnesia from which the crucibles were made and seems to occur as an

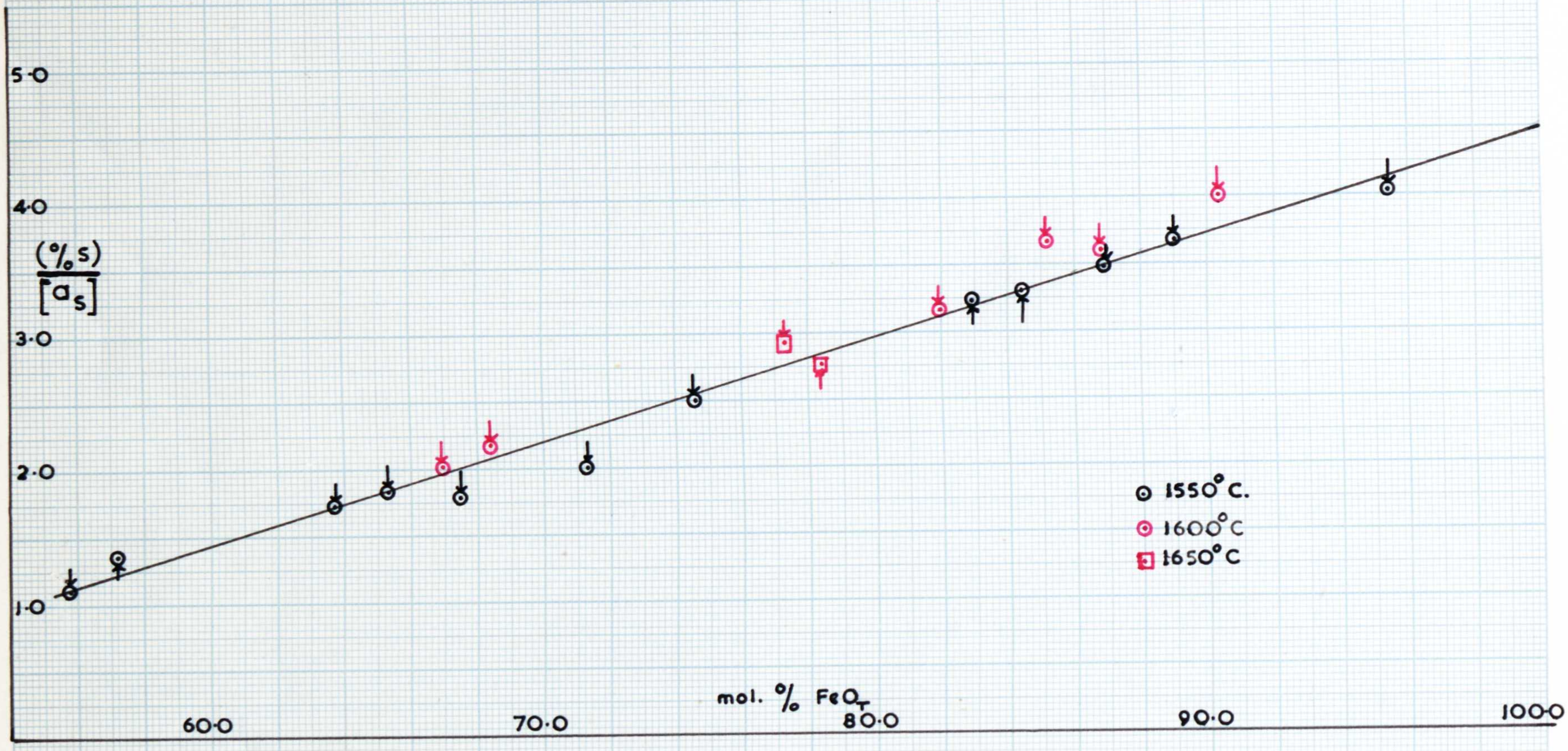

Fig13. EQUILIBRIUM DISTRIBUTION COEFFICIENT OF SULPHUR BETWEEN IRON OXIDE—SILICA SLAGS AND MOLTEN IRON.

intergranular material in the crucible wall and therefore is very easily absorbed by the reactive iron oxide slag. In this way the slag can pick up as much as 1·0 per cent silica. With the addition of silica to the iron oxide melt the solubility of magnesia in the slags increased very markedly and instead of a two component system of iron oxide and silica being studied as desired, a three component system of iron oxide, silica, and magnesia is encountered A further complexity is the formation of appreciable quantities of ferric oxide even in contact with molten iron. This ferric oxide was converted to ferrous oxide in the slag analysis, thus assuming that the desulphurizing power of both oxides was the same, which is not necessarily so. In work of this nature it is very necessary to make these arbitrary assumptions in order to simplify a complex multi-component system into a much simpler binary or ternary system.

Three temperatures, 1550°, 1600°, 1650°C, were used in this investigation. At 1600°C/and 1650°C low silica slags were used owing to the much greater solubility of magnesia at high temperatures, and the greater possibility of crucible failure. It is seen from Fig.13 that the distribution coefficient is proportional to the mol per cent FeO_T in the slag. The effect of temperature is not very marked with a possible slight increase in the distribution coefficient at higher temperatures. The relationship between the distribution coefficient and the mol per cent FeO_T from 1550° to 1650°C is given by

$$\frac{(\underline{\%S})}{[a_S]}_{(1550^\circ-1650^\circ C)} = 0{\cdot}078\ (\text{mol}\ \%\ FeO_T) - 3{\cdot}25$$

Only two similar investigations on the distribution coefficient of sulphur between iron oxide slags and liquid iron have been made, One by Bardenheuer and Geller[61] and the other by Fetters and Chipman[34]. These workers' slag data were recalculated in a similar manner to those in this investigation and their results between 1550°C and 1660°C are plotted against mol % FeO_T in Fig.14. Bradenheur and Geller found little or no ferric iron present in their melts while the ferric iron content of Fetters and Chipman was generally less than in this investigation. The reasons for these differences in ferric iron concentration are not clear as the Eighic iron contents in this investigation were similar from run to run.

The results of Bardenheuer and of Fetters can be seen to fall into two separate groups with the results of this investigation lying between them. No tendency is noted in either set of points for temperature to have any effect on the sulphur distribution ratio and the scatter of points in both investigations is very wide. However Bardenheuer and Geller managed to obtain a relationship for the temperature dependence of the sulphur distribution coefficient between pure iron oxide and molten iron, given by

$$L_{FeS} = \frac{2390}{T} - 0{\cdot}714 \quad \text{where} \quad L_{FeS} = \frac{(FeS)}{[FeS]}$$

The distribution coefficients from this equation at 1550°, 1600°, and 1650°C at 100 mol per cent FeO are shown in Fig.14, where they are

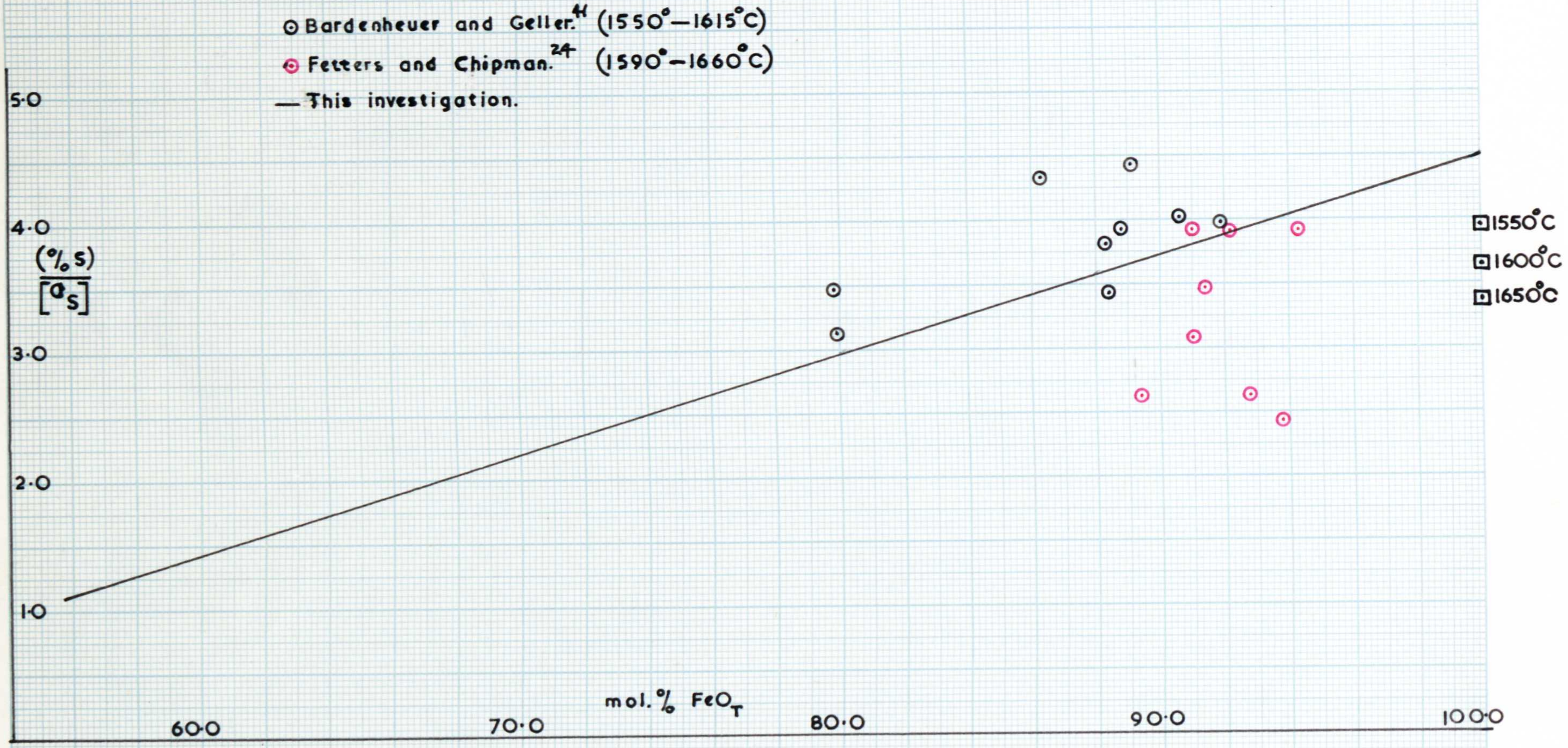

Fig.14. EQUILIBRIUM DISTRIBUTION COEFFICIENT OF SULPHUR BETWEEN IRON OXIDE–SILICA SLAGS AND MOLTEN IRON.

seem to lie well below the experimental line obtained in this investigation. It is obvious from the results of Bardenheuer and Geller that in the formation of their distribution coefficient equation the effect of magnesia and silica were neglected and the slag was considered as pure FeO. Owing to magnesia having a low molecular weight the mol percentage of magnesia can be quite appreciable. Fetters and Chipman unfortunately conducted their distribution coefficient experiments with very low slag sulphur contents (0·09%) and did not report their sulphur slag analyses to the third decimal place. This could partially account for the greater scatter of their points which lie at roughly the same mol percentage ferrous oxide.

Fig. 15 shows the effect of silica on the distribution coefficient of sulphur at constant magnesia percentages, while Fig.16 shows the effect of magnesia on the distribution coefficient at constant silica percentages. ~~on the distribution coefficient at constant silica percentages.~~ From these figures it can be seen that at constant silica mol percentage as magnesia displaces ferrous oxide from the slag the distribution ratio is lowered. Magnesia is therefore not such an efficient desulphurising agent as ferrous oxide in high ferrous oxide slags. Silica at constant magnesia mol percentage lowers the distribution ratio of sulphur, the effect of silica being slightly greater than the effect of magnesia on an equal mol per cent basis. This is

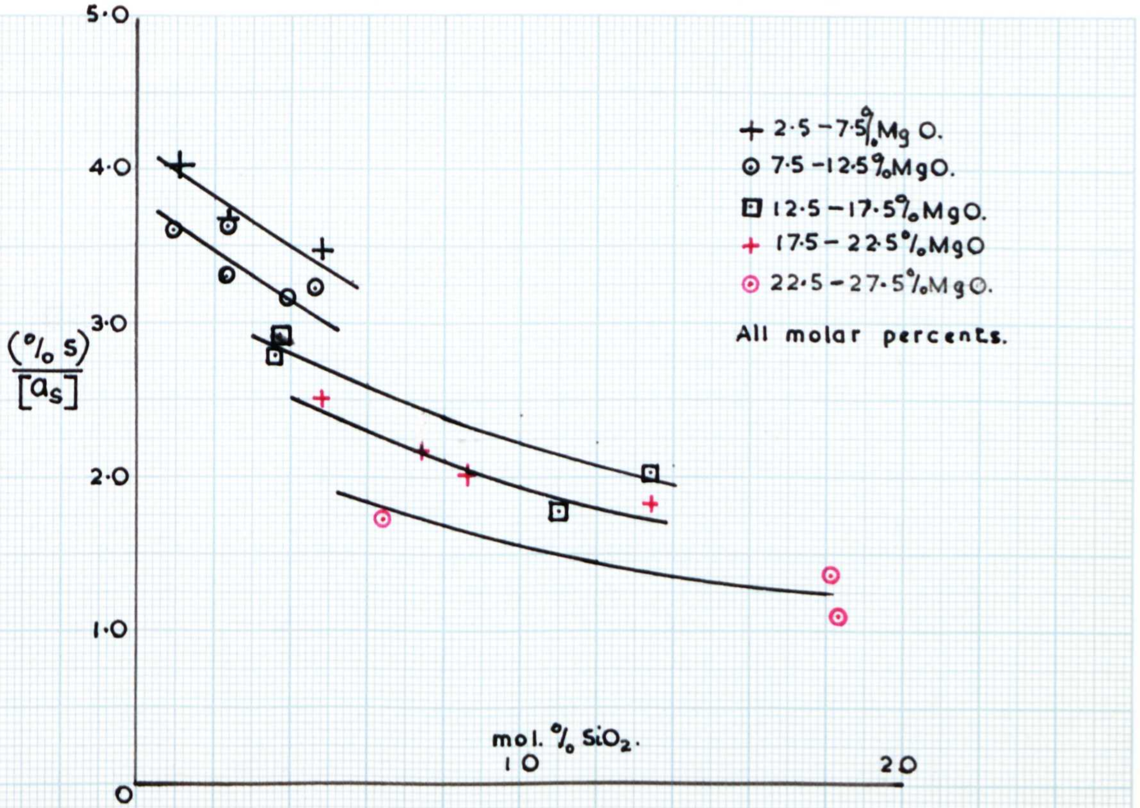

Fig.15. EFFECT OF SILICA ON THE DISTRIBUTION COEFFICIENT OF SULPHUR BETWEEN FeO_T–MgO–SiO_2 SLAGS AND MOLTEN IRON. 1550°–1650°C.

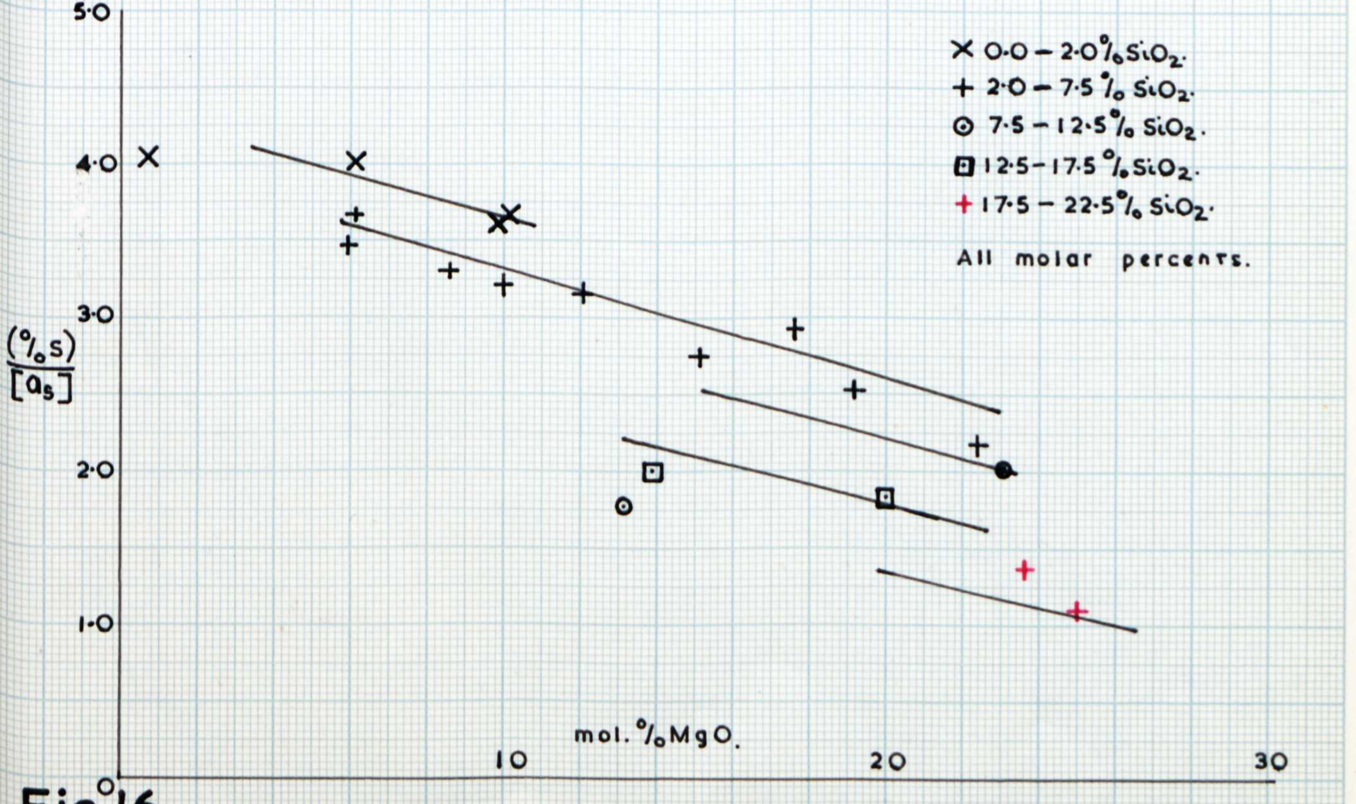

Fig.16. EFFECT OF MAGNESIA ON THE DISTRIBUTION COEFFICIENT OF SULPHUR BETWEEN FeO_T–MgO–SiO_2 SLAGS AND MOLTEN IRON. 1550°–1650°C.

rather surprising as magnesia is a basic oxide while silica is an acidic oxide and it would normally be expected that silica would lower the distribution coefficient much more than an equal molar amount of magnesia. The equivalence of magnesia and silica is also shown in Fig.13 where there is little variation from the standard line in any of the slags despite fairly wide variations in composition with respect to magnesia and silica. It is unfortunate that high magnesia, low silica ferrous oxide slags are not liquid below 1600°C and also that high silica ferrous oxide slags cannot be obtained without the necessary adjunct of high magnesia due to fluxing action of these slags.

3. Gas - Slag

A one per cent sulphur dioxide-nitrogen gas mixture was passed at 200 ml/minute over 8g. of molten iron oxide slag in a magnesia crucible until equilibrium was reached. Equilibrium was assumed to be attained when the rates of sulphur dioxide entry to and exit from, the furnace were equal. This state was normally reached in three hours and the equilibrium slag sample was taken one to two hours after reaching equilibrium but slag samples were also taken before equilibrium was reached. No silica was added to these slags in order to reduce the pick-up of magnesia from the crucible to a minimum. The slags were crushed carefully and analysed for ferrous iron, total iron, and hence ferric iron, silica, sulphur and magnesia. The analyses of the slags sampled in these runs are given in Table VI, which contains both equilibrium and non-equilibrium slags.

At steelmaking temperatures sulphur dioxide dissociates very slightly into several gases, SO, S_2, S, O, SO_3 and O_2 being the important ones. St. Pierre and Chipman[34] have given the gas equilibrium composition at 1550°C resulting from a pure sulphur dioxide inlet gas, but not at any other temperature.

Larson and Chipman[33] have found the relationship between j of iron oxide-lime slags and the partial pressure of oxygen gas in equilibrium with these slags used 1550°C, where $j = \frac{Fe^{+++}}{Fe^{++} + Fe^{+++}}$ St. Pierre and Chipman used this data to find the oxygen pressure in their gas systems as they too were working ~~were working~~ at 1550°C.

TABLE VI - Pure Iron - Oxide Slags.

Run	Clock time h.m.	Slag Sulphur %	(FeS) wt.%	(SiO_2) wt.%	(FeO) wt.%	(Fe_2O_3) wt.%	(FeO_x) wt.%	(MgO) wt.%	$j=\frac{Fe^{+++}}{Fe^{++}+Fe^{+++}}$	Temp. °C	Remarks
35	6·49	2·48	6·8	0·8	78·3	12·2	89·3	1·9 Ø	·1157	1550	
	8·30	3·22	8·8	1·0	66·7	21·4	85·9	2·3	·2060	1550	Equilibrium
36	7·30	2·54	7·0	0·4	n.d.	n.d.	83·9	8·7 Ø Al_2O_3	-	1550	Alumina crucible
	8·21	2·70	7·4	0·4	n.d.	n.d.	83·8	8·4 Ø Al_2O_3	-	1550	used
37	5·27	6·65	18·3	0·5	75·8	5·5	80·7	0·0 Ø	·0517	1550	
	7·38	7·87	21·6	0·4	62·0	12·1	72·9	3·9	·1202	1550	
	8·40	8·69	23·9	0·8	58·0	12·0	68·8	5·3	·1222	1550	
38	10·15	3·42	9·4	0·9	62·8	22·3	82·8	4·6 Ø	·2217	1550	Equilibrium
41A	9·07	0·333	0·9	1·4	61·0	25·6	84·0	11·0	·2717	1620	Equilibrium
42	8·08	0·858	2·4	1·0	65·9	24·8	88·2	5·9 Ø	·2476	1605	Equilibrium
	8·20	0·780	2·2	1·0	65·7	23·8	87·2	7·4	·2412	1605	Equilibrium
	10·05	0·658	1·7	1·2	65·5	22·8	86·0	8·7	·2347	1650	from 8·30 crucible
	-	0·582	1·6	1·3	63·3	21·1	83·6	12·8	·2272	1650	slag

Ø By difference

In this investigation it was necessary to find the oxygen pressure in equilibrium with the slag from the actual oxygen potential of the slag, but as the temperatures used were up to 1620°C the data of Larson and Chipman was insufficient. However, Darken and Gurry[36] have also conducted researches into the oxygen pressures in equilibrium with iron oxide melts and their results are shown in Fig. 17 at various temperatures $\frac{N_2}{N_1}$ is their measure of slag oxygen potential and is the atomic ratio of oxygen to iron. St. Pierre and Chipman used the $j = \frac{Fe^{+++}}{Fe^{++} + Fe^{+++}}$ ratio as a measure of slag oxygen potential, the relationship between theetwo systems being given by $j = 2(\frac{N_2}{N_1} - 1)$. In Fig. 17 the results of Larson and Chipman at 1550°C are seen to agree closely with those of Darken and Gurry, especially at $\frac{N_2}{N_1} = 1{\cdot}1$, which is approximately the oxygen potential of the slags in this investigation. The 1650°C isotherm is approximate, as the highest temperature used by Darken and Gurry was 1635°C. The phase boundaries have been drawn in the figure purely as reference points for the oxygen potential of the slag.

Fig. 18 shows the change in partial pressure of sulphur with oxygen partial pressure in pure sulphur dioxide at 1550°C, 1600° and 1650°C, calculated as in Chapter IV. from the change in free energy equations for the various gases. As a result of the experimental method used in this investigation, magnesia and silica in appreciable quantities were picked up from the magnesia crucibles by all the slags. Larson and Chipman[33] found that magnesia and silica at a given oxygen potential in the gas raised and lowered respectively the j - ratio of the equilibrium slags. This is shown in Fig. 19 which has been calculated from the data of these

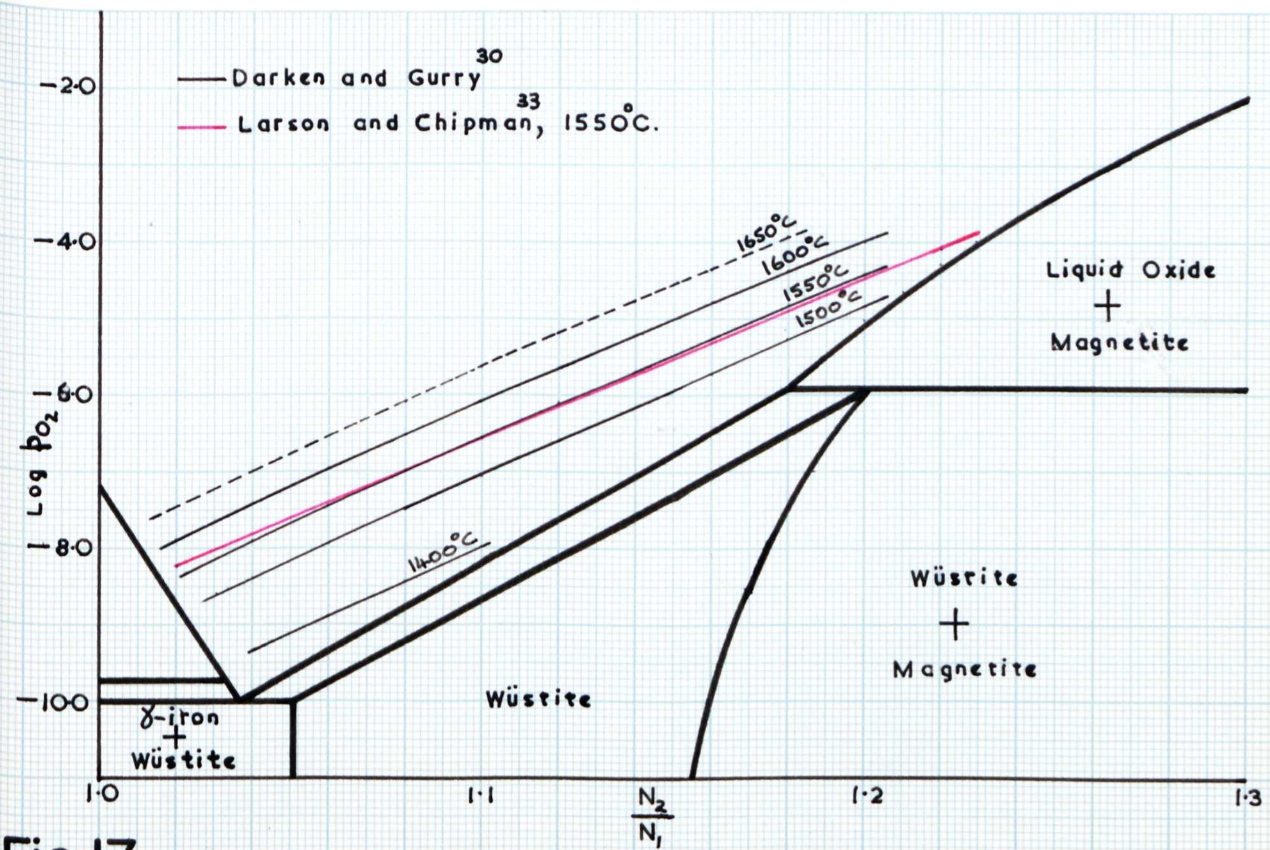

Fig. 17. THE PARTIAL PRESSURE OF OXYGEN IN IRON OXIDE MELTS AT EQUILIBRIUM.

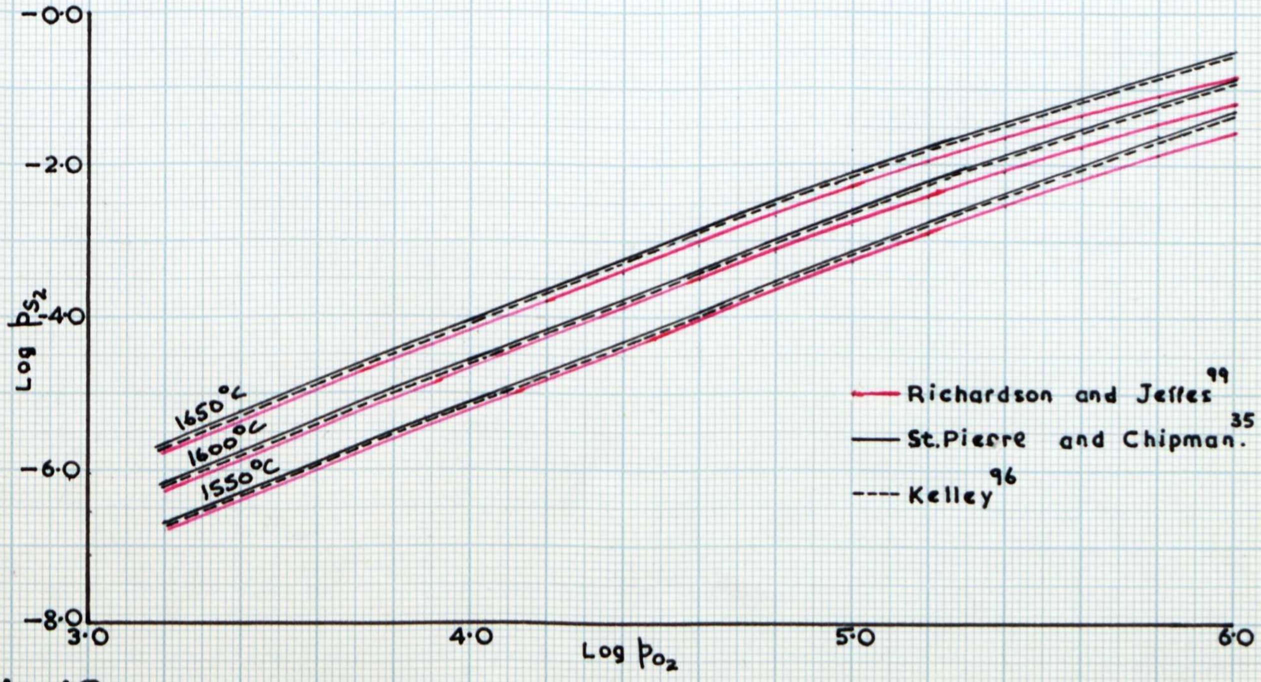

Fig. 18. PARTIAL PRESSURE OF SULPHUR GAS IN PURE SULPHUR DIOXIDE AT VARYING OXYGEN PRESSURES.

workers. The solubility of magnesia at 1550°C is 8·7 mol per cent hence the small difference in the j-ratio at constant oxygen pressure between 8 and 24 mol per cent magnesia. There seems no apparent cause for the inflections in the curves at j = ·4, a possible explanation being that the scatter of the experimental points is much more pronounced at higher oxygen pressures. The effect of silica was studied at only one oxygen pressure and it has been assumed in the figure that the silica lines lie parallel to the pure FeO line. From Fig.19 it can be seen that silica, 8 per cent, and magnesia, 8 per cent, are roughly equivalent on a mol per cent basis in altering in opposite directions the j - ratio at a pO_2 of less than 1×10^{-8} atm. No experimental work was done above 1550°C by Larson and Chipman and it has been assumed in all the calculations that Fig. 19 is applicable to 1620°C. This assumption seems reasonable as in iron oxide/lime slags with a certain lime concentration and a constant oxygen gas pressure, temperature had no effect on the j-ratio.

The oxygen potential of the slags in this investigation can be obtained from the slag analysis by two methods. As it is assumed that ferrous sulphide exists in the slag, the oxygen potential of the slag obtained from the FeO and Fe_2O_3 concentration will be different from that obtained from the j-ratio. The two values will be quite close as in Run 41A due to its low slag sulphur concentration but quite far apart as in Run 35 due to its high slag sulphur concentration. This is shown in Fig.20, where the log of sulphide capacity, $C_s = \frac{(\%S).p^{\frac{1}{2}}_{O_2}}{p^{\frac{1}{2}}_{S_2}}$

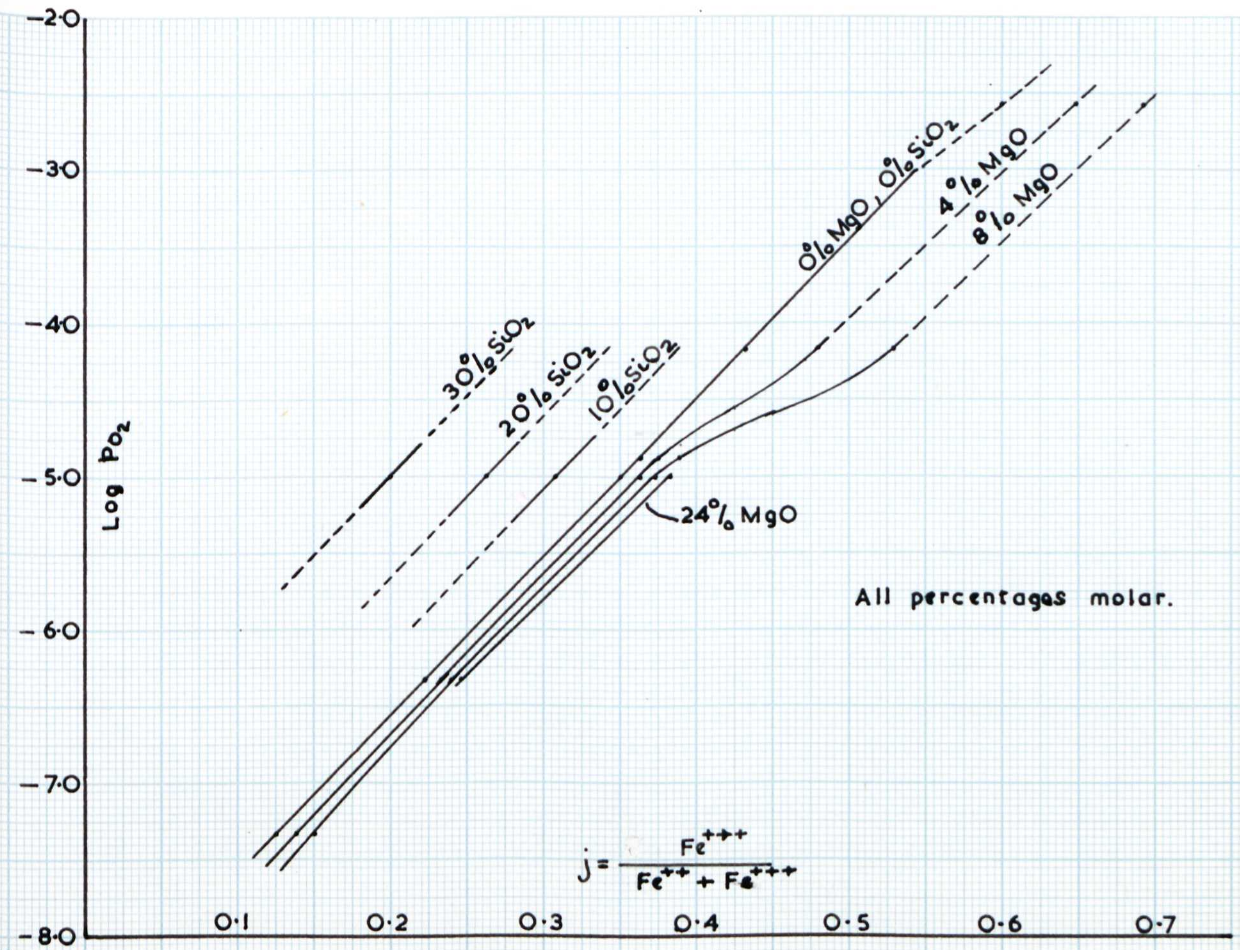

Fig.19. THE EFFECT OF SILICA AND MAGNESIA ON j AT VARYING OXYGEN PRESSURES 1550°C. (From the data of Larson and Chipman[33])

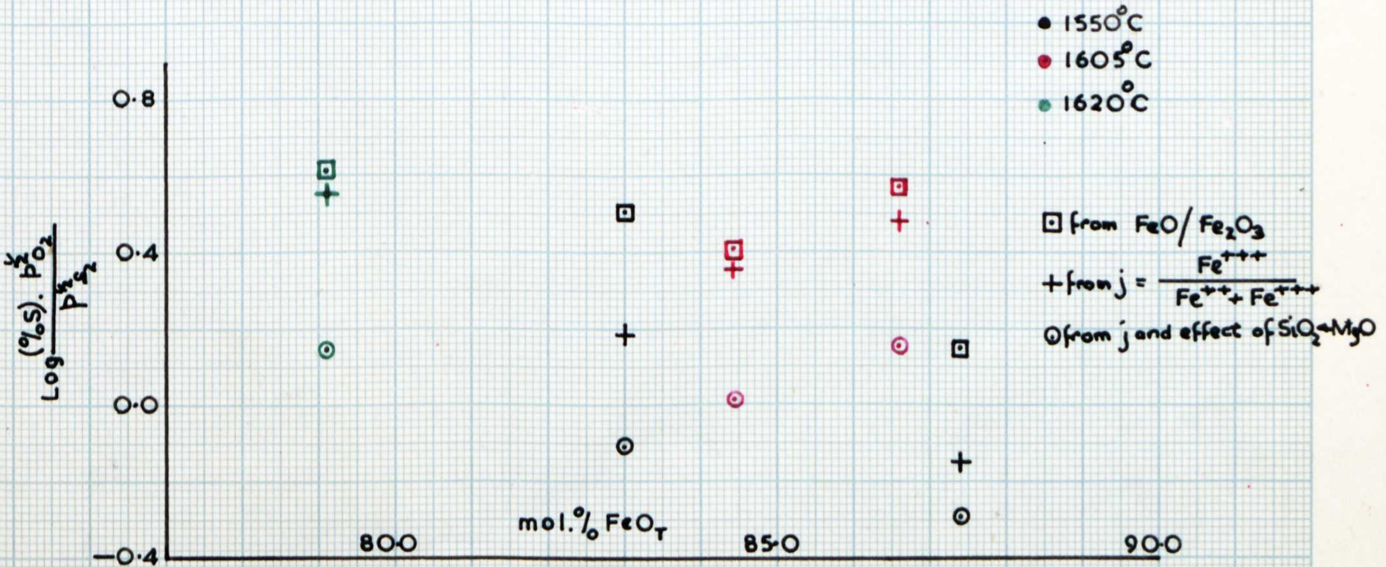

Fig.20. THE EFFECT OF OXYGEN POTENTIAL AND MAGNESIA-SILICA ON THE SULPHIDE CAPACITY OF IRON OXIDE SLAGS IN EQUILIBRIUM WITH SO_2-N_2 MIXTURES.

is shown against mol per cent FeO_T. It was decided to use the j-ratio as a measure of the oxygen potential of the slag, due to the relatively large differences in sulphur concentration among the equilibrium slags. The combindd effect of the magnesia and silica in altering this j-ratio and hence the sulphide capacity is also shown in Fig.20.

The calculations to find the sulphide capacity of the slags were carried out as follows. The j-ration from the slag analysis was corrected for the magnesia and silica content of the slag and then convertedtothe Darken and Gurry $\frac{N_3}{N_4}$ by the use of the formula. From Fig.17 the partial pressure of oxygen in equilibrium with this slag at the particular temperature was obtained. This was taken as the partial pressure of oxygen in equilibrium with the slag. The partial pressure of sulphur dioxide in the furnace was known from the gas analysis and the partial pressure of oxygen in the furnace was divided by this to give the equivalent oxygen pressure in pure sulphur dioxide. From Fig.18 using St. Pierre and Chipman's line the equivalent sulphur pressure at this equivalent oxygen pressure was found,and multiplied by the sulphur dioxide partial pressure to give the actual partial pressure of sulphur in equilibrium with the slag. The sulphur content of the slag was known and this with thepartial pressures of oxygen and sulphur gave the sulphide capacity. This sulphide capacity enables comparisons to be made of melts of various compositions at differing values of oxygen and sulphur pressure in the gas phase. The sulphide capacities obtained from the slags in equilibrium with the nitrogen sulphur dioxide gas mixtrues at various temperatures are given in Table VII and shown in Fig. 21. The Fe_3O_4 concentration in

TABLE VII

Iron oxide slags in equilibrium with sulphur dioxide.

Run	Clock time h.m.	(FeO_x) mol %	$j = \frac{Fe^{+++}}{Fe^{++} + Fe^{+++}}$	$pO_2 \times 10^7$ atm.	pSO_2 atm.	$pS_2 \times 10^7$ atm,	Slag sulphur wt.%	$\log_{10} C_s$	Temp. °C	Remarks
35	8·30	87·4	·2060	2·455	·0203	97·16	3·22	-·2909	1550	Nitrogen flow 200 ml/min.
38	10·15	83·0	·2217	2·961	·0191	57·80	3·42	-·1119	1550	
41A	9·07	79·1	·2717	38·55	·0197	2·180	0·333	·1461	1620	
42	8·08	86·6	·2476	17·86	·01945	6·500	0·858	·1532	1605	
	8·20	84·4	·2412	15·60	·01945	8·749	0·780	·0174	1605	

the slag has been converted to FeO on the iron basis to give FeO_T.

As there was no other data on high iron oxide slags in equilibrium with sulphur dioxide/nitrogen gas mixtures, it was decided to use the slag-metal experiments as a comparison of sulphide capacity.

As the oxygen concentrations in the metal samples have not been determined in this investigation they were calculated from the iron oxide activity of the slag using mol per cent FeO_T as the iron oxide concentration. The activity of FeO_T was obtained from the work of Taylor and Chipman[67] on $CaO-MgO-FeO-SiO_2$ slags. The solubility limit of oxygen in molten iron is given by[67,71]

$$\log [\%O]^{T}_{sat} = -\frac{6320}{T} + 2{\cdot}734$$

and hence the oxygen content of the metal sample is obtained from

$$[\%O]^{T}_{met.} = a_{FeO_T} \cdot [\%O]^{T}_{sat}$$

It was assumed that sulphur in themetal had no effect on the solubility of oxygen. The partial pressures of oxygen and sulphur was obtained from the oxygen and sulphur concentrations of the metal as shown in Chapter IV. No data is available on the effect of sulphur on the activity of oxygen and vice versa, although the data of Hilty and Crafts[70] shows that at the concentrations of sulphur used in this investigation, sulphur has little effect on the solubility of oxygen in molten iron. It has been assumed in the calculations that the activity of one solute is unaltered by the presence of the other solute in the ternary iron-sulphur-oxygen alloy. This is an assumption but the only one which can be made in the circumstances.

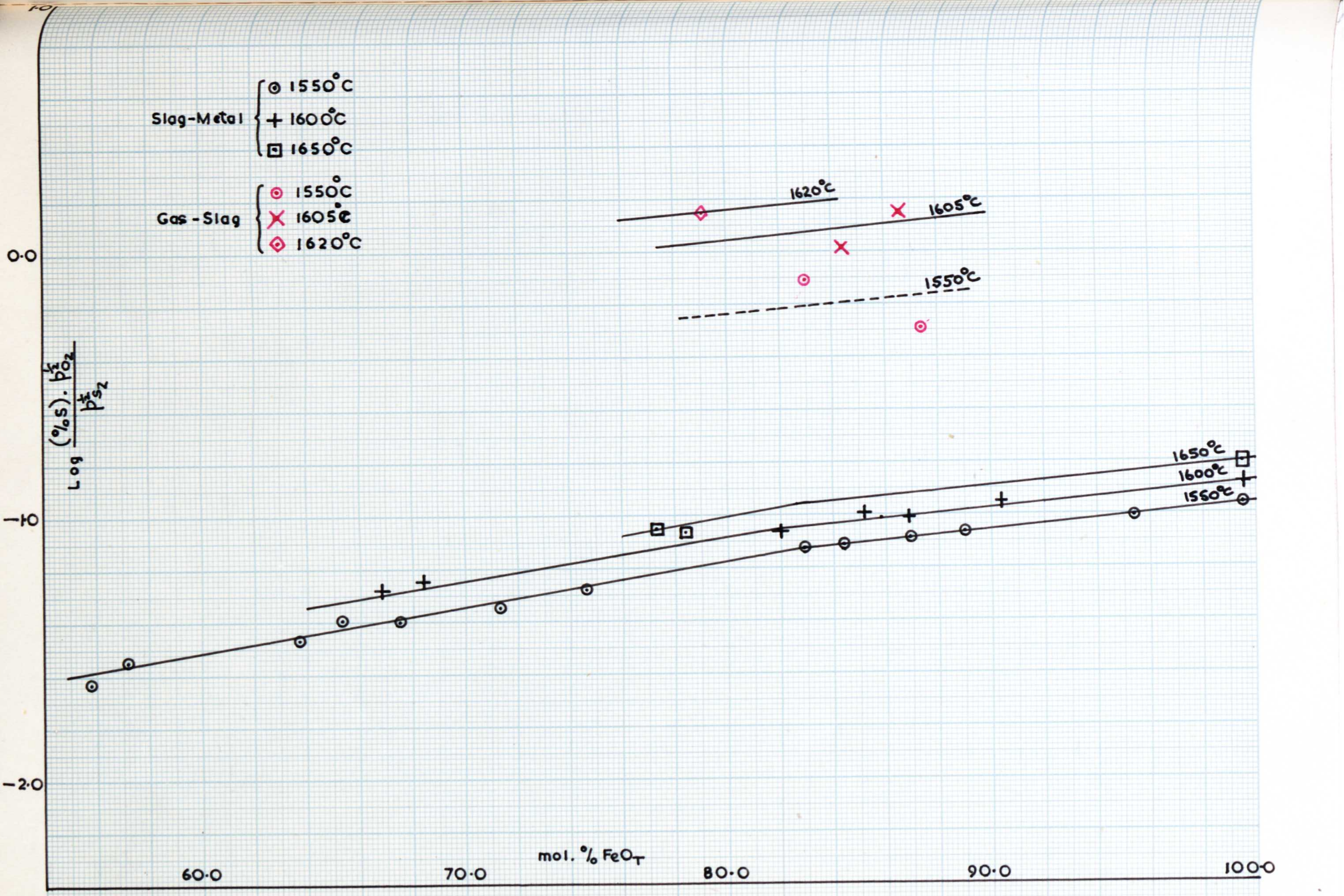

Fig. 21. SULPHIDE CAPACITY OF IRON OXIDE SLAGS FROM GAS-SLAG AND SLAG-METAL DATA AT EQUILIBRIUM

The sulphide capacities as calculated from the slag metal equilibrium data are given in Table VIII and shown in Fig.21. The values at 99·5 mol per cent FeO_T are calculated from the distribution coefficients of pure FeO_T assuming an activity of sulphur in the metal of 0·100. The data lie on three lines depending on temperature with very little scatter about each line. The sulphide capacity decreases with decreasing FeO_T, the rate of decrease becoming greater at lower FeO_T concentrations. On lowering the temperature the sulphide capacity is also lowered. The agreement between the sulphide capacities obtained from the gas-slag equilibria and from the slag-metal equilibria is very poor, the temperature effect being the only similarity.

The calculated sulphide capacities from the slag metal equilibrium data of Bardenheuer and Geller (41) and Fetters and Chipman[24] are given with the results of this investigation in Fig.22, and the agreement between the three sets of data is seen to be excellent. Fetters and Chipman analysed their metal samples for oxygen and this analysed oxygen concentration has been used in the calculations on their results. Because of the agreement between their results and the other slag metal results the oxygen contents of the metal samples as calculated from the slag analysis seem to be correct.

Chipman[27] has calculated from the iron-sulphur phase diagram that the activity coefficient of iron in sulphide, γ°_{FeS}, in dilute solution in iron is 7·5 at 1550°C. The sulphur distribution ratio of 4·55 obtained in this investigation for a pure FeO slag at 1550°C gives a value of 5·854 for $\frac{(N_{FeS})}{[N_{FeS}]}$. This value combined with γ°_{FeS} leads to the activity coefficient of iron sulphide in FeO as 1·28

TABLE VIII - Iron Oxide-Silica Slags in Equilibrium with Molten Iron

Run	Clock time h.m.	(FeO_T) activity	Metal Oxygen %	Metal Oxygen Activity	$p^{\frac{1}{2}}_{O_2}$ x 10^5 atm.	Metal sulphur activity	$p^{\frac{1}{2}}_{S_2}$ x 10^4 atm.	Slag sulphur %	$\log_{10} C_s$	(FeO_T) mol%	Temp. °C
29	9·44	0·80	·1482	·1387	4·662	1·6590	39·160	2·89	-1·4633	63·7	1550
30	9·35	0·91	·1686	·1568	5·271	2·201	51·96	3·93	-1·3993	67·5	1550
31	7·25	0·90	·1668	·1545	5·193	0·343	8·097	0·688	-1·3554	71·3	1550
	8·30	0·90	·1668	·1545	5·193	0·361	8·522	0·659	-1·3961	65·3	1550
32	7·15	0·85	·1575	·1468	4·934	0·363	8·569	0·495	-1·5452	57·2	1550
	8·44	0·85	·1575	·1468	4·934	0·386	9·112	0·426	-1·6370	55·8	1550
33	6·30	0·98	·1816	·1672	5·620	0·307	7·247	1·24	-1·0170	95·4	1550
	8·00	0·96	·1779	·1640	5·513	0·319	7·531	1·17	-1·0672	89·0	1550
	9·35	0·95	·1760	·1625	5·462	0·678	16·01	2·24	-1·1168	84·4	1550
34A	6·15	0·96	·1779	·1640	5·513	0·356	8·404	1·15	-1·1224	82·9	1550
	7·50	0·96	·1779	·1640	5·513	0·317	7·483	1·10	-1·0913	86·9	1550
	9·45	0·85	·1575	·1468	4·934	0·275	6·492	0·689	-1·2810	74·6	1550
39	4·49	0·90	·2061	·1878	7·751	0·321	9·321	1·155	-1·0175	86·8	1600
	5·50	0·87	·1992	·1820	7·511	0·415	12·05	0·909	-1·2467	68·4	1600
	6·25	0·88	·2015	·1838	7·586	0·431	12·515	0·867	-1·2794	66·8	1600
	7·30	0·89	·2494	·2222	11·14	0·496	17·58	1·37	-1·0613	78·4	1650
40	6·15	0·95	·2176	·1970	8·130	0·289	8·391	1·16	-0·9493	90·4	1600
	7·15	0·93	·2130	·1931	7·969	0·306	8·885	1·12	-0·9971	85·2	1600
	8·17	0·93	·2130	·1931	7·969	0·293	8·653	0·941	-1·0622	82·0	1600
	9·05	0·86	·2410	·2153	10·80	0·238	8·434	0·699	-1·0482	77·3	1650
Pure FeO	Calculated	1·00	·1853	·1702	5·721	0·100	1·183	0·223	-0·9673	99·5	1550
Pure FeO	from graph	1·00	·2290	·2060	8·502	0·100	1·455	0·223	-0·8851	99·5	1600
Pure FeO	assuming $[a_S] = 0·100$	1·00	·2802	·2462	12·35	0·100	1·775	0·223	-0·8091	99·5	1650

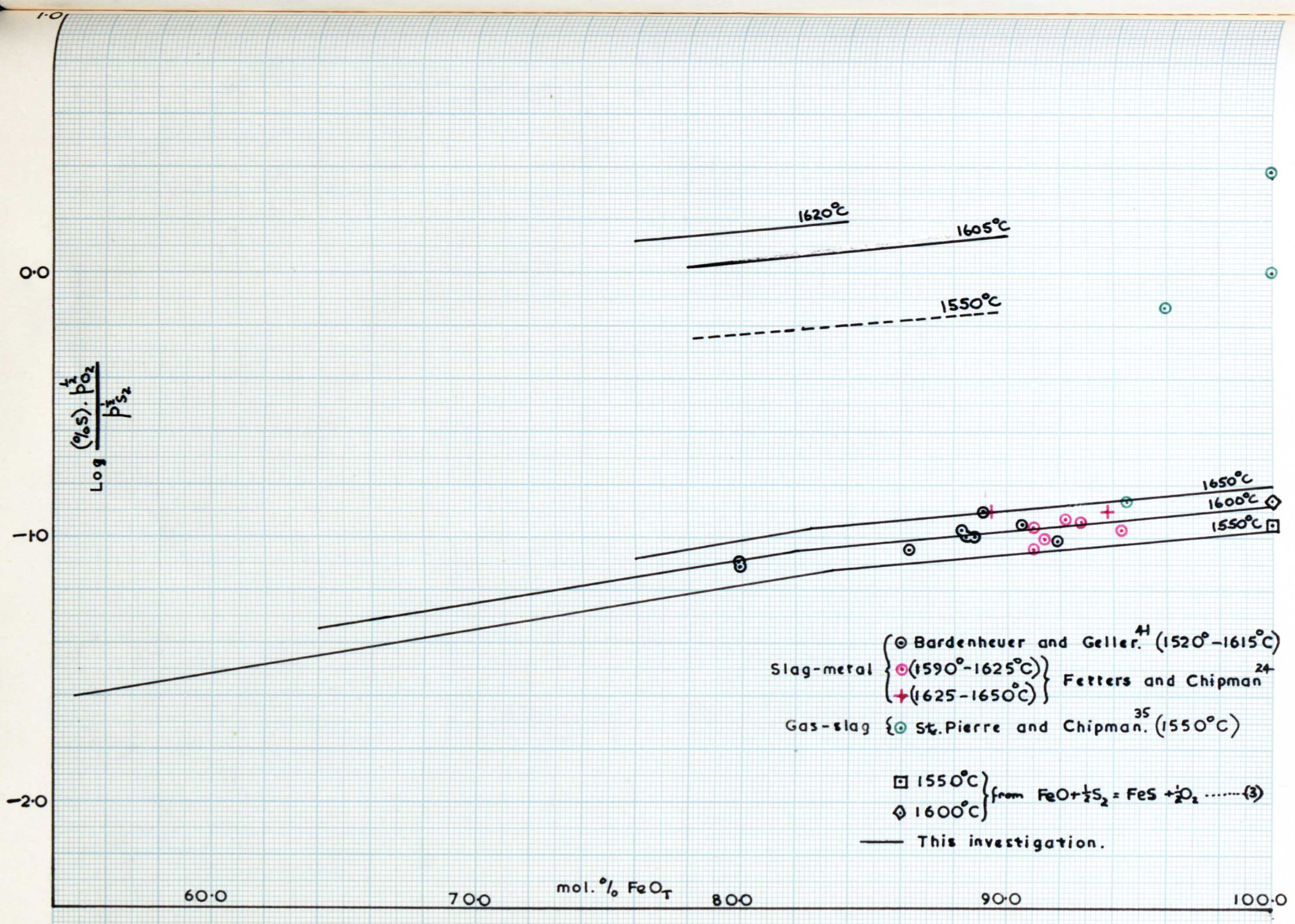

Fig. 22. SULPHIDE CAPACITY OF IRON OXIDE SILICA MAGNESIA SLAGS FROM VARIOUS DATA.

with Chipman's calculated value of 1·51 using the data of Bardenheuer and Geller. Considering the equation

$$\mathrm{FeO} + \tfrac{1}{2}\mathrm{S_2(g)} = \mathrm{FeS} + \tfrac{1}{2}\mathrm{O_2(g)} \quad \Delta G^\circ = 21{,}450 - 0{\cdot}62T$$

$$K = \frac{a_{FeS} \cdot p^{\frac{1}{2}}_{O_2}}{a_{FeO} \cdot p^{\frac{1}{2}}_{S_2}}$$

$$= \frac{\gamma_{FeS} \cdot N_{FeS} \cdot p^{\frac{1}{2}}_{O_2}}{1 \cdot p^{\frac{1}{2}}_{S_2}} \qquad \text{as } a_{FeO} = 1 \text{ in pure FeO}$$

$$= \frac{\gamma_{FeS} \times 0{\cdot}008169 \times 87{\cdot}92 \times (\%S) . p\, O_2}{32{\cdot}07 \times p\, S_2} \qquad \text{as } = {\cdot}008169(\%FeS) \text{ in FeO/FeS slag}$$

$$\frac{(\%S) . p^{\frac{1}{2}} O_2}{p^{\frac{1}{2}} S_2} = \frac{32{\cdot}07 . K}{\gamma_{FeS} \times {\cdot}008169 \times 87{\cdot}92}$$

K can be calculated at the appropriate temperature from the change in free energy equation. This final equation gives the sulphide capacity for pure FeO independently of slag-metal equilibrium data, and is seen to be in excellent agreement with the slag metal equilibrium data in Fig. 22. This is further evidence that the sulphide capacities of high iron oxide slags with silica and magnesia additions are accurately represented by the slag-metal data in Fig. 21. If this is so then the slag gas equilibrium data must be in error for some reason. The partial pressure of sulphur gas in sulphur dioxide gas mixtures at a constant oxygen pressure obtained from the data of either Kelley, or Richardson and Jeffes, Fig. 18, has a lower value than that obtained from the data of St. Pierre and Chipman. This lower value of sulphur pressure leads to an increase in log C_s, the maximum difference in log C_s being + 0·2 between St. Pierre and Chipmand and Richardson and Jeffes at the ~~the~~ one temperature. The choice of the data of St. Pierre and Chipman therefore leads to the closest agreement between the slag-metal and the slag-gas equilibrium experiments. The discrepancy does not lie in the thermodynamic data for the equilibrium gas compositions.

St. Pierre and Chipman equilibrated only four pure iron oxide slags with SO_2/CO gas mixtures at 1550°C and their results are shown in Fig. 22. The 100 mol per cent FeO_T was equilibrated with pure SO_2 gas, the 96 mol per cent FeO_T with SO_2/Co = 34·1 gas, and the 94·5 mol per cent FeO_T with SO_2/CO = 20·7 gas. The decrease in mol per cent FeO_T from 100 per cent is due entirely to the sulphur concentration in the slags. The slags equilibrated with pure SO_2 and SO_2/CO = 34·1 are in good agreement with the 1550°C gas-slag results of this investigation, whereas the SO_2/CO = 20·7 slag agrees better with the slag-metal investigation.

In the work of St. Pierre and Chipman the oxygen potential of the slag in the pure sulphur dioxide experiments was controlled by the oxygen formed by the breakdown of sulphur dioxide at high temperatures whereas in the SO_2/CO experiments the oxygen potential of the slag was controlled by the CO/CO_2 ratio of the gas. Due to this the ferric oxide concentration of the slags in equilibrium with pure sulphur dioxide were much higher (55%) than the slags in equilibrium with SO_2/CO mixtures (31%). St. Pierre and Chipman charged their slags with a ferric oxide concentration slightly below the expected equilibrium value in order to lessen the experimental time to come to equilibrium.

There are several possibilities as to why the sulphide capacity of the slags as measured by the slag metal runs is ten fold that measured by the slag metal runs. The main difference between the slags in the two sets of experiments is in the high ferric oxide concentration of the slags in equilibrium with the gas phase. The sulphide capacity as postulated from the reaction

$$(FeO) + \frac{1}{2}S_2(g) = (FeS) + \frac{1}{2}O_2(g)$$

involves the activity of FeO as

$$a_{FeO} \cdot C_S = \frac{(\%S)\, p^{\frac{1}{2}}_{O_2}}{p^{\frac{1}{2}}_{S_2}}$$

and it is a possibility that the activity coefficient of FeO in FeO-Fe_3O_4 melts varies. From the almost straight line relationship of pO_2 against $\frac{N_2}{N_1}$ in Fig. 17 at one temperature it seems that FeO and Fe_3O_4 form ideal solutions, or at most the activity coefficient of FeO in FeO-Fe_3O_4 melts departs very slightly from unity, but definitely not by a factor of ten.

The partial pressures of oxygen and sulphur in the equilibrium gas phase were obtained by different procedures for the two sets of experiments. The relevant thermodynamic data has been investigated independently by several workers and agreement between them, while no means perfect, is good and the slight discrepancies cannot account for the large difference in sulphide capacities.

No work has been published on the effect of ferric oxide on the activity coefficient of sulphur in iron oxide melts. In order to bring the slag-gas data into line with the slag metal data the ferric oxide in the slags would have to lower the activity coefficient of sulphur some ten-fold. This would have to happen over the small concentration range from 8 per cent Fe_2O_3 in the slags in equilibrium with the metal to 25 per cent Fe_2O_3 in the slags in equilibrium with the gas, and it is extremely unlikely that such a large change in activity coefficient would take place. As the ferric oxide contents of St. Pierre and Chipman's slags equilibrated with pure sulphur dioxide were of the order of 55 per cent Fe_2O_3, and their results agree quite closely with those of this investigation, this implies a constant activity coefficient of sulphur of approximately 0·1 between 25 per cent and 55 per cent Fe_2O_3, which is again unlikely. Furthermore from the increasing sulphur concentration of the slags with a low j-ratio it might be expected that increase in ferric oxide concentration would have the opposite effect and raise the activity coefficient of sulphur in these iron oxide melts. The affinity of sulphur for ferrous iron would also be expected to be greater than for ferric iron, this again raising the activity coefficient of sulphur on increasing the ferric oxide concentration in the slags.

None of the above explanations satisfactorily explains the difference between the two sets of experimental results, the remaining and most possible probability being that the slags were not in equilibrium with the gas phase. From Run 37 it was known that the sulphur concentration of the slag could rise far above the equilibrium value due to the low oxidation potential in the slag. In one experiment of St. Pierre and Chipman starting with a pure FeO slag, on approaching the equilibrium oxygen potential of the slag the sulphur content began to decrease to the equilibrium value. The reactions taking place can be postulated as oxidation of the slag,

$2\,Fe^{++} + \frac{1}{2}O_2(g) = 2Fe^{+++} + O^{=}$ ....(8)

with pick up of sulphur until the concentration of the ferric ions become appreciable and the reactions

$S'' + 2Fe^{+++} = \frac{1}{2}S_2 + 2Fe^{++}$ ....(9)

and $S'' + 6Fe^{+++} + 2O^{=} = SO_2 + 6\,Fe^{++}$ ....(10)

begin to take place. If these last reactions (9) and (10) are slow, sulphur will be removed slowly from the slag into the gas phase. The ferrous ions formed will be reoxidised to ferric ions as in (8) by the sulphur dioxide gas, the quantities involved in ten minutes being so small as to be unmeasureable by the gas analysis. Unfortunately in the experimental apparatus used it was not possible to find if elemental sulphur was issuing from the furnace in the exit gas, although zones of sulphur deposition were noted on the furnace tube walls at the end of each run. This means that while the oxidation potential of the slag was in equilibrium with the gas phase the sulphur content of the slag was not, higher concentrations of sulphur being present. This then would give both in the results of St. Pierre and Chipman and of this investigation higher sulphur capacities than at equilibrium.

The result of St. Pierre and Chipman which agrees closely with the slag-metal data of this investigation had a high sulphur concentration and the ferric iron and sulphur concentration of the charged slag may have been near the equilibrium value, both these facts making for an early approach to equilibrium with little increase in the sulphur content above the equilibrium value.

Run 36 was carried out in an alumina crucible in order to find the effect of alumina on the equilibrium sulphur content. Equilibrium had not been reached at 2·7 per cent sulphur and shortly afterwards the slag penetrated the crucible and the run had to be abandoned. It was found that alumina crucibles could only withstand iron oxide attack for the relatively short time of two hours before crucible failure occurred and for this reason no equilibrium results in alumina crucibles were obtained.

In an attempt to approach the equilibrium composition from the high sulphur side Run 37 was charged with an approximately 4 per cent sulphur/ferrous oxide slag and the gas mixture passed over the slag in an attempt to reach equilibrium. Slag samples taken at intervals showed that pick-up of sulphur was occurring with a simultaneous oxidation of the slag. At the beginning of the run when the slag oxidation potential was low, conditions were perfect for pick-up of sulphur hence the rise far above the equilibrium sulphur concentration. If the run had been continued the oxidation potential of the slag would have reached the equilibrium value whereupon the sulphur concentration of the slag would have decreased to the equilibrium value. The run, however, was shut down prematurely as it was carried out "blind" and it seemed at the time that equilibrium was not being attained. This working "blind" is a great drawback in this type of work as it is several days before the analysis of the slag is complete and then one realizes what should have been done at the time of the run.

This excess of sulphur above the final equilibrium value at low slag oxidation potentials seems to be a feature of this type of run as it was noticed several times on sampling the melt early in the heat that sulphur dioxide was evolved from the melt for some considerable time after the mix due to sampling. This evolved sulphur dioxide raised the sulphur dioxide concentration of the exit gas above the sulphur dioxide concentration of the inlet gas. This sulphur dioxide evolution was not due to air entering the reaction tube during sampling as dummy sampling attempts were made several times without disturbing the slag, after which no sulphur dioxide was evolved from the slag. Again sulphur dioxide was not evolved after the equilibrium slag samples were taken. It is thought that the surface layer of the iron oxide slag in contact with the gas becomes oxidised to the equilibrium value, diffusion of oxygen from this surface layer into the melt occurring much more slowly than the diffusion of sulphur. When sampling of this non-equilibrium slag takes place this oxidised layer is mixed into the main body of the slag, thereby raising the total oxidation potential of the slag. Because of this higher oxidation potential sulphur is given off from the slag, no doubt reacting with some of the oxide to form sulphur dioxide which appears in the exit gases. In the equilibrium slag, however, the oxygen potential of the slag was uniform throughout and mixing caused no difference to the sulphur concentration of the slag and hence no alteration in the sulphur dioxide content of the exit gas.

In Run 42 after attaining equilibrium the temperature was raised from 1605° to 1650°C and held at this temperature for 1.3/4 hours.

Equilibrium was not reached but it is noticeable that the slag sulphur fell from 2·2 to 1·7 per cent while the oxidation potential remained substantially constant. From this it seems that the transfer of sulphur from slag to gas is slow unless there is a simultaneous transfer of oxygen from gas to slag. This final slag at 10·05 was also cooled in the crucible and analysed. The magnesia content was higher possibly due to sampling of the magnesia rich solid solution on breaking up the crucible to obtain the slag sample. The oxygen potential and the sulphur concentration of the slag had decreased slightly due to the dilution effect of this higher magnesia content.

Fig.23 shows the effect of temperature on the experimental equilibrium constant of the reaction

$$(FeO_T) + \tfrac{1}{2}S_2(g) = (FeS) + \tfrac{1}{2}O_2(g) \qquad \ldots\ldots\ldots(3)$$

$$K_3 = \frac{(N_{FeS})\cdot p^{\frac{1}{2}}O_2}{(N_{FeO_T})\cdot p^{\frac{1}{2}}S_2}$$

where N_{FeS} and N_{FeO_T} are the mol fractions of iron sulphide and iron oxide respectively in the slag. It is assumed that the activity coefficients of iron sulphide and ferrous oxide in the slag are both equal to one. The variation in equilibrium constant calculated from the change in free energy equation is shown for comparison. The temperature effect on the equilibrium constant is similar in both cases but the experimental values are too great, the difference decreasing with decreasing temperature. This difference, as outlined, previously, could be due to too high a sulphur concentration in the slag.

An ionic reaction may also be considered for the absorption of sulphur by the slag such as

$$(O^{=}) + \tfrac{1}{2}S_2(g) = (S^{=}) + \tfrac{1}{2}O_2(g) \qquad \text{..........(11)}$$

$$K_{11} = \frac{(N_{S^{=}}).p^{\frac{1}{2}}_{O_2}}{(N_{O^{=}}).p^{\frac{1}{2}}_{S_2}}$$

where $N_{S^{=}}$ and $N_{O^{=}}$ are the anionic atom fractions of sulphur and oxygen reppectively in the slag. It is assumed that the activity coefficients of the oxygen and sulphur ions are both equal to one.

The change in free energy of reacion (11) has not been measured directly but may be obtained from the change in free energy for the reaction

$$O^{=} + \underline{S} = \underline{O} + S^{=} \qquad \Delta G^{\circ} = 18,000 - 9.25T$$

as given by Bishop, Grant and Chipman[74]. This change in free energy combined with the changes in free energy for the reactions, $\tfrac{1}{2}S_2(g) = \underline{S}$.[98], and $\tfrac{1}{2}O_2(g) = \underline{O}$[26] leads to the value for the change in free energy of equation ( ) of

$$\Delta G^{\circ} = 17,750 - 5.24T$$

The experimental points and the calculated theroetical equilibrium constants are shown in Fig. 24. The temperature effect is similar in both cases but the experimental values are too low, the difference decreasing with increasing temperature.

It is obvious that there is a great similarity between equations (3) and (11). but that the experimental determinations of the equilibrium constants for the reactions differ from the theoretical constant in opposite directions. ~~It has been fairly well established from the theoretical constant in opposite directions.~~ It has been fairly well established from the slag-metal data that the change in free energy values for reaction (3) are correct. If the calculated

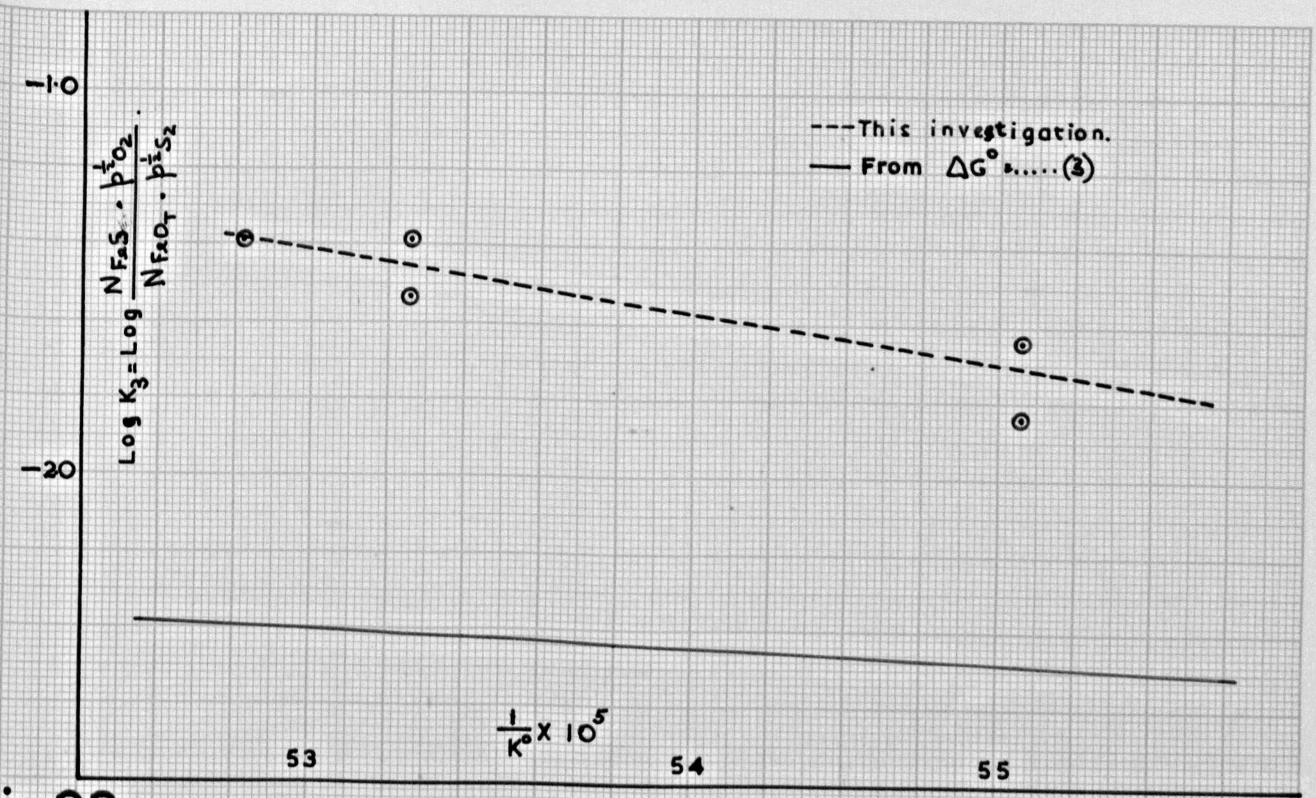

Fig 23. VARIATION OF K_3, THE EQUILIBRIUM CONSTANT FOR THE REACTION $FeO_T + \frac{1}{2}S_2 = FeS + \frac{1}{2}O_2$ ......(3) WITH TEMPERATURE.

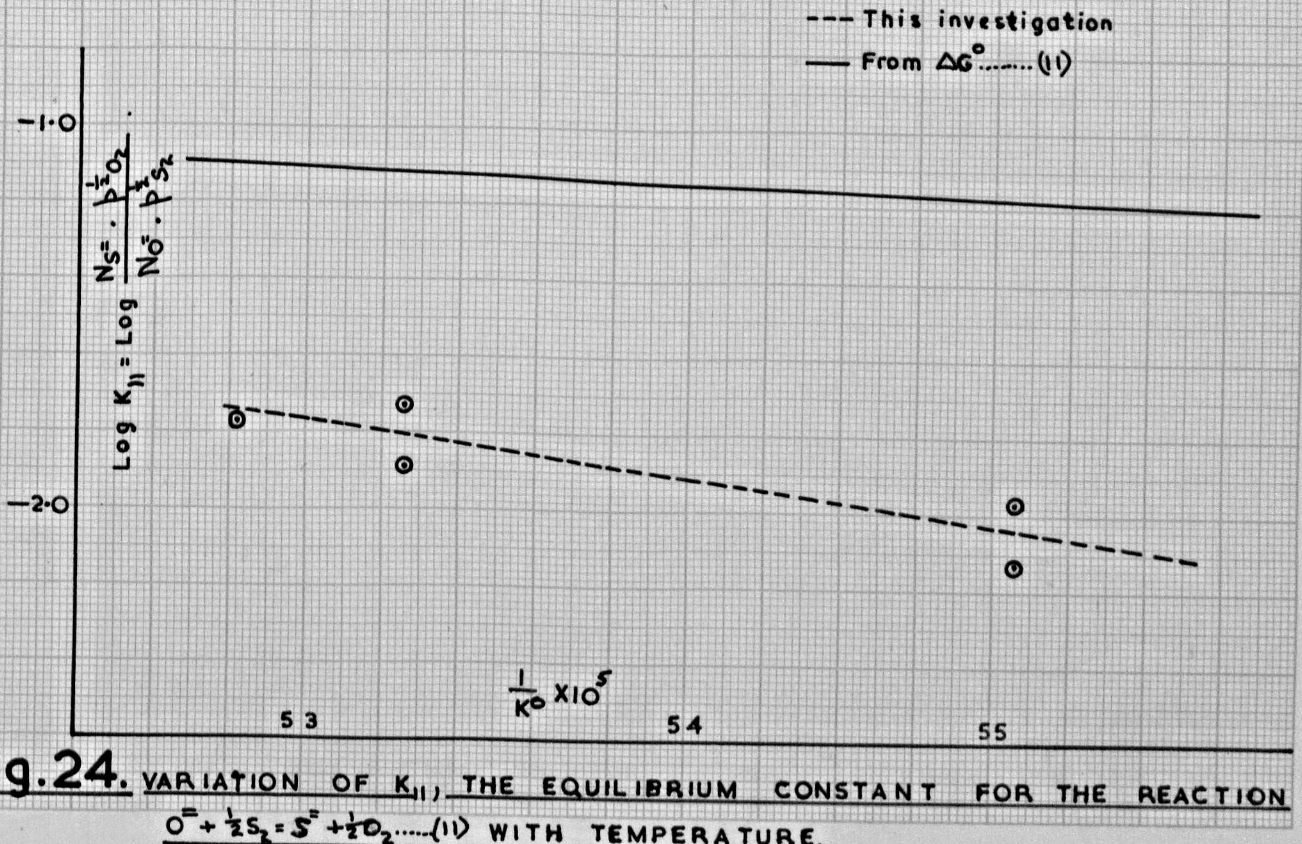

Fig.24. VARIATION OF K_{11}, THE EQUILIBRIUM CONSTANT FOR THE REACTION $O^{=} + \frac{1}{2}S_2 = S^{=} + \frac{1}{2}O_2$ .....(11) WITH TEMPERATURE.

value for the activity coefficient of ferrous sulphide[27] is used instead of unity this will increase the difference between the experimental and theoretical equilibrium constants.

If the experimental and theoretical equilibrium constants are accepted from Fig.23, then either the theoretical or experimental equilibrium constants, or both, are in error in Fig.24. The presence of sulphur may have an effect on the activity of oxygen and vice versa in these slags but this is unlikely to be great due to the small percentage of sulphur in these slags. The most likely explanation is that the change in free energy for reaction (11) as given by Bishop, Grant, and Chipman is in error.

4. Gas-slag-metal

Three experiments were carried out at 1550°C by passing a sulphur dioxide-nitrogen gas mixture over slag and metal held in magnesia crucibles. The slag and metal were given a bubble-mix every fifteen minutes for fifteen seconds. The charged slags consisted of iron oxide with additions of zero, ten, and twenty per cent silica so that the range of slags used in the equilibrium studies were covered adequately. The total rate of gas flow and partial pressure of sulphur dioxide were similar to those of Run 24, from which a slag and metal sample had been obtained. Run 28, with zero per cent silica was intended as a further comparison with the work of Carter and Tahir[16]. Samples of slag and metal were taken almost simultaneously at intervals of time, the normal analyses being carried out as before. The analyses of the slags and the sulphur concentration in the metal are given in Tables IX and VIIA.

It can be seen from Table IX that the sulphur concentrations in both slag and metal rose appreciably during each run, but the most remarkable change is in the silica concentration of the slag. In Runs 29 and 30 the silica percentage of the slag decreased during the run and in Run 30 reached half the charged value two hours after commencement of the run. This decrease could only have been caused by a dilution effect due partly to the pick-up of sulphur from the gas but mostly to the formation of an oxide slag phase at the expense of the metal.

As the ferric oxide contents of the slag phase are approximately the same as in the slag metal equilibrium experiments, the oxygen potential of the slag was not far from equilibrium with the metal. The

TABLE IX - Gas-Slag-Metal

Run	Clock time h.m.	Metal sulphur wt.%	Slag sulphur wt.%	$\frac{(\%S)}{[a_S]}$	(FeS) mol%	(SiO_2) mol%	(FeO_n) MOL%	(MgO) mol %	pSO_2 atm. Nitrogen 340 ml/min.	Temp. °C.	Remarks
24	8·35	3·01	9·5	3·83	21·4	0·7	68·3	9·7 Ø	·0302	1550	
28	6·52	0·244	1·20	5·00	2·7	1·6	91·6	4·1 Ø	·0299	1550	
	7·42	0·838	3·26	4·11	7·4	1·9	85·7	5·0Ø			
	8·31	1·37	4·27	3·40	9·5	2·0	80·2	8·4			
	9·00	1·90	4·72	2·81	10·6	1·8	81·1	6·4			
29	6·23	0·245	0·804	3·34	1·7	11·9	80·0	6·4Ø	·0304	1550	
	7·18½	0·929	2·20	2·51	4·6	8·7	73·3	13·8			
	8·10	1·59	2·58	1·79	5·4	7·0	67·4	20·3			
30	5·45	n.d.	n.d.	-	n.d.	20·3	53·8	25·7	·0305	1550	Starting slag
	6·08	0·280	0·455	1·65	0·9	17·8	55·5	25·8			
	7·03	1·37	1·93	1·54	3·8	12·9	60·0	23·3			
	7·53	2·43	3·79	1·82	7·9	11·2	64·5	16·4			

Ø By difference

mechanism of the reactions taking place in the system can be pictured as oxidation of the upper slag surface in contact with sulphur dioxide, pick up of sulphur at this surface occurring as well. The sulphur and oxygen diffuse through the slag layer until the slag-metal interface is reached. The oxygen potential of the slag is too high for slag-metal equilibrium and iron passes from the metal into the slag to lower this oxygen potential, thereby raising the slag bulk. With this transfer of iron a simultaneous transfer of sulphur across the slag-metal interface must also occur in order to build up the concentration of sulphur in the metal to the equilibrium value. Throughout the run the ferric oxide content of the slag does increase slightly with time possibly due to the ferric oxide becoming more stable at lower silica concentrations in the slag.

The sulphur distribution coefficients in these gas-slag-metal runs are shown in Table IX and are plotted against mol per cent FeO_T in Fig.25. The equilibrium sulphur distribution coefficient at 1550°C is also shown for comparison. Although the one point from Run 24 is quite far from equilibrium, the points representing Runs 28-30 are relatively close to equilibrium especially in the latter stages of the runs. The slag sample from Run 24 had an exceedingly high ferrous sulphide content (26·0% FeS) which may alter considerably the distribution ratio $\frac{(\%S)}{[a_s]}$

Approximately 15 g of the premixed slag were charged into the Armco iron crucible as outlined previously in Chapter 111. A greater weight of slag would have entailed a greater attack on the crucible walls with the risk of crucible failure. Due to the

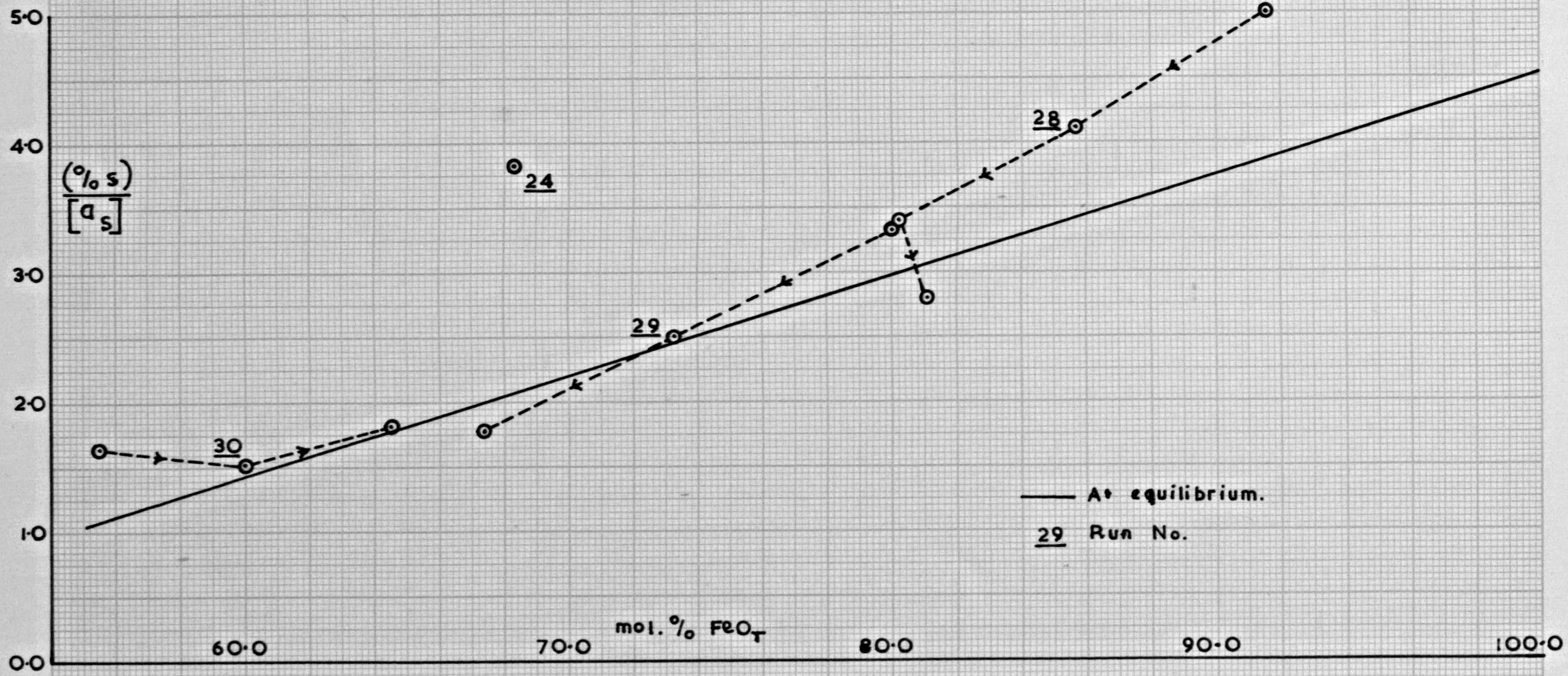

Fig. 25. THE DISTRIBUTION COEFFICIENTS OF SULPHUR IN GAS-SLAG-METAL EXPERIMENTS AT 1550°C.

contact angles of molten slag and metal with solid magnesia the metal upper surface assumes a convex shape, while the slag upper surface assumes a concave shape. Because of this there is an appreciable depth of molten slag at the crucible walls, and a fairly shallow depth at the centre of the melt where the slag sample is taken. Care must be exercised in order not to remove too much slag when sampling, as this leaves an area of metal exposed to the gas atmosphere. In the slag-metal equilibrium runs this was relatively unimportant as fresh slag could be added, but in these gas-slag-metal runs the addition of a slag would have upset conditions completely. The continuous formation of iron oxide in the gas-slag-metal investigations did help to maintain the slag bulk but on two occasions the metal was uncovered.

In Run 28 after the 8·31 sample was taken approximately 50 per cent of the metal surface was exposed to the sulphur dioxide/nitrogen gas, and as a consequence the sulphur concentration of the metal rose steeply due to reaction between the metal and the gas. The sulphur distribution ratio thirty minutes later was below the equilibrium value showing that during this time the main direction of sulphur movement was from the gas to the metal and then to the slag. Due to this increased pick-up of sulphur, iron oxide was formed in greater quantities than previously, this halting the decrease in percentage FeO_T with time and in this particular case reversing it slightly. In Run 29 after the 7·18 sample was taken approximately 10 per cent of the metal surface was exposed to the gas phase. The sulphur distribution ratio fifty minutes later was again below the equilibrium value. Throughout Run 30 no exposure of metal to the gas phase took place and all the values of the distribution coefficient are above the equilibrium line.

From Table VIIIA it can be seen that as the concentration of silica rises from Run 28 to Run 30 the efficiency of absorption of sulphur by the metal increases. This is no doubt due to the increased fluidity of the high silica slags making the passage of sulphur from gas to metal via slag much easier. As the silica concentration of the slag increases the rate of pick-up of sulphur by the slag decreases. Whether this is an inherent propety of these slags or is due to the increased rate of transfer of sulphur to the metal is not known. The efficiency of absorption by the slag-metal system is uniformly high with a slight decrease in efficiency as the run progresses. This decrease in efficiency was also noted in the gas-metal experiments and was due to a fall in the activity of sulphur at higher sulphur concentrations.

In Run 28, despite the formation of FeO from the metal, the concentration of FeO_T in the slag decreased throughout the run due to the pick-up of sulphur by the slag and also to a slight increase in magnesia concentration. In Run 29 the decrease in FeO_T concentration was due to the increase in magnesia throughout the run as the increase in sulphur concentration was counterbalanced by a decrease in silica concentration. In Iron oxide slags held in magnesia crucibles an increase in silica concentration normally means a proportional increase in the magnesia concentration of the slags, but in Run 29 the magnesia concentration of 3·7 per cent at 10·3 per cent silica was well below magnesia saturation. It can only be assumed that the increasing magnesia concentration throughout this run was due to the concentration approaching the saturation limit. In Run 30 the concentration of FeO_T increased throughout the run due to the formation of FeO from the metal. This increase in FeO_T lowered the silica concentration of the slag, the magnesia concentration being lowered not only by the increase in FeO_T but also by the decrease in silica concentration. The passage of sulphur and of oxygen into the metal was much faster in this run due to the very fluid slag and so the amount of FeO formed was consequently greater.

Due to the closeness of approach to equilibrium in these runs it can be postulated that the amount of sulphur absorption by an iron oxide/silica slag in contact with molten iron is controlled not only by the gas phase but to a great extent by the metal. It has been shown in the previous section that the lower the oxidation potential of these slags the greater the absorption of sulphur from a sulphur dioxide/nitrogen atmosphere. In these gas-slag-metal runs the molten iron controls the oxygen potential of the slag and as a result of this the slag picks up a greater quantity of sulphur than it would if it were in equilibrium with the gas. The partition coefficient then comes into action and the sulphur passes from the slag to the metal until the equilibrium ratio is attained.

Several attempts to use lime-silica slags of approximately 50 per cent lime ended in failure as the magnesia crucibles could not withstand the slag attack. The slag passed through the walls of the crucible leaving the metal surface exposed to the sulphur dioxide/nitrogen gas. Additions of magnesia to the slags in the hope of lessening the erosive action of the molten slag were also unsuccessful.

CHAPTER VI

GENERAL DISCUSSION

GENERAL DISCUSSION

In this investigation it was found that the rate of absorption of sulphur by molten metal from a sulphur dioxide/nitrogen gas mixture was very dependent on the mode of contact of the gas and metal phases. Bubbling the gas through the metal increased the contact area of the two phases and hence increased the rate of absorption of sulphur by the metal. Other factors affecting this rate of absorption were also examined. Raising the partial pressure of sulphur dioxide in the gas phase at a constant nitrogen flow increased the rate of pick-up of sulphur by the metal, but not proportionally. Increase in concentration of carbon and silicon in the metal, and increase in temperature was found to decrease the rate of absorption of sulphur.

The rate of carbon removal from the iron-carbon molten alloys was increased by an increase in the partial pressure of sulphur dioxide in the gas phase at a constant nitrogen flow but, similarly to sulphur, not proportionally. Increase in temperature and in the silicon concentration of the metal raised and lowered respectively the rate of carbon removal. It was very noticeable that the change in the rate of carbon removal was almost proportional to the change in the rate of sulphur absorption. obviously the absorption of sulphur by the metal from the gas could not take place without a simultaneous absorption of oxygen by the metal, and hence removal of carbon in the iron-carbon alloys. One surprising fact emerged from these gas-metal runs, as the metal was so far from equilibrium with the gas it might be thought that the rates of reaction would be uniformly fast and be unaffected by concentration or temperature factors, but this was found not to be the case as outlined previously.

Molten Armco iron was found to absorb sulphur and oxygen from a sulphur dioxide-nitrogen gas mixture, the oxygen eventually forming a separate oxide phase which not only reacted with the gas but into which sulphur partitioned from the metal. No "equilibrium" concentrations of sulphur were found, the rate of absorption being almost uniform throughout, with a slight decrease in the rate at higher concentrations of sulphur in the metal.

In the gas-slag experiments iron oxide-silica slags were observed to absorb large quantities of sulphurfrom the gas phase during the early period of the run when the oxygen potential of the slag was low. Absorption of oxygen by the slag from the gas phase took place simultaneously, and the oxygen potential of the slag rose slowly until equilibrium with the oxygen potential of the gas was attained.
From the experimental results it can be concluded that the concentration of sulphur in the slag must have reached a maximum some time before the oxidation potential of the slag reached the equilibrium value. On the slag approaching closer to oxygen equilibrium with the gas, sulphur was evolved from the slag and the concentration of sulphur in the melt fell slowly. It was noticeable that whereas absorption of sulphur in the initial stages of these iron-oxide slag runs was rapid, the rate of evolution of sulphur from the melt at high oxygen potentials in the slag was extremely slow and could not be measured by the apparatus used in this investigation. Seemingly once sulphur has been picked up by these slags it is extremely difficult to remove it from the slag even at high oxygen potentials in the slag.

It was found in the studies of the gas-slag-metal system that the absorption of sulphur from the gas by the slag and metal system was almost complete. The ferric iron concentration of the slag was controlled by the molten metal, this keeping the oxygen potential of the slag well below the value in equilibrium with the gas phase. Because of this low oxygen potential the concentration of sulphur in the slag was appreciable. The sulphur partitioned into the metal from the slag and it has been shown from the experimental data that the sulphur in the slag-metal system was nearly in equilibrium. Although the depth of slag layer was not great, approximately 1/10", the diffusion of sulphur through the slag to the slag-metal interface must have been f fairly rapid in order to maintain this equilibrium. It was noticeable that if the metal was uncovered by the slag, the absorption of sulphur by the metal was much faster than the absorption by the slag. Therefore the slag, although picking up sulphur itself and passing it on to the metal, protected the metal from an even greater pick-up of sulphur.

As this investigation was carried out using nitrogen-sulphur dioxide gas mixtures of low oxygen potential the results cannot be applied directly to open-hearth conditions, where on the average the oxygen potential of the combusted gases is high. The main pick-up of sulphur in the open-hearth furnace is known to take place during melt down of the charge when the gases are impinging directly on either the melting metal or lumps of undissolved lime floating in the dispersed pools of slag. Complete combustion of the flame has always been desired as experience has shown that greater sulphur pick-up occurs with a partially combusted flame striking the solid metal charge.

The cold metal charge to the open-hearth furnace normally consists of steel scrap and pig-iron, and it is thought that the oxidising flame in the furnace converts the surface layer of iron into a watery iron oxide-silica slag whose melting point is approximately 1400°C. This slag then acts as a barrier against the gases and prevents the pick-up of sulphur by the main bulk of the metal. During the formation of this protective slag skin, the ability of the skin itself to absorb sulphur from the gases is important. If the oxygen potential of the skin is high, i.e. a high percentage ferric oxide, then it is extremely unlikely that much sulphur will be abstracted from the gases. The oxygen potential of the skin will be high if the the slag comes to equilibrium with the oxidising gas phase.

From the experimental work in this investigation it was found that the iron oxide-silica slag did not come to equilibrium with the gas phase but with the liquid metal phase. During melt down with the metal melting, it might be said that the liquid slag is in contact with solid metal, so that a solid metal-liquid slag interface is the controlling interface. It would be unlikely that equilibrium would be reached in this liquid-solid system, but more likely that equilibrium would be reached between the liquid slag and the gas phase. However, it could equally well be postulated that there are two interfaces, 1, a liquid slag-liquid metal interface and 2, a liquid metal-solid metal interface. If this is the case then the slag could be in equilibrium with the molten metal, and thus have a low oxidation potential. Pick-up of sulphur from the gas is then controlled not by the oxygen potential of the gas but by the oxygen potential of the slag in equilibrium with molten iron. The gas phase in this investigation, with a partial pressure of oxygen of approximately 10^{-5} atmospheres, corresponds roughly to a $\frac{CO}{CO_2}$ ratio of 7 at 1550°C. This $\frac{CO}{CO_2}$ ratio could be obtained in the open-hearth furnace just in front of the ports with poor combustion conditions, and in the light of this investigation rapid sulphur pick-up from the gases could be expected. Under more normal oxidising conditions the same mechanism could take place but the pick-up of sulphur might be less due to a thicker slag layer which then might not wholly come to equilibrium with the molten metal. The hotter this protective slag, of course, the less the pick-up of sulphur, and for this reason the use of oxygen for cutting down the cold metal charge would be ideal.

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APPENDIX

TABLE IIA - Iron-Carbon Alloys.

Run	Time of SO_2 flow mins.	Wt. of metal in crucible gms.	Carbon Wt.%	Sulphur Wt.%	Actual from metal analysis		Theoretical from gas analysis		Crucible	Remarks
					Wt. of carbon lost gms	Wt of sulphur gained gms	Wt. of carbon lost gms.	Wt of sulphur gained gms		
1	0-15	78·24	4·06-3·89	·0289-·0445	·140	·0122	·018	·0235	Alundum	
	15-49	55·98	3·89-3·79	·0445-·0944	·060	·0279	·040	·0535		
	49-158	35·61	3·79-3·48	·0944-·358	·110	·0940	·113	·1510		
	158-257	14·74	3·48-2·91	·358 -·910	·085	·0812	·117	·1560		·025[Si]
2	0-51	81·71	4·27-4·07	·0287-·314	·170	·233	·328	·438	Alundum	
	51-130	57·29	4·07-3·81	·314 -·707	·150	·225	·505	·675		
	130-264	48·89	3·81-3·38	·707-1·11	·211	·196	·858	1·148		·038[Si]
	264-393	39·69	3·38-3·32	1·11 -1·16	·024	·020	·828	1·105		·043[Si]
3	0-35	70·00	4·16-4·00	·029-·264	·110	·165	·446	·595	Alundum	
	35-140	59·74	4·00-3·43	·264-·842	·340	·345	1·340	1·785		
	140-215	41·79	3·43-2·75	·842-1·68	·285	·350	Gauges unstable			
	215-265	25·36	2·75-2·06	1·68- 2·44	·175	·192	·634	·850		
7	0-46	67·69	3·70-3·64	·028-·089	·040	·0413	·093	·124	Alundum	
	46-100	51·79	3·64-3·50	·089-·255	·071	·0860	·108	·144		·048[Si]
	100-158	30·41	3·50-3·30	·255-·530	·062	·0835	·104	·139		
	158-198	25·62	3·30-3·16	·530-·818	·036	·0740	·0835	·111		
	198-234	13·36	3·16-2·74	·818-·973	·056	·0208	·048	·064		·058[Si]

TABLE IIA - Iron-Carbon Alloys (cont'd)

Run	Time of SO_2 flow mins.	Wt. of metal in crucible gms.	Carbon Wt.%	Sulphur Wt.%	Actual from metal analysis		Theoretical from gas analysis		Crucible	Remarks
					Wt. of carbon lost gms.	Wt. of sulphur gained gms.	Wt. of carbon lost gms.	Wt. of sulphur gained gms.		
10	0-57	80·42	3·92-3·86	·029-·082	·050	·0426	·058	·077	Alundum	
	57-106	64·41	3·86-3·79	·082-·140	·043	·0373	·052	·069		
	106-136	51·44	3·79-3·75	·140-·204	·022	·0330	·028	·0377		
	136-171	37·15	3·75-3·64	·204-·289	·040	·0318	·036	·0478		
14	0-79	78·0	3·95-3·88	·024-·031	·055	·0055	·040	·053	Magnesia	
15	6-20	70·2	3·63-3·42	·056-·307	·150	·177	·128	·157	Magnesia	
	20-43·5	52·4	3·42-2·86	·307-1·00	·290	·363	·161	·215		
	43·5-67·5	44·0	2·86-2·03	1·00 -2·10	·365	·485	·193	·258		
	67·5-105	25·0	2·03-·474	2·10 -3·74	·389	·410	·281	·374		
17	0-32	82·2	4·10-4·00	·024-·110	·083	·0708	·0635	·0845	Magnesia	·040[Si]
	32-76	68·8	4·00-3·85	·110-·290	·105	·1239	·0917	·1225		
	76-127	59·4	3·85-3·65	·290-·575	·117	·1690	·1070	·1430		
	127-152	51·0	3·65-3·48	·575-·756	·085	·0925	·0525	·070		·042[Si]
	152-181	31·9	3·48-3·22	·756-1·11	·083	·1125	·0611	·0815		
18A	0-40	83·0	3·96-3·89	·022-·122	·055	·0828	·0570	·106	Magnesia	

TABLE 11A - Iron-Carbon Alloys (cont'd)

Run	Time of SO_2 flow mins.	Wt. of metal in crucible gms.	Carbon Wt.%	Sulphur Wt.%	Actual from metal analysis		Theoretical from gas analysis		Crucible	Remarks
					Wt. of carbon lost gms.	Wt. of sulphur gained gms.	Wt. of carbon lost gms.	Wt. of sulphur gained gms.		
20	0-58	66·5	4·14-3·98	·026-·233	·105	·138	·1155	·154	Magnesia	·011[Mn]
	58-111·25	51·4	3·98-3·77	·233---·496	·105	·135	·1080	·144		
	111·25-159	38·2	3·77-3·58	·496-·797	·071	·115	·0965	·129		
	159-176	31·3	3·58-3·49	·797-·925	·030	·040	·0338	·045		
	176-201	22·1	3·49-3·30	·925-1·18	·042	·056	·0506	·0675		
21	0-58	65·0	4·06-3·86	·012-·184	·130	·1117	·115	·154	Magnesia	
	58-111·5	52·9	3·86-3·65	·184-·387	·110	·107	·1025	·137		·039[Si]
	111·5-144	37·7	3·65-3·50	·387-·535	·058	·056	·0582	·078		
	144-177·5	24·5	3·50-3·33	·535-·795	·041	·0635	·0660	·088		·044[Si]
25	0-51·75	57·6	4·89-4·86	·027-·215	·0172	·1073	-	·1365	Graphite	
	51·75-108·5	49·7	4·86-4·75	·215-·503	·0546	·1380	-	·1475		
	108·5-148·5	41·6	4·75-4·66	·503-·723	·0374	·0820	-	·104		
	148·5-189·25	25·9	4·66-4·58	·723-1·08	·0207	·0785	-	·106		
26	0-69·25	60·9	4·77-4·60	·580-1·19	·1035	·372	-	·394	Graphite	
	69·25-124·25	44·9	4·60-4·34	1·19-1·86	·1167	·301	-	·3125		

TABLE IIIA

Iron-Carbon-Silicon Alloys

Run	Time of SO_2 flow mins.	Wt. of metal in crucible gms.	% Carbon wt.	% Sulphur percent	% Silicon
8	0 - 47	69·73	4·02 - 3·80	·024 - ·130	·876 - 1·28
	47 - 104	55·84	3·80 - 3·74	·130 - ·164	1·28 - 1·30
	104 - 163	28·61	3·74 - 3·54	·164 - ·368	1·30 - 1·31
	163 - 208	20·22	3·54 - 3·19	·368 - ·612	1·31 - 1·36
	208 - 227	9·98	3·19 - 2·90	·612 - ·835	1·36 - 1·34
9	0 - 44	61·43	3·68 - 3·65	·026 - ·108	2·63 - 2·75
	44 - 102	53·00	3·65 - 3·68	·108 - ·248	2·75 - 2·94
	102 - 162	39·24	3·68 - 3·60	·248 - ·375	2·94 - 2·87
	162 - 192	25·27	3·60 - 3·50	·375 - ·522	2·87 - 2·84
18B	0 - 56	46·6	3·90 - 3·65	·030 - ·345	1·39 - 1·38
	56 - 102	31·1	3·65 - 3·32	·345 - ·809	1·38 - 1·37
	102 - 151	16·1	3·32 - 2·68	·809 - 1·94	1·37 - 1·23
19	0 - 41	66·9	3·93 - 3·85	·018 - ·140	2·78 - 2·79
	41 - 85	53·8	3·85 - 3·72	·140 - ·319	2·79 - 2·71
	85 - 128·5	43·8	3·72 - 3·58	·319 - ·573	2·71 - 2·68
	128·5 - 170	39·8	3·58 - 3·40	·573 - ·835	2·68 - 2·65
	170 - 186	25·8	3·40 - 3·33	·835 - 1·00	2·65 - 2·53

TABLES IIIA (cont'd)

Run	Actual from metal analysis			Theoretical from gas analysis		Crucible	Remarks
	Wt. of carbon lost gms.	Wt. of sulphur gained gms.	Wt. of silicon lost gms.	Wt. of carbon lost gms.	Wt. of sulphur gained gms.		
8	·165	·0738	-·282	·0972	·1295	Alundum	Silicon segregations very marked
	·030	·0190	-·011	·1180	·157		
	·058	·0584	-·003	·0796	·106		
	·070	·0495	-·010	·0676	·090		
	·028	·0223	+·002	·0285	·038		
9	·020	·0503	-·074	·0867	·1155	Alundum	Silicon segregation very marked
	-·015	·0743	-·100	·1120	·1490		
	·033	·0495	+·027	·1070	·1425		
	·025	·0373	+·008	·0542	·0725		
18B	·120	·147	·0045	·108	·149	Magnesia	Gas bubbled every 15 min. for 15 secs.
	·102	·1443	·0030	·0870	·121		
	·102	·182	·0225	·0784	·130		
19	·054	·0817	-·007	·0840	·112	Magnesia	"
	·070	·0961	·040	·0574	·122		
	·060	·1110	·014	·0781	·120		
	·070	·1040	·013	·0740	·114		
	·019	·0430	·032	·0060	·044		

TABLE IVA

Armco Iron.

Run	Time of SO_2 flow mins.	Wt. of metal in crucible	Sulphur wt.%	Actual from metal analysis wt. of sulphur gained gms.	Theoretical from gas analysis wt. of sulphur gained gms.	Crucible	Remarks
5	0 - 18	63·25	·022-·028	·0038	·0340	Magnesia	Metal partially covered by 48/52% silica/lime slag
	18 - 38	44·28	·028-·043	·0067	·0372		
	38 - 58	21·16	·043-·088	·0095	·0372		
22	0 - 56·5	67·1	·042-·274	·156	·140	Magnesia	·016[Mn]
	56·5 -107·25	57·3	·274-·499	·129	·1175		
	107·25-150·5	40·8	·499-·768	·110	·095		
	150·5 -180·5	29·2	·768-1·08	·090	·0685		
	180·5-210·5	20·7	1·08-1·48	·083	·0765		
24	0 -20·8	58·9	·041-·520	·282	·272	Magnesia	
	20·8-50·7	44·0	·520-1·29	·3385	·383		
	50·7-93·7	30·8	1·29-2·20	·279	·535		
	93·7-121·7	16·8	2·20-3·01	·132	·354		

TABLE VA - Analysis of Iron Oxide, Silica Slags.

Run	Clock time h.m.	%FeS	% FeO	$\%Fe_2O_3$	$\%FeO_T$	% SiO_2	% MgO	Temp. °C
		percentages by weight						
29	9·44	7·9	57·2	14·2	70·0	5·9	ø 14·8	1550
30	9·35	10·8	58·7	13·2	70·6	9·8	7·7	1550
31	7·25	1·9	66·7	11·0	76·6	12·0	ø 8·4	1550
	8·30	1·8	60·9	12·5	72·2	12·4	12·4	1550
32	7·15	1·4	57·2	9·0	65·3	17·4	15·1	1550
	8·44	1·2	54·6	10·5	64·0	17·6	16·1	1550
33	6·30	3·4	89·2	6·1	94·7	1·0	ø 0·3ø	1550
	8·00	3·2	82·4	9·0	90·5	1·9	3·5	1550
	9·35	6·2	76·2	10·9	86·0	2·0	4·9	1550
34A	6·15	3·2	77·0	10·0	86·0	4·0	ø 5·8ø	1550
	7·50	3·0	77·7	11·8	88·3	4·1	3·4	1550
	9·45	1·9	67·0	15·1	80·7	4·3	11·6	1550
39	4·49	3·2	84·3	6·0	89·7	0·8	ø 5·7	1600
	5·50	2·5	71·6	5·0	76·1	6·9	14·0ø	1600
	6·25	2·4	67·2	8·1	74·4	7·9	14·4	1600
	7·30	3·8	75·5	8·5	83·2	3·3	9·0	1650
40	6·15	3·2	85·8	6·7	91·9	1·0	3·5ø	1600
	7·15	3·1	82·4	6·6	88·4	2·0	5·9	1600
	8·17	2·6	78·1	8·8	86·0	3·4	7·1	1600
	9·05	1·9	74·1	10·1	83·1	3·3	10·6	1650

ø By difference

TABLE VIA - Pure Iron Oxide Slags.

Run	Clock time h.m.	(FeS) mol %	(SiO_2) mol %	(FeO_T) mol %	(MgO) mol %	Nitrogen flow 200 ml/min p_{SO_2} atm.	Temp. °C.	Remarks
35	6·49	5·6	0·9	90·1	3·4 ø	·0203	1550	
	8·30	7·3	1·1	87·4	4·2		1550	Equilibrium
36	7·30½	6·0	0·5	87·2	6·3 ø Al_2O_3	·0181	1550	Alumina crucible used
	8·20½	6·3	0·5	87·1	6·1 ø Al_2O_3		1550	
37	5·27	15·5	0·6	83·9	0·0 ø	·0186	1550	
	7·38	18·0	0·4	74·4	7·1		1550	
	8·40	19·8	0·9	69·7	9·5		1550	
38	10·15	7·7	1·1	83·0	8·2 ø	·0191	1550	Equilibrium
41A	9·07	0·7	1·7	79·1	18·5	·0197	1620	Equilibrium
42	8·08	1·9	1·2	86·6	10·3 ø	·01945	1605	Equilibrium
	8·20	1·7	1·2	84·4	12·8		1605	Equilibrium
	10·05	1·3	1·4	82·4	14·9		1650 from 8·30	
	-	1·2	1·3	76·6	20·9		1650	

ø By difference

Table VIIA - Slag Analysis.

Run	Clock time h.m.	%FeS	%SiO_2	%FeO	%Fe_2O_3	%FeO_T	%MgO
		wt. percentages					
24	8·35	26·0	0·6	n.d.	n.d.	68·0	5·4 Ø
28	6·52	3·3	1·3	84·9	8·3	92·4	2·3 Ø
	7·42	9·0	1·6	76·1	10·5	85·4	2·8
	8·31	11·7	1·7	69·5	12·4	80·7	4·7 Ø
	9·00	12·9	1·6	69·0	13·0	80·7	3·6
29	6·00	0·1	11·1	n.d.	n.d.	85·3	n.d.
	6·23	2·2	10·3	69·7	14·2	82·4	3·7
	7·18½	6·0	7·7	67·0	11·4	77·4	7·9 Ø
	8·10	7·1	6·3	59·8	14·7	72·8	12·3
30	5·45	0·14	19·9	57·2	6·1	62·7	16·9
	6·08	1·25	17·0	58·0	6·8	64·1	16·7
	7·03	5·3	12·0	58·1	10·0	67·1	14·7
	7·53	10·4	10·0	59·8	10·0	68·7	9·8

Ø by difference

Table VIIIA - Gas-Slag-Metal

Run	Increment time of SO_2 flow mins.	Actual / Theoretical Sulphur gained metal	Actual / Theoretical Sulphur gained slag + metal	Actual from slag and metal analysis $\frac{d[S]}{dt}$ g./min.	Actual from slag and metal analysis $\frac{d(S)}{dt}$ g./min.	Actual from slag and metal analysis $\frac{d\Sigma S}{dt}$ g./min.
28	21·75	40·8	104·0	·00565	·00869	·01434
	46	51·[illegible]	100·0	·00687	·00661	·01348
	47	34·2	56·0	·00466	·00298	·00764
	29	42·4	57·2	·00583	·00204	·00787
29	21·75	49·0	99·3	·00570	·00584	·01154
	53·25	53·2	87·6	·00576	·00372	·00948
	51·5	SO_2 gauge fluctuating badly				
30	21·75	67·4	94·0	·00665	·00263	·00928
	52·75	70·1	91·2	·00682	·00266	·01148
	47·75	44·3	72·8	·00540	·00346	·00886

Table VIIIA (cont'd) - Gas-Slag-Metal

Run	Time of SO_2 flow mins.	Wt of metal in crucible gms.	Wt. of slag in crucible gms.	Actual from slag and metal analysis Weight of sulphur gained			Theoretical from gas analysis Total gms.
				Metal gms.	Slag gms.	Total gms.	
28	0 - 22	60·2	15·8	·123	·189	·312	·301
	22 - 68	53·4	14·8	·316	·304	·620	·619
	68- 115	41·2	13·7	·219	·140	·359	·640
	115 -144	31·9	12·7	·169	·059	·228	·399
29	0 - 21·75	60·3	15·8	·124	·127	·251	·253
	21·75 - 75	44·8	14·1	·307	·198	·505	·577
	75 -126·5	27·3	13·1	·181	·050	·231	-
30	0 - 21·75	60·2	12·6	·144	·057	·201	·215
	21·75 - 74·5	42·6	9·5	·466	·140	·606	·665
	74·5 -122·25	24·4	8·9	·258	·165	·423	·582

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